Forensic Analysis of Red Nail Polishes by FT-IR Microspectroscopy–A Preliminary Study

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Abstract

In the sexual assault, murder or other violence cases, nail polishes are a type of transfer evidence that can be commonly found at the crime scene [1-4]. The chemical analysis of nail fragments coated with nail polish, or other items with nail polish smear can offer useful information to assist in a crime reconstruction. The components of the nail polishes vary according to their brand, color and purpose of the products. FT-IR microspectroscopy offers a nondestructive method of trace evidence and uses in majority of forensic laboratories. In this study, 14 red nail polishes with 8 different brands were obtained and evaluated using FT-IR microspectroscopy. The results showed that 14 red nail polishes can be visually classified into 12 groups by infrared spectra with a discriminating power of 0.978. The results also showed a great potential for the discrimination of red nail polishes with a very similar-looking shades. Identifying the brand of the nail polish found as a trace at a crime scene, or even the exclusion of one or two brands is clearly a good choice. Thus, the infrared analysis of nail polishes can include the suspect(s) when link is established between the victim(s) or the crime scene.

Keywords: forensic science, nail polish, FT-IR Microspectroscopy, trace evidence

Introduction

Trace and transfer evidences such as drugs, explosives, fibers, paints, pigments, inks, gunshot residues and cosmetic can provide the link between the victims and suspects. By analyzing the trace evidences, forensic scientists can offer useful information to assist in crime reconstruction. Cosmetic products, including lipsticks, eye products, creams, cosmetics powders and nail polishes are widely used by women for beauty purposes. The trace of cosmetic products can provide a useful information in criminal investigation, particular in cases related to sexual and physical assault against women [1,2]. Nail polishes are coloring products used to protect and beautify the fingernail by women. When the fragment of the fingernail with nail polish was found in the crime scene, the analysis of nail polish can be useful to gain information about a suspect, victim at a crime scene, or to help linking individuals to other locations [2]. Although the actual composition of nail polishes varies between manufacturers, the majority of nail polishes have similar compositions. Most of the nail polishes are composed of

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15% film former (nitrocellulose, methacrylate polymers, vinyl polymers), 7% thermoplastic resin (formaldehyde, p-toluene sulfonamide, polyamide, acrylate, alkyd and vinyl resins), 7% plasticizers (dibutyl phthalate, dioctyl phthalate, tricresyl phosphate, camphor), 70% solvent (acetates, ketones, toluene, xylene, alcohols), 0-1% pigments (organic D&C pigments, inorganic pigment) and 1% specialty fillers (Guanine fish scale or titanium dioxide-coated mica flakes or bismuth oxychloride for iridescence) [2-8]. Basic components of nail polish have changed very little since its first introduction in 1920s, except for the use of polymers that increase the flexibility of the film over the nail to resist peeling and chipping [5]. Chemical characteristic of the nail polish may reveal not only the color but the brand, therefore increasing the chance to get information about the possible suspect related to the crime [7,8].

Forensic scientists prefer using nondestructive methods of analyzing of trace evidences rather than using destructive methods. FT-IR microspectroscopy is a vibrational spectroscopic technique used for the non-destructive identification of molecular species, including nail polish [9-12]. Nail polishes are complex mixture, and all the infrared-active ingredients of the formula are expected to contribute to IR spectra. It is hard to identify the single ingredient of the nail polish, because the IR signals came from one compound can be masked by other or may even overlap. FT-IR spectroscopy can confirm the presence of the specific functional group such as carbonyl, amide, nitro, aromatic, ketone, alcohol, acid, ester, and alkene group [12].

Previous researches had been used several techniques to discriminate the nail polishes. In 1992, Misra et al. showed that the energy-dispersive X-ray fluorescence (EDXRF) spectroscopy provided a most appropriate technique for the analysis of nail polishes to which elemental analysis can be applied. By comparing the ratio of the element Fe, Ti and Cu ratios in the samples of nail polishes, it can differentiate number similar-looking shades of nail polishes [3]. Shimamoto et al. used portable X-Ray fluorescence spectrometer to scan the filter paper had the nail polishes painting on it. By comparing the elements P, S, K Ca, Ti and Fe from the sample, they excluded Fe, K_α and K_β lines to perform the principal component analysis (PCA) due to iron oxides were used to produce brown pigment and the concentration of Fe was directly linked to the color of

the nail polish and these differences were easily observed without chemometrics. They had shown XRF is a great tool for discriminating nail polish when finding a trace of the nail polish on the wall or on paper, or even a piece of painted fingernail. The principal component analysis applied to XRF was able to group between 42 Brazilian nail polishes among 5 brands and showed Ca and Ti K_α lines as the most relevant ones to their study [4]. In Lopez-Lopez et al.'s research, 77 nail polishes were analyzed with confocal Raman spectroscopy using 532 nm and 780 nm laser wavelengths [7]. They concluded that longer laser wavelength (780 nm) was more appropriate for the analysis of nail polishes. The 532 nm laser wavelength may have a burning or fluorescence effect shown on the Raman spectra. Some Raman spectra of the nail polish sample showed the same spectra although they present different color or glitter particles. In this research only 64% of nail polish samples analyzed showed a characteristic spectrum. This can be due to the common presence of compounds in a high concentration of very Raman active that overwhelms the rest of the compounds signal. After visually comparing the nail polish appearance such as clear differences in color changes or glitter presence, the Raman spectroscopy increases the percentage of distinction up to 86%. In terms of nail polish evidence collecting methods, they used nail flakes by scraping the nail with a blade or acetone-soaked cotton swab by removing the nail polish from nail. The results showed that both types of evidence can be analyzed by Raman spectroscopy [7]. Chophi et al. conducted an experiment on 19 brands of nail polish with 73 different series using ATR-FTIR spectroscopy and chemometrics [8]. The spectrum of nail polish showed various functional groups, such as aliphatic amine, aliphatic and aromatic nitro groups of nitrocellulose, alcohol, acid and aromatic ester. The spectra obtained using ATR-FTIR have been successfully differentiated using PCA and Correlation Coefficient methods with discriminating powers of 99.5% and 99.3% respectively. Chophi et al.'s study showed ATR-FTIR technique in combination with statistical tool successfully differential almost all the sample. However, the evidential value of nail polish would depend on the circumstance of its finding. Because nail polishes are mass produced, and two or more nail polishes can have similar spectra. They suggested that it is required for analysis nail polishes using different techniques or a

combination of different techniques that can effectively discriminate all the samples [8].

In the present study, an attempt has been made to differentiate 14 red nail polishes of 8 different brands using Micro Compression Diamond Cell FT-IR microspectroscopy in transmittance mode. The uses of IR spectroscopy techniques are more appropriate to determine qualitative nail polish composition than quantitative one. Although ATR-FTIR showed great potential for characterizing nail polish, ATR technique was restricted to examine a layer or surface of nail polish samples. Because of the complexity of the nail polish formulation, ATR-FTIR may not reflect its actual composition [12]. In order to reveal more IR band and more intense band in the IR spectrum, we selected to use Micro Compression Diamond Cell in transmission mode in this study. Hopefully, the method here presented can narrow down the list of suspects when the nail polishes found in the crime scene.

Experimental

Fourteen red nail polishes were obtained from retail store in Taiwan. The list of nail polishes samples analyzed in this study is shown in Table 1. The infrared spectra were collected using a Nicolet Nexus 470 FT-IR spectrometer equipped with a Continuum IR microscope (Thermo Scientific Madison, WI, USA) with a mercury cadmium telluride detector was used to record the IR spectra of the samples. The nail polishes were applied on microscope slide and allowed to dry for 2 hours in Electronic moisture-proof box at 25°C. For each nail polish, three replicates were acquired. The specimen of the dry nail polish sample was obtained from the microscope slide by scraping nail with a blade. Then the sample was placed into the Micro compression diamond cell and put under the infrared microscope (Fig. 1). The samples were compressed in order to obtain a suitable thickness in the transmittance mode. In order to get a good signal to noise ratio, 512 scans were collected with a spectral resolution of 4 cm^{-1} and the frequency range was measured between 650 and 4000 cm^{-1} of the mid-IR region. Infrared data acquisition and data processing were achieved through Thermo Electron's OMNIC. SOFTWARE 7.2.
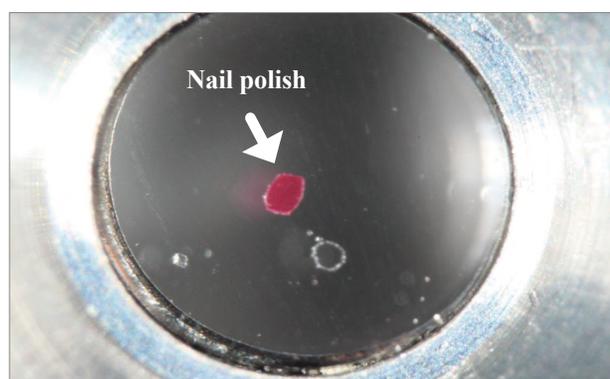

Fig. 1 Nail polish specimen on the diamond window.

Table 1 List of nail polish samples.

Sample no.	Brand	Product line	Serial no.
RS001	Revlon	Classic	680 Revoln Red
RS002	Revlon	Classic	280 Cherry Berry
RS003	Revlon	Top Speed	210 Jelly
RS004	Revlon	Top Speed	430 Chili
RS005	Bourjois	-	#25
RS006	Bourjois	-	#08
RS007	Bourjois	-	#11
RS008	Bourjois	-	#16
RS009	Vov	-	5561
RS010	Kate	-	KATE # RD 5
RS011	NYX	-	NP116
RS012	Canmake	-	C111616
RS013	Integrate	-	RD381
RS014	Missha	-	RD01

Results and Discussion

FT-IR microspectroscopy was used to obtain 14 red nail polishes from 8 different brands to differentiate compositions between different nail polishes. Nail polishes are made of different compounds according to their brands, product lines, colors and functions. Nitrocellulose is the popular ingredient that can be act as film forming agent in nail polish [5,6]. In this study, the infrared spectrum of nail polish is more likely indicative one of the main components, nitrocellulose. Nitrocellulose with a 82.81 quality index value was the top match when the nail polish spectrum was performed by OMNIC infrared library search. A typical spectrum of red nail polish is given in Fig. 2(A). The spectrum can classify into two regions: the first region is functional group (4000 cm^{-1}-1800 cm^{-1}) and the second region is fingerprint region (1800 cm^{-1}-700 cm^{-1}). Fig. 2(A) showed a board band at 3499 cm^{-1} corresponding to O-H stretching in alcohols and N-H stretching in amides. In the region 2970 cm^{-1} and 2098 cm^{-1} were contributed to CH_3 and CH_2 stretching in aliphatic hydrocarbon. The peak at 1725 cm^{-1} (C=O stretch) attributed to the presence of aromatic esters. The presence of nitrocellulose in the nail polish can be found at 1660 cm^{-1} (NO_2 asymmetric stretch). The peaks at 1603 cm^{-1} and 1584 cm^{-1} (C=C stretch) indicate the presence of aromatic compound. The peaks at 1454 cm^{-1} (CH_2 scissoring) and 1372 cm^{-1} (CH_3 symmetric bend) indicate the presence of aliphatic CH group. The peaks at 1320 cm^{-1} (C-O-H stretch), 1180 cm^{-1} (C-C-O stretch) and 1115 cm^{-1} (O-C-C stretch) may come from aromatic ester, alcohol, acid anhydride or from ketone. The peaks at 1284 cm^{-1} (NO_2 symmetric stretch) and 1072 cm^{-1} (C-O-C asymmetric stretch) indicate the nitrocellulose. The peak at 1030 cm^{-1} (C-O stretch) indicates esters. The peak at 845 cm^{-1} (NO_2 scissoring) indicate nitro group. The peaks at 749 cm^{-1} and 716 cm^{-1} (aromatic C-H wag) indicate aromatic compound [1,2,6,12]. Fig. 2 shows the comparison of two infrared spectra from the red nail polish in this study and nitrocellulose in the IR library. Characteristic infrared bands for nitrocellulose can be seen at 1660 cm^{-1} (NO_2 asymmetric stretch) , 1284 cm^{-1} (NO_2 symmetric stretch) , 1072 cm^{-1} (C-O-C asymmetric stretch) and 845 cm^{-1} (NO_2 scissoring) .
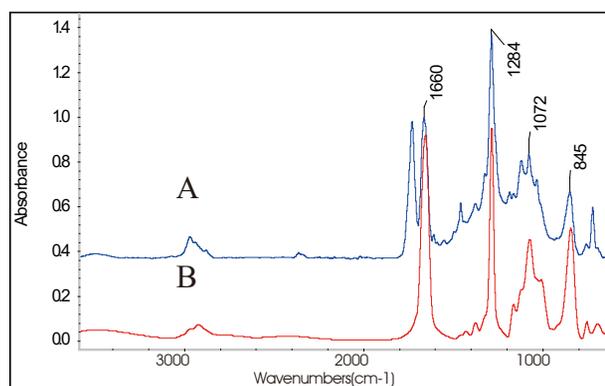

Fig. 2 IR spectra of nail polish and reference; (A) RS001 and (B) Nitrocellulose.

The visual image of red nail polishes analyzed in this study usually appeared a little different shade of red color under the light stereomicroscope (Fig. 3). Infrared spectra were obtained from three different positions of the same red nail polish specimen to test chemical homogeneity. The results showed that visual image of the nail polish under the microscope was not directly related the presence or absence of the IR peak, the spectra of red nail polish were identical at three different measure points. Fig. 4 showed identical spectral at three different points measured.

Fig. 3 The picture of RS001 nail polish painted on the microscope slide under stereomicroscope (40X magnification).
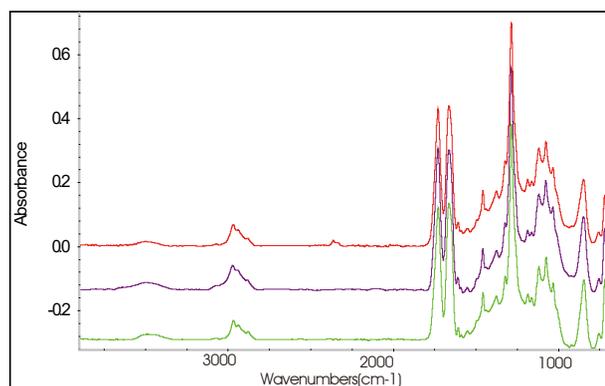

Fig. 4 IR spectra of three different points of RS001.

To study the effect of thickness applied on the finger-nail, we compared the IR spectra between applied one layer and two layers on the microscope slide. No visual difference in the nail polish spectra was observed as shown in Fig. 5. This result showed that the thickness of the nail polish applied on the nail cannot change the features of the IR spectrum.
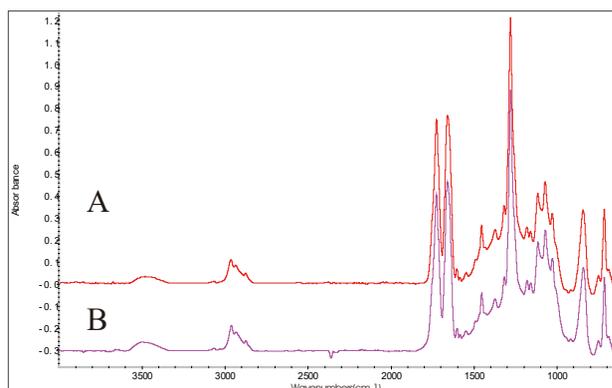

Fig. 5 IR spectra of RS001; (A) sample from two layers and (B) sample from one layer.

The IR spectra of all nail polish samples were visually compared to check the differences among their infrared spectra. Intra-brand trails were carried out by comparing different shade of red nail polishes from the same manu-facturer and same product line in different serial number. Sample RS001 and RS002 came from the same manu-facturer – Revlon and same product line – Classic. The serial number for RS001 is 680 and number for RS002 is 280 that represent different shade of red color. Base on their ingredients information showed on nail polish bottle, the major ingredients of these two samples were the same, but their pigments used were different. As shown in Fig. 6, the IR spectra showed no differences between sample RS001 (Revlon 680 Revlon red) and sample RS002 (Revlon 280 cherry berry). The same result was observed when we compared Top Speed 210 (RS003) to Top Speed 430 (RS004). Infrared spectra can-not discriminate among nail polishes with the same product line, even though they have different shade of color. The acquisition of identical IR spectra was not directly related with the color of the same nail production line, because the chemical components of the pigment was under 1% of the nail polish ingredient. FT-IR micr-ospectroscopy does not provide sensitive dete-ction of minor components concentration less than 5 percentage [13].
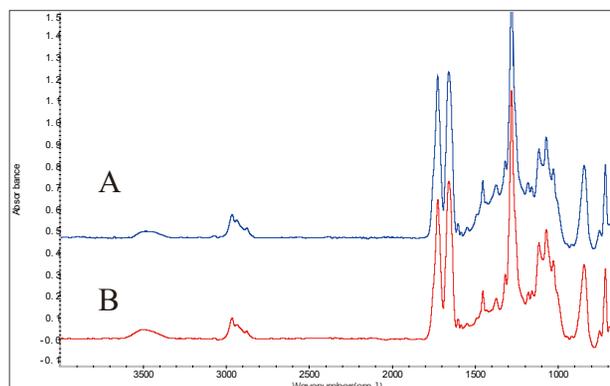

Fig. 6 IR spectra of nail polish; (A) RS001 and (B) RS 002.

In Fig. 7, we showed that infrared spectra of the same brand but two different product lines – Revlon Classic and Revlon Top Speed. These two different lines were de-signed for different sales purposes. Top Speed is specially designed for quick drying of nail polish. The absorption bands were different at 1603 cm^{-1} (C=C stretch), 1491 cm^{-1} (N=O stretch), 1453 cm^{-1} (CH2 scissor), 1321 cm^{-1} (C-O-H bend), 974 cm^{-1} (aromatic CH wag), 786 cm^{-1} (ring vibration) and 715 cm^{-1} (aromatic CH wag). This suggests that although nail polishes are from the same brand, different product lines may have different components of the nail polish for different purposes. FT-IR microspectroscopy could be used to discriminate between red nail polishes with similar color from the same brands but that belong to two different product lines.

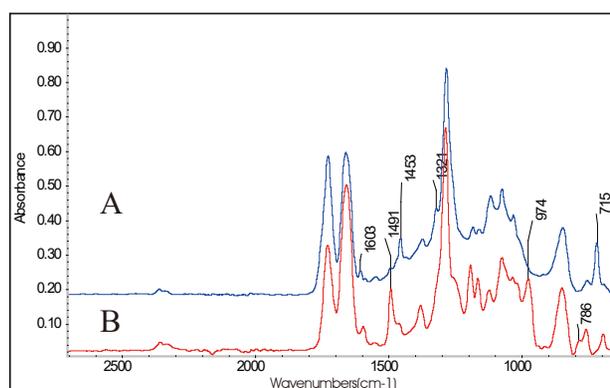**Fig. 7** IR spectra of nail polish; (A) RS001 and (B) RS 003.

Inter-brand comparisons were made different brands with visually similar red color. As shown in Fig. 8, the spectra typically have the same absorption band at 1725 cm^{-1} (C=O stretch) and 1660 cm^{-1} (NO$_2$ asymmetric stretch). However, it was possible to differentiate samples using absorption bands between 1660 cm^{-1} and 650 cm^{-1}.
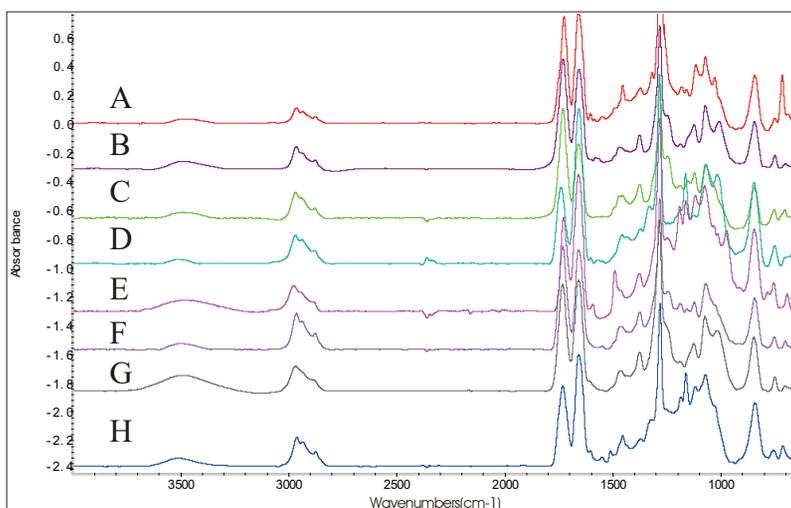
Fig. 8 IR spectra of 8 different nail polishes brands: (A) RS001, (B) RS005, (C) RS009, (D) RS010, (E) RS011, (F) RS012, (G) RS013, (H) RS014.

Systematic visual comparison of the 14 red nail polishes was performed on the Omnic software. Base on the presence or absence of infrared peaks as well as their frequency, and intensity, the 14 nail polishes can be first classified into four different groups between 1620 cm^{-1} and 1590 cm^{-1}, Group A was found absence of 1603 cm^{-1} (RS005, RS006, RS009, RS012), Group B was found shoulder at 1613cm^{-1} (RS007, RS008, RS013), Group C was found peak at 1603 cm^{-1} (RS001, RS002, RS010, RS014), and Group D was found peak at 1596 cm^{-1} (RS003, RS004, RS011). 1613cm^{-1}, 1603 cm^{-1} and 1596 cm^{-1} are C=C stretch indicate the presence of aromatic compound. Spectra were then examined within each group (Fig. 9). Subgroups were defined based on the peak presence or absence, peak position or peak height ratio to the most intense band. Visual analysis revealed peaks that were characteristic for appropriate groups. Fig. 10 shows a flow chart which summarized the results for the infrared analysis of the red nail polishes objectively base on the absence or presence of infrared peak. Majority of the infrared spectra could be discriminated while few samples, such as Group 8 (RS001 and RS002) and Group12 (RS003 and RS004) could not be differentiated. These nail polishes have the same brand (Revlon) and the same product line within their groups which made the spectra are indistinguishable.
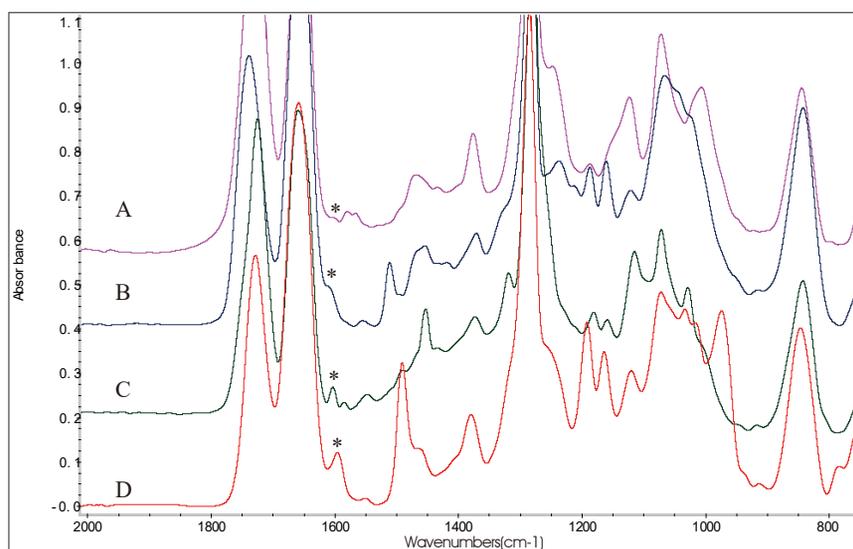

Fig. 9 IR spectra of (A) Group A: absence of 1613 cm^{-1} band, (B) Group B: shoulder at 1613cm^{-1}, (C) Group C: peak at 1603 cm^{-1}, and (D) Group D: peak at 1596 cm^{-1}.

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                          │  14 Red Nail Polishes │
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No peak at 1613,1603, 1596 cm⁻¹   1613 cm⁻¹   1603 cm⁻¹   1596 cm⁻¹

Group A
005、006、
009、012

Group B
007、008、013

Group C
001、002、
010、014

Group D
003、004、011

1066
1580, 1566 cm⁻¹

1511, 1237
1187, 1160 cm⁻¹

1584, 1453
1028, 715 cm⁻¹

1246, 1074 cm⁻¹

Yes   No   Yes   No   Yes   No   Yes   No

005   006,009,012   007,008   013   001,002   010,014   011   003,004

Group 1   **Group 5**   **Group 8**   **Group 11**   **Group 12**

1552 cm⁻¹   1555 cm⁻¹   1511, 713 cm⁻¹

Yes   No   Yes   No   Yes   No

006   009,012   007   008   014   010

Group 2   **Group 6**   **Group 7**   **Group 9**   **Group 10**

1188/1154 cm⁻¹
peak high ratio

0.6   2.8

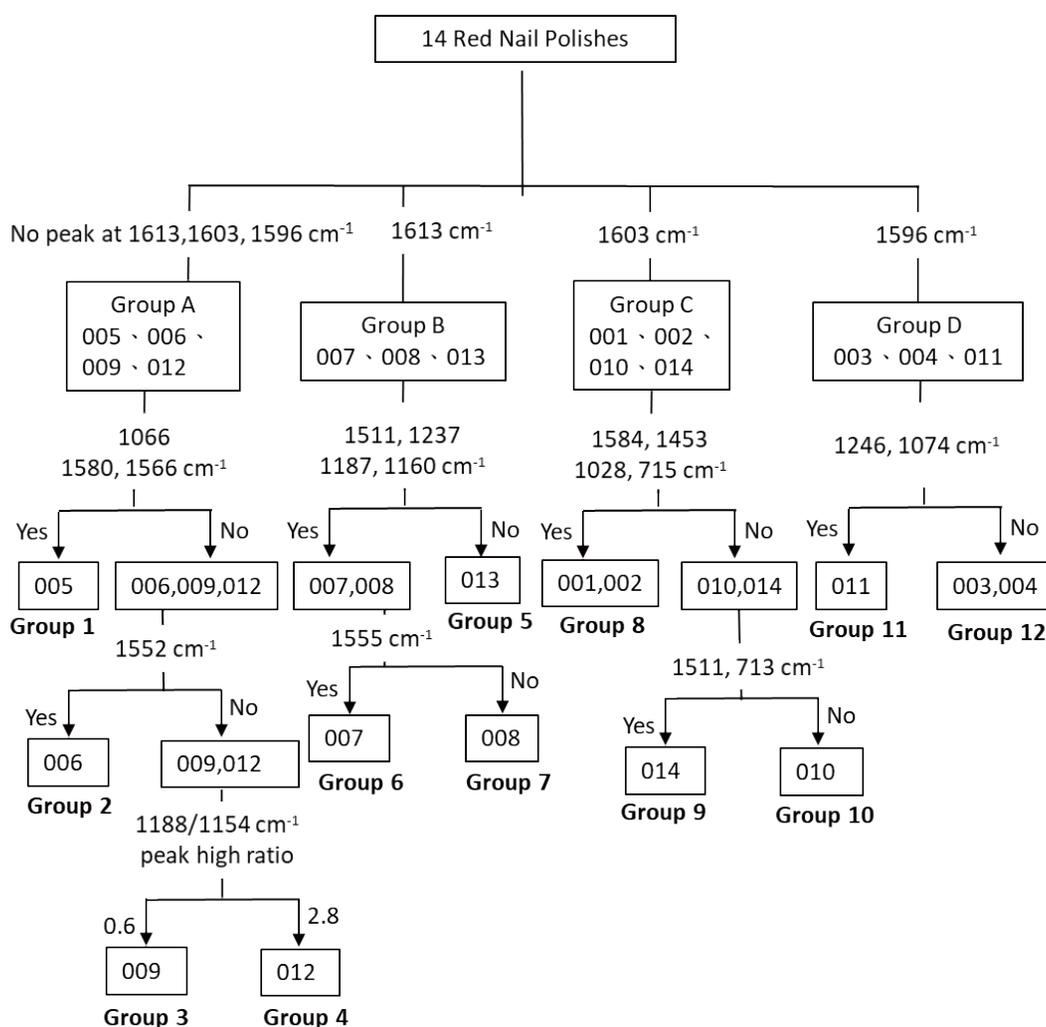009   012

Group 3   **Group 4**

Fig. 10 Visual classification flow chart of the14 red nail polishes.

The discriminating power (DP) for the 14 red nail polishes was calculated according to the method of Smalldon and Moffat [14],

where:

$$DP = \frac{\text{(Number of discriminated pairs)}}{\text{(Number of possible pairs)}}$$

14 nail polishes were able to be categorized into 12 groups, resulting 2 pairs of undifferentiated samples. Based on these finding, a discrimination power of 0.978 was calculated. If the sample are indistinguishable that belong to the same group (RS001 and RS002; RS003 and RS004) the individual discrimination can be achieved by Raman microspectroscopy. In the following study, the Raman spectra make a certain distinction between RS001 and RS002, also can be differentiate between RS003

and RS004. If the supplementsry technique such as Raman microspectroscopy can be performed after FT-IR microspectroscopy, the 14 red nail polishes can be classified into 14 groups. The discriminating power of the red nail polishes can be improved from 0.978 to 1.00 when both techniques FT-IR and Raman microspectroscopy were used in this study. According to the comments of the article by Fikiet et al., infrared spectroscopy is used to distinguish the resin types of paint samples, while Raman spectroscopy is used to distinguish similar colors of paints [15]. FT-IR and Raman microspectroscopy are complementary spectroscopic techniques for forensic science. The use of chemometric methods, such as Principal Component Analysis or Cluster Analysis was not applied in this study. In this study, the results showed that a very good discriminating power can be obtained

by visually comparing infrared spectra. If the brand or color of the nail polish sample is increased in future research, chemometric method should be applied in order to facilitate discrimination and provide more extensive analysis of the obtained data. PCA is a very-useful multivariate statical method for demonstrating the relationships between analyzed samples. However, the determination of the optimal number of components that should be chosen is a crucial step. Inappropriate estimation of Principal components could lead to loss of information. By using Scree test, Kaiser's stopping rule and the percentage of cumulative variance, principal components are still a very useful tool for demonstrating the relationship between analyzed samples [16].

Conclusions

Finding the trace evidence in the crime scene is an important task for forensic scientists. There are many types of trace evidence, such as fibers, hair, paint and cosmetic. Nail polish is one of the cosmetic evidence. Vibrational spectroscopy has been used to analyze many evidences in forensic laboratory since 1980s [13]. Therefore, we used Fourier transform infrared microspectroscopy with a diamond cell in transmission mode to analyze 14 red nail polish samples with different brands. The results showed that 14 similarly red colored nail polishes with different brands can be visually classified into 12 groups by FT-IR microspectroscopy with a discriminating power of 0.978. The use of FT-IR microspectroscopy to differentiate the same color shade or differentiate brands is practical and successful in this study. However, the discrimination can still be improved by combining with Raman microspectroscopy in the further study. A combination of instrumental techniques is typically needed to reach a high discriminating power for forensic identification and comparison.

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