



EVALUATING THE POTENTIAL OF CHEMOMETRICS TECHNIQUES AS RAPID SCREENING TOOLS FOR BLACK GEL INKS DISCRIMINATION

(Menilai Potensi Teknik Kemometrik sebagai Alat Saringan Pantas untuk Diskriminasi Dakwat Hitam Gel)

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Abstract

Examining the questioned documents can offer essential scientific proof that the documents are authentic. Examining inks and handwriting to establish authenticity, authorship, suspected counterfeiting, and/or modifications are forensic problems that require critical attention. Due to gel pens popularity and widespread usage, their emergence in criminal cases associated with questioned documents are therefore anticipated. A dissolution test by dissolving gel ink into organic solvent can sometimes be used for rapid discrimination of gel ink into either pigment-based or dye-based colourants. However, due to its extremely destructive nature, this test is unfavourable for forensic document examination purposes. The main aim of this study was to develop a model that could be used to determine the nature of colourant in black gel ink without having to perform the destructive dissolution test. To achieve this, black gel pen inks of different brands/models ($n = 30$) that were procured from 23 different manufacturers from Malaysia, India, and China were initially dissolved in a series of organic solvents, and the nature of their colourants was recorded. Thereafter, their infrared (IR) spectra profiles were acquired using the attenuated total reflectance - Fourier transform infrared (ATR-FTIR) spectroscopy, and then preprocessed prior to feature selection using the principal component analysis (PCA). The selected features were used for the development of a classifier using the linear discriminant analysis (LDA), whereby 98.1% of correct classification was recorded for the cross-validated samples. Furthermore, it signified the potential of this approach for rapid screening of black gel ink without having to perform the destructive dissolution test, which could be utilised by forensic document examiners.

Keywords: black gel inks, forensic science, questioned document, attenuated total reflectance infrared spectroscopy, principal component analysis

Abstrak

Meneliti dokumen yang dipertikai boleh memberikan bukti saintifik penting bahawa dokumen itu sah. Memeriksa dakwat dan tulisan tangan untuk menentukan keaslian, kepengarangan, disyaki pemalsuan dan/atau pengubahsuaian adalah masalah forensik yang memerlukan perhatian kritikal. Disebabkan oleh populariti pen dakwat gel dan penggunaannya yang semakin meluas, kemunculan mereka dalam kes jenayah yang berkaitan dengan dokumen yang dipertikai adalah dijangkakan. Ujian pembubaran

dengan melarutkan dakwat gel ke dalam pelarut organik kadangkala boleh digunakan untuk diskriminasi pantas dakwat gel kepada sama ada berasaskan pigmen atau pewarna. Walau bagaimanapun, disebabkan sifatnya yang sangat merosakkan, ujian ini tidak sesuai untuk tujuan pemeriksaan dokumen forensik. Matlamat utama kajian ini adalah untuk membangunkan model yang boleh digunakan untuk menentukan sifat pewarna dalam dakwat gel hitam tanpa perlu melakukan ujian pelarutan yang merosakkan. Untuk mencapai matlamat ini, dakwat pen gel hitam daripada jenama/model berbeza ($n = 30$) yang diperolehi daripada 23 pengeluar berbeza dari Malaysia, India, dan China, pada mulanya dilarutkan dalam satu siri pelarut organik, dan sifat pewarnanya direkodkan. Berikutan itu, profil spektrum inframerah (IR) mereka diperolehi menggunakan spektroskopi jumlah pemantulan yang dilemahkan - inframerah transformasi Fourier (ATR-FTIR), dan kemudian pra-diproses sebelum pemilihan ciri menggunakan analisis komponen utama (PCA). Ciri-ciri yang dipilih telah digunakan untuk pembangunan pengelasan menggunakan analisis diskriminasi linear (LDA), di mana 98.1% pengelasan yang betul telah direkodkan untuk sampel-sampel yang disahkan silang, yang menandakan potensi pendekatan ini untuk pemeriksaan pantas dakwat gel hitam tanpa perlu melakukan ujian pelarutan yang merosakkan, yang boleh digunakan oleh pemeriksa dokumen forensik.

Kata kunci: dakwat gel hitam, sains forensik, dokumen yang dipersoalkan, spektroskopi inframerah jumlah pemantulan yang dilemahkan, analisis komponen utama

Introduction

Nowadays, increase in document forgery activities and fight against these illegal activities causes serious problems and negatively affects individuals, including the private and government institutions [1]. Any documents related to criminal cases that are doubtful of authenticity and authorship, are known as questioned documents [2]. It also refers to any objects bearing handwriting, typed, and printed materials. Document examination offers a great deal of interest in the forensic document examiners' community. It includes examining of the ink written on documents, signatures and handwriting, and determining the age of the ink written on paper [3]. The commonality for forensic document examiners is to test for document alteration and defacement, distinguishing between inks with identical impressions, and determining whether the provenance of the two ink samples is either identical or otherwise [4]. All of these processes require ink analysis, which serves to discover the authenticity of documents [5]. The chemistry of ink is determined by its composition, which is different for each brand/model. Nonetheless, the existence of colours, pigments, solvents, and additives in ink recipes aids forensic document examiners in the discrimination, and classification of confiscated pens in actual cases [6].

There are several types of writing instruments used in a document, such as roller ball pens, ballpoint pens, fountain pens, and gel pens. However, gel pens are popular writing material due to their smooth and interesting writing appearance [2]. Due to this, the usage

of gel pens in documents is increasing. The history of the gel pen began in 1984, whereby the Japanese Sakura Colour Products Corporation introduced the first gel pen, a type of writing instrument that used a rolling ball mechanism to transfer ink from the reservoir to paper [7]. Gel ink often contains colouring ingredients, such as dyes and pigment, a water-based solvent as a vehicle or carrier, and additional additives, such as plasticisers, surfactants, waxes, and driers to enhance its writing performance and appearance [8]. The uniqueness of each manufacturer is the type of colourant used, and the quality and quantity of additives, such as surface activators, fluorescent material, solubilisers, preservatives, and anti-corrosion agents added to the ink composition [9]. Dyes and pigments are preferred over other components since they can be seen by the naked eye, making them the most prominent aspects in the ink analysis. This feature enables the examiners to make a quick decision, and straightforward comparisons between the various inks, which is helpful for the initial assessment of an ink analysis.

The subjective judgement of forensic document examiners regarding ink analysis has somewhat diminished due to the advancement of analytical techniques. The latter technique is gaining popularity because other than being straightforward, it requires no or minimal sample preparation, and most importantly it maintains the integrity of documents [10]. Amongst the methods are the attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy [4, 11–15], and surface increase Raman scattering [10, 16–20].

Due to these, the non-destructive method is often preferred over the destructive method for document analysis.

The ATR-FTIR spectroscopy has been proven as an effective tool for ink analysis, which offers a simple tool that can provide qualitative and quantitative information for comparative analysis of ink. Additionally, these methods work in combination with the chemometrics methods, such as the principal component analysis (PCA) [5, 15], [21, 22], linear discriminant analysis (LDA) [14], and partial least square-discriminant analysis (PLS-DA) [4] for discrimination and classification of ink. Consequently, a mixture of statistical and analytical methods has been consistently applied to achieve substantial outcomes in forensic questioned document examination [4]. Despite numerous studies demonstrated a successful combination of ATR-FTIR analysis with chemometrics methods, there was a noticeable research gap that explored the practical significance of these results in effectively distinguishing between different types of inks, as the preliminary stage in ink analysis. This is significant considering that ATR-FTIR offers a non-destructive approach, and has the potential to replace traditional, destructive techniques to discriminate the ink at an early stage.

Chemometrics are mathematical and statistical approaches to chemical data that provide reliable tests for classification, discrimination, or model development for sample datasets [23]. In ink analysis, the main principle of chemometrics is to analyse and examine the data obtained from analytical methods to avoid making an unbiased decision about similarities between the ink samples. Chemometrics have a positive influence on the forensic examination of various inks. It is also a powerful tool when dealing with multi-component systems and allows for extracting maximum information from complicated datasets.

The PCA is a widely used method for pattern recognition in chemometrics. It allows for a large number of datasets, and reduces data dimension by transforming the original set of correlated variables into orthogonal variables, known as the principal components (PCs)

[24]. This process is achieved by removing the noise, redundant, and highly correlated data [25]. Each PC is calculated to describe the highest proportion of variance, and most of the information is stored in the first few PCs. The number of useful PCs is less than the number of original variables [26].

The LDA is a well-known method for pattern recognition [15]. Additionally, it is a powerful classification method that applied linear classification structure that can separate a series of samples within different classes based on their spectral features. In LDA, the dimensional embeddings are reduced in a manner that effectively separates orientations of the classes projected data on any given line or space. The maximum ratio of within-class variability to between-class variability in the training set serves as the criterion for determining these vectors.

Prior to analytical analysis, the standard procedure in ink analysis commences with the dissolution test, which serves as a rapid screening technique to differentiate between unidentified ink sources and categorises ink by its colourant composition. This preliminary test was conducted by observing the degree of ink solubility that was deposited on paper after it was submerged in organic solvent. Dye-based ink readily dissolved in the solvent, causing a noticeable change in the solvent colour, whereas the pigment-based ink remained adhere to the paper substrate. A study by Mohammad Asri et al. [16] found that red gel ink dissolved in acetone compared to other organic solvents. This result was also supported by Reed [27] who claimed that acetone and hydrochloric acid were able to dissolve red and blue gel inks, respectively.

This screening test could provide rapid discrimination between unknown ink, but it is not recommended for it could obliterate the document. Therefore, this study proposed the development of a non-destructive screening test protocol based on dissolution test data. Consequently, a screening test was performed on 30 different brands of black gel ink pens to determine the colourant nature of each ink; these inks were then deposited on paper and subjected to non-destructive ATR-FTIR analysis. The ATR-FTIR data mining was

performed using PCA and LDA, and a classification model was developed. The outcome of this study would provide valuable insights of screening test using the non-destructive approach. The developed model could be utilised by forensic document examiners, as a rapid screening tool to identify the nature of colourant in black gel ink without having to perform the destructive dissolution test.

Materials and Methods

Sample collection

Thirty different brands and models of black gel inks were purchased from stationery stores and online. In this study, seven pens from each brand/model were used, totaling 210 samples of black ink. For reference, a code was assigned to each brand or model. The information and IDs used in this study are shown in Table 1.

Table 1. Details of samples

No	Brand	Model	Code ID
1	M&NISUN	606	A
2	Faber Castell	True Gel	B
3	Faber Castell	Eco Gel	C
4	Pilot	Super Gel	D
5	Pilot	Wingel	E
6	M&G	AGP02372-R3	F
7	M&G	AGP13271- Office	G
8	Pentel	BL110-Energel	H
9	NMANAN	MiWi Get	I
10	Zhi Xin	Diamond	J
11	Zhi Xin	Lovein Test Good	K
12	Zhi Xin	POS G-518	L
13	BIC	GLI X - Fine	M
14	Faster	SP-F-072	N
15	Monami	Jeller Pen 502	O
16	Monami	Jell Line	P
17	Paper Mate	Gel 300	Q
18	Unicorn	TGP-812C	R
19	CHOSCH	CS-G169	S
20	U-Fine	UC-Q8	T
21	Digno	Trinok Gel	U
22	Buncho	Fine Tech	V
23	Buncho	Jellie	W
24	TYNO	GP100	X
25	BEIFA	GA102601	Y
26	Mr DIY	Gel-067	Z
27	Zui Xua	CS801	A'
28	Test 2	GP-300	B'
29	MUJI	5110	C'
30	Stabilo	Palette	D'

Dissolution test

In questioned document examination, this test acts as a screening step to distinguish inks that are similar in colour, but with different ink colourant composition [16]. Gel ink colourants were either pigment- or dye-based. While pigment-based ink does not dissolve in organic solvents, dye-based ink does. This test aimed at identifying the colourants used in each ink sample based on their solubility in organic solvents. The results could provide an early insight to discriminate the ink samples into two groups; ink that was soluble in an organic solvent, classified as dye-based ink, whereas ink that was insoluble in organic solvent had pigment-based colourant. This test was adapted from a study by Reed [27] that used a variety of organic solvents to discriminate gel ink samples of red, blue, and black. The solvents used were polar organic solvents, such as methanol and ethanol.

Each ink was scribbled on a 4 mm x 4 mm square on a 70 gsm A4 paper until the entire square was thoroughly inked. After drying at room temperature for 10 min, the square sheet was cut and placed in a glass vial. Thereafter, 2 mL of solvents (methanol and ethanol) were drawn into the sample vial with a pipette, and subsequently stirred vigorously using a vortex mixer for 1 min. After leaving each sample at room temperature for 5 min, the solubility of ink samples in these solvents was observed and recorded. The outcomes of the dissolution test were compared with ATR-FTIR analysis and chemometrics results, which were crucial as they served as a reference point to demonstrate that ATR-FTIR analysis could provide equivalent results. Furthermore, they had the potential to substitute the dissolution test as a screening method for forensic ink analysis.

Infrared (IR) spectral acquisition

In forensic science, problems arose when the reference and unknown samples contained the same type of colourant. Therefore, discrimination of the ink by dissolution test is irrelevant. This could be resolved by using the Fourier transform infrared (FTIR) analysis to separate the ink samples, depending on the functional groups present in each sample. FTIR is preferable as it is a non-destructive analysis and requires no sample

preparation. Consequently, the integrity of the document as evidence is maintained. Each absorbance spectrum was collected in the range of $4000\text{ cm}^{-1} - 600\text{ cm}^{-1}$ wavelengths using a LUMOS FTIR microscope (Bruker, Germany) equipped with an ATR. The ink line samples were prepared by drawing seven lines with seven gel pens from the same brand/model on a white A4 70 gsm paper. Before the spectra acquisition, all samples were stored in normal laboratory environment. The environmental conditions were maintained the same for all the samples, as they could offer an equal effect of moisture content and other environmental factors [4]. The sample was then placed on the stage under a microscope, and the seven lines drawn from each pen were measured in a low ATR pressure mode with 64 background sample scans at a resolution of 4.0 cm^{-1} . In each sample measurement, the background was measured according to the aperture. All collected spectra were baseline corrected using the OPUS 7.5 software connected to the instruments.

Data preprocessing and analysis

The absorption spectrum acquired from the LUMOS FTIR microscope instrument was saved in a *.dpt format and converted into an Excel spreadsheet. The spectral range from this analysis was collected in the range of $4000\text{ cm}^{-1} - 600\text{ cm}^{-1}$. However, for observation purposes and data analysis, the fingerprint region in the range of $1500\text{ cm}^{-1} - 600\text{ cm}^{-1}$ was selected, as this region exhibited characteristic peaks for each sample. The data from each spectrum were then preprocessed to normalised dataset. The ATR-FTIR spectra obtained from the ink samples might contain broad, low resolution, and merged peaks. Therefore, the normalised preprocessing of numerical data was necessary to minimise and refine the results [4].

Principal component analysis (PCA)

In this study, the statistical software package, Unscrambler (Version 10.4) 2016 was used to process normalised dataset. The average value from each sample spectrum was inputted to the Unscrambler to run PCA. A score plot was used to display the clustering outcome, as the samples with similar scores were placed close to each other, while those with dissimilar scores were located apart.

Linear discriminant analysis (LDA)

The classification model was built on the normalised FTIR dataset to observe whether all the IR data could be classified according to their colourant nature. The IBM Statistical Package for the Social Sciences, also known as IBM SPSS (Version 26) was used that applied the Fischer's function coefficient algorithm and leave-one-out approach, which is one of the types of cross-validation techniques.

Results and Discussion

Dissolution test

Typically, black gel pen ink contains multiple dye components, or pigments of various hues that are combined proportionally to produce black colour. To ascertain the degree of dissolution of the black gel ink samples, the colour changes in the organic solvents were observed, as the ink was introduced. In this test, 21 black gel inks failed to dissolve effectively, which suggested that they might contain pigments as colourants, whereas nine black gel inks (Codes C, D, E, H, O, U, V, W, and D') dissolved in methanol and ethanol, indicating that they contained dyes. The observation made from this test concurred with a study conducted by Reed [27]. From this test, the ink samples were able to discriminate based on the type of colourant contained in the ink.

Spectral characterization

Figure 1 and Figure 2 show the spectra from dye-based black gel ink and pigment-based black gel ink, respectively. None of the sample's spectra displayed any discriminating peaks between 4000 and 1600 cm^{-1} . The cellulose band presence in the range of 3000 cm^{-1} – 3500 cm^{-1} and 2880 cm^{-1} – 2890 cm^{-1} characterised the C-H and O-H stretching, which was from the paper composition [14]. The fingerprint region from 1500 cm^{-1} – 600 cm^{-1} exhibited the most characteristic peaks of ink [28]. Peaks in the range of 1300 cm^{-1} – 1500 cm^{-1} could be attributed to the vibration of carbon compounds, such as CH-stretching and bending vibrations in the aliphatic and aromatic compounds. Presence of peaks in the range 1550 cm^{-1} – 1610 cm^{-1} was due to nitrogen bonding in azo compounds used in ink. Primary, secondary, and tertiary alcohols appeared in the region of 1600 cm^{-1} – 1000 cm^{-1} with the presence

of C-O bond peaks in stretching mode. The region below 1000 cm^{-1} was due to C-H bond in the bending mode that indicated alkenes. Lastly, the epoxy group existed in the region of 800 cm^{-1} – 900 cm^{-1} . It was suspected that this might be due to the source of additives in the gel pen ink composition. Based on the spectra observations, there were no discernible differences between the dye-based ink and pigment-based ink samples. Unfortunately, this observation was unsuccessful in distinguishing against all the black ink samples. These findings were supported by Reed [27], as visual discrimination of the spectra based on the presence or absence of peaks, and their intensities were challenging and difficult.

Principal component analysis (PCA)

The score plot of normalised dataset is reported in Figure 3, showing visual pattern recognition of normalised dataset plotted using the first two principal components, namely PC1 and PC2. The first two PCs explained 89% (PC1 75% and PC2 14%) of the total variance. A close observation of this score plot clearly showed two well-separated clusters corresponding to the dye-based groups (Group I) and pigment-based group (Group II), which were in line with the results obtained from the dissolution test. The score plot separated Group I mostly as negative value, while most of Group II as positive value at PC1. The PCA could discriminate these samples based on their colourant types. Additionally, it clearly demonstrated the link between the samples (Code D and Code E) and (Code V and Code W), which originated from the same brand located near each other under the same cluster (Group I), as they had similar ink formulation. In contrast, samples (Code F and Code G) and (Code J, Code K, and Code L) in cluster Group II were separated despite belonging to the same brand. This trend might be impacted by the presence of additive ingredients in the ink to enhance their appearance and writing performance. Code R and Code X were pigment-based ink, but their positions were distant from the cluster, suggesting that they might not be gel ink. As observed, a small number of Group II samples overlapped with each other, indicating that the samples from different brands might have varying proportions, but with similar ink compositions. Gawad et al. [29] achieved 100% discrimination power for ink

differentiation amongst 33 pens by integrating ATR-FTIR data with PCA. Qureshi et al. [6] also applied PCA with pre-treated ATR-FTIR spectral data for discrimination of local and foreign ballpoint inks. The PCA scatter plot exhibited a cumulative variance of 97%

of the first two principal components. PCA with ATR-FTIR data demonstrated a significant contribution of non-destructive approaches, as useful tool for ink discrimination.

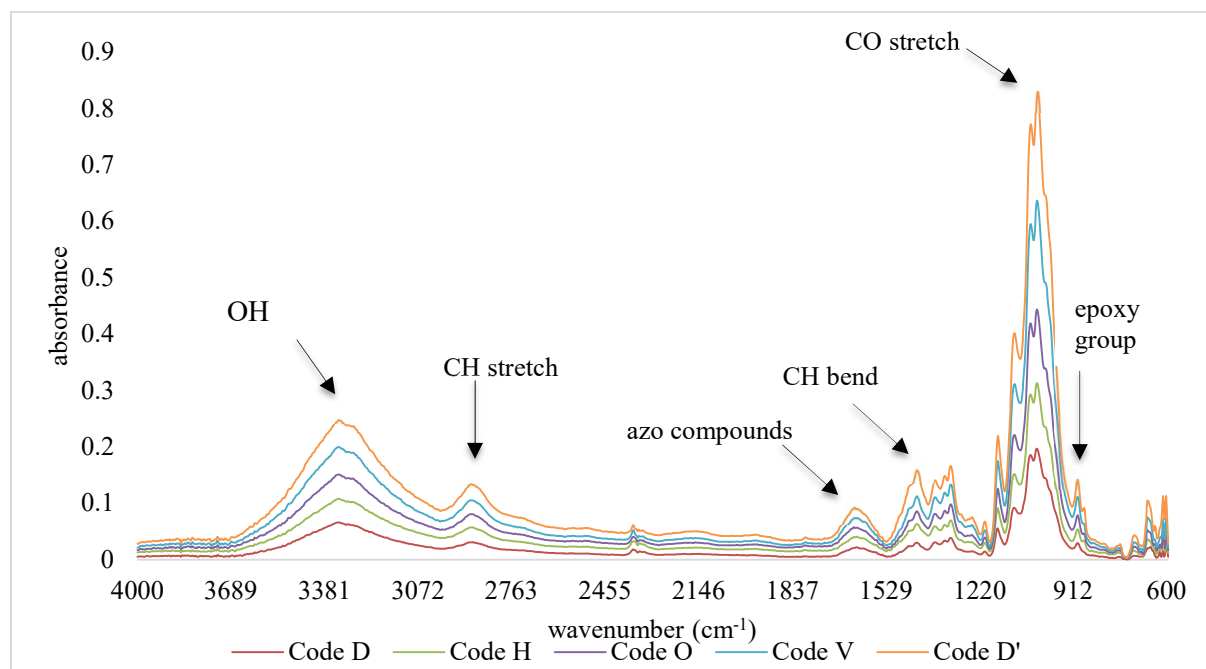


Figure 1. FTIR spectra of dyed-based black gel ink spectrum

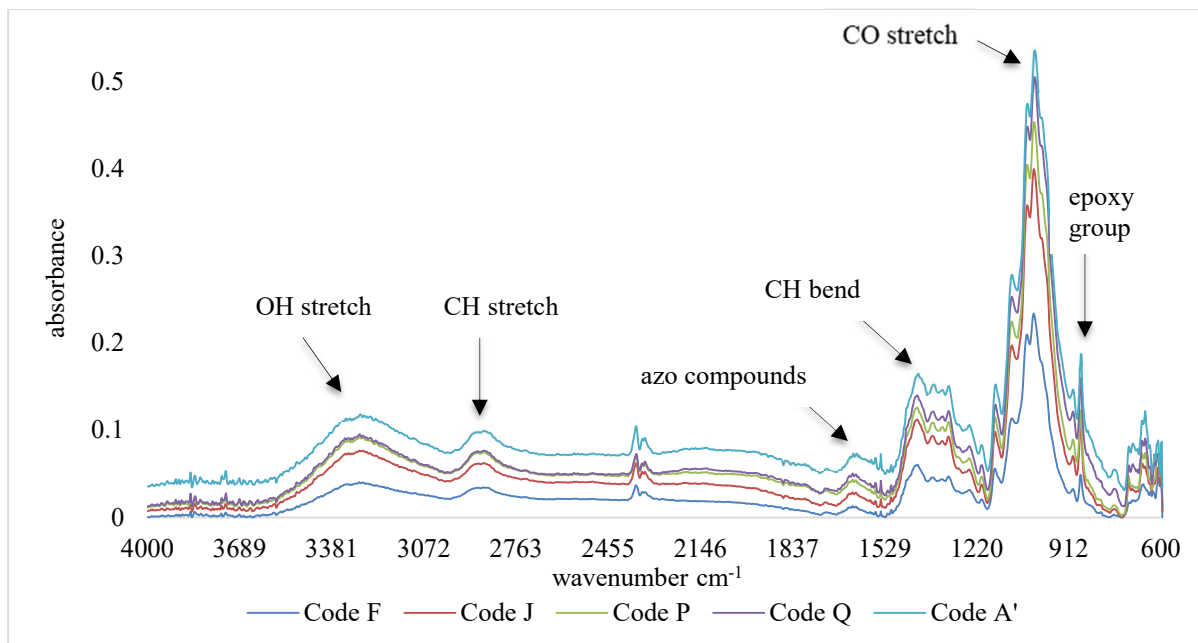


Figure 2. FTIR spectra of pigment-based black gel ink spectrum

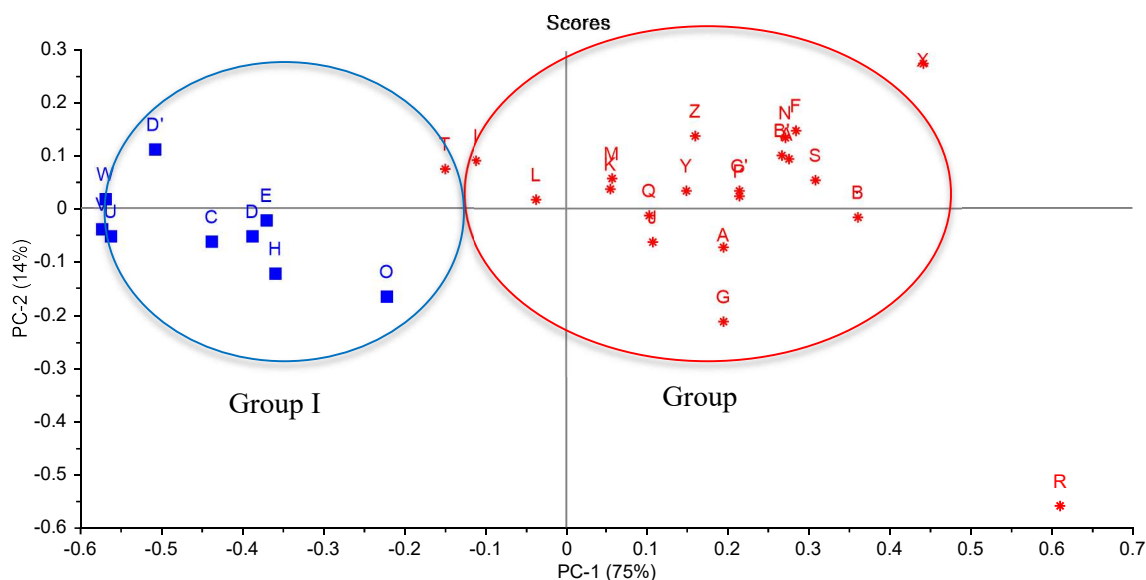


Figure 3. PCA score plot of the normalized dataset for black gel ink samples

Linear discriminant analysis (LDA)

The Wilks' Lambda measures how well each function separates cases into groups. It is equal to the proportion of the total variance in the discriminant scores that are not explained by differences amongst the groups. It shows whether these two groups (dye and pigment) differ significantly based on their means value on a set of continuous variables, which indicated the

significance of the discriminant function. The value ranges from 0 to 1; the smaller the value of Wilks' Lambda indicates the greater discrimination ability of the function. Table 2 shows a high significance function ($p < 0.05$), and provided a small Wilks' Lambda value, which was 0.254 that indicated greater discrimination ability of the function.

Table 2. Wilks' Lambda table from linear discriminant analysis

Test of Function(s)	Wilks' Lambda	Chi-square	df	Sig.
1	.254	201.661	6	.000

The classification in Table 3 reveals the results using the generated discriminant model. Of the original group used to create this model, 43 from 45 dye-based ink samples were classified correctly, and 106 from 107 pigment-based ink were classified correctly. Overall, 98% of the original group cases were classified correctly. On the other hand, the cross-validated group cases that applied leave-out-one approach, however, showed similar discriminating power (98%). Pigment colourants were perfectly classified with a good accuracy (99.1%) than dyed colourants (95.6%). The model validation for 30 unknown samples showed 100%

classification. All the unknown samples were correctly assigned into its designated group according to its colourant nature. In the realm of ink analysis, previous studies have yielded promising results through the utilisation of LDA in conjunction with ATR-FTIR spectral data. Specifically, Kher et al. [30] demonstrated that 48.4% of blue ballpoint pens could be accurately classified using this approach. Furthermore, Silva et al. [14] applied LDA with ATR-FTIR data for pen classification, and reported a remarkable outcome, achieving a perfect 100% in their classification model.

These findings underscored the robustness and efficacy of LDA for ink classification.

Table 3. Classification table generated from normalized dataset of black gel ink samples

			Pigment	Dye	Total
Original	Count	Pigment	106	1	107
		Dye	2	43	45
	%	Pigment	99.1	.9	100.0
		Dye	4.4	95.6	100.0
Cross-validated	Count	Pigment	106	1	107
		Dye	2	43	45
	%	Pigment	99.1	.9	100.0
		Dye	4.4	95.6	100.0

a. 98.0% of original grouped cases correctly classified.

b. Cross validation is done only for those cases in the analysis. In cross validation, each case is classified by the functions derived from all cases other than that case.

c. 98.0% of cross-validated grouped cases correctly classified.

Conclusion

The development of classification model to discriminate the black gel ink based on its colourant nature as an alternative destructive screening test holds a significant promise. By applying this model, the screening test of the unknown ink samples could be conducted without damaging or altering the integrity of the sample. Furthermore, ATR-FTIR spectroscopy in combination with chemometrics techniques could be successfully used for the discrimination of ink when it involved large datasets. Additionally, PCA was applied resulting in good clustering of all samples based on the nature of ink colourants. The LDA classification model could quantify the predictive ability for correct classification rate of the gel ink samples by providing higher discrimination rate, which was 98% for both the original and cross-validated group cases.

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