CHEMOMETRICS ANALYSIS OF PETROLEUM-BASED ACCELERANTS IN
FIRE DEBRIS

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DEDICATION

It gives me great pleasure to convey a special dedication to my family members, Ahmad Shuhaimi Ishak and Maznah Shyidon, my respected supervisor, lecturers, and friends.

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ABSTRACT

Petroleum-based accelerants such as diesel, gasoline, kerosene and others are usually related to fire debris analysis because they are inexpensive, readily available and commonly used to enhance the burning intensity of fire. However, combustion process and the presence of pyrolysis products can lead to misclassification of accelerants to the arson investigator. Furthermore, fire debris which has been exposed for several days may undergo some component lost and makes the detection more difficult. In this study, gas chromatography-mass spectrometry (GC-MS) was used to identify the accelerants present in simulated arson incidents. Total ion chromatogram and the peak area from the GC-MS data were used to perform chemometrics techniques which include principal component analysis (PCA), linear discriminant analysis (LDA), partial least square-discriminant analysis (PLS-DA) and support vector machine (SVM). The performance of these methods was further tested by analyzing samples which have been exposed for several days in the environment. Three accelerant classes were formed by these classification models which consist of gasoline, kerosene and diesel. Supervised pattern recognition technique showed satisfactory results, in terms of correctly classified samples, which were 90.4% (LDA), 85.3% (PLS-DA) and 96.7% (SVM) for training sets. A test set produced a value of 87.5% correct classification for LDA, 83.3% for PLS-DA while the best classification is 91.7% by SVM. Fire debris analysis using GC-MS with the aid of chemometrics methods give a promising result in the identification and classification of accelerants used to initiate the fire in arson cases.

ABSTRAK

Bahan penggalak kebakaran berasaskan petroleum seperti diesel, petrol, minyak tanah dan lain-lain biasanya berkait rapat dengan analisis sisa kebakaran kerana bahan ini adalah murah, mudah didapati dan biasa digunakan untuk meningkatkan keamatan api pembakaran. Walau bagaimanapun, proses pembakaran dan kehadiran produk pirolisis boleh membawa kesan sampingan dalam pengkelasan bahan penggalak api oleh penyiasat kebakaran. Tambahan pula, sisa kebakaran yang telah terdedah beberapa hari boleh melalui proses kehilangan beberapa komponen dan menyukarkan pengesanannya. Dalam kajian ini, kromatografi gas-spektrometri jisim (GC-MS) telah digunakan untuk mengenal pasti kehadiran bahan penggalak pembakaran dalam simulasi insiden bahan terbakar. Kromatogram ion jumlah dan luas puncak daripada data GC-MS telah digunakan untuk melaksanakan teknik kimometrik termasuk analisis komponen utama (PCA), analisis diskriminan linear (LDA), analisis diskriminan-kuasa dua terkecil separa (PLS-DA) dan mesin vektor sokongan (SVM). Prestasi kaedah ini telah diuji dengan menganalisis sampel yang terdedah selama beberapa hari di alam sekitar. Tiga kelas bahan penggalak kebakaran telah dibentuk hasil daripada model klasifikasi yang terdiri daripada petrol, minyak tanah dan diesel. Teknik pengecaman corak berselia menunjukkan keputusan yang memuaskan, daripada segi pengkelasan sampel iaitu 90.4% (LDA), 85.3% (PLS-DA) dan 96.7% (SVM) untuk set latihan. Set ujian menghasilkan nilai 87.5% pengkelasan betul untuk LDA, 83.3% untuk PLS-DA sementara pengkelasan terbaik ialah 91.7% untuk SVM. Analisis sisa kebakaran menggunakan GC-MS dengan bantuan kaedah kimometrik memberikan keputusan yang baik dalam pengenalpastian dan pengkelasan bahan penggalak kebakaran yang digunakan untuk memulakan api dalam kes kebakaran.

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LIST OF ABBREVIATIONS

GC	-	Gas Chromatography
GC-MS	-	Gas Chromatography Mass Spectrometry
MS	-	Mass Spectrometry
GC-FID	-	Gas Chromatography Flame Ionization Detector
FID	-	Flame Ionization Detector
RON	-	Research Octane Number
PCE	-	Tetrachloroethylene
TCMX	-	Tetrachloro-m-xylene
ACS	-	Activated carbon strip
SPME	-	Solid phase microextraction
MATLAB	-	Matrix Laboratory
HCA/ CLA/ CA	-	Hierarchal Cluster Analysis
PCA	-	Principal component analysis
SIMCA	-	Soft independent model of classification analogy
SVM	-	Support vector machine
LDA	-	Linear Discriminant Analysis
PLS	-	Partial Least Square
PLS-DA	-	Partial Least Square Discriminant Analysis
ILR	-	Ignitable Liquid Residue
TIC	-	Total Ion Chromatogram
PC	-	Principle Component
GA	-	Genetic Algorithm
RMSEP	-	Root Mean Square Error Of Prediction
RMSEC	-	Root Mean Square Error Of Calibration
CC	-	Correctly Classified / Correct Classification

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CHAPTER 1

INTRODUCTION

1.1   Background of Study

Arson represents a serious problem which is defined as a criminal act of purposely setting fire to a house, building or other properties. Arsons are included as difficult crime to investigate and prosecute. It is because every fire scene need to be treated as a potential arson scene until clear proof of natural and accidental cause is discovered. Furthermore, the crime itself, if it is successful, destroys the physical evidence at its origin [1]. In some cases, the evidence is still there but it requires methodical and rigorous analysis. Arson is a crime that destroys evidence rather than creates one as it progresses and normally there is not much eyewitness evidence. Moreover, the incendiary origin of the fire is often hard to prove.

The main objectives of arson investigation are to determine the cause and origin of fire and also to identify the accelerants used to start the fire. However, fire investigator faced great challenges when there are lacking of physical evidence in the fire scene due to thermal degradation and combustion process. Besides that, complex nature of petroleum-based fire accelerants poses a problem for the arson investigator to determine the origin and the cause of the fire. Many accelerants composed of hundreds of compounds that can make identification of fire debris very difficult. The detection of fire accelerants becomes more difficult due to the contamination from the pyrolysis of common household items such as plastics, carpet and carpet padding at the fire scene [2-4].

The study of weathering effect is important since the exposed accelerants will definitely have some changes in their chemical composition. Hence it will greatly affect the chromatographic data. The chromatographic data obtained from fire debris will be used to perform chemometric techniques to see the accelerants grouping. Studies on the evaporation effect on samples are necessary to avoid misinterpretation of accelerants [5, 6].

Identification of petroleum-based accelerants are normally conducted according to chemical components of the accelerants. Chromatographic technique remains as the best method to analyze the components. Gas chromatography mass spectrometry (GC-MS) analysis of fire debris has been used to identify residues of fire accelerants. Identification of fire accelerants using GC-MS depends on two main types of pattern matching methods [7]. One approach makes use of extracted ion profile matching. With this method, intensity profiles for characteristic ions of fire debris samples are visually compared with the profile of known standard. Another method depends on target component analysis. A target compound chromatogram (TCC) is developed using the retention time and relative amount for each target compound. Visual pattern recognition is employed to confirm the fit to TCCs of known accelerant. This is done for the identification of an unknown accelerant.

Both these methods require visual inspection for the identification of complex samples of fire accelerant. This process is time consuming and may lead to misclassification. Furthermore, the interpretation of the complex data obtained from arson suspected fire required the experience of a trained analyst. Hence, a powerful tool such as chemometrics method is essential in interpreting these complex data obtained from GC-MS to classify and identify fire accelerants present in arson crime scene.

Preliminary work [8] on the classification of accelerants extracted from the fire debris produced promising results. Clusters which correspond to the type of accelerants were obtained by using principal components analysis (PCA). In the proposed study, more powerful pattern recognition method such as support vector machine [9] will be employed to develop classes using samples of fire debris with

known accelerants. The developed class will be validated by predicting the type of accelerants in the unknown samples. Furthermore, the effect of weathering on the classification will be studied.

1.2   Problem Statement

Petroleum-based accelerants are commonly associated with arson-related fire. In most arson cases, accelerants such as gasoline, kerosene and diesel are used to enhance the intensity and rate of fire. The complex nature of petroleum-based accelerants posed a problem for the arson investigator to determine the origin and the cause of the fire. The identification of fire accelerants become more difficult due to contamination from pyrolysis of common household items such as plastics, carpet and carpet padding at the fire scene. Furthermore, the weathering effect on the fire debris samples will alter the chemical composition due to the loss of light components via vaporization process. Therefore, correct identification of accelerants is crucial to arson investigation.

In this study, the application of gas chromatography-mass spectrometry (GC-MS) followed by data analysis using chemometric techniques were conducted. A comparatively new pattern recognition method, support vector machine (SVM) was applied to perform the non-linear classification of accelerants in fire debris analysis. Other chemometric methods such as soft independent model of class analogy (SIMCA) has been used to perform the classification of petroleum-based accelerants in previous study [8]. However the grouping was not clearly seen and there is difficulty in building the model. SIMCA is a linear supervised pattern recognition technique which performs the classification based on the model of known samples from principal component analysis. Perhaps the grouping of petroleum-based accelerants requires a non-linear classification technique.

Hence, new pattern recognition technique is proposed to perform the analysis. Support vector machine is a supervised pattern recognition technique which is

expected to give better results on the classification of accelerants in fire debris samples. This SVM model is developed from the linear classification model itself before transforming into higher dimensional space to create a non-linear boundary to perform the non-linear classification of petroleum-based accelerants. The non-linear classification model is supposed to provide better classification results than the linear technique.

1.3 Objectives of the Study

The main objectives of the research are:

1) to analyze petroleum-based accelerants in fire debris using gas chromatography-mass spectrometry (GC-MS).
2) to study the grouping pattern of gas chromatographic data of accelerants.
3) to classify the accelerants using supervised pattern recognition techniques namely LDA, PLS-DA and SVM.

1.4 Scope of Study

This study is based on petroleum-based accelerants. Accelerants such as gasoline, kerosene and diesel were collected from the petrol stations and nearby shops. This arson analysis is focused on classification of the sample of fire debris based on their accelerants group. Carpet was selected as the sample matrix. The extraction technique involved in this analysis was dynamic headspace adsorption using activated carbon as absorbent.

Some of the fire debris samples were left for two days and five days after burnt (time variable) to investigate the weathering effect on the accelerants classification using chemometrics methods. The weathering effect on the fire debris

samples was expected to alter the results on the classification due to the loss of some volatile compounds to the surrounding.

The analysis of chemical components in the fire debris was conducted by using GC-FID and GC-MS. The grouping of the accelerant is based on the data variables obtained from the extracted ion profile and target ion chromatogram. Next, pattern recognition techniques will be used to develop classes using samples of fire debris with known accelerants and identification of unknown accelerant. Principal component analysis, linear discriminant analysis and partial least square discriminant analysis will be used to perform the linear classification while support vector machine will be used to carry out the non-linear classification.

The SVM classification model will be validated by predicting the accelerants used in the real sample. This supervised pattern recognition technique should demonstrate the clustering of real samples before further analysis is done for accelerant confirmation used.

1.5   Significance of Study

This study attempts to identify the type of accelerants used to start a fire in arson cases. The results obtained can be used in the forensic investigation and used as evidence to prosecute the arsonist. Basically, fire can be divided into several categories which are natural, accidental and incendiary [10]. The main role of fire investigators are to identify the causes of fire whether they are natural, accidental or incendiary in loses [11]. They utilized the evidence to make such determinations.

Significant pieces of information at fire scene like the points of origin of the fire and how the fire starts [12] will be required as proof in arson cases. Normally, multiple points of origin are strongly indicative of an intentionally set fire. After obtaining the evidence, fire investigators have the responsibility to identify the

person who commit the arson intentionally when it comes to incendiary fire cases and provide proof to prosecute the arsonist.

Analysis of fire debris using gas chromatography in conjunction with flame ionization detector (GC-FID) and mass spectrometry (GC-MS) will give detailed and accurate data to perform the accelerants classification. The large amount of target ion chromatogram data will be used to carry out the classification while the classification model from chemometric methods such as principal component analysis (PCA), linear discriminant analysis (LDA), partial least square discriminant analysis (PLS-DA) and support vector machine (SVM) will be useful to the party who are involved in arson cases like Jabatan Kimia Malaysia, Jabatan Bomba Malaysia or consultants from the private sector. It is hoped that this research will facilitate the analyst to make the identification and classification of fire accelerants from fire debris samples more accurately.

1.6   Chapter Summary

This chapter summarized the background details of fire debris analysis on identification and classification of petroleum-based accelerants. A few objectives were made to answer several research questions related to this study. New chemometric technique (SVM) is proposed and expected to give better results on the classification of accelerants. In addition, several researches are needed to compare and improve the findings.

The next chapter will discuss further on other research works related to this study. Most of the literatures will be focused on the petroleum-based accelerants, chromatographic techniques, extraction methods and chemometrics techniques which later will be applied to the sample matrix.

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