ORIGINAL ARTICLE

Forensic Analysis of Accelerant on Different Fabrics Using Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) and Chemometrics Techniques

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ABSTRACT

Introduction: Accelerants and fabrics are commonly used to spread fire attributable to their highly flammable properties. Hence, having the ability to discriminate the different types of accelerants on various types of fabrics after fire and/or arson using the non-destructive Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy coupled with chemometric techniques appears forensically relevant. **Methods:** Six types of fabrics *viz.* cotton, wool, silk, rayon, satin, and polyester, were burnt completely with RON95 and RON97 gasoline as well as diesel. Subsequently, the samples were analyzed by ATR-FTIR spectroscopy followed by Principal Component Analysis (PCA) and Linear Discriminant Analysis (LDA) for discriminating the different types of accelerants on such burned fabrics. **Results:** RON95 showed the fastest rate of burning on all fabric types. Results also revealed that while wool had the slowest burning rate for all the three different accelerants, polyester, cotton, and satin demonstrated the highest rate of burning in RON95, RON97, and diesel, respectively. FTIR spectra revealed the presence of alkane, alcohol, alkene, alkyne, aromatic, and amine compounds for all fabrics. The two dimensional PCA (PC1 versus PC2) demonstrated 71% of variance and it was improved by cross-validation through the three dimensional LDA technique with correct classification of 77.8%. **Conclusion:** ATR-FTIR spectroscopy coupled with chemometric techniques had enabled identification of the functional groups, as well as statistically supported discrimination of the different accelerants, a matter of relevance in forensic fire and arson investigations.

Keywords: Accelerant, Fabrics, ATR-FTIR, PCA, LDA

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INTRODUCTION

Forensic investigation of fire and arson involves recovery of physical evidence (e.g. fire debris) from the scene and its laboratory analysis. The incendiary fires usually involve the use of substance, such as accelerants or fabrics to accelerate the intensity of the ignition phase and the spreading of fire (1). Factors, such as the wide availability of the substance, high flammability, and low cost, contribute to its use by arsonists to commit a crime. Since the chemical profiles of accelerants burned on different fabrics may vary from the burning of accelerants per se, examining such chemical profiles in view of discriminating the different accelerants used appears forensically imperative.

Interestingly, review of literature indicates that most researches focusing on the identification of accelerants confined to the laboratory-controlled conditions (3-5) that may not represent the actual conditions at the crime scene. Despite the laboratory-scale researches conducted, only two researches that attempted to reconstruct in full-scale fire experiments (2,6). In this context, they mentioned the complexity in conducting a full-scale fire experiment, whereby the results are, at times, difficult to interpret due to varying environmental conditions.

One of the pertinent aspects to establish during fire and arson investigations is the link between the accelerant and the fire debris, the chemical profiles of these two parameters must be consistent (2). While the American Society for Testing and Materials (ASTM) recommended analytical method for fire debris analysis is using Gas Chromatography-Mass Spectroscopy (GC-MS) (2), the analysis may not be able to provide suitable data for chemometric techniques such as Principal Component Analysis (PCA) and Linear Discriminant Analysis (LDA) Therefore, suitable statistical prove as well as the means of forensic intelligence to predict the types of burned accelerants on debris like fabric may not be able to be provided. In this context, successful application of the non-destructive Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy coupled with chemometric techniques for a number of different samples has been reported in the literature (8). However, such application for categorically differentiating the different types of accelerants on varying fabrics conducted in a full-scale fire experiment, especially in tropical climate like Malaysia remains unreported so far. Hence, this present research that evaluated the chemical profiles of the completely burned accelerants on common fabrics that underwent complete full scale burning, as well as categorically classifying them using chemometrics techniques merits forensic consideration. The chemical profiling was made following the use of ATR-FTIR, while PCA and LDA were used for developing suitable prediction models.

MATERIALS AND METHODS

Samples
Gasoline research octane number (RON) 95 and 97, and diesel fuel were purchased from a local petrol station in Shah Alam, Selangor. All accelerants were stored in a closed container at room temperature to avoid evaporation. The fabrics used in this study were cotton, wool, silk, rayon, satin, and polyester, purchased from a local textile store in Shah Alam, Selangor. All the accelerants as well as fabrics were used without any treatment to mimic the real case scenario observable in fire and arson cases.

Sample preparation
Each different fabric (40 cm x 40 cm) was prepared for burning purposes. Three pieces of each fabric (viz. cotton, wool, silk, rayon, satin, and polyester) were used for each type of accelerants (viz. RON95, RON97 and diesel), bringing the total number of 18 pieces of fabric analyzed in this present research. i A combination of different fabrics with the accelerants (burnt residue) were directly analyzed using the ATR-FTIR spectrometer. Detailed description on the procedure used for burning is provided in the method section. The definition of "burnt completely" mentioned here refers to the condition that 90% of the fabric was burned, and its residue was taken for the ATR-FTIR analysis. The relative standard deviation (%RSD) was calculated for repeatability and reproducibility studies.

ATR-FTIR procedure
ATR-FTIR was performed to identify the functional groups present in the accelerants. Bruker Technologies FTIR spectrometer with ATR sampling interface was used in this study. The sampling interface was wiped clean with tissues soaked in ethanol. Then, the sample was placed on the ATR baseplate of the specimen compartment and the spectrum obtained was in the spectral range of 4000 cm^{-1} to 600 cm^{-1}.

Methods
The flame test experiment was conducted around noon in a sunlit environment in Shah Alam, Selangor Malaysia (ambient temperature: 30-34°C; relative humidity: 70 -75%; with no evidence of rain) to replicate a common real fire case. The site was away from the public access to avoid any damages to the public facilities and injury to humans. Each sample (40 cm x 40 cm) was soaked into respective accelerant (RON95, RON97 or diesel) and burnt completely. A control sample for each unburnt fabric was also prepared for analysis. Time (s) taken for complete burning and physical characteristics such as the soot production and flame color were also observed. This step was repeated for wool, silk, rayon, satin and polyester.

Although the flame test was performed on 18 fabric samples, only 12 of them were subjected to ATR-FTIR analysis. The 12 samples included three samples and one sample that demonstrated high and slow burning rates for each type of accelerant, respectively. This present research focused on the high burning rate samples since they are easily evaporated and hence the more problematic ones for forensic investigation. The sample was collected and stored in an air-tight container to avoid evaporation and contamination.

Data analysis
For data analysis, 36 FTIR profiles (triplicates of the 12 samples) were collected and processed using Microsoft® Excel spreadsheet (Microsoft Corporation, Washington, USA) prior transferring them into IBM SPSS statistics version 23. Then, the data were imported into Minitab® version 16.2.3 statistical software (Minitab Incorporated, State College, PSA, USA) to perform Principal Component Analysis (PCA) and Linear Discriminant Analysis (LDA). The samples name in datasets from the Microsoft Excel were renamed using number-sample ID (Table I) prior to analyzing them using IBM SPSS and Minitab® software.

TABLE I: Sample ID

Samples	Number	Samples	Number
Cotton95	1	Polyester97	7
Wool95	2	Rayon97	8
Polyester95	3	CottonD	9
Silk95	4	WoolD	10
Cotton97	5	PolyesterD	11
Wool97	6	SatinD	12

RESULTS

Flame test

The flame test was performed to determine the burning behavior of accelerants on different fabrics. The result of the flame test for gasoline of RON95 andRON97, as well as diesel are tabulated in Table II, where comparisons were made on the burning rate, soot production, and flame color. The result showed that the burning rate of the fabrics varied according to the different types of accelerants. The burning rates of the accelerants on different fabrics revealed the fire risk order of the fabrics with the presence of accelerants. As for gasoline RON95, the fire risk order of six different fabrics was presented in a decreasing order; polyester, silk, cotton, rayon, satin, and wool. For RON97, the fire risk order of six different fabrics were: cotton, rayon, polyester, silk, satin, and wool. Meanwhile, for diesel, the fire risk order for the same six different fabrics were: satin, polyester, cotton, rayon, silk, and wool.

Table II: Burning rate and characteristics of accelerants on different fabrics

	RON 95	RON 97	Diesel
Cotton	37. 30 sec	47.40 sec	92 sec
Wool	40.19 sec	95 sec	129 sec
Silk	34.51 sec	79 sec	124 sec
Rayon	38.06 sec	51.70 sec	178 sec
Satin	38. 23 sec	87 sec	69 sec
Polyester	30.00 sec	58.25 sec	73 sec
Soot production	Black	Grey	White (almost invisible)
Flame colour	Orange-red	Orange	Light orange

ATR-FTIR analysis of gasoline RON95, RON97, and diesel

All ATR-FTIR spectra containing samples exhibited similar peaks at ~3300 cm^{-1}, 2800 cm^{-1},1600 cm^{-1},1300 cm^{-1} ,1100 cm^{-1} but they varied in relative intensities The ATR-FTIR spectra of gasoline RON95 and RON97, as well as diesel are shown in Figure 1 with the list of functional groups identified are tabulated in Table III. The peaks appeared similar for all accelerants, which indicated the presence of similar functional groups in the accelerants. The broad peak that was in the range of 3700 cm^{-1} to 3000 cm^{-1} may indicate the presence of different functional groups: alcohol (-OH) group in the range of 3700 cm^{-1} to 3400 cm^{-1}; alkenes (C=C-H) group in the range of 3100 cm^{-1} to 3020 cm^{-1}; alkynes (C≡C-H) group at 3300 cm^{-1}; and amines (N-H) group in the range of 3350 cm^{-1} to 3300 cm^{-1} .

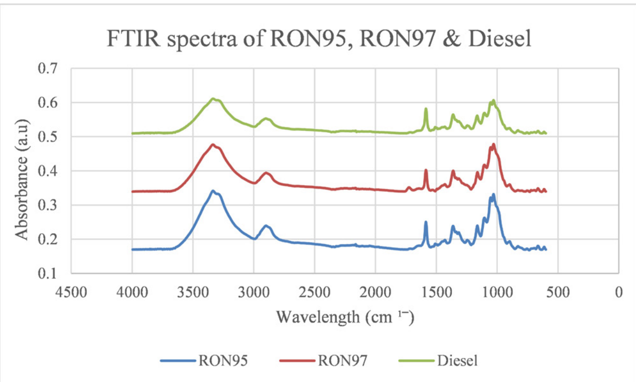

Figure 1: ATR-FTIR spectra of RON 95, RON 97 and Diesel

Table III: Functional group identified in accelerants

Wavenumber (cm^{-1})	Intensity	Types of vibration	Functional groups
3700 - 3400	Strong	Stretching	Alcohol (O-H)
3100 - 3020	Strong	Stretching	Alkenes (C=C-H)
3350 - 3300	Strong	Stretching	Amines (N-H)
3300	Strong	Stretching	Alkynes (C≡C-H)
3000 - 2800	Medium	Stretching	Alkanes (C-H)
2000 - 1650	Weak	Stretching	Aromatics
1680 - 1640	Medium	Bending	Alkenes (C=C)
1500 – 1300	Medium	Bending	Alkanes (C-H)
>1000	Strong	Bending	Alkanes (C-H) and aromatics

Chemometrics analysis of accelerant

The FTIR profiles for each accelerant on different fabrics were processed in Microsoft® Excel spreadsheet to create the average datasets before transferring them to the IBM SPSS statistics version 23. PCA was performed to uniquely reduce the dimension of large datasets into Principal Components. Following the use of PCA, supervised LDA was performed for each dataset to enable further group membership prediction of the sample groups (8). The LDA models were developed to ensure satisfactory and reliable classification through cross-validation approach by means of "leave-one-out" technique. The sample classification predictions and misclassification of groups using LDA model were obtained and tabulated in Table IV. In this study, PCA and LDA models were performed using Minitab® version 16.2.3 statistical software to ensure classification and discrimination of samples. The PCA model described the data system in a simplified and more interpretable form (9). In contrast, LDA is a method used for pattern recognition, in which it describes a separation hyperplane by calculating the linear discriminant functions, resulting in optimal discrimination of classes (10–12). A 2-dimensional (2D) PCA (PC1 versus PC2) score plot of samples was plotted to establish the classification of accelerant sample, as shown in Figure 2. Prior to PCA, a scree plot was also constructed to identify the total number of PCs to justify the maximum variance in dataset. The visual inspection of 2D PCA score plot showed a variance of 71% (PC1=39.1%; PC2=31.9%), indicating a higher percentage of discrimination of accelerants according to its group. A further approach using LDA model (Figure 3) was derived from the PCA (obtained from the first three

Table IV: Sample classification into its predicted group and misclassification of the group using LDA model

Sample	No. of sample analysed	Predicted group	Misclassification	Percentage (%)
1	3	3	-	100
2	3	3	-	100
3	3	2	1 (misclassify into group 2)	66.7
4	3	3	-	100
5	3	3	-	100
6	3	3	-	100
7	3	3	-	100
8	3	3	-	100
9	3	2	1 (misclassify into group 10)	66.7
10	3	3	-	100
11	3	3	-	100
12	3	1	2 (misclassify into group 8 & 9)	33.3
Total				**88.9%**

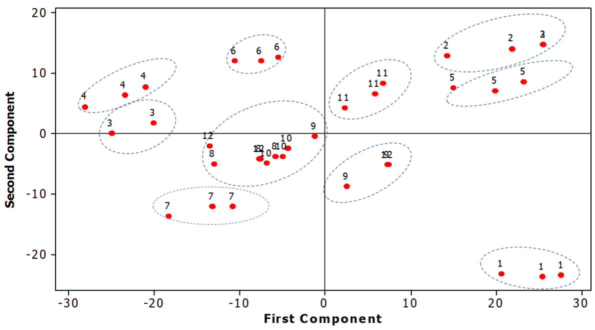

Figure 2: Two-dimensional (2D) PCA model of accelerant samples using the first two components (PC1=39.1%, PC2=31.9%)

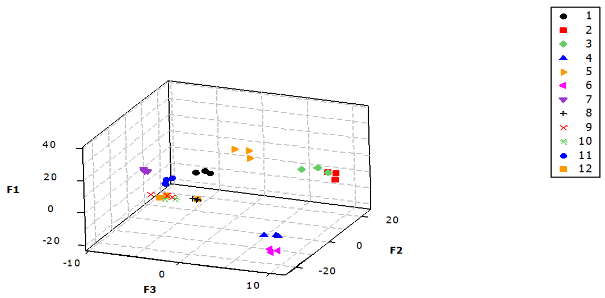

Figure 3: Three-dimensional (3D) LDA model of accelerant samples using three discriminant function (F1, F2 & F3)

PCs), demonstrating an improvement by 77.8% by cross-validating the correct classification of the accelerants. The results also showed 88.9% of original group cases that were correctly classified (before cross-validation). The LDA model is represented in three-dimensional (3D) scatterplot using three discriminant functions (F1, F2, and F3) (Figure 3).

DISCUSSION

Flame test

The result obtained shows a significant difference in the burning rate, in which among all the accelerants, gasoline RON95 showed a higher burning rate on all fabrics, compared to that by gasoline RON97 and diesel. This is due to the octane number and n-heptane number present in the gasoline. RON95 has a lower octane number, which is 95%, compared to RON97 that has 97% of octane number; therefore, this may have influenced the burning rate of the fuel. This led to prompt detonation under compression before the spark was triggered for RON95; in other words, it burnt faster than RON97. The number of carbons in the fuel may also contribute to the burning rate of the accelerants. The presence of octane in gasoline and cetane in diesel both have eight and sixteen carbons, respectively. Since RON95 has a lower percentage of octane number, it will burn faster than RON97 and diesel. In addition, the low flash point (-43°C) properties of the gasoline have resulted in fast ignition and high burning rate (2).

The soot production and flame color obtained from this study were different for all accelerants. The lower CO2 and CO emissions in RON97 (13) is the key factor affecting the soot production and flame color produced. Thus, incomplete combustion is more likely to occur with RON95, which leads to black soot production and orange-red flame color. For each accelerant, the different types of fabrics did not affect the soot production and flame color. Different fabrics had been identified as fire risk fabrics for all accelerants, indicating that different fabrics do influence the burning rate. Polyester, cotton, and satin had high burning rates with RON95, RON97, and diesel, respectively. This concludes that the material of the fabric influences the burning rate of the accelerant. Sources of fabrics, either natural or synthetic, can be one of the contributing factors as well. Despite that, wool reveals to have slow burning rate for all accelerants. Wool is known for its highly efficient properties in absorbing oils, however, its weaving process during production will result in holding the oil longer (2). Thus, the resulting evaporation of the accelerant becomes slower and the burning time becomes longer.

ATR-FTIR Analysis of Gasoline RON95, RON97, and Diesel

The current analysis of fire debris follows the American Society for Testing and Materials (ASTM) standard that has been developed and published since 1990. The recommended analytical method for fire debris analysis is using Gas Chromatography-Mass Spectrometry (GC-MS) (14), which is the standard technique in fire debris analysis. However, considering this technique is time-consuming and destructive as well as requires sample preparation and costly, ATR-FTIR spectroscopy is preferred in forensic investigation for chemical profiling (2). Gasoline and diesel have very complex mixtures, consisting of thousands of individual chemicals with a wide range of carbon atoms in the chain (15). Therefore, with the use of ATR-FTIR, this study was able to identify the functional groups that were present in both gasoline and diesel (e.g., alcohol, alkanes, alkenes, alkynes, amines, and aromatics). The results obtained in this study were in line with the previous findings (16), in which alkanes were detected at peaks between 3000 cm^{-1} to 2800 cm^{-1} and 1500 cm^{-1} to 1300 cm^{-1}. In addition, the bands at 1650 cm^{-1} represented the out-of-plane C-H bending of the aromatic ring. Moreover, in the previous research (17), the IR spectra of diesel fuel showed a C-H stretching vibration at peaks 2924 cm^{-1} to 2854 cm^{-1}. The addition of alcohol, such as methanol or ethanol, in both gasoline and diesel has its own function. It acts as an additive in the fuel, which helps to improve fuel efficiency (2). Besides, it may also improve the fuel economy and thermal efficiency, as well as increase the octane number.

Chemometric analysis of accelerants

The main objective of chemometric analysis in this present research was to determine whether the ATR-FTIR spectra of different accelerants can be discriminated into its classification or otherwise subsequent to the changes in their physical and chemical properties. Using PCA model to examine the datasets, the accelerants were able to be classified and the generic separation between the accelerants was attempted. In order to make the PCA score plot usable and valid to represent the sample classification, a certain percentage should be achieved. A suggested 70%–80% of variation is adequate to represent the datasets in a much reduced dimension (8). This indicates that the model was able to correctly predict and classify the chemical-physical properties of unknown gasoline samples. Although the PCA model was able to reveal the separation of the accelerant, this was not sufficient for the forensic database. This is due to the fact that PCA is a unsupervised method that enables the observation of the organization of data alone and not meant for prediction (8). Thus, to solve this issue, LDA was chosen to combine with PCA due to its classificatory nature. PCA-LDA techniques may provide better discrimination of accelerants than using PCA alone. This study has found an improvement in the classification and discrimination of accelerant samples, which was identified by 77.8% of cross-validation of correct classification, as compared to using the PCA model alone. Hence, this study provides better classification and discrimination of the different accelerant samples, which is beneficial to the forensic field in distinguishing unknown accelerants.

CONCLUSION

In conclusion, the study of different types of accelerants on different fabrics was a success, having able to discriminate them despite after undergoing some physical and chemical changes in their structures due to the burning. ATR-FTIR spectroscopy that was used in this study, is proven as a useful tool in fire debris analysis to identify the presence of accelerants. The ability of this technique to identify the functional groups in accelerants fulfils the standard criteria for fire debris analysis. In addition, ATR-FTIR spectroscopy coupled with chemometric techniques, such as PCA-LDA, has made it possible to predict and discriminate the accelerant samples into its classification. As a suggestion, these PCA and LDA models can be used as a reference or database for the identification of unknown accelerant samples. Apart from that, the data from this study could be useful in real fire or arson cases to link between the unknown samples from the crime scene with accelerants from available library data.

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