

CLASSIFICATION OF PETROLEUM-BASED ACCELERANTS IN FIRE DEBRIS USING GAS-CHROMATOGRAPHY MASS SPECTROMETRY AND CHEMOMETRIC TECHNIQUE

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Abstract. The classification of petroleum-based accelerants in fire debris samples have been studied using gas chromatography-mass spectrometry (GC-MS) and chemometric technique. Samples were collected from carpets burnt with three different types of accelerants: gasoline, kerosene and diesel. Some of the charred carpets were left for several days to study effect weathering on the classification. Total ion chromatograms obtained for each sample were subjected to principal component analysis (PCA). The chromatograms identified the hydrocarbons present in the samples while PCA perform the classification based on the peak area of each component. This study showed that, by using PCA, we were able to cluster the samples according to type of accelerants used even though some of the samples were collected several days after the incident.

Keywords petroleum-based accelerant; fire debris; weathering effect; gas chromatography-mass spectrometry; principal component analysis

1.0 INTRODUCTION

Arson is a crime of maliciously setting a fire to a building or other property for some improper reason. Criminals usually set up the fire with a careful plan to minimize the chance of detection. Arson is a serious problem in the United States of America (USA). In 2011, about 364 500 arson cases were stated by United States Fire Administration which caused \$6651 million loss in property damage [1]. Eventhough it showed a decline in arson cases for the past few years, it involved over 2000 people lives loss and about 13 900 people were injured.

Determination of the causes of fire is crucial and proves to be a major hurdle in solving arson cases. Most of the arson fire involves a suspicious building fire which caused a lot of death. In USA, incendiary fires illustrated the highest percentage of 28% among the causes of all fires in 1994. Since it involves both the property and live, incendiary stated as the second leading causes of fire [2].

In Malaysia, 127 arson cases involving residential and non-residential building fire caused by the incendiary were stated by Jabatan Bombadanan Penyelamat Malaysia. Residential building fire indicated the highest number of 73 cases among all [3]. Arson becomes a serious case because it involves public safety and lost of profits. Hence, it proves that arson case is a major problem which required a serious investigation to arrest the criminal.

Criminal often used petroleum-based accelerants to start a fire because of their low cost and easy availability. It is used to initiate or increase the intensity or speed of fire [4]. Petroleum-based accelerants like gasoline, kerosene and diesel are the most common accelerants found in arson cases.

Basically, petroleum-based accelerants can be divided into several categories which are light, middle and heavy according to the petroleum distillates processes. However, some changes have been made to accelerants classification by addition of kerosene group and others. Current accelerants classification is described based on the chemical classes and weight [5]. Hence correct identification of petroleum-based accelerants is needed as evidence to find the person who commits the arson.

Petroleum-based accelerants are made up from a mixture of hydrocarbons and volatile compounds making their detection complicated. Forensic chemists have to face problem during isolation and detection of volatile residues in fire debris samples. In fact, the presence of contamination from pyrolysis product makes it worse in liquid residues identification. This is because it will interfere with the chromatograms and brings confusion during analysis. Fernandes *et al.* [6] have been studied the compounds which could interfere the identification of accelerants after burning effect of carpet matrix. Similar research demonstrated four compounds as pyrolysis product after being burnt with gasoline [7]. According to Prather and co-worker [8], identification of ignitable liquid residues was successfully done by PCA with the presence of matrix interferences. Furthermore, a research had been done in comparing weathered accelerants with the fresh accelerants for correct classification of petroleum-based accelerants [9].

Therefore, a high performance instrument is required to analyze such a complex data. Chromatographic techniques remains as the powerful method in identification of liquid residues present in fire debris samples. Total ion chromatogram (TIC) is one of the well-known approaches in chromatography [10, 11]. Huppert *et al.* [12] applied total ion chromatogram (TIC) and extracted ion chromatogram (EIC) in diesel fuel analysis for forensic and environmental applications. Besides GC-MS analysis, other researchers utilized Raman spectroscopy [13, 14], infrared spectroscopy [15, 16, 17], ultraviolet spectroscopy [18] and also physiochemical analysis [19] in accelerants analysis in conjunction with chemometric technique.

Chemometric method is a powerful tool in handling enormous sophisticated data. A lot of researches employed chemometric techniques to perform classification. Techniques like principal component analysis (PCA), hierarchical cluster analysis (HCA) and soft independent model class analogy (SIMCA) were successfully applied in solving fire debris analysis [20, 21]. Other research on food analysis [22, 23, 24] and vegetable oil identification [25, 26, 27] integrated chemometric procedures and proved that this technique is effective in classification problem.

This study was done to apply a powerful chemometric technique in accelerants identification of fire debris samples. Weathered accelerants samples

were used to study the effect of evaporation in classification of accelerants. The results discussed that this technique could be successfully used to classify petroleum-based accelerants in fire debris sample.

2.0 EXPERIMENTAL

2.1 Materials

Various hydrocarbon standard C₈-C₂₃, pristane, phytane, 3-ethyltoluene, o-xylene (analytical grade) obtained from Dr. EhrenstorferGmbH, Augsburg, Germany and 1,2,4-trimethylbenzene from Supelco, Bellefonte PA, U.S.A. were used as standard reference. These compounds were commonly existed in petroleum-based accelerants. Tetrachloro-m-xylene (TCMX) obtained from Sigma-Aldrich (M) Sdn. Bhd. Malaysia was used as an internal standard while carbon disulfide (CS₂) from Tedia Company Inc. (Fairfield, USA) was used as a solvent.

Several petroleum-based accelerants used in this research. They were gasoline, diesel and kerosene. Gasoline and diesel were purchased from several petrol stations (Petronas, Shell, Caltex) in Taman Universiti, Skudai area while kerosene was obtained from different shop around Taman Universiti, Skudai. Carpet sample was purchased from a retail store as a sample matrix.

2.2 Method

2.2.1 Sample Preparation

Carpet sample was soaked with 5mL of each accelerant and then burned for about 2 minutes. Fire debris was extracted using passive headspace adsorption for an hour to create headspace before it was desorbed for 30 minutes. Activated carbon (100mg) was used as absorbent. The sample was heated and maintained to 80 °C. Carbon disulfide (5 mL) was used as a solvent to extract the analyte. The extractant was put into 2mLlabelled vial and spiked with 100ppm internal standard

before further analysis with gas chromatography flame ionization detector (GC-FID) followed by gas chromatography-mass spectrometry (GC-MS).

2.2.2 GC-MS Analysis

Instrument used was GC-MS equipped with a HP-5 fused silica capillary column (25m × 0.2mm × 0.33μm, Agilent Technologies). The data was acquired by MS chemstation. Helium was used as a carrier gas. **Table 2.1** shows details of the instrumental parameter applied in this study. Target ion compound (TIC) was used as the variables to perform the chemometric analysis.

2.2.3 Effect of Weathering

Fire debris sample was exposed to the surrounding room temperature before further analysis to obtain the chromatogram. The weathering effect was study by leaving the sample after burned with accelerants for 0, 2 and 5 days respectively. Hence, there were three types of data involving debris extracted immediately after the fire, debris which left for two days and five days.

2.3 Chemometric Analysis

All target ion components were imported into Matlab R2008a version 7.6 (The Mathworks. Inc). PLS-toolbox (Eigenvector Research, Inc) version 6.2 was used to perform PCA statistical analysis. Before that, data was normalized based on the peak area of internal standard and it was set to be meancentred pre-processing. Principal component analysis is one of the statistical tools available in this software. Genetic algorithm[28]was then applied for the variables selection. All the variables used in this research are listed in **Table 2.2**.

3.0 RESULTS AND DISCUSSION

Total ion chromatograms (TICs) of weathered and unevaporated accelerants from fire debris samples are compared as shown in **Figure 3.1, 3.2** and **3.3** for gasoline, diesel and kerosene respectively. The weathering effect might cause the samples to be group wrongly since some of the low concentration compounds loss to the surrounding. Hence, classification of petroleum-based accelerants on fire

debris samples needs an advanced method to handle large amount of data and accounted for changes occurred due to some factor like weathering.

Details of components exist in accelerants have been used for the accelerants identification and association of samples to a certain class. Visual data is difficult to evaluate and the differences are often not observable. The chances of getting inaccurate analysis are higher due to the presence of matrix interferences and weathering effect. Thus, multivariate chemometric procedures are required. In this study, pattern recognition technique: principal component analysis (PCA) was used to perform the classification and variables reduction.

Firstly, PCA was executed on the preprocessed GC-MS dataset of fire debris. Variance of original data was acquired through a few principal components (PCs). PC1 which has the largest eigenvalue carries the largest amount of variance in the original data followed by PC2 and PC3. Furthermore, PCA assisted the study of weathering effect on the accelerants. Low volatile compounds in ignitable liquid residues were lost to surrounding due to the weathering effect and ultimately altered the chromatographic patterns. Fire investigator will have difficulty in the detection of weathered samples based merely on chromatograms. PCA gives a clear classification overview of weathered accelerants samples and helps the forensic chemist in analysis while GC-MS is a good instrument for determination of components that lost caused by weathering.

Figure 3.4 illustrates the scores plot of all 52 fire debris samples using all variables. A 50.05% of total variance was obtained by the two PCs (PC1: 32.13%; PC2: 17.92%). There are three groups of ignitable liquid residues can be seen from the scores plot which consisted of gasoline, kerosene and diesel. However, kerosene and diesel samples seem to be clustered as one class. Kerosene on fire debris samples were closed to each other except for two samples (KTU2 and KJ5) which slightly shifted to left and upper side of the plot respectively. The grouping explained that kerosene from different brands was not much affected by the weathering effect since they still have similar amount of components in the samples. A higher amount of dichlobenzene in KJ5 sample caused it to be slightly shifted to upper side of the scores plot while KTU2 sample might be caused by high amount of alkane.

Table 2.1: Parameter for GC-MS analysis

Injector Temperature (°C)	250
Flow Rate (ml/min)	1.0
Detector temperature (°C)	310
Injection Volume (µl)	1.0
Split Ratio	1:50
Oven Program:	
Initial (°C)	50 (2.5 min hold)
Ramp (°C/min)	15
Final (°C)	310 (6 min hold)
Mass Spectrum on	2.5 (solvent delay)
Scan mode-scan	50-500 amu

As for diesel samples, most of them were classified on the left quadrant and some of them located near to the kerosene samples. Diesel and kerosene were classified as high petroleum distillated (HPD) according to ASTM E1618 since they have similar components like C₁₁, C₁₂, C₁₃ and trans-decalin. That makes diesel and kerosene closed to each other in the scores plot. The scattered of diesel samples along PC2 were caused by loss of some aromatic components.

Since weathering discriminates the samples based on boiling points, severe weathered samples like gasoline were scattered on the upper right quadrant of the scores plot. There were two sub clusters in the gasoline group. These happened due to the different of compounds present in gasoline which originated from different supplier. As can be seen in this figure, Gasoline 1 sub group was originated from Shell while Gasoline 2 was from Caltex supplier. Besides that, there was few gasoline samples located in the middle of the scores plot (Gasoline 3). These samples were separated from others even they were from the same supplier (Caltex). The grouping was slightly far because these samples were RON 97 gasoline while others RON 95.

Table 2.2: Components used as variables in accelerants classification

Peak No.	Variables	Peak No.	Variables
1	Ethylbenzene	26	Benzene, 4-ethyl-1,2-dimethyl
2	p-xylene	27	Benzene, 1-ethyl-2,3-dimethyl-
3	o-xylene	28	Benzene, 1-methyl-2-(1-methylethyl)-
4	m-xylene	29	Benzene, 1,2,4,5-tetramethyl-
5	xylene	30	Benzene, 1,2,3,4-tetramethyl
6	Nonane	31	5-Methylindan
7	Cyclohexane, propyl-	32	Indan, 4,7-dimethyl-
8	Benzene, propyl-	33	Naphthalene
9	Isopropylbenzene	34	Naphthalene, 1-methyl
10	4-Ethyltoluene	35	Naphthalene, 2-methyl-
11	o-ethyltoluene	36	Undecane
12	Benzene, 1-ethyl-2-methyl-	37	Dodecane
13	Benzene, 1,2,3-trimethyl-	38	Tridecane
14	p-Ethyltoluene	39	Tetradecane
15	Benzene, 1,2,4-trimethyl-	40	Pentadecane
16	Decane	41	Hexadecane
17	Benzene, 1,2-dichloro-	42	Heptadecane
18	Indane	43	Octadecane
19	Benzene, 1-methyl-4-(1-methylethyl)	44	Pristane
20	Benzene, 1,3,5-trimethyl-	45	Phytane
21	Cyclohexane, butyl-	46	Nonadecane
22	Benzene, 1-methyl-3-propyl-	47	Eicosane
23	Benzene, 1-methyl-2-propyl-	48	Heneicosane
24	Decane, 4-methyl-	49	Docosane
25	Benzene, 1-ethyl-3,5-dimethyl-	50	Trans-decalin

Loadings plot (**Figure3.5**) shows the relationship between variables as well as a clue to which variables contributed to the classification. Aromatic components and derivatives were located on the positive PC1 and disseminate along PC2. As compared to the scores plot, most of gasoline samples located on the positive PC1 which indicates aromatic compounds as significant variables in gasoline classification. For kerosene and diesel samples here the loadings plot explained that n-alkane as the important variables for the classification.

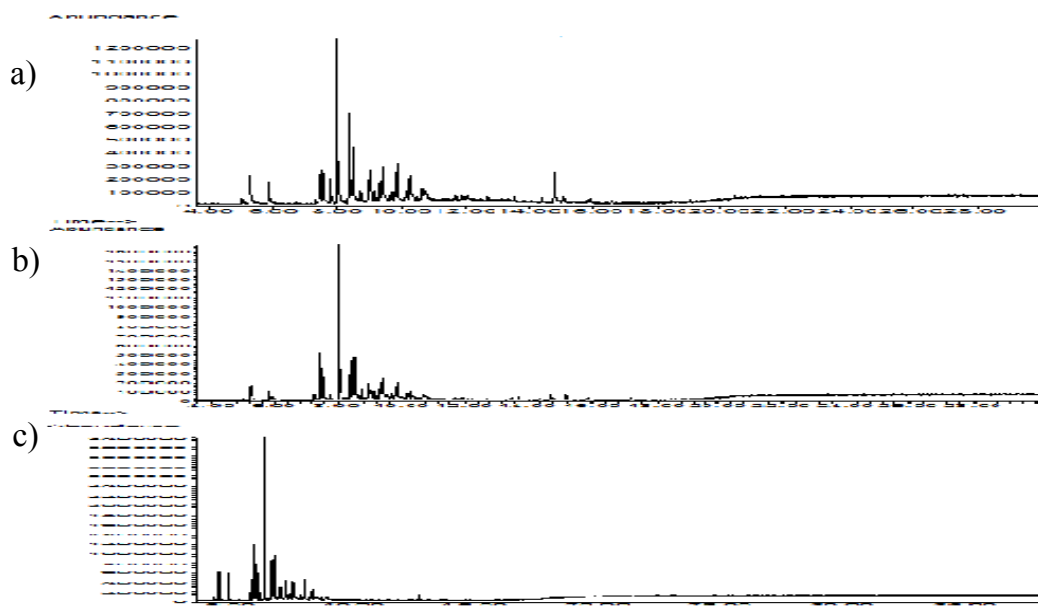


Figure 3.1: Total ion chromatograms for diesel a) immediately after burnt b) exposed for two days c) exposed for five days.

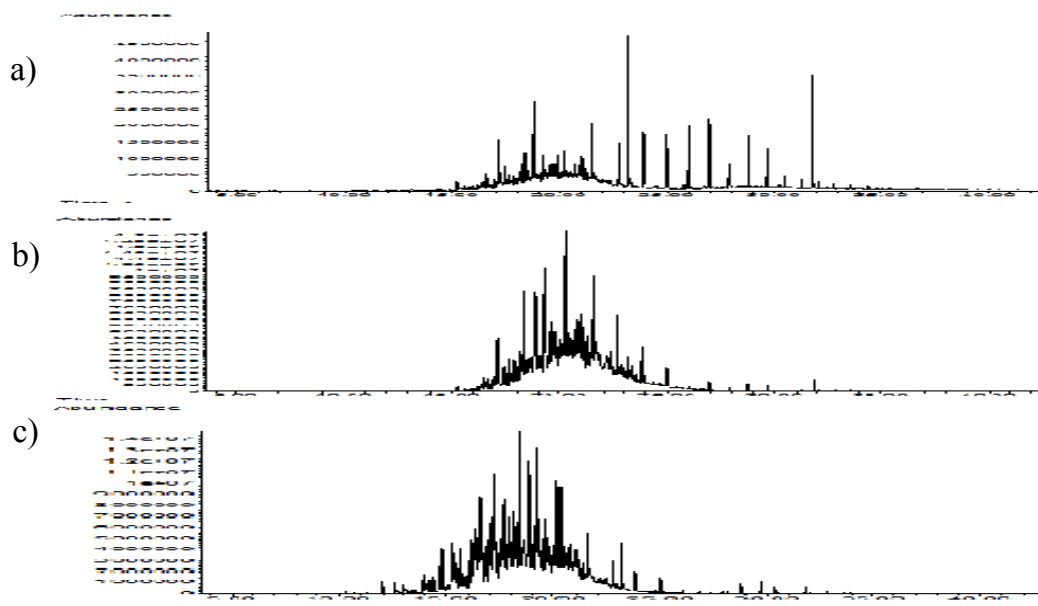


Figure 3.2: Total ion chromatograms for diesel a) immediately after burnt b) exposed for two days c) exposed for five days.

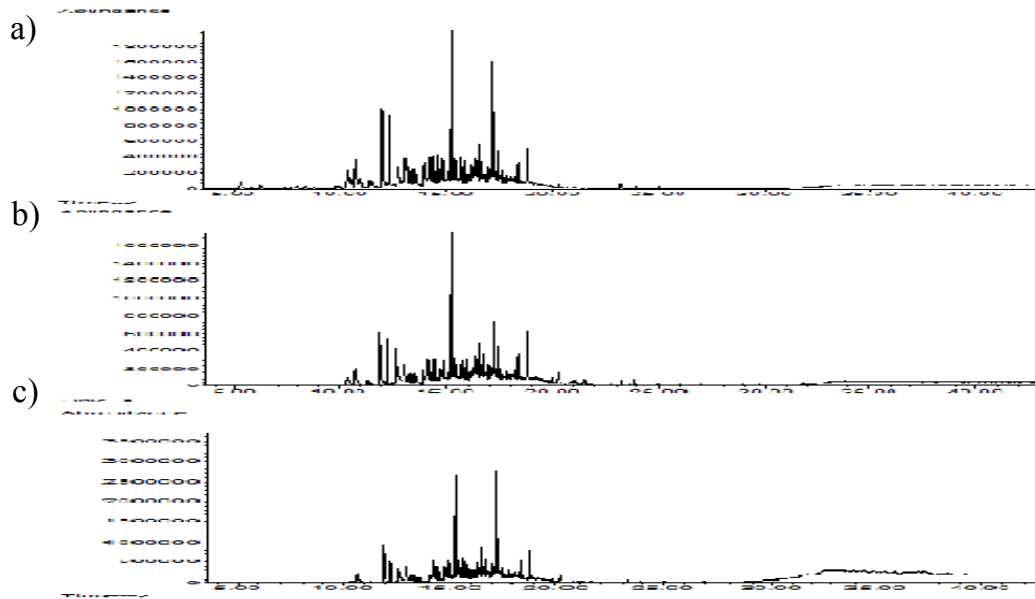


Figure 3.3: Total ion chromatograms for kerosene a) immediately after burnt b) exposed for two days c) exposed for five days.

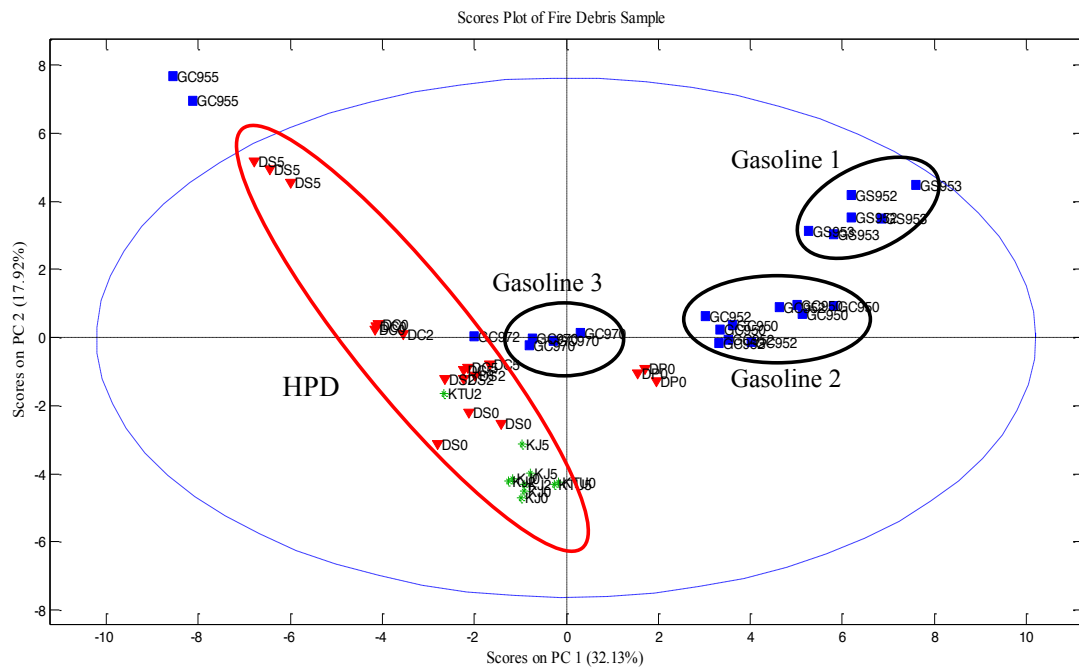


Figure 3.4: Scores plot of principal component analysis before variables reduction.

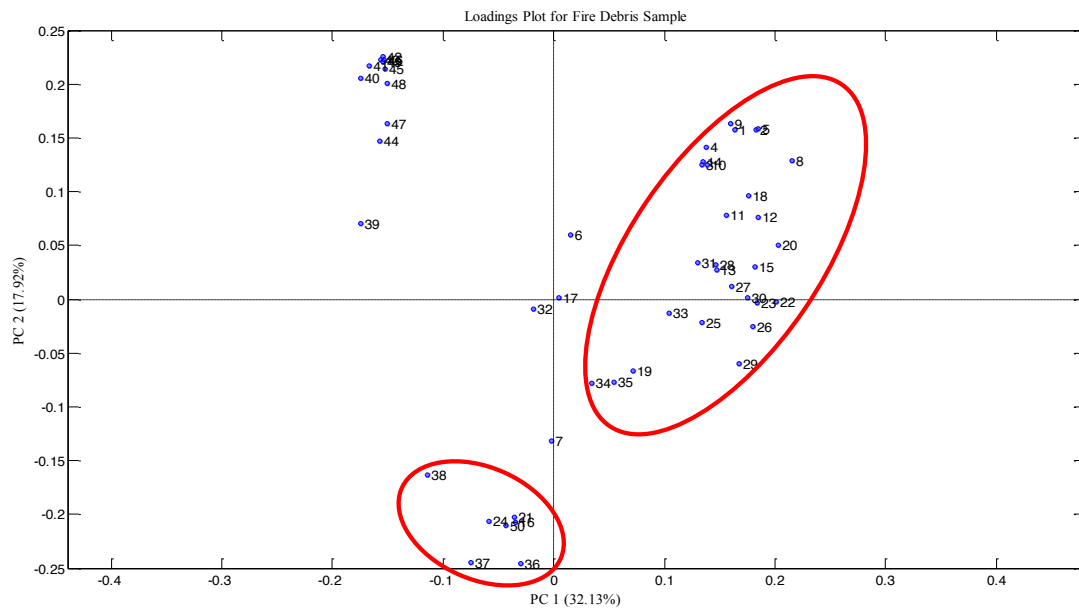


Figure 3.5: Loadings plot of principal component analysis before variables reduction

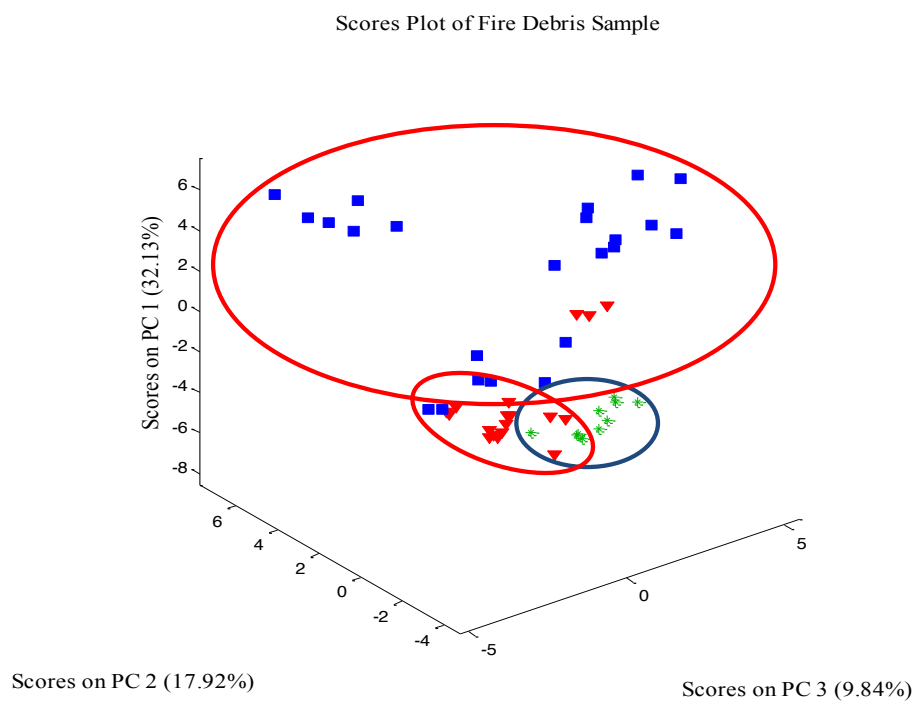


Figure 3.6: 3D scores plot of fire debris sample.

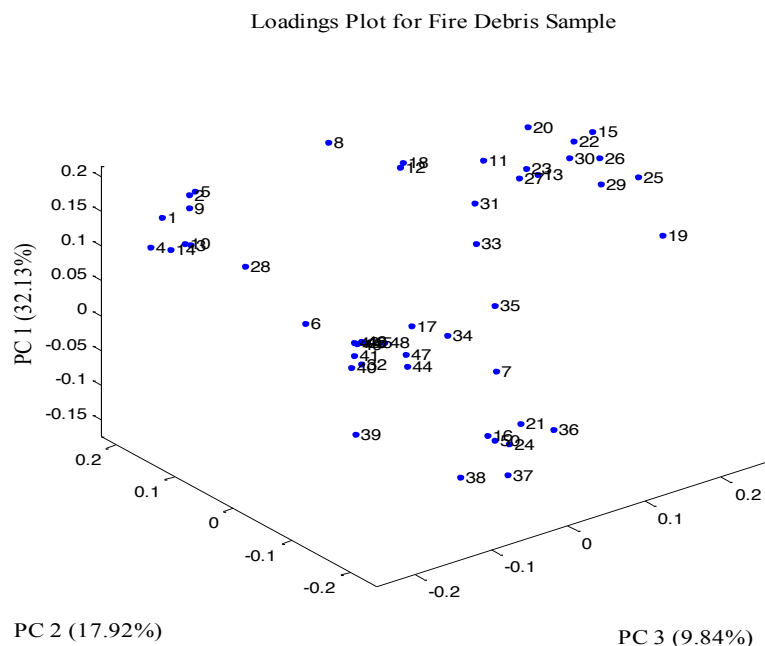


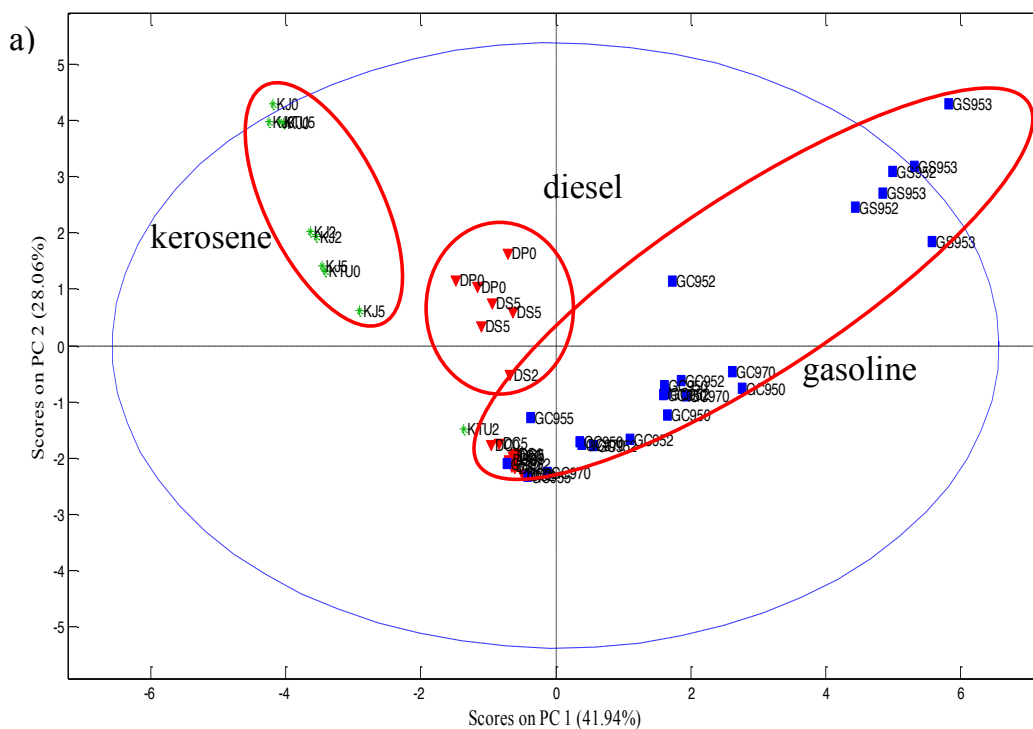
Figure 3.7: 3D loadings plot of fire debris sample.

A 3 dimensional scores and loadings plots were built to obtain clearer view of the classification as shown in **Figure 3.6** and **3.7** respectively. These three PCs accounted for 59.89% of total variance in the original data. The PC1-PC2 scores plot (Fig3.4) illustrated the discrimination of gasoline and high petroleum distillates (kerosene and diesel) samples. In addition, PC3 in Figure 6 clustered the kerosene samples while PC1 distinguished gasoline samples from the remaining. The variables that contributed to the classification of accelerants in fire debris remain unchanged as can be seen in Figure 7. Aromatic components and derivatives lead to the gasoline grouping; higher volatile compounds for diesel samples and some of n-alkanes like C₁₁-C₁₃ were significant for kerosene classification.

Fire debris samples were distinguished into several classes using 50 compounds treated as variables. All of the variables were from aromatics, n-alkanes and other compounds like trans-decalin which contributed to the classification. As can be seen in **Figure3.5** and**3.7**, there were some overlapping

variables that can be omitted. Minimum variables were needed to obtain good classification of accelerants while maintaining information of original data.

Genetic algorithm technique maintains a few variables after 10 replicates run time which significant in this study. Slight changes in scores plot observed as shown in **Figure 3.8**. Clear separation was observed in both 2D and 3D scores plots between kerosene and diesel samples after removal some variables except for one kerosene sample which located in diesel group. PC1 discriminated gasoline group from others. Three samples from gasoline were located near to diesel group. Fire debris samples grouped themselves in better way after removing some variables. Genetic algorithm variable selection provides significant information for sample clustering compared to the previous model using all variables.



b)

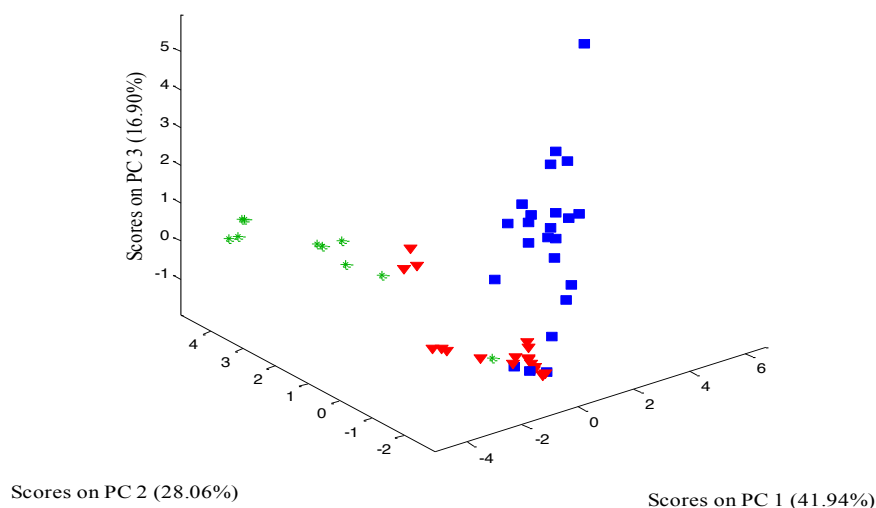


Figure 3.8: Scores plot of fire debris sample after variables reduction. a) PC1 vs PC2 b) PC1-PC2-PC3

4.0 CONCLUSIONS

Identification of components presence in ignitable liquid residues revealed that different supplier or brand had different compounds in their accelerant products. It is evident that chemometric method useful in the weathering study. Petroleum-based accelerants on fire debris samples successfully classified into three groups which are gasoline, kerosene and diesel even some of the samples had undergone weathering.

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