Original Article

FORENSIC DISCRIMINATION OF LIPSTICK SMEARS USING ATTENUATED TOTAL REFLECTANCE–FOURIER TRANSFORM INFRARED (ATR-FTIR) SPECTROSCOPY WITH CHEMOMETRICS TECHNIQUES

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ABSTRACT

Lipstick smear is one of the trace evidence that may transfer due to contact between suspect, victim and crime scene. The main objective of this study was to discriminate and classify 12 red lipstick samples of local and international brands using ATR-FTIR spectroscopy coupled with chemometrics techniques of principle component analysis and hierarchical cluster analysis. The result obtained from hierarchical cluster analysis is in conformance with principle component analysis. The application of chemometrics techniques had successfully separated and discriminated the red lipstick samples into six distinctive clusters according to their brands.

INTRODUCTION

Cosmetic products are used by individuals with intention to improve their appearances as well as to “express” their beauty to the public. Lipstick is an emblem of feminism, allure and elegance. Individuals apply lipstick to make their appearances much more attractive. The main ingredients of lipstick are wax, oil and colourants [1, 2]. The vivid colour of lipstick is due to the presence of one or combination of organic dyes and inorganic pigments [3]. Some examples of dyes commonly used in lipstick are eosin, phloxine and erythroxine.

In forensic caseworks, lipstick is commonly found in the form of smear and present in minute or trace amount [4-8]. The smears can be encountered on various types of substrates such as paper, fabric, tissue paper, drinking glass, paper cup, cigarette butt and skin. Lipstick smear is the result of physical contact between a person wearing lipstick with another person and/or with object(s) [9-12]. Hence lipstick smear is very helpful and useful in providing link between victims, suspects and also crime scene [13].

Two techniques are generally approached in forensic lipstick analysis, namely, destructive and non-destructive techniques. Most chemical analyses involve in lipstick smears are destructive in nature [14-19], which mean that the analyses result in loss due to extraction and dissolution in organic solvents. In order to maintain sample integrity, non-destructive techniques which have known to be straight forward analysis is highly recommended as it does not require any form of sample preparation, allows *in-situ* analysis and most importantly does not result in sample loss.

FTIR spectroscopy is one of the examples of non-destructive method. In this study, FTIR spectroscopy together with ATR accessory was chosen for the lipstick analysis. Previous study using FTIR spectroscopy in this area is very limited. A study conducted by Pasieczna-Patkowskaa and Olejnik (2013) [20] to red lipstick samples using different IR spectroscopy techniques including ATR-FTIR obtained similar spectra pattern regardless of lipstick formulations. Anthocyanin is one of the natural pigment contain in the lipstick formulation. Its absorption towards skin had successfully been studied by Westfall (2015) [21]. Most of the research study had focused and discovered only at spectroscopy spectral pattern. However, the interpretation of spectral pattern using conventional direct manual examination is very tedious, challenging as well as very time consuming. In this case, chemometrics techniques of principle component analysis (PCA) and hierarchical cluster analysis (HCA) were applied and give more

objectives and definite outcomes.

PCA and HCA are described as unsupervised pattern recognition methods which are commonly used in forensic caseworks due to their ability to reduce a large number of datasets and presenting the data in the form of graphical presentation for an easy interpretation [22]. The result of PCA is presented in the score plot which reveals the relative position of the samples where the samples having similar scores are located closely together. Meanwhile in HCA, the data analysis will be signified in a dendrogram showing the successive stages of grouping. Both techniques enable a classification and characterisation of sample in more objectives and reproducible manner [23].

The aim of this study is to characterise and discriminate a set of red lipstick smears of local and international brands of similar shades using ATR-FTIR spectroscopy and analyse the spectroscopic data using chemometrics techniques of PCA and HCA.

METHODOLOGY

Sample Collection

A total of 12 red lipstick samples, comprising of local and international brands by six different manufacturers (SilkyGirl, Sendayu Tinggi, Simplysiti, Avon, NYX, Revlon) were used in this study. The selection of the brands was based on their commonality in the market. Each of the lipstick samples having similar hue and shade indistinguishable by eyes were selected. Table 1 lists the lipstick samples, their shades, manufacture and reference codes. The reference codes were given for ease of identification of the lipstick samples. Another 6 lipstick samples of local brand named Peinifen13 (code P13) with same red shade was purchased specifically for repeatability and reproducibility examination.

ATR-FTIR Spectroscopy

The FTIR analysis in this study was performed using a Bruker Tensor 27 FTIR spectrometer (Bruker Tensor, UK) equipped with a crystal diamond ATR sampling interface. The spectrometer was calibrated using a polystyrene film standard prior to performing any analysis.

The ATR sampling interface was thoroughly clean by wiping it using a tissue paper soaked with methanol before and after scanning was done to the sample to ensure that the interface was free from any contaminants or sample carry-over effect. Background scanning was done to confirm that the sampling interface was thoroughly clean.

The lipstick sample was smeared directly from its container onto the sampling interface. This was to ensure that the spectra were obtained without the interference from substrate or background matrix. The smear was scanned using the parameter mentioned in Table 2.

The repeatability and reproducibility of the analysis were assessed by calculating the percent relative standard deviation (%RSD) of peak absorbancies. All the samples were analysed in six replicates.

Chemometrics Analyses

The chemometrics analyses of principal component analysis (PCA) and hierarchical cluster analysis (HCA) were performed using Minitab Version 16.2.3 statistical software (Minitab Inc., State College, PA, USA). Prior to importing the dataset into the Minitab environment, the raw data were first pre-processed

Table 1: List of the lipstick samples used in this study.

Categories	Brands	Lipstick shade	Manufacture code	Reference code
Local	SilkyGirl	Foxy red	08	SK3
		Spicy marsala	10	SK5
	Sendayu Tinggi	Red desire	NA	ST2
		Red ruby	NA	ST3
	Simplysiti	Deep plum	LC15	SS2
		Chilli red	LC25	SS4
International	Avon	Berry-berry nice	1402	AV2
		Poppy love	1400	AV4
	NYX	Russian roulette	SR01	NYX2
		Seduction	SR05	NYX3
	Revlon	Really red	006	REV1
		Retro red	004	REV3

to compensate for run-to-run variations and to minimise the masking effect.

RESULTS

Repeatability and Reproducibility Studies

Peinifen 13 (reference code: P13) lipstick samples were used for repeatability and reproducibility studies. These studies aimed to evaluate the precision and robustness of the techniques used in this study. Figures 1 and 2 display the spectra obtained for the repeatability and reproducibility study, respectively. The figures have presented that the spectra of the P13 lipstick was overlapping one another and the calculated %RSD for both repeatability and reproducibility studies were less than 5%, indicating that the technique was robust.

Hierarchical Cluster Analysis (HCA)

HCA was performed to the spectra lipstick samples using the Euclidean distance and single linkage clustering strategy mechanism. The wavenumber region 1730 cm^{-1} – 1701 cm^{-1} was chosen and the outcome of HCA is presented in a dendrogram as shown in a Figure 3.

Principle Component Analysis (PCA)

Similar to HCA, the wavelength region of 1730 cm^{-1} – 1710 cm^{-1} was used for PCA analysis. The outcome is presented in a score plot and the final interpretation was made using the first two PCs; i.e. PC1 and PC2. In order to elucidate the outcomes, the clusters were manually circled and labelled as shown in Figure 4.

DISCUSSIONS

Hierarchical Cluster Analysis (HCA)

Wavenumber region 1730 cm^{-1} – 1701 cm^{-1} was chosen because it describe most of the variability concerning on the characteristics of samples hence allowing the samples to be discriminated from one another. As can be seen from the Figure 3, all the samples formed distinctive clusters. At similarity index approximately 87%,

Table 2: Parameter of ATR-FTIR Tensor 27 System

Item	Specifications
Software	OPUS 7.0 (20110823)
Resolution	4 cm^{-1}
Sample scan time	16
Background scan time	16
Range of wavenumber	4000 cm^{-1} – 600 cm^{-1}
Accessory	MIRacle, Diamond #141ADDF0

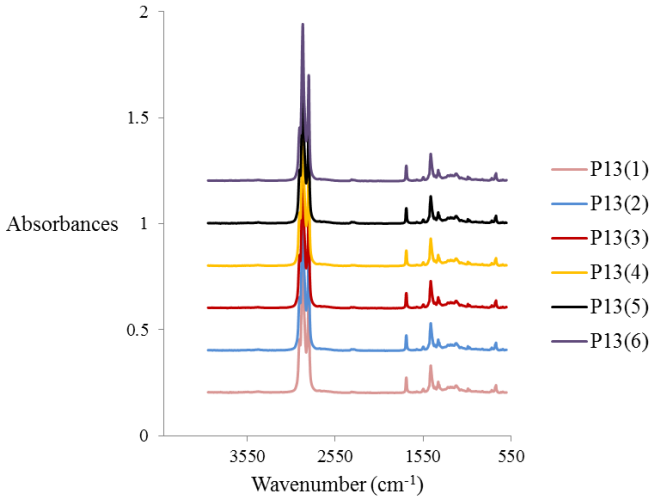

Figure 1: ATR - FTIR spectra for repeatability study

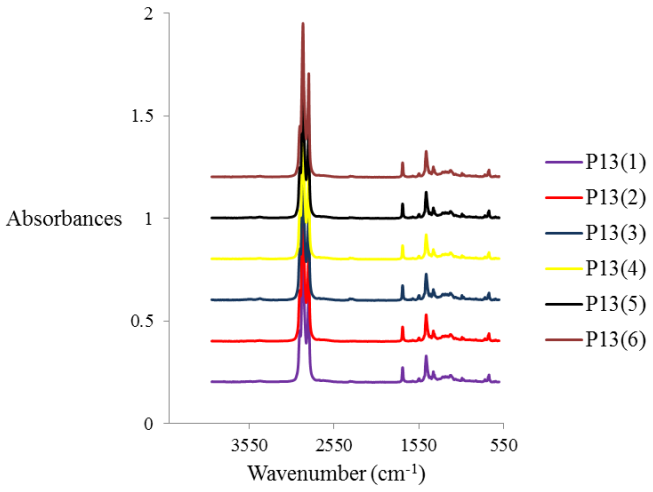

Figure 2: ATR – FTIR spectra for reproducibility study

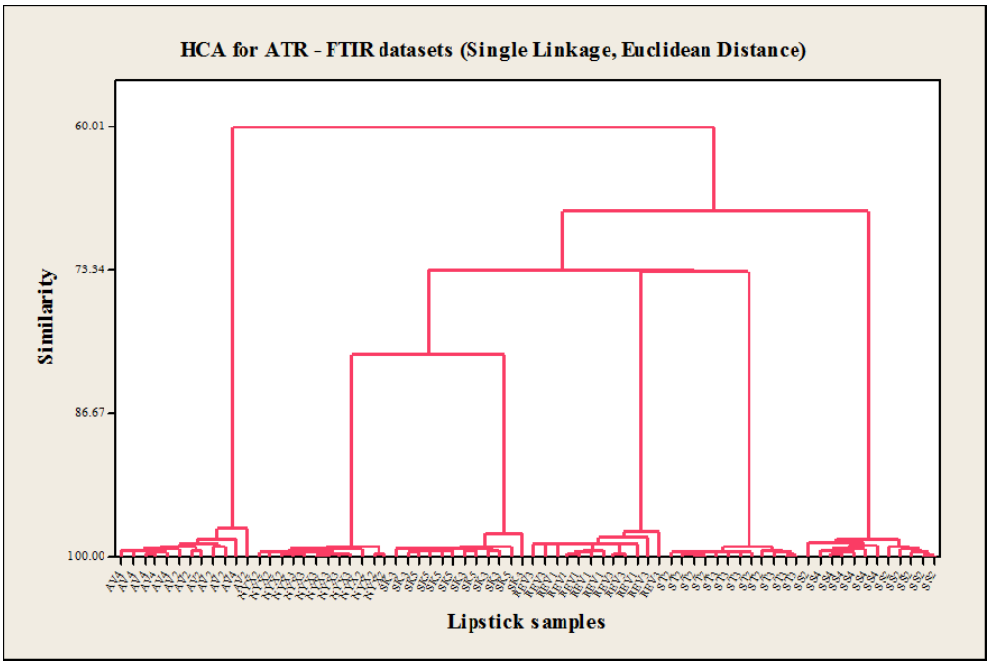

Figure 3: A dendrogram generated from the red lipsticks smeared dataset using Single Linkage and Euclidean Distance

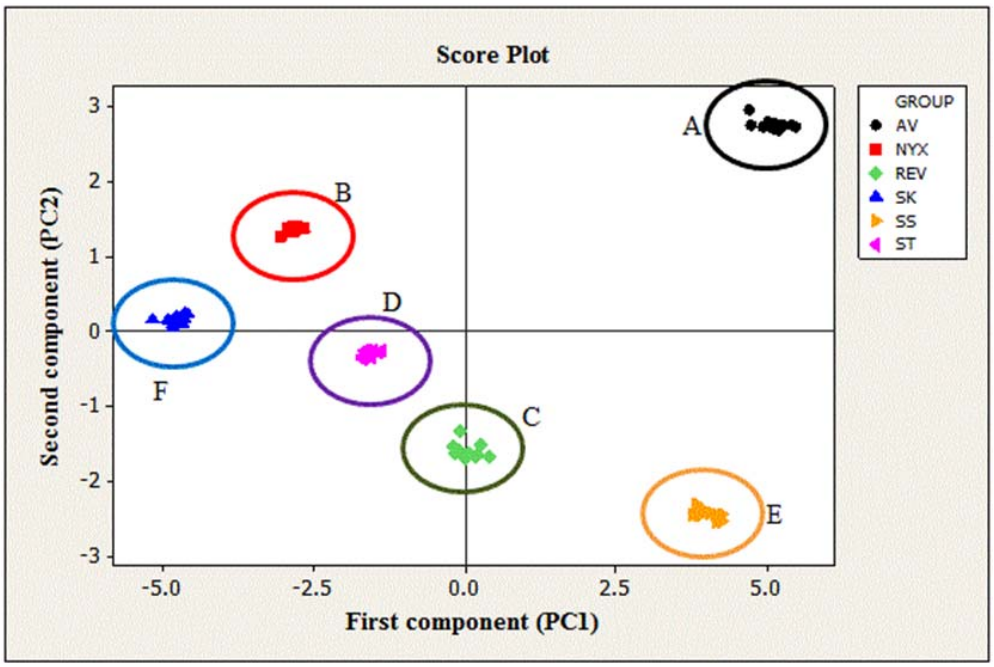

Figure 4: The principle component score plot for the lipstick samples

six clusters which were designated as cluster 1, 2, 3, 4, 5 and 6 (cluster 1: Avon, cluster 2: NYX, cluster 3: Silkygirl, cluster 4: Revlon, cluster 5: Sendayu Tinggi, cluster 6: Simplysiti) are evident in the dendrogram.

Principle Component Analysis (PCA)

The first principle component (PC1) accounted for 80% of the variation in the dataset. The second principle component (PC2) accounted for 19% of the variation in the dataset. Hence, the combination of these two PCs accounted for 99% variation in the dataset. As shown in the score plot, the lipstick smears are successfully classified into six distinctive clusters equivalent to the six different lipstick brands used in this study.

The six different clusters are labelled as cluster A (Avon), B (NYX), C (Revlon), D (Sendayu Tinggi), E (Simplysiti) and F (Silkygirl). These six distinctive

clusters have been separated very well. The separation could have been due to the different dyes formulation and composition in the lipstick samples used in this study.

CONCLUSION

The variations in lipstick colours arise from different combinations of dyes and pigments available in the market. Generally, lipsticks of different colours for examples red and brown can be readily discriminated between one another however it is not the case with lipsticks of similar colours and shades. The latter when discovered at crime scene poses a very challenging task to forensic scientists.

In this study, red lipsticks from local and international brands were studied using ATR - FTIR coupled with chemometrics techniques with the aim to differentiate them. The combination of ATR – FTIR coupled with PCA and HCA had successfully discriminated the lipstick samples into six distinctive clusters according to their brands. These chemometrics techniques give more objective outcomes (delivered by the score plot) compared to direct visual examinations of FTIR spectra alone. Hence, it shows that these approaches are powerful procedures in characterising and discriminating the lipsticks with different brands.

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