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## Forensic Differentiation of Black Shoe Polish Stains using Attenuated Total Reflection - Fourier Transform Infrared Spectroscopy and Chemometrics

التمييز الجنائي لبقع تلميع الأحذية السوداء باستخدام الانعكاس الكلي المخفض - تحويل فورييه الطيفي بالأشعة تحت الحمراء والقياسات الكيميائية



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### Abstract

Shoe polish smears or stains are encountered as evidentiary material on a variety of substrates, particularly in cases related to sexual and physical assault, murder, theft, and robbery. This trace evidence can be used as proof of contact to narrow down the search in a criminal investigation. The identification and differentiation of samples with similar composition and the same hue can be a difficult task for the investigator.

In the present work, the scope of Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy for discriminating shoe polish samples of 15 different brands is investigated in combination with chemometric tools that is principal component analysis. The discriminating power of visual analysis is 99.04 %, while in principal component analysis it is 98.09 %, which is highly significant. The blind test is carried out with unknown samples to the analyst, to predict their respective sample source. Intra-brand variation, homogeneity and the effect of different substrates on sample analysis are also studied. The reported method provides considerable results for the identification and differentiation of shoe polish samples of different brands. The stains on substrates could be identified and linked to their parent source as well.

### المستخلص

يتم مصادفة وجود مسحات تلميع الأحذية أو البقع كأدلة إثبات على مجموعة متنوعة من السطوح وخاصة في الحالات المتعلقة بالاعتداء الجنسي والجسدي والقتل والسرقة وحالات السطو. ويمكن استخدام دليل التتبع هذا كدليل على التلامس، وذلك لتضييق نطاق البحث في التحقيقات الجنائية. ويمكن أن يكون تحديد وتمييز العينات ذات البنية التركيبية المماثلة وتدرج اللون نفسه مهمة صعبة على المحقق.

في العمل الحالي، تم عمل إجراء فحص بواسطة الانعكاس الكلي المخفض - تحويل فورييه بالأشعة تحت الحمراء لتمييز عينات تلميع الأحذية من 15 علامة تجارية مختلفة، مع استخدام أدوات القياس الكيميائي. تبلغ القوة التمييزية للتحليل البصري 99.04%، بينما في التحليل الأساسي للمكونات 98.09%، وهو أمر مهم للغاية. تم إجراء الاختبار مع التعمية على عينات غير معروفة للمحلل، للتنبؤ بمصدر العينة. كما تمت دراسة تباين العلامات التجارية الداخلية، والتجانس، وتأثير الأسطح المختلفة على تحليل العينات.

توفر الطريقة التي تم فحصها في هذه الدراسة نتائج معتبرة لتحديد وتمييز عينات تلميع الأحذية من علامات تجارية مختلفة. ويمكن التعرف على البقع الموجودة على الأسطح وربطها بمصدرها الأصلي كذلك.

**Keywords:** Forensic Sciences, Trace Evidence, Shoe Polish Stains, Fourier Transform Infrared Spectroscopy, Chemometrics.

الكلمات المفتاحية: علوم الأدلة الجنائية، الآثار المادية، بقع تلميع الأحذية، تحليل الطيفي فورييه، القياسات الكيميائية.



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## 1. Introduction

To identify and establish the source of trace evidence is one of the most important tasks in forensic investigation. It can be useful to establish a link between the suspect, victim and the crime scene. There are various types of evidence recovered from the crime scene, and shoe polish is one such important trace evidence. As per Locard's exchange principle, "every contact leaves a trace", substances containing wax and oils can be easily transferred from one substrate to another. As awareness of methods of committing crime has increased among criminals, it is important to develop new methods to identify the trace evidence recovered from the crime scene. Trace evidences also hold an important corroborative position in a court of law, as they are often left undisturbed at a crime scene because of their diminutive and inconspicuous nature.

Shoe polish, along with other wax-based products, can get easily transferred to the clothing of a victim and suspect and thus serve as an important corroborative evidence. It can be encountered in physical and sexual assault cases such as murder, rape, physical violence, theft, and robbery in the form of stains on a variety of substrates [1,2]. These stains can be used as proof of contact limiting the massive number of suspects. Sometimes it can also be used as a writing instrument to write anonymous letters, threatening remarks, and suicide notes on unusual surfaces. In such cases, the authorship of document is in question, which is often hard to establish especially when written on unusual surfaces with unusual writing instruments. Indirect authorship in such cases, can be established by linking this trace material with its source origin [3].

Shoe polish is composed of dyes, pigments, fats, and oils [4]. The dyes and pigments vary greatly depending upon the colour of the shoe polish. However, among shoe polish of the same colour and different brands the difference is so minute that it is difficult to differentiate just on the basis of visual examination. Different techniques have been reported to analyze shoe polish stains such as microscopic examination, TLC (Thin Layer Chromatography) [5,6], GC-MS (Gas Chromatography-Mass Spectrometry) [4,5,7,8] and UV/Visible Spectroscopy [7,9]. Various characteristics have been observed in previous studies such as volatile components, dye solubility, visible region absorption spectra, pigment particle size, and color [4]. Correct identification of shoe polish is also influenced by the age of the stain. The effect of aging from room temperature rising to 56°C and withering at different environmental conditions has been examined by TLC, UV/Visible spectroscopy and GC [7]. In recent

studies, Raman and Surface-Enhanced Raman Spectroscopy (SERS) have also been used for the analysis and identification of shoe polish dyes [10]. Recently, a hold-up case was reported in which trace material was found on the jacket of the person reported to have been pushed by the offender. The trace material was analyzed by a sequence of analytical methods like stereomicroscope, microscopic examination, and infrared spectroscopy. It was observed that successful differentiation of shoe polish can be achieved based on component analysis of dyes and pigment, even without any sample extraction [11].

Due to the transferable nature of this evidence, it is important to use non-destructive, sensitive, reliable and quick methods. To the best of author's knowledge, no prior studies are available where Attenuated Total Reflection - Fourier Transform Infrared (ATR-FTIR) Spectroscopy has been applied for the analysis of shoe polish samples. The main advantage of ATR-FTIR spectroscopy is that the samples are not destroyed during analysis and thus the samples can be used for any further examination, and no prior sample preparation is required. FT-IR spectroscopy has been commonly used and demonstrated as a diagnostic tool within the biomedicine field [12–18]. In the field of forensic science, this technique has been used to identify fibers [19], hair [20,21], banknotes [22], paints [23], gunshot residues [24], inks [25–28], drugs and their derivatives [29], body fluids [30–34], cosmetics [3,35,36], and illicit liquors [37]. Keeping in view the importance of ATR FT-IR spectroscopy, the present research has been conducted to differentiate black shoe polish samples of 15 different brands. Principal component analysis (PCA) has been applied to achieve discrimination and to analyze data more objectively.

## 2. Materials and Methods

### 2.1. Sample collection

Total ( $n=45$ ) samples of fifteen different brands (3 sample of each brand) of black shoe polish samples were collected from local markets in Punjab and Delhi from cobblers. Table-1 indicates the details regarding samples collected for the present study.

### 2.2. Sample preparation

Each of the selected shoe polish sample was analyzed in the neat form by placing a direct smear (approximately 1.5 mg) on the ATR crystal surface with air background. To study the effect of substrates on the analysis of shoe polish, simulated samples were prepared on commonly encountered substrates such as white cotton, denim, polyester, leather, and canvas. Analysis was done by smudg-



ing samples on substrates, which were left undisturbed for 24 hours at room temperature ( $25\pm 5^\circ\text{C}$ ). In each case, blank substrate was run as a background and shoe polish residue on the same surface was analyzed as a sample, and the subtraction was done in the whole mid infrared range of  $4000\text{--}600\text{ cm}^{-1}$ . A new background measurement was done prior to the analysis of each new sample. The ATR crystal was cleaned with pre-wetted ATR cleaning tissues (part no. 1008033), containing deionized water and isopropyl alcohol before analyzing each sample in order to avoid cross-contamination. Fifteen samples (16-30) were selected for the blind test. These samples were pretended to be unknown for the analyst and their actual identity was not revealed until the predictions were completed.

Reproducibility was checked by analyzing three replicates of each selected shoe polish sample. Homogeneity test was performed on all the shoe polishes by analyzing the same sample from different points to study homogeneous distribution of components within samples. To investigate the intra-brand variation, 3 different samples of all brands were collected and analyzed.

### 2.3. Instrumentation

The experiments were carried out using a Bruker Alpha eco-ATR FT-IR spectrometer with a Small Orbit, ZnSe crystal accessory, and OPUS (v 7.2) software equipped with an air-cooled deuterated tri-glycine sulfate (DTGS) detector. All samples were scanned at  $4\text{ cm}^{-1}$  resolution within the mid-infrared (MIR) range of  $4000\text{ to }600\text{ cm}^{-1}$ . Reproducibility was checked by analyzing three replicates of each sample. The spectra were pre-processed using baseline offset and linear baseline correction, smoothing by Savitzky-Golay algorithm with 2 polynomial order and 11 smoothing points in a symmetric kernel, and area normalization. The measurements were obtained in absorbance units. PCA was applied by using the Unscrambler X (Version 10.5.1 (64 bit) CAMO Software AS, Oslo, Norway) [38] software on the infrared spectroscopic data. Data was imported in opus format.

### 2.4. Multivariate data analysis - Principal Component Analysis (PCA)

Principal Component Analysis (PCA) is a mathematical operation and a variable reduction technique used to identify the significant differences and similarities within score plots to discriminate or to classify the samples. It is a very useful technique for analyzing large data sets and data compression. It is used when variables are highly correlated. It identifies the original clusters in the data set with the first principal component, which expresses the

major amount of variation followed by the second principal component, which indicates the second most important factor of the remaining analysis and so forth [39–41].

### 2.5. Discrimination Power

Smalldon and Moffat defined Discrimination power as [42]

$$DP = \frac{\text{Total no. of discriminating pair of samples}}{\text{Total no. of possible pair of samples}} \times 100$$

$$\text{Total number of possible sample pairs (n)} = \frac{n(n-1)}{2}$$

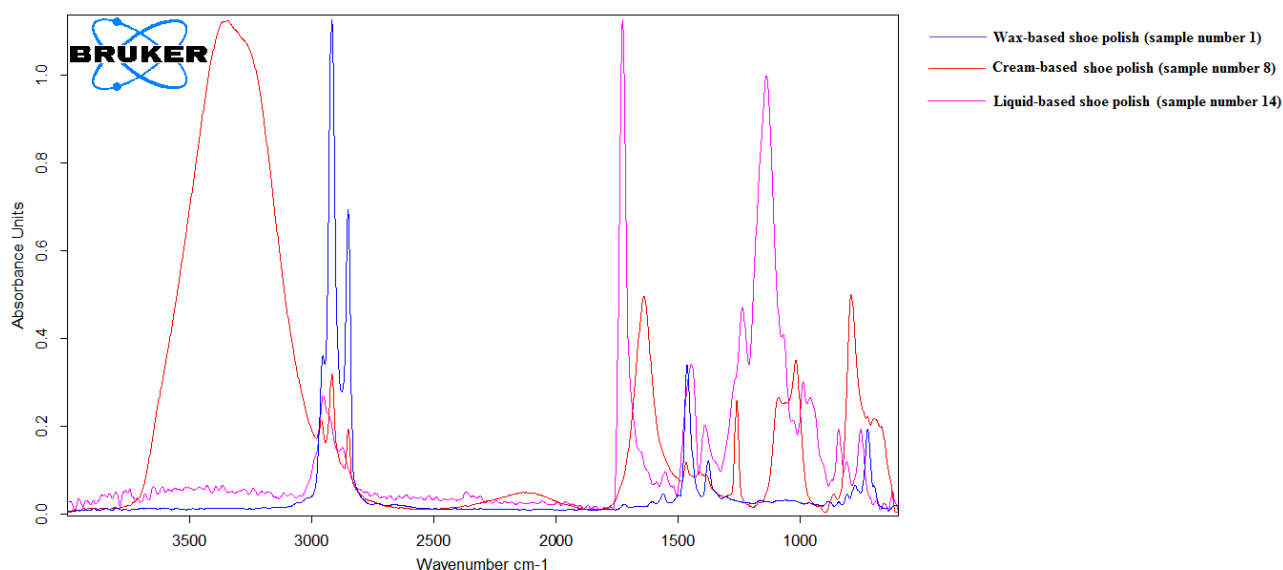
Where,  $n$  is the total number of samples

## 3. Results and Discussion

Shoe polish samples were analyzed using ATR FT-IR spectroscopy to determine the vibrational spectrum of components in the mid infrared region of the electromagnetic spectrum. The discrimination of the samples was performed by visual inspection and by using the PCA method. The spectra were obtained from  $4000\text{ to }600\text{ cm}^{-1}$  range with a resolution of  $4\text{ cm}^{-1}$ . The signal was the average of 24 scans. Homogeneity, intra-brand variation, and reproducibility tests were performed, and through analysis, it was found that the samples were homogenous and that there is no compositional difference between various shoe polish samples of the same brand. The obtained spectra of these samples completely overlapped and was characterized by excellent repeatability and homogeneity.

A visual comparison was made on the basis of position and shape of the peak on all the analyzed and processed spectra. Figure-1 represents the overlaid ATR FT-IR spectrum of wax, cream, and liquid-based shoe polish. The peak composition data were obtained from the available literature [3,35,43]. A further difference between samples was also studied in the fingerprint region below  $2000\text{ cm}^{-1}$ . According to the data generated by ATR FT-IR spectroscopy, the peak positioned at approximately  $3354\text{ cm}^{-1}$  corresponds to O–H stretch in alcohols and N–H stretch in amides. A large distribution of sharp and most intense peaks positioned at approximately  $2916\text{ cm}^{-1}$  corresponds to asymmetric C–H stretching and at  $2848\text{ cm}^{-1}$  attributed to symmetric C–H stretching. A peak positioned at approximately  $2119\text{ cm}^{-1}$  in the range of  $2100\text{--}2140\text{ cm}^{-1}$  belongs to C–C stretching, and so on. Table-2 indicates the ATR FT-IR peak component identification for spectral interpretation.





**Figure 1-** Representative ATR FT-IR spectrum of wax, cream and liquid based shoe polish sample.

### 3.1. Visual discrimination of spectra

Discrimination between each shoe polish spectra was preliminary performed by qualitative analysis based on the presence or absence of a peak. On visual inspection, all spectra could be discriminated from each other except one sample pair [sample number 4 and 11]. Table-3 shows the detailed qualitative information regarding the presence of peaks at various ranges of wavenumbers. The discrimination power of this method was calculated to be 99.04 %.

This type of analysis produces good results for the discrimination of a lesser number of samples, while an increase in sample number increases the chances of error, and the comparison between spectra becomes tedious and time consuming. Therefore, in order to overcome limitations of visual comparison, a chemometric analysis was employed to ensure objective interpretation of results, and to reduce the chances of manual errors.

### 3.2. Differentiation of selected black shoe polish sample using PCA

Further discrimination of all selected shoe polish samples was performed using the PCA method. To determine sample adequacy and ensure the application of PCA is appropriate, various pre-requisite tests such as Bartlett's sphericity test and Kaiser-Meyer-Olkin (KMO) tests were performed. The value of KMO test must be greater than 0.5, and Bartlett's test of sphericity should

be less than 0.05. Table-4 shows the values of KMO test and Bartlett's test. The obtained value of KMO test was 0.875. In Bartlett's test, the significance value is 0.000.

Therefore, in the present study the application of PCA was found to be suitable. The number of principal components to be considered was carried out using Kaiser Criterion test (scree test). Based on the scree plot, only two components were selected as the line steps beyond component 2. Sufficient information was provided based on these two components. Approximately 97% of the total variance was observed in the obtained spectra for the first (86%) and second (11%) principal components. A two-dimensional PCA scatter plot was generated, as it makes the visual analyses easier.

In order to discriminate spectra of shoe polish from each other, a PCA scatter plot with loading values of all possible PC sets was evaluated, for example, PC1 and PC2, PC2 and PC3, and PC1 and PC3, as shown in Figure-2, Figure-3, and Figure-4, respectively. The best discrimination was observed in PC1 vs. PC3 scatter plot, as shown in Figure-4.

These findings suggest that most of the analyzed samples can be successfully distinguished (Figure-4). Only two sample pairs (8 and 10; 1 and 3) out of 105 sample pairs were placed relatively closer to each other and remained difficult to distinguish. The closeness of samples on the scatter plot gave an idea about the similar compositional makeup of the samples. The obtained results con-

**Table 1-** Details of analyzed black shoe polish samples.

S.No./ Sample code	Sample Name	Product Type	Color	Manufacturer	Number of samples
1	Char-may Mil- lenium	Wax	Black	Char-May Millenium Shoe Polish Co. New Del- hi-110041	03
2	Charmy Extra Shine	Wax	Black	Charmy Industries E-134, Sector-3, D.s.i.d.c Bhawana Delhi - 110039	03
3	Cherry BLOSSOM	Wax	Black	Vill. Nandpur, P.o. Lodi Majra, Nalagarh, So- lan-173205 H.p.	03
4	KIWI	Wax	Black	Tide Industries, 231, Pratappura, Holol, Gu- jrat-389350	03
5	ROBIN BOOT Polish	Wax	Black	Basti Nau, Jalandhar 144002	03
6	Royal	Wax	Black	Santosh Chemicals Co. New Delhi-110064	03
7	Venom	Cream	Black	Black Stone Xim Services Pvt. Ltd. 358c Udyog Ken- dra 1, Ecotec 3, Greater Noida (U.p) 201306	03
8	Helios	Cream	Black	Black Stone Xim Services Pvt. Ltd. 358c Udyog Ken- dra 1, Ecotec 3, Greater Noida (U.p) 201306	03
9	Dazlo	Wax	Black	Waterloo Products Co. 15a/16, Damodar Park, Delhi-95	03
10	Pro-Color	Cream	Black	M. V. Shoe Care Pvt. Ltd. B-32, Sector 6, Noida- 201301,Up, India	03
11	Taj Mahal	Wax	Black	Tajmahal Polish Co. Pin No. 251002 (U.p)	03
12	Classic	Wax	Black	Santosh Chemical Cp. New Delhi – 110064	03
13	Kiwi	Liquid	Black	Sai Corporation, Khasra No. 353/196/186/1-2, Village - Joharon, Trilokpur Road, Kala-Amb, Distt. Sirmour (Hp) – 173030	03
14	Helios	Liquid	Black	C. P. Marketing Inc. A-65, Swarn Park Inds. Area, Phase-1, Mundka, Delhi-41	03
15	Cherry blossom	Liquid	Black	Paramount Polish Processors Pvt. Ltd. 102, Thaper Arcade, 47 Kalu Sarai, New Del- hi-110016	03





**Table 2-** ATR FT-IR peak component identification for spectral interpretation.

Observed Peak (cm <sup>-1</sup> )	Frequency Area (cm <sup>-1</sup> )	Types of Vibrations
1735.90	1750-1700	CO absorption in cyclic amides, ester bonds and aromatic compounds
1640.42	1680-1620	C=C stretches in alkenes and CO stretches in amides, (ketones, esters), polyethylene glycol
1513.03	1550-1510	NH deformation in secondary amides
1463.18	1450±20	CH deformation in asymmetrical alkanes, aromatic compounds, paraffin compound
1376.2	1350±50	OH bend in alcohols and phenols and CN stretch in primary amides, paraffin compounds, aliphatic compounds, mica
1278.5	~1270	CN stretch in secondary amides
802.33	840-790	CH deformation in tri-substituted alkenes
720.71	750-690	NH bending in amides
666.47	700-650	CH deformation in alkynes, paraffin compounds, aromatic compounds

firmed that the collected black shoe polish samples are more similar to each other based on their formulations that are wax, liquid, and cream-based. Figure-5 showed the combined loading plot of PC1 and PC2. It can be further divided into three regions, based on the correlation between PC1 and PC2. Region 1 (3650-2950 cm<sup>-1</sup>) is due to the O-H stretch in alcohols and N-H stretch in amides, where both PC1 and PC2 show negative correlation; Region 2 (2950-2800 cm<sup>-1</sup>) is attributed to symmetric and asymmetric C-H stretching, where PC1 shows positive correlation, and PC2 shows negative correlation; Region 3 (1700-600 cm<sup>-1</sup>) is due to C=O, and C-H stretching, where PC1 and PC2 both show positive correlation. The discriminating power of the PCA method was 98.09%, which is highly significant.

To cross-validate the model, 15 unknown samples

(16-30) were collected and analyzed. All samples were selected from already available shoe polish samples. The identities of these samples were concealed from the analyst until the predictions were made. To get the clear distinction between samples of wax-based samples of shoe polish lying in the positive axis of PC1 and the positive and negative axis of PC2, zoom in function/option was utilized [Figure-6(B)].

On analysis, it was observed that unknown samples number 16, 17, 18, 20, 21, 22, 23, 24, 25, 26, 27, 28, and 29 were completely overlapped or nearby with already existing samples thus belong to 11, 10, 1, 13, 14, 15, 2, 24, 25, 5, 6, 7, and 8, respectively. Sample number 19 and 30 were observed to lie at a distant position on the score plot from their source samples Figure-6). The accuracy for the blind validation test was found to be 86.6%.



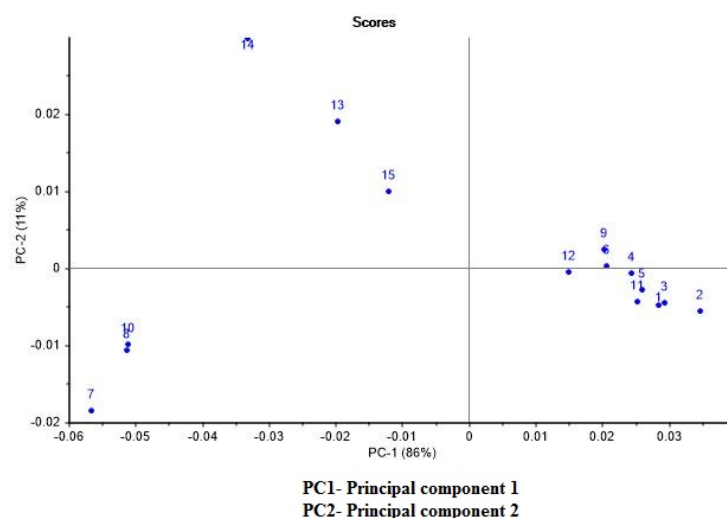
**Table 3-** Qualitative analysis of shoe polish samples. Symbol (□) represents the presence of a particular peak at a particular wavenumber range ( $\text{cm}^{-1}$ ). Extra peaks of samples are given in extra peaks column.

Samples	Wavenumber range ( $\text{cm}^{-1}$ )					Extra peaks
	1700-1600	1500-1400	1400-1300	1100-1000	800-700	
1		□	□		□	698
2		□	□		□	1737, 1171
3	□	□	□		□	1735, 1575, 1539
4		□	□		□	1736, 1712, 1171
5		□	□		□	—
6		□	□		□	806, 698
7	□			□	□	—
8	□			□	□	1260
9	□	□	□	□	□	1260, 811
10	□	□			□	—
11		□	□		□	1736, 1712, 1171
12		□	□		□	—
13	□	□	□	□	□	1729, 1598, 1110, 698
14		□	□		□	1725, 1142, 1553, 1238, 988, 962, 841, 806
15		□	□	□	□	1733, 1246, 1167, 1115

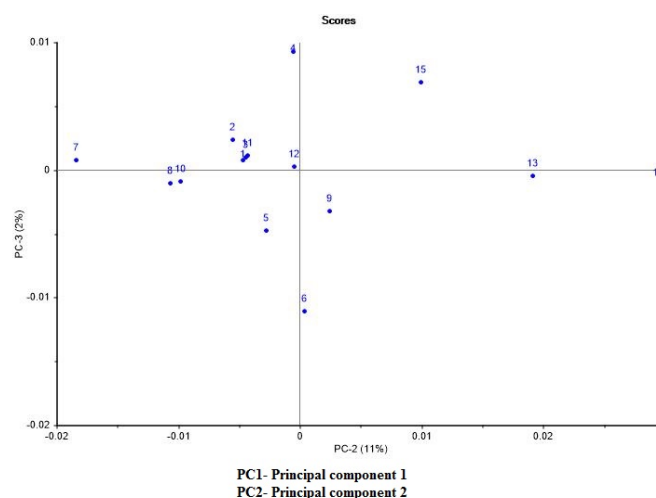
**Table 4-** Values of Kaiser-Meyer-Olkin (KMO) and Bartlett's Test.

Samples	Extra peaks
Kaiser-Meyer-Olkin (Measure of Sampling Adequacy).	0.875
Bartlett's Test of Sphericity	Approx. Chi-Square Df Sig.
	295868.574 465 0.000





**Figure 2-** A two - dimensional PCA score plot to discriminate different brands of black shoe polish samples using PC1 vs. PC2.



**Figure 3-** A two - dimensional PCA score plot to discriminate different brands of black shoe polish samples using PC2 vs. PC3.

#### 4. Analysis of black shoe polish traces on various substrates

During criminal investigations, traces of shoe polish samples may be recovered from various cloth substrates such as white cotton, denim, canvas, leather, and polyester. Therefore, the effect of the substrate's interference during sample analysis was also studied. Additional bands were observed in the spectra due to the substrates in the case of polyester and leather, but peaks related to the samples were still found. However, a comparison can be done between spectrum obtained from samples on various substrates and an in-built library of neat shoe polish samples, especially in the fingerprint region, which enables successful identification and differentiation of shoe polish samples.

#### 5. Conclusions

In the present research work, the application of ATR FT-IR spectroscopy and chemometrics to discriminate different brands of black shoe polish samples was found to be highly accurate, reproducible, effective, and robust. ATR FT-IR spectroscopy is able to differentiate each shoe polish sample from one another by unique, dominant peaks being present or absent in the spectra. On the basis of visual examination of different spectra, a discriminating power of 99.04% was obtained. Whilst using PCA, the discriminating power of 98.09% was obtained, which is highly significant. Additionally, a preliminary study was also conducted by analyzing shoe polish stains on various substrates to simulate actual case





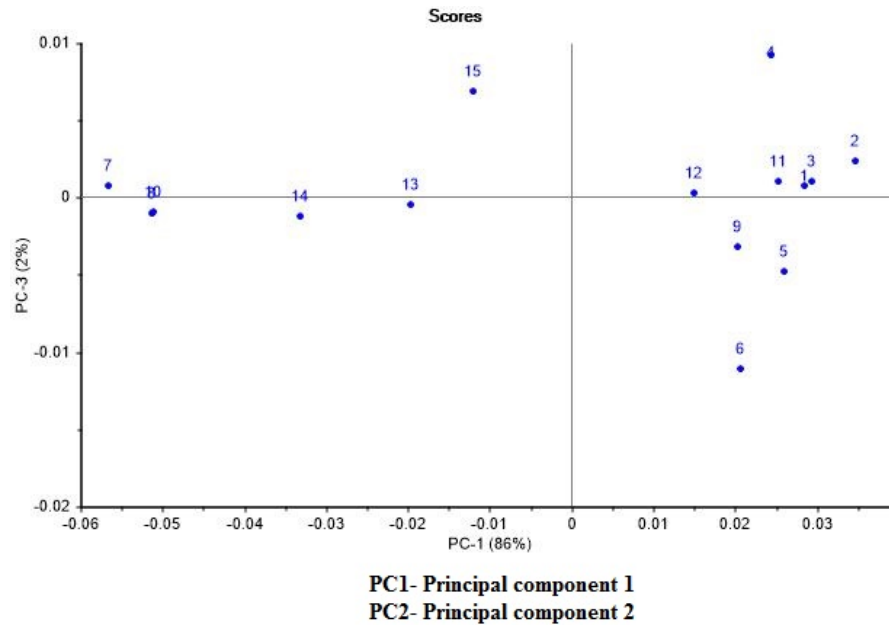


Figure 4- A two - dimensional PCA score plot to discriminate different brands of black shoe polish samples using PC1 vs. PC3.

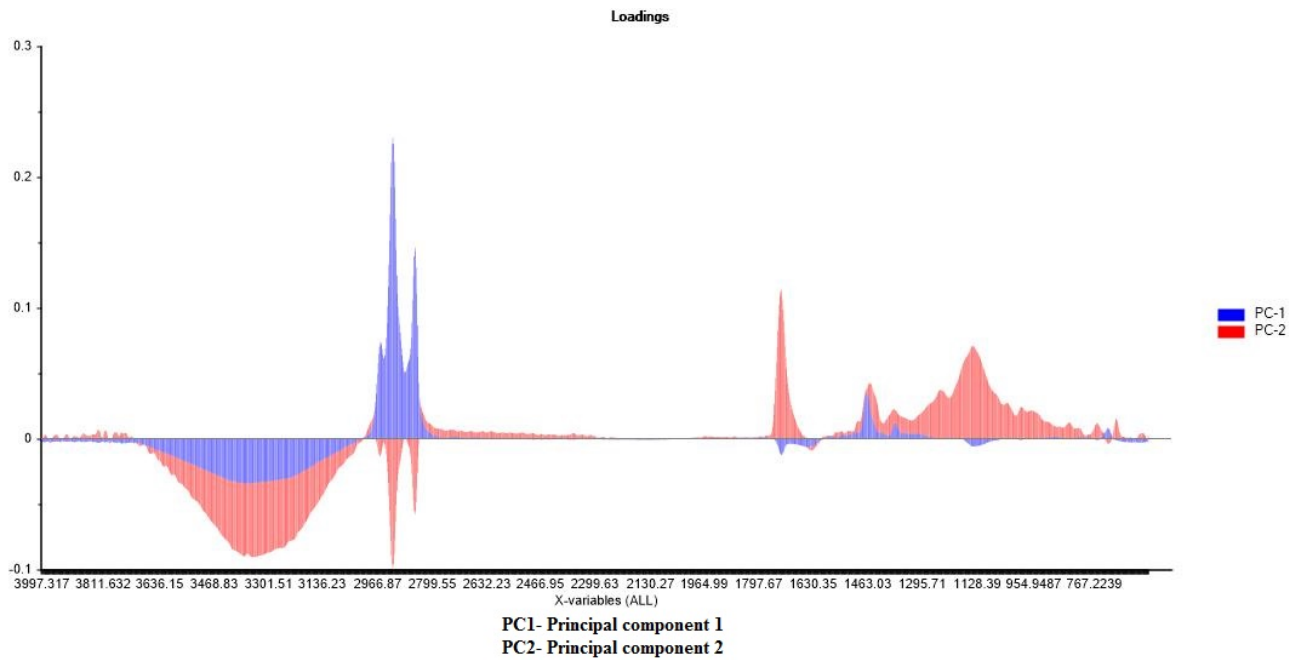
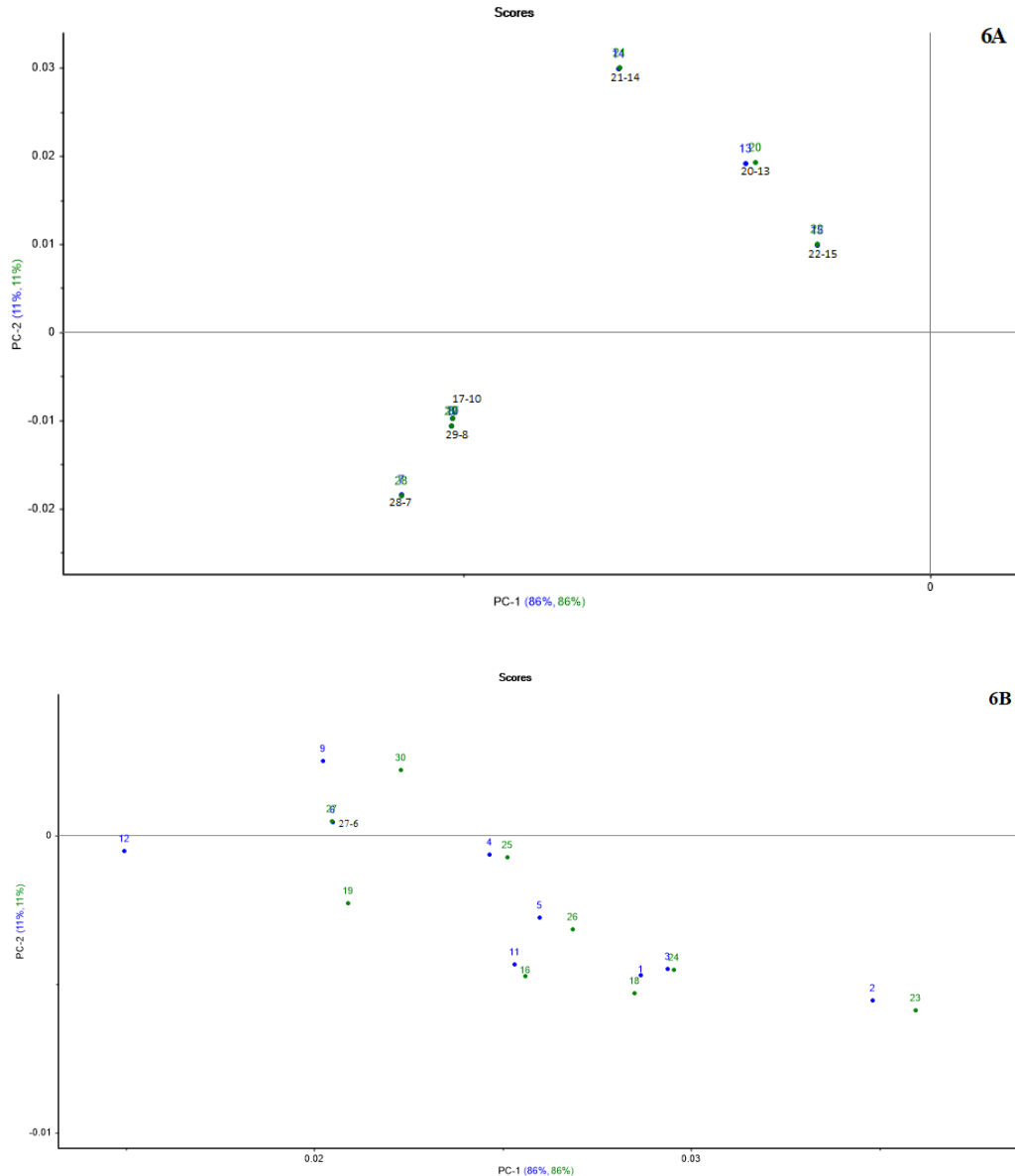


Figure 5- Combined factor loadings of the PC1 and PC2 for principal component analysis of shoe polish samples.



**Figure 6-** Blind testing to check the reliability of PCA method (Zoom in view).

conditions. On analysis, similar peaks were observed in the presence of substrates as well. Furthermore, to check the consistency of the PCA model a blind test was conducted which showed 86.6% accuracy. Using a blind test, two unknown samples (19 and 30) were placed at distant positions from their original source of sample. It was concluded that ATR FT-IR spectroscopy is a useful tool in the identification and differentiation of shoe polish stains on a variety of crime exhibits and offers a rapid, non-destructive, sensitive, and eco-friendly alternative to routinely adopted methods.

We suggest that further comprehensive studies should be performed on validation parameters and the applicability of the current methodology to assess the effects of various substrates and environmental conditions by simulating actual case work conditions on sample analysis.

#### **Conflict of interest**

None to declare.

#### **Funding**

None to declare.



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