

**FORENSIC ANALYSIS OF GASOLINE IN
MOLOTOV COCKTAIL USING GAS
CHROMATOGRAPHY – MASS
SPECTROMETRY AND CHEMOMETRIC
PROCEDURES**

by

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for the degree of
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DECLARATION

I declare that the material presented in this thesis is all my own work. The thesis has not been previously submitted for any other degree.

Date: 27 October 2014

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LIST OF ABBREVIATIONS, ACRONYMS AND SYMBOLS

%	percentage
°C	degree Celsius
cm	centimetre
cm²	square centimetre
<i>et al.</i>	and others
g	gram
<i>i.e.</i>	that is
kg	kilogram
m³	cubic metre
µm	micrometre
min	minute
mm	millimetre
mL	millilitre
r²	r-squared value
v/v	volume/volume
ASTM	American Society for Testing and Material
EIC	Extracted Ion Chromatogram
GC	Gas Chromatography
GC-MS	Gas Chromatography-Mass Spectrometry
ID	Internal Diameter
MS	Mass Spectrometry
NIST	National Institute of Standards and Technology
PAH	Polycyclic Aromatic Hydrocarbons
RON	Research Octane Number
RT	Retention Time
SD	Standard Deviation
SIM	Selected Ion Monitoring
SPME	Solid Phase Micro Extraction
TIC	Total Ion Current *Chromatogram
UCM	Unresolved Complex Mixtures

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**ANALISIS FORENSIK TERHADAP GASOLIN YANG DIGUNAKAN
SEBAGAI MOLOTOV KOKTEL DENGAN MENGGUNAKAN
KROMATOGRAFI GAS-SPEKTROMETRI JISIM DAN KAEDAH
KEMOMETRIK**

ABSTRAK

Terdapat peningkatan yang ketara dalam rampasan Molotov koktel oleh Polis Diraja Malaysia, terutamanya semasa demonstrasi jalanan, ketegangan agama dan konflik sosial. Semasa penyiasatan forensik, pengumpulan maklumat dan siasatan terhadap komposisi bahan boleh menjadi penghubung antara kes-kes yang berbeza, atau sumber dan kumpulan orang yang terlibat. Tesis ini mengkaji kepelbagaian gasolin yang biasa digunakan sebagai bahan api dalam Molotov koktel dengan menggunakan kromatografi gas-spektrometri jisim (GC-MS) dan teknik kemometrik untuk analisis data lanjutan termasuk analisis komponen utama (PCA) dan analisa hirarki kelompok. Dua puluh tujuh sample telah dikumpul dari stesen minyak berbeza. Gasolin yang didapati daripada dua stesen minyak terpilih pada selang masa yang berbeza selama 28 hari telah dikaji untuk melihat perubahan profil dari masa ke masa. Dua jenama gasolin juga telah dikaji bagi mengetahui perubahan profil selepas terdedah kepada penyejatan dan pelarutan. Kesemua sampel telah dianalisa dengan GC-MS dan puncak terpilih telah digunakan untuk analisis data seterusnya. Keputusan kajian menunjukkan bahawa analisis GC-MS dapat mendiskriminasi sampel gasolin segar kepada dua kumpulan utama mengikut jenama. Dengan menggunakan puncak terpilih dari kromatogram, sampel segar diambil dari masa ke masa dari stesen minyak tertentu dapat dibezakan walaupun ada yang dikelompokkan dengan agak

rapat. Kedua-dua sampel menunjukkan trend yang dapat diramalkan pada plot skor PCA yang boleh digunakan untuk menganggar tahap penyejatan suatu sampel. Data ion kromatografi terekstrak bagi sampel gasolin yang terdedah kepada air kelihatan hanya berubah sedikit. Penyiasatan terhadap perolehan semula bahan api daripada Molotov koktel yang sudah diletupkan menunjukkan hanya 80% daripada Molotov koktel terbakar sepenuhnya. Bilasan pelarut ke atas serpihan kaca yang diperolehi memberikan keputusan negatif terhadap kesan gasolin. Ia memberi indikasi bahawa pengumpulan serpihan kaca dari Molotov koktel yang telah diletupkan untuk pemulihan bahan api tidak digalakkan bagi pegawai-pegawai penyiasat kecuali untuk tujuan lain seperti untuk mendapatkan kesan cap jari. Kesimpulannya, kajian ini menunjukkan gasolin segar daripada sumber yang berbeza boleh dibezakan sekurang-kurangnya mengikut jenama yang berlainan atau ke dalam kelompok kecil dalam jenama yang sama dengan menggunakan prosedur kemometrik. Maklumat ini berguna bagi menyiasat kes-kes yang melibatkan Molotov koktel yang telah dirampas. Sampel yang telah tersejat dilonggokan dalam kumpulan yang berbeza oleh PCA dengan corak yang boleh dijangkakan sementara pelarutan hanya memberikan sedikit kesan ke atas profil gasolin. Dalam kes Molotov koktel yang telah terbakar, bahan api akan lesap disebabkan keamatan pembakaran dan haba.

**FORENSIC ANALYSIS OF GASOLINE IN MOLOTOV COCKTAIL USING
GAS CHROMATOGRAPHY – MASS SPECTROMETRY AND
CHEMOMETRIC PROCEDURES**

ABSTRACT

There has been a significant increase in the number of seizure of Molotov cocktail by the Royal Malaysia Police (RMP) during street demonstrations, religious tensions and society conflicts in Malaysia recently. In a forensic science investigation, information gathered for intelligence purposes and investigation on the composition of a material of interest may serve as a link between different cases, or to a particular source or group of people involved. This thesis studies the variability (in term of chemical profiles) of gasoline commonly used as accelerant in Molotov cocktail using gas chromatography-mass spectrometry (GC-MS) coupled with chemometric techniques for advanced data analysis including principal component analysis (PCA) and hierarchical cluster analysis (HCA). A total of 27 samples of fresh gasoline were collected from different service stations. Collection of gasoline samples from two selected service stations at different time interval over 28 days was conducted to study their profiles changes over time. Two brands of gasoline were also used to investigate the profiles change after being subjected to evaporation and dissolution. All samples were analysed using GC-MS and selected peaks were used for subsequent data analysis. The results show that the GC-MS analyses were able to discriminate the fresh gasoline samples into two main groups on the basis of the different brands of gasoline. Using selected peaks from chromatogram, , the fresh samples collected over time from a particular service station were able to be

discriminated though some were tightly clustered. Both samples showed a predictable trend on PCA score plot that could possibly be used to estimate the extent of evaporation of a sample. The extracted ion chromatography data of the gasoline samples in contact with water appeared to be only slightly changed. The investigation of the recovery of accelerant on spent Molotov cocktail found that only 80% of the Molotov cocktails were completely combusted. Solvent rinse (of the recovered glass fragments) has shown negative result which could suggest that collection of glass fragment of exploded Molotov cocktail for accelerant recovery is not advisable unless for other forensic purposes such as fingerprint recovery. In conclusion, the fresh gasoline from different sources could be differentiated according to their different brands or into small clusters (within brand) using the chemometrics techniques. This information is useful for the investigation of seized Molotov cocktail cases. Evaporated samples are grouped differently by the chemometrics techniques however in a predictable manner while dissolution gave only slight change to the gasoline profiles. In the case of spent Molotov cocktail, accelerant would be lost due to evaporation as a result of intense burning and heat.

CHAPTER 1

INTRODUCTION

1.1 Introduction

This thesis studies the variability of gasoline fuels commonly used as the accelerant in Molotov cocktail. The main focus on the study is on the variability of fresh accelerant recovered from seized Molotov cocktails for tracing their common sources in a forensic scenario where a syndicate is suspected or to confirm a witness statement. A study on the variability of gasoline collected from two selected gasoline stations at different time interval over a period of time was also conducted to see if the accelerant source changes over time. In the case where a Molotov cocktail is spent, evaporation and/ or dissolution of the accelerant would inevitably occur. This study also investigated the profile changes of the accelerant subjected to evaporation and dissolution.

1.2 Statement of the Problems

In recent years, there has been a significant increase in the seizure of so called home-made improvised combustible materials using bottles by law enforcement in Malaysia, especially during street demonstrations or on the occasions of political supporters disagreement, rebellious, tensions or social conflicts, such incendiary bottles are also known as Molotov cocktails. During a forensic investigation, the ability to get the most information out from a recovered Molotov cocktail is the ultimate aim of a forensic investigation. In forensic investigation of seized materials

such as Molotov cocktail, an important point that could help intelligence gathering and investigation or as a preventive measure of a more serious unwanted event is based on the assumption that similar composition of the material may serve as a link between different cases, or a particular source or even to a particular group of people involved in a plot. In the case when unused Molotov cocktails are uncovered, the investigator's task is to examine the chemicals used to prepare the bottles, identify them, and indicate the source that it could have come from. To establish the links between the seized Molotov cocktails and their suspected source, the composition of the two sources shall be the same. Unfortunately, it is practically not easy to chemically fingerprint the accelerant, particularly, since they could have come from various sources.

It is therefore important to investigate the variability of the fuels used in a Molotov cocktail from various sources. For example, in the case if a source is determined (perhaps through witness statement or closed circuit television (CCTV) and also, in the case of unexploded Molotov cocktail, would the weathering i.e. evaporation and/or dissolution affect the profile from its original source.

1.3 Definition of Molotov Cocktail

A Molotov cocktail is defined by Tsaroom (1986) "as a bottle that contains inflammable liquid and has an ignition source (Tsaroom, 1986)". A typical Molotov cocktail is made using a bottle or can be other breakable container filled with accelerant such as gasoline (Siegel and Mirakovits, 2010). A wick is inserted through

the mouth of the bottle so that it can be ignited before throwing to a target (Siegel and Mirakovits, 2010).

1.4 Molotov Cocktail as an Improvised Explosive Device (IED)

Being a simple, cheap and easy to make incendiary device, known also as a gasoline bomb (Helmenstine, 2006), Molotov cocktails have been used as weapons for many years. Its history could be traced back during the Spanish Civil War in 1936 where the “bottle-bombs: were used to attack tank (Trotter, 2012). The name “Molotov cocktail” was attached to the bottle bombs was believed to originated during the Winter War when Soviet Union invaded Finland (Trotter, 2012). The Finnist manufactured the bottle bombs to fight against Soviet Union’s tanks and used the name Vyacheslov Molotov, the Minister of Foreign Affairs of Soviet Unions at the time. A simple Molotov cocktail consists of a breakable bottle filled with accelerant such as gasoline. A fuel-soaked rag is then stuffed on the top of the bottle. The fuel soaked rag is ignited before throwing. When container breaks due to the impact, the flammable liquid in the bottle spread to form flammable vapor which is then quickly ignited by the flame producing a fireball (Helmenstine, 2006). Figure 1.1 shows a typical Molotov cocktail.



Figure 1.1: A typical Molotov cocktail as an IED

Tsaroom (1986) also reported different versions of Molotov cocktail design, in which a rag is saturated with flammable liquid as shown in Figure 1.2 (left) and wrapped around the bottle's neck as shown in Figure 1.2 (middle). Matches were also used as the ignition source (Tsaroom, 1986) as shown in Figure 1.2 (right).

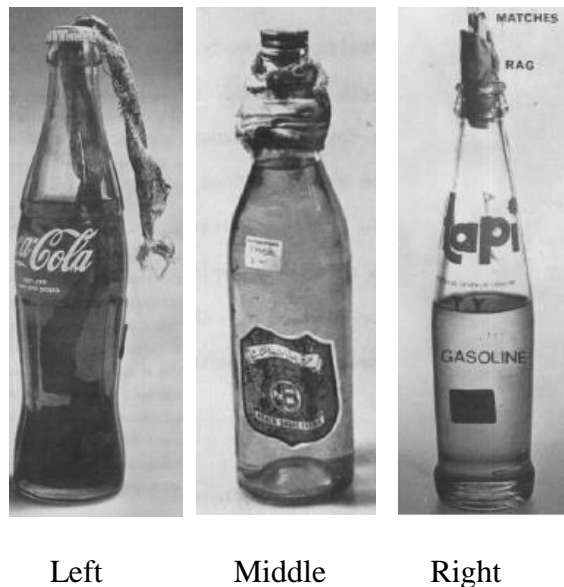


Figure 1.2: Different mechanisms used as the ignition source: (Left) A wick inserted through the bottle neck; (middle) a rag saturated with fuel liquid and wrapped around the bottle neck, and (right) matches tied together and inserted inside the bottle neck (Tsaroom, 1986)

The effects of causing burning is maximised by throwing it against hard surfaces such as wood or wall (DeHaan, 2007). The flammable liquids used in a Molotov cocktail can be gasoline, kerosene or a mixture of other materials including diesel and motor oil (Tsaroom, 1986), calcium hydroxide and calcium carbonate (Tsaroom, 1986), sugar and potassium chlorate (Martin-Alberca *et al.*, 2012) and sulphuric acid (DeHaan, 2007; Martin-Alberca *et al.*, 2012). However, the most common Molotov cocktail contains gasoline (Tsaroom, 1986; DeHaan, 2007), probably due to the ease of handling since gasoline is safe to transport in bottle, easily available at service station and relatively inexpensive.

Incidents involving Molotov cocktail were frequently reported in Malaysia especially during the road demonstrations, riots or racial disputes over the past several years (Personal Communication). In Kelantan alone, data from the Criminal Investigation Department (CID) of Royal Malaysia Police in Kelantan showed that there were at least 42 reported cases from 2004 to 2012 involving the use of Molotov cocktail with most of them involving gasoline as fuels (Table 1.1).

Note that in the case of Molotov cocktail, several sections of the law are used for information including Section 302 of the Penal Code, Section 435 of the Penal Code or Section 6 of Explosive Act (1957). Section 302 of Penal Code states that “whoever commits murder shall be punished with death”.

Table 1.1: Number of cases and sections charged for cases involving Molotov cocktail in Kelantan.

No.	Year	Total of cases	No. of Cases	Section Used for Investigation
1.	2012	5	1	302 Panel Code
			4	435 Panel code
2.	2011	8	1	6 Explosive Act (1957)
			7	435 Panel code
3.	2010	4	4	435 Panel code
4.	2009	8	2	6 Explosive Act (1957)
			6	435 Panel code
5.	2008	7	1	6 Explosive Act (1957)
			6	435 Panel code
6.	2007	4	4	435 Panel code
7.	2006	2	2	435 Panel code
8.	2005	2	2	435 Panel code
9.	2004	2	2	435 Panel code
Total of Cases		42		

Section 435 of Panel Code states that “whoever commits mischief by fire or any explosive substance, intending to cause, or knowing it to be likely that he will thereby cause, damage to any property to the amount of fifty ringgit or upwards, shall be punished with imprisonment for a term which may extend to seven years, and shall also be liable to fine”. Section 6 of Explosive Act (1957) states that “any person who unlawfully and maliciously causes by any explosive an explosion of a nature likely to endanger life or to cause serious injury to property shall, whether any injury to person or property has been actually caused or not, be liable, on conviction, to imprisonment for seven years, or to a fine of ten thousand ringgit, or to both” (Explosive Act, 1957; Penal Code, 2008). Note that the right column of Table 1.1 indicate that these cases were investigated under different section of Panel Code or section 6 of Explosive Act 1957.

1.5 Gasoline as Fuels in Molotov Cocktail

Theoretically, any flammable liquid can be used as the fuel for Molotov cocktails. Although there were other possible mixture such as the thickened “napalm” i.e a mixture of gasoline paraffin wax, poor burning effects making it less famous (Siegel and Mirakovits, 2010) when extra time and effort are required. Gasoline, kerosene, diesel and toluene are some commonly available flammable liquids but gasoline is perhaps the most preferred one as it is easily available and produce instant flame upon ignition. Kerosene and diesel do not burn as fast as gasoline especially when the surface is not hot. Kerosene is also not available in many places while the purchase of diesel may attract the seller’s attention due to its limited use except for heavy trucks. In addition, the purchase of diesel is controlled by the subsidy scheme in Malaysia. Toluene is suitable but it is costly and not widely available as gasoline which could be purchased from any service station without restriction.

In the case when a plot is planned, the persons involved would not want her/ him to be attracted by others and the most convenient place will be the publicly assessable service stations. All these explain why gasoline is the most common fuel encountered in Molotov cocktail (Tsaroom, 1986) and incendiary fires (Trotter, 2012).

1.6 Chemistry of Gasoline

Gasoline is a flammable liquid most voluminously produced and distributed (DeHaan, 2007). It is a transparent liquid at room temperature that boils below 180°C (Trotter, 2012) and derived from crude oils vial various processes. Figure 1.3 shows

a schematic flowchart of various process to produce a particular gasoline petroleum product such as gasoline (DeHaan, 2007).

The word “fingerprinting” is used to explain the complex feature of compounds in a particular source that can be different from another different source (Sandercock and Pasquier, 2003a). As reported by Shell Malaysia, they are many types of crude oil which come from many different sources around the world, and the selection of the source depends on many factors including quality, availability, volume and price (Shell Malaysia, 2014).

Due to various distillation processes that blended multiple intermediates in the manufacturing process, different brands or sources can exhibit different chemical profiles (DeHaan, 2007) and this a useful feature in distinguishing different sources known as hydrocarbon fingerprinting commonly used by environmental forensic scientist.

1.6.1 Molecular Component of Gasoline

In general, gasoline contains molecules of 4 to 12 carbon atoms as its main composition (Newman, 2004; DeHaan, 2007; Trotter, 2012) that can broadly be classified into saturated and aromatic hydrocarbons (Bertsch *et al.*, 1993; Newman, 2004) and some alkanes and other compounds at trace quantities (Bertsch *et al.*, 1993). In contrast to diesel fuel where alkanes are in large abundance, aromatic hydrocarbons form a large fraction of gasoline.

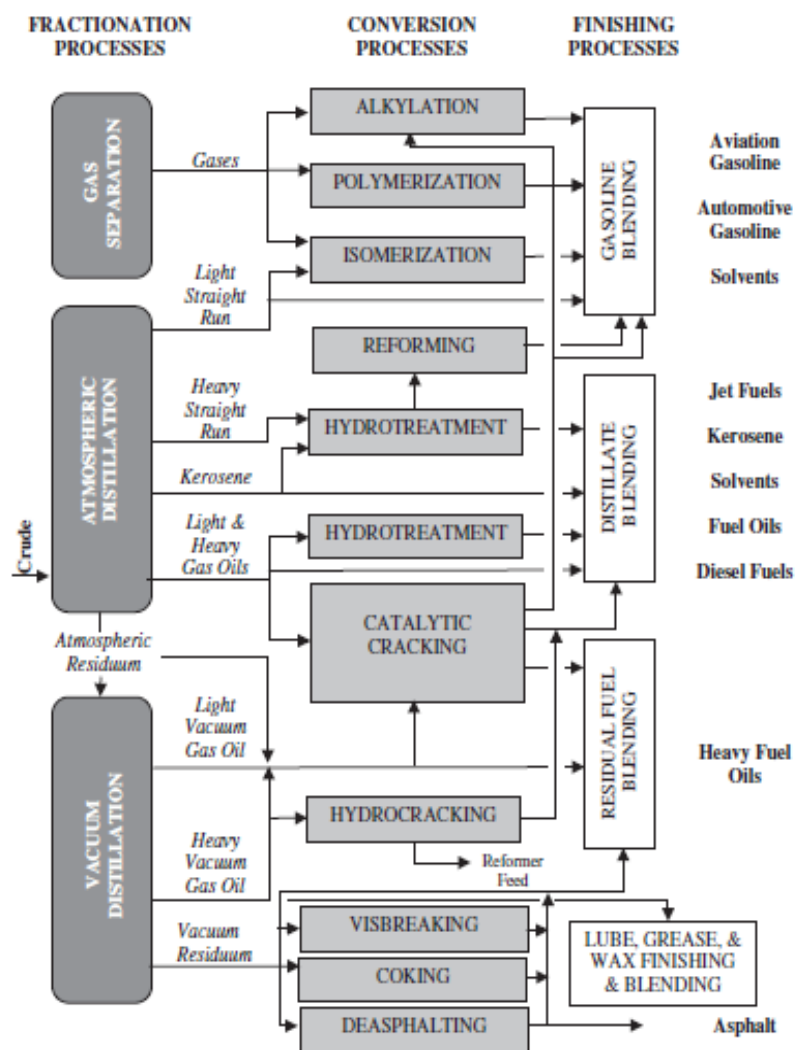


Figure 1.3: Schematic flowchart of a modern complex refinery used in the production of gasoline petroleum products (DeHaan, 2007)

1.6.2 Alkanes

Alkanes are commonly found in crude oil with carbon numbers ranging from C_5 to C_{40} although a few alkanes beyond C_{40} have also been identified (Tissot and Welte, 1984). Alkanes contain only nonpolar (C: carbon H: hydrocarbon) C - C and C - H bonds and as a result, they exhibit only weak Van Der Waals forces between molecules and therefore present as gas or liquid at room temperature except for high

molecular weight alkanes. In general, alkanes can be classified into normal alkanes, isoalkanes and cycloalkanes.

1.6.2.1 Normal Alkanes

Normal alkanes (n-alkanes) consist of a series of carbon atoms connected by single bonds in a straight-chain configuration. They have the formula C_nH_{2n+2} , where 'n' is the number of carbon atoms in the molecule. In hydrocarbon analysis, alkanes appear “tree – like structure” in a chromatogram at regular intervals, especially in a chromatogram of a diesel (Abdullah, 2004). In gasoline, the carbon numbers for n-alkanes generally span from C_5 to C_{13} but they could be masked by aromatic compounds which are present in significantly larger abundance in a chromatogram. An example of n-alkanes is shown in Figure 1.4.



Figure 1.4: n-decane with ten carbons in a long chain

1.6.2.2 Branched-alkanes

Iso-alkanes are branched alkanes. In generally, they are similar to n-alkanes except they have one or more carbon branches along the straight chain backbone (Abdullah, 2004). The branching structure leads to lower boiling points as compared to their n-alkanes counterpart although both have the same molecular formula. Branched alkanes are found in gasoline. Figure 1.5 shows an example of iso-alkanes.

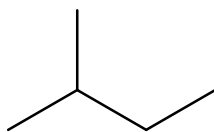


Figure 1.5: Structure of 2-methylbutane

1.6.2.3 Cycloalkanes

Cycloalkanes are alkanes containing rings of carbon atoms with chemical formula of C_nH_{2n+2} (Newman, 2004; Katherine *et al.*, 2011). They have higher boiling points than their corresponding normal alkanes. The cycloalkanes compound found in gasoline include cyclopentane, methyl-cyclopentane, cyclohexane and 1,2-dimethylcyclohexane as shown in Figure 1.6.

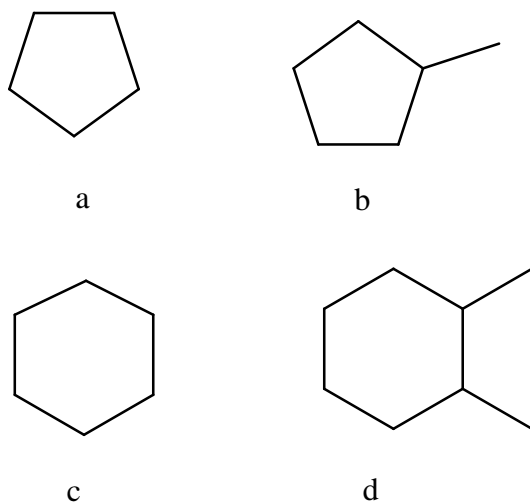


Figure 1.6: Cycloalkanes found in gasoline (a: cyclopentane, b: methylcyclopentane, c: cyclohexane and d: 1,2-dimethylcyclohexane)

1.6.3 Aromatic Compounds

Aromatic compounds are compounds that contain the characteristic benzene ring or its structural relatives in their chemical structures (Seager and Slabaugh, 2000). The most common aromatic compounds are based on the six-membered aromatic ring- *i.e*, the benzene ring (Katherine *et al.*, 2011). In hydrocarbon analysis, aromatic compounds are generally classified into simple aromatic, polynuclear aromatic hydrocarbon (PAHs) and indanes (Abdullah, 2004; Stout and Wang, 2007). Simple aromatic compounds consist of a benzene ring in their chemical structures. Benzene, carrying the molecular formula C_6H_6 is the simplest aromatic compounds. In crude oil, benzene, naphthalene and phenanthrene types are the most abundant (Abdullah, 2004). Figure 1.7 shows the representative structures of aromatic compounds with single, double and triple benzene rings.

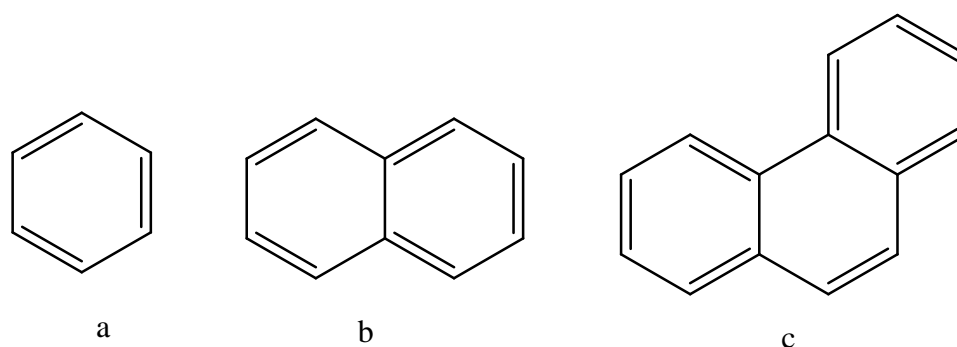


Figure 1.7: Chemical structure of aromatic compounds (a: benzene, b: naphthalene and c: phenanthrene)

Naphthalene and phenanthrene are known as polynuclear aromatic hydrocarbons (PAHs) because they are composed of two or more aromatic rings joined together. Naphthalene has a distinctive aroma and is frequently used as mothballs in the house.

Phenanthrene can be found as product of incomplete combustion of fossil fuels and wood in the environment. In crude oil, aromatic compounds with an alkyl side chain attached in a cyclic configuration to a benzene ring are called indanes. The side chain attaches to the benzene ring in two consecutive locations forming a cyclic configuration. Figure 1.8 shows the structure of an indane.

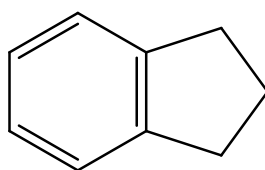


Figure 1.8: The structure of indane

In gasoline, the big molecule of PAHs were removed during the distillation process, leaving the lighter aromatic molecules such benzene, toluene, ethylbenzene and xylene (BTEX) and other alkylbenzenes and some naphthalenes.

1.7 Analytical Methods for Gasoline as Fuels in Molotov Cocktail

The analytical methods available for gasoline analysis in forensic setting have evolved in line with those used by the geo-chemist in the production of hydrocarbon products (Stout and Wang, 2007). Gas chromatography (GC) coupled with flame ionisation detector (FID) and mass spectrometry (MS) have been widely used in oil spill fingerprinting (Abdullah, 2004; Donald *et al.*, 2004; Christensen and Tomasi, 2007), arson analysis (Bertsch, 1994) and gasoline analysis (Mann, 1987; Coulombe, 1995; Sandercock and Pasquier, 2003a; Sandercock and Pasquier, 2003b; Aleme *et al.*, 2008). By comparing the chromatographic features of two samples, forensic

investigators can establish the similarities and differences between the two samples through the technique known as pattern comparison (Section 1.8). Similarities indicate that both the samples could have come from the same origin while differences could indicate that they were from different sources (Abdullah, 2004).

1.7.1 Gas Chromatography–Flame Ionisation Detector

GC-FID analysis provides useful hydrocarbon fingerprints of the sample and can provide an initial picture of the profile (Donald *et al.*, 2004). Flame ionisation is a robust detection method (Christensen and Tomasi, 2007). In environmental forensics, GC-FID is used as a screening technique to characterise hydrocarbons (Wang *et al.*, 1994; Irwin, 1998; Wait, 2000; Daling and Faksness, 2002). The flame ionisation detector is a universal detector and responds to large number of hydrocarbons and is widely used due to its large linear range of sensitivity (Donald *et al.*, 2004).

1.7.2 Gas Chromatography–Mass Spectrometry

GC-MS is currently the most important instrument for forensic analysis of organic compounds including hydrocarbon compounds (Dolan, 2004; Donald *et al.*, 2004; Douglas *et al.*, 2007). It consists of a gas chromatograph to separate the compounds and a mass spectrometer as a detector. Mass spectrometer detects selected ions at particular (mass-to-charge ratio) m/z values. Identification is based on the fact that a particular type of structure leads to a particular m/z values of detected ions.

As pointed out by Newman (2004), in terms of accelerant analysis, GC-MS provided the additional levels of pattern recognition because each class of hydrocarbons (alkanes, cycloalkanes, aromatic) produce ion fragments that can be used to indicate the compound class (Newman, 2004). For instance, the normal alkanes produce ion fragments at m/z of 3, 57, 71 and 86. Therefore, extracting these ions can produce an extracted ion chromatograms (EIC) for the examination of a sample especially when the sample is mixed with background material (Dolan, 2004), that could have made the total ion chromatogram different due to contaminations.

1.7.3 Gas Chromatography of Gasoline

Gasoline contains aliphatic and aromatic compounds, but the former are less abundant than the latter (Newman, 2004). In a gas chromatography, the presence of aliphatic compounds is indicated by the “trees” in a chromatogram at different interval (Abdullah, 2004). However, the “trees” are not obvious in gasoline due to narrow carbon range from $C_5 - C_{12}$ and with lower abundance. Most compounds in gasoline are simple aromatic *i.e.* alkyl-substituted benzene as can be seen on a GC-FID chromatogram, or a full scan of GC-MS chromatogram for the presence of C_2 alkylbenzene, C_4 alkylbenzene peaks (Newman, 2004) as shown in Figure 1.9.

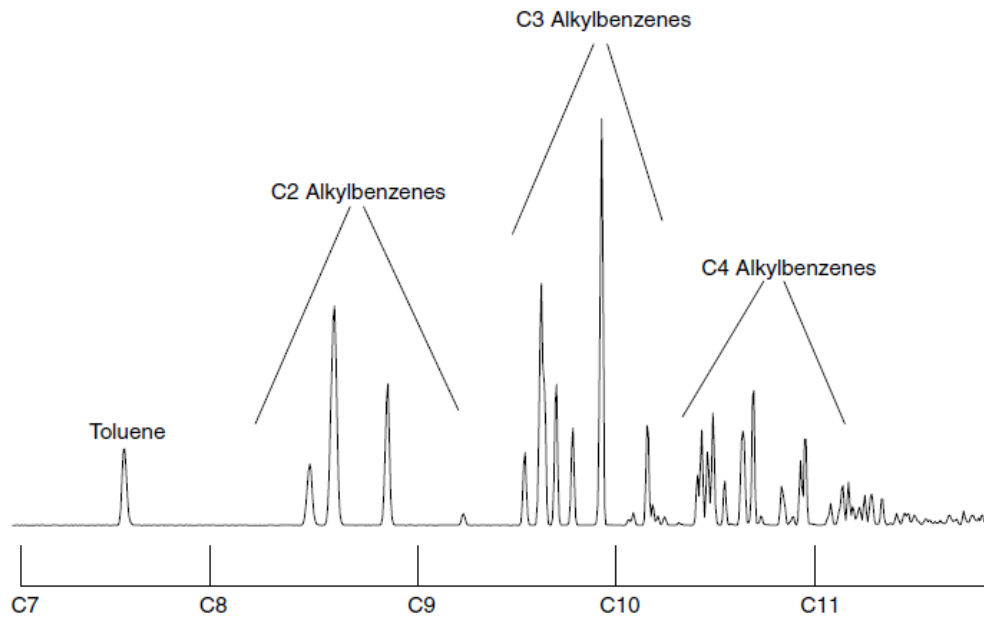


Figure 1.9: Peak patterns for alkylbenzenes found in gasoline (Newman, 2004)

1.7.4 Peak Normalisation

Peak normalisation was necessary to make samples of different concentrations to be comparable. For example, if a sample is diluted to different extents, then the peak areas (or the peak heights) between the different dilutions will definitely differ. Nonetheless, if two peaks within the samples were chosen, the ratios of these selected two peaks should remain the same when compared to the ratio of the two peaks of different dilutions (Figure 1.10).

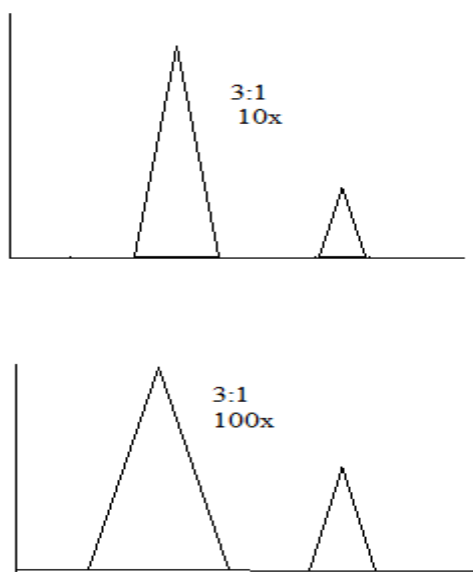


Figure 1.10: Ratio of the two peaks of different dilutions

Even the samples were prepared with the same concentration; more of one sample may have been introduced into the GC thus producing chromatograms of different response between the two injections (of the same sample). Under such circumstances, peak normalisation is necessary to make the data from different chromatogram comparable.

The peaks selected for integration should fulfil some criteria's. Peaks might either contain shoulders, Figure 1.11 (a) or unresolved (b), making integration inaccurate if the same peaks were to be used for comparison. If a peak appears too small, it could be associated with a larger error of integration especially when peak area is used (Abdullah, 2004), see also Figure 1.11 (b).

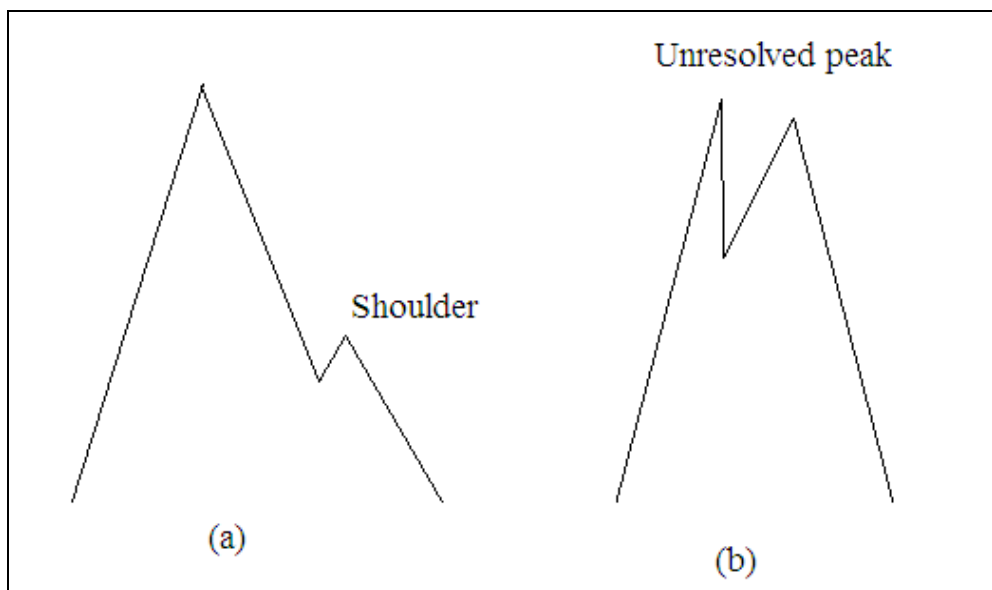


Figure 1. 11: A peak with (a) peak shoulder and (b) an unresolved peak

1.8 Pattern Recognition

The term “pattern recognition” is used in forensic and arson analysis to describe the visual composition of chromatograms (Bertsch *et al.*, 1993). It is a subfield of chemometrics that uses statistical methods to extract information from data (Bertsch *et al.*, 1993). Pattern recognition is identification based which does not focus on the presence of individual compounds, but emphasises on the presence of compounds in relation to other compounds (Almiral and Furton, 2004). In forensic science, pattern recognition is widely used with the application from fingerprint and ballistics analysis, environmental oil spill fingerprinting, arson investigation to image comparison (Bertsch *et al.*, 1993; Christensen and Tomasi, 2007).

In hydrocarbon analysis for environmental or arson application, the chromatogram from the sample analysed is compared to a collection of known samples. The analyst determines a threshold that must be exceeded for sample inclusion or exclusion

(Bertsch *et al.*, 1993). It is important to note that the physical arrangement and graphic presentation may effect human perception and therefore a number of steps should be followed (Bertsch *et al.*, 1993; ASTM D3328-00, 2000). In visual comparison, patterns (such as chromatograms and peaks) of similar size are preferred than those displayed at different size (Bertsch *et al.*, 1993) and the overlay techniques for accelerant are normally used if the chromatograms could be produced at the same magnitude (Bertsch *et al.*, 1993; ASTM D3328-00, 2000).

With the advancement of computer software, data displaying software in modern gas chromatographer has facilitated chromatogram comparison. An early literature by Tontarski and Strobel (1982) described the computer aided pattern recognition to adjustment of the scale of the chromatogram (Tontarski and Strobel, 1982). The chromatogram was divided into different windows for comparison (Figure 1.12) and this step by step analytical procedure is still being practised until today.

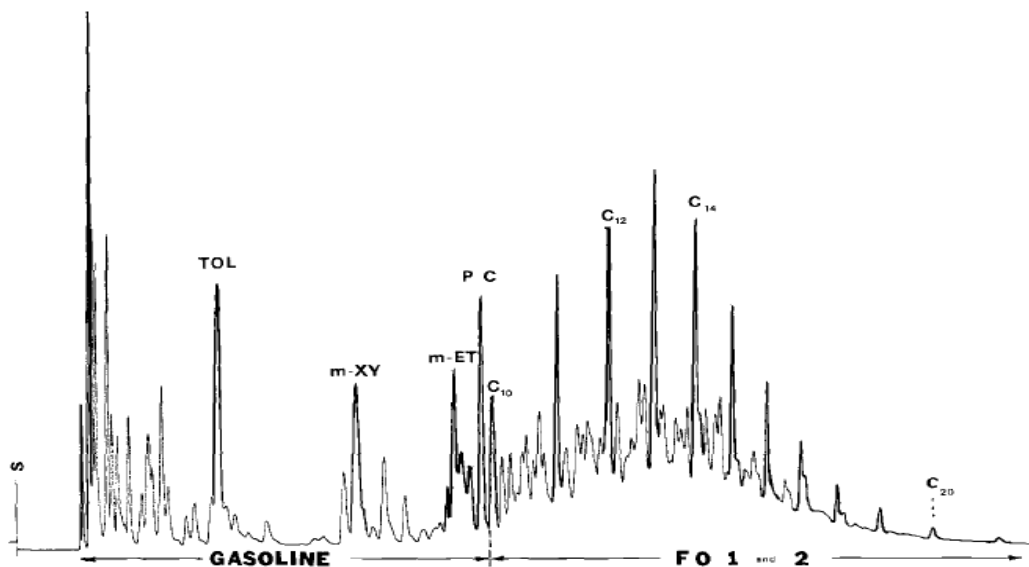


Figure 1. 12: The chromatogram was divided into different windows for step by step comparison (Tontarski and Strobel, 1982)

Statistical analysis has been used to classify hydrocarbon products for forensic purpose (Stout, 2001; Sandercock and Pasquier, 2003a; Sandercock and Pasquier, 2003b; Wang and Fingas, 2003; Wang *et al.*, 2004; Wang *et al.*, 2005; Wang *et al.*, 2006; Barbeira *et al.*, 2007; Bartolome *et al.*, 2007; Ebrahimi *et al.*, 2007; Ebrahimi and Hibbert, 2008; Hupp *et al.*, 2008). Multivariate statistical technique such as Principal Components Analysis (PCA) has been used to visualise the relations between samples using chromatographic data (Sandercock and Pasquier, 2003a; Barbeira *et al.*, 2007). For instance, Abdullah (2004) have used PCA and dendrograms to differentiate diesel samples collected from service stations in Auckland and fishing boats (Abdullah, 2004). A study of the variability of fresh diesel from service stations in Kota Bharu using GC-MS and PCA was also conducted by the same research group (Azah and Abdullah, 2011). For gasoline, Sandercock and Pasquier (2003) have also applied the PCA for the fingerprinting of unevaporated automotive samples in Australia and New Zealand (Sandercock and Pasquier, 2003a) while Barbeira reported the use of PCA for the identification of gasoline origin (Barbeira *et al.*, 2007).

1.8.1 Principal Component Analysis

PCA is a multivariate analysis used to analyse and visualise the differences between samples (Abdullah, 2004; Christensen and Tomasi, 2007; Azah and Abdullah, 2011). PCA creates new independent variables which contain much of the information from the original data thus reduces the multiple dimensions of the raw data into a few principal components (PC1, PC2, PC3...). The first principal component (PC1) explains the most possible amount of variability in the data followed by the second

principal component (PC2) that explains the second largest amount of variability in the data, and so on for the third principal component (PC3), the fourth principal components, etc.

1.9 Analytical Methods

Tontarski and Stobel (1982) reported a method for rapid screening of arson samples using a sorption elution sampling setup followed by GC analysis in early 1982. (Tontarski and Stobel, 1982). This method is very similar to ASTM E1388-00 method developed later. In many instances, accelerant or oil samples with or without cleaning with a suitable solvent such as dichloromethane (DCM) are subjected to GC analysis (Stout, 2001; Sandercock and Pasquier, 2003a; Abdullah, 2004; Wang *et al.*, 2004; Hupp *et al.*, 2008). Sandercock and Pasquier (2003) also applied a solid phase extraction to separate aliphatic and aromatic compounds prior to GC-MS analysis (Sandercock and Pasquier, 2003a; Sandercock and Pasquier, 2003b). A comparison of unevaporated gasoline from Australia and New Zealand was also conducted by the same research group using GC-MS which reported the ability to differentiate the country of origin (Sandercock and Pasquier, 2004).

The ASTM E 1385-00 is the standard practice for separation and concentration of ignitable liquid residues from fire debris samples by steam distillation published by American Society for Testing and Materials (ASTM). Steam distillation is not a popular method and it is the least sensitive and most complex technique for ignitable liquid separation (ASTM E1385-00, 2000). Its use is extremely limited in forensic laboratories and is not intended as a primary extraction technique.

The ASTM E 1386-00 is the Standard Practice for Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Solvent Extraction that explains the procedure to extract residue of combustible liquid from fire debris using suitable solvent for subsequent gas chromatography analysis (ASTM E1386-00, 2000). The procedure may not be a primary technique to extract combustible liquid as it is often related to its low sensitivity, messy with significant background substrate contamination, and is destructive in nature (Newman, 2004). The procedure is particularly useful when the analyst need to extract over a wide range of concentration and allows for distinguishing among the types of fuel oil (ASTM E1386-00, 2000).

The ASTM E 1387-01 is a Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography which is used together with ASTM E1385, ASTM E1386 and ASTM 1388 (ASTM E1385-00, 2000; ASTM E1386-00, 2000; ASTM E1388-00, 2000). It covers the steps for extracting a small quantity of accelerant vapour at the headspace of the sample container. The method notes that repeat and inter laboratory analyses are possible (ASTM E1388-00, 2000).

The ASTM E 1618-06 is a Standard Test Method for Ignitable Liquid Residue in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry. The standard describes the procedures for the identification of ignitable liquids residues from fire debris samples (ASTM E1618-06, 2006). It is applicable for most samples, also co-extract back-ground materials from the substrate. Sample handling procedures, accelerant classification and target compound identification are described (ASTM E1618-06, 2006). The standard notes that pattern matching of

chromatograms “rarely gives perfect correction with reference liquids”, and therefore analysts should evaluate visual pattern with care. In this thesis, this method is slightly modified for GC-MS analysis.

1.10 Weathering of Gasoline as Fuel in Molotov Cocktail

Depending on the environmental conditions and length of time elapsed, the chemical composition of gasoline from an exploded Molotov cocktail will subject to evaporation or even dissolution if the fuel survived from combustion. In such cases, information on the impact of the evaporation and dissolution on the composition profile of the fuel is important if profile composition to a suspected source need to be carried out.

The rate of evaporation depends on the composition of an oil (Charles *et al.*, 2000). Evaporation removes low-boiling point components which can be observed from GC chromatograms (Nortest, 1991). Gasoline fuel contains low to medium boiling hydrocarbon components. The lighter compounds such as n-pentene, n-heptane and toluene are easily evaporated even at room temperature due to their high volatility and this explains why gasoline can cause inhalation hazards as opposed to diesel. As evaporation occurs to a large extent, the chromatographic features changes (Abdullah, 2004) and this might make comparison difficult if not impossible. An example of distortion is the loss of the lower boiling alkylbenzenes (Bertsch *et al.*, 1993) such as toluene, followed by C2-alkylbenzenes and C3-alkylbenzenes.

When gasoline is mixed with water, dissolution of compounds may occur. Dissolution removes components according to their solubility in the following sequence: hetero compounds > aromatic hydrocarbon > saturated compounds (Nortest, 1991). According to Nortest (1991), water solubility will reduce with higher substitutions. Therefore C1-phenanthrene is less soluble than phenanthrene, and C3-phenanthrene is even less soluble than C1-phenanthrene. In an event of oil spill, gasoline is more likely to cause aquatic toxicity as aromatic compounds are toxic to aquatic life (Charles *et al.*, 2000). However, due to its volatility, gasoline will also evaporate off relatively fast.

1.11 Significance of Study

The use of gasoline in producing Molotov cocktail has been reported. In this study, the gasoline samples from two different companies were investigated, namely Shell and Petronas. All the samples were obtained from the service station in Kota Bharu and Bachok district. This study is important to investigate the cases involving Molotov cocktail and to link them between different cases, or to a particular source or the people involving.

1.11 Aim and Objectives

There has been an increased in the numbers of the Molotov cocktails being used illegally or seized by the law enforcement personnel in Malaysia in various occasions. For intelligence gathering and investigation purposes at the forensic laboratory of Royal Malaysia Police, information on the analysis of fuels in Molotov