

UNIVERSITI SAINS MALAYSIA



UNIVERSITI SAINS MALAYSIA

**Identification of Fuel Oil in Non-Absorbent Surfaces
in a Site of ANFO Blasts**

**Dissertation submitted in partial fulfillment for the
Degree of Bachelor Science in Forensic Science**

Cheah Chaw Phang

School of Health Sciences

Universiti Sains Malaysia

Health Campus

16150, Kubang Kerian, Kelantan

Malaysia

2011

Acknowledgements

I would like to express my thanks to the Dean, staff of PPSK, and Dr Mohammad Hadzri Yaacob, Chairman of Forensic Science Program, USM, for giving this opportunity to perform this project. My gratitude is extended to my dedicated supervisor, Mr. T. Nataraja Moorthy, who was instrumental in designing this project, as well as his continuous guidance and advices to complete the project successfully. My sincere thanks are due to my co supervisor, Mr Mohd Hizam B Abdul Kadir, Deputy Director of Mine and Quarry, Minerals and Geoscience Department, Kelantan, for their support and guidance to conduct this research.

My sincere and regretful thanks are due to Mr Oon Hoe Sing, Managing Director, and Mr Chung, Senior Technical Manager, Tenaga Kimia Sdn Bhd (TKSB) for their permission and providing explosive chemicals to conduct this valuable explosive project in Malaysia. I also wish to thank, Mr Slamet B Ahmad, Executive-Technical Advisory Service, TKS, and Mr Hamdan B Kamaruddin, Quarry Manager, Cimaco Quarry Sdn Bhd, my field supervisors during the blasting exercises, who provided the facilities and guidance throughout this project.

I wish to acknowledge Pn Rusikah Minhad, Head of Criminalistics Section, Jabatan Kimia Malaysia (JKM), for giving permission to conduct the analysis in the forensic laboratory. Special thanks are due to Mr Sivabalan Nagayah, Scientific officer, JKM and Mr Wan Ahmad Ashadi B Wan Mohd Kamil, Scientific officer, Makmal Penyiasatan Kebakaran, for their support to complete the instrumental analysis for my project. The members of the

department staff deserve special recognition for their continued support and advice in this research.

I would like to thank Supt Soo Me Tong, Head of Chemistry Division of the Forensic Laboratory, Royal Malaysian Police, for this valuable guidance and support during the research.

My loving thanks are due to my parents and family members for their encouragement throughout the research. Their moral support and encouragement has giving me a confidence boost and complete my project.

Not forgotten my project partner, Miss Hidayatul Hazwani Binti Hamdan, for the continuous idea and discussion to complete this research. Also regards to all my friends who lend me a hand when needed and support. Sincere thanks to all those helped me directly or indirectly and complete this wonderful research.

Contents

Title	
Certificate	
Acknowledgements	
Contents	i
List of figures	iii
List of tables	iv
List of symbols and abbreviations	vi
Abstract	viii
Chapter 1. Introduction	
1.1 Background	1
1.2 Problem statement	5
1.3 Scope of the study	6
Chapter 2. Literature Review	
2.1 History of ANFO	7
2.2 Physical and chemical properties of AN and diesel fuel	9
2.3 Theory of energy output of ANFO	11
2.4 Instrumental analysis of explosives	13
2.5 GC-MS	16
Objectives of the Study	18
Chapter 3. Materials and Methods	
3.1 ANFO blasting exercises	
3.1.1 Preparation of non-absorbent surfaces	19
3.1.2 Preparation of ANFO and firing devices	20

3.1.3	Materials used in blasting site	22
3.1.4	Materials used for sample collection	22
3.1.5	Conducting blasting exercises	23
3.1.6	Sample collection	26
3.2	Experimental	
3.2.1	Analyses of group A samples by GCMS	
3.2.1.1	Instrumentation	27
3.2.1.2	Preparation of standard solutions	28
3.2.1.3	Preparation of samples	28
3.2.1.4	Data analysis	29
3.2.2	Analyses of group B samples by GCMS	
3.2.2.1	Instrumentation	29
3.2.2.2	Preparation of standard solutions	30
3.2.2.3	Preparation of samples	30
3.2.2.4	Data analysis	31
Chapter 4. Results and Discussions		
4.1	Data interpretation of group A samples	32
4.2	Data interpretation of group B samples	43
4.3	Discussion	51
Chapter 5. Conclusion		
References		
Appendices		

List of figures

Figure 1.1	Three-step explosive train	4
Figure 2.1	Relative ANFO energy as a function of the percent fuel oil used	11
Figure 3.1	Three-step explosive train used in the blasting exercises	20
Figure 3.2	Location of blasting exercises	23
Figure 3.3	Blasting design at distances of 5 m and 7 m radius from the blasting point	24
Figure 4.1	EIP of standard fresh diesel for ion m/z 113	32
Figure 4.2	EIP of soil sample of ANFO in mixing ratio of 94:6 by weight	34
Figure 4.3	EIP of soil sample of ANFO in mixing ratio of 90:10 by weight	36
Figure 4.4	EIP of soil sample of ANFO in mixing ratio of 80:20 by weight	38
Figure 4.5	EIP of sample 915D	40
Figure 4.6	EIP of sample 827A	42
Figure 4.7	TIC of standard fresh diesel	43
Figure 4.8	TIC of soil sample of ANFO in mixing ratio of 60:40 by weight	45
Figure 4.9	TIC of soil sample of ANFO in mixing ratio of 50:50 by weight	47
Figure 4.10	Diesel fuel found splashed and scattered around the crater mark (60:40)	53
Figure 4.11	Diesel fuel found splashed and scattered around the crater mark (50:50)	53

List of tables

Table 2.1	Physical and chemical properties of AN	9
Table 2.2	Physical and chemical properties of diesel fuel	10
Table 3.1	Non-absorbent surfaces and the quantities used	19
Table 3.2	Varying proportions of AN and FO	21
Table 3.3	Date of the blasting exercises	25
Table 4.1	Result of standard fresh diesel with hydrocarbon chain ranging from C12 to C28	33
Table 4.2	Result of soil sample of ANFO in mixing ratio of 94:6 by weight with hydrocarbon chain ranging from C21 to C28	35
Table 4.3	Result of soil sample of ANFO in mixing ratio of 94:6 by weight with hydrocarbon chain ranging from C29 to C34	35
Table 4.4	Result of soil sample of ANFO in mixing ratio of 90:10 by weight with hydrocarbon chain ranging from C25 to C28	37
Table 4.5	Result of soil sample of ANFO in mixing ratio of 90:10 by weight with hydrocarbon chain ranging from C29 to C33	37
Table 4.6	Result of soil sample of ANFO in mixing ratio of 80:20 by weight with hydrocarbon chain ranging from C14 to C28	39
Table 4.7	Result of sample 915D with hydrocarbon chain ranging from C17 to C28	41
Table 4.8	Result of sample 915D with hydrocarbon chain ranging from C29 to C36	41
Table 4.9	Result of standard fresh diesel with hydrocarbon chain ranging from C12 to C25	44
Table 4.10	Result of soil sample of ANFO in mixing ratio of 60:40 by weight with hydrocarbon chain ranging from C12 to C25	46
Table 4.11	Result of soil sample of ANFO in mixing ratio of 50:50 by weight with hydrocarbon chain ranging from C13 to C25	48
Table 4.12	Result of group A samples of ANFO in mixing ratio of 94:6, 90:10 and 80:20 by weight	49

Table 4.13 **Result of group B samples of ANFO in mixing ratio of 60:40 and 50:50 by weight** **50**

List of symbols and abbreviations

°C	Degree Celsius
%	Percent
cal/g	Calorie per gram
cm ³ /g	Cubic centimeter per gram
g/cm ³	Grams per cubic centimeter
kcal/kg	Kilocalorie per kilogram
kg	Kilograms
kg/L	Kilograms per Liter
J/mol	Joule per molar
m	meter
min	minutes
mL	milliliter
m/s	Meter per second
<i>m/z</i>	Mass ratio
mmHg	Millimeter of mercury
NH ₄ NO ₃	Ammonium Nitrate
Al	Aluminum
AN	Ammonium nitrate
ANFO	Ammonium nitrate and fuel oil
CL	Chemiluminescence
ECD	Electron capture detector
EIP	Extracted ion profile
FO	Fuel oil

GC	Gas chromatography
GCFID	Gas chromatography
GCMS	Gas chromatography mass spectrometry
HPLC	High performance liquid chromatography
MS	Mass spectrometry
PE	Polyethylene
PETN	Pentaerythritol tetranitrate
PP	Polypropylene
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
RDX	Hexahydro-1,3,5 trinitroazine
RT	Retention time
TD-GC	Thermal desorption-gas chromatography
TEA	Thermal energy analyzer
TIC	Total ion chromatogram
TKSB	Tenaga Kimia Sdn Bhd
TNT	Trinitrotoluene

Abstract

ANFO, a commercial explosive consists of mixture of fuel and oxidizer, none of which is classified as explosive. ANFO is usually used in construction, quarrying and mining works but sometimes it is identified as one of the most common explosion found in a crime scene. They are often mixed at different ratio by a non-standard user during explosion. Therefore, the objective of this project is to serve as a preliminary study to investigate how far ANFO at different mixing ratio can travel after the blasts. Five different mixing proportions of AN and FO (94:6, 90:10, 80:20, 60:40 and 50:50) were used in this studies. Six selected non-absorbent surfaces commonly found at an explosion scene were placed at the distance of 5 m, 7 m and 9 m radius from the seat of blast. Residues travelled on selected surfaces were collected and analyzed using GC-MS. As a result, the FO residues can travel as far as 7 meter with the idea ANFO mixture of 94:6 by weight (500 g AN and 38.35 mL FO) during blasting. When improper ANFO mixture of 50:50 by weight (500 g AN and 600.96 mL FO) was used, explosion did occur but FO found splashed and scattered around the crater mark. Thus, the extent of FO residues travel to some distances after the blast depends upon the proportions and quantities of ANFO.

Chapter 1

Introduction

1.1 Background

Ammonium nitrate-fuel oil (ANFO) is generally recognized as commercial explosive. It has many legitimate uses including mining, quarrying and construction, but also being used in criminal acts by terrorists (Girard, 2011). Over the past century, there had been several major accidents as well as terrorist bombings with ANFO (Girard, 2011). For example, terrorist use of ANFO began in the bombing campaign of the Provisional Irish Republican Army (PIRA) in 1969 until 1994 (Oxley et al., 2002). During that period there were 14,000 ANFO bombing incidents occurred (Oxley et al., 2002). Thus, the reliable identification and analytical challenges of this explosive is an important step in the investigation of terrorist bombings. The proper combination of ammonium nitrate (AN) and fuel oil (FO) turn into powerful explosives (Oommen & Jain, 1999). ANFO is a mixture of AN and FO to formulate a safe non-nitroglycerin alternative to dynamite in commercial explosives (Henderson & Saari-Hordhaus, 1992). AN is a colourless, crystalline salt, and highly soluble in water (Oommen & Jain, 1999). It has been extensively used in a large variety of nitrogen-based fertilizers and explosives process (Turcotte *et al.*, 2003). Domestic FO or native oils like rapeseed oil methyl ester are usually used in ANFO mixture. Therefore, it is important to understand the fundamental principles of explosives and the mechanism of explosion.

According to Singh (2007), explosive is a material (chemical or nuclear) that can be initiated to undergo very rapid and self-propagating decomposition resulting in the formation of more stable material with the liberation of heat and pressure. Basically, explosives are categorized into low and high explosives (Singh, 2007). Examples of low explosives include propellants, smokeless powder, black powder, and pyrotechnics. The chemical reaction of low explosives requires confinement for an explosion or deflagration (Singh, 2007). Such rapidity that the rate of reaction in material below the speed of sound (Singh, 2007).

High explosives are sub-classified into two groups according to their sensitivity, which are primary explosives and secondary explosives (Singh, 2007). Primary explosives include lead azide, mercury fulminate, and lead styphnate, are highly sensitive to initiation by shock, friction, spark, heat or any combination of these and they are often referred as 'initiating explosives' because they can be used in igniting secondary explosives (Singh, 2007). Secondary explosives are also sub-divided into two groups depending upon their manufacture and intended usage, which are military explosives and commercial explosives (Singh, 2007). Example of military explosives include trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), and hexahydro-1,3,5 trinitroazine (RDX). On the other hand, commercial explosives include emulsion explosives, slurry explosives, water-gel explosives, and ANFO mixture that may be used in mining and construction purposes (Singh, 2007). ANFO mixture is easy to manufacture at a low-cost (Singh, 2007). However, large quantities of ANFO are used for terrorist bombings (Girard, 2011).

According to National Fire Protection Association (NFPA, 2002), explosion is the sudden conversion of potential energy (chemical, mechanical or nuclear) into kinetic energy that released gas violently. These high-pressure gases then cause mechanical work such as moving, changing, or shattering materials nearby. Explosion is also refer to a sudden, violent release of energy (Noon, 2001). It is usually accompanied with loud noise and an expanding pressure wave of gas (Noon, 2001). Explosions due to the sudden release of chemical energy can be classified into two main types, which are deflagrating explosions and detonating explosions (Noon, 2001). Deflagrating explosion is characterized by a relatively slow, progressive burn rate of the explosive material (Noon, 2001). It is accomplished by normal heat transfer depends on external factors such as ambient pressure and temperature during the progressive release and dispersion of energy through the explosive material (Noon, 2001), for example, black powder.

Detonating explosion is characterized by a detonation, high energy releases rate, and a high peak explosion pressure. Noon, (2001) stated that the progressive release and dispersion of energy through the explosive material is accomplished by shock waves and their associated pressure forces and stresses in detonating explosion (Noon, 2001). The energy of explosion reinforces the shock waves which then become self-sustaining, therefore, transmission of energy through the detonating material is independent upon ambient conditions of pressure or temperature (Noon, 2001) and ANFO is an example for detonating explosion.

ANFO mixture is the most popular commercial secondary explosive (Turcotte, *et al.* 2003). It is an insensitive explosive mixture, which make it safe to use. ANFO is not water resistance unless it is packed in waterproof containers (Murray, 2000). Nevertheless, ANFO mixture requires the use of a booster, dynamite or any water-gel explosives to provide reliable detonation (Murray, 2000). There is a three-step explosive train occurring during detonation of ANFO explosives. Explosive train is a series of combustible or explosives components arranged specifically in decreasing order according to sensitivity designed to initiate explosives (Murray, 2000). Generally three-step explosive train consists of primer (also known as detonator or blasting cap), booster and main charge as shown in Figure 1.1. The most effective detonation or explosion of a particular explosive is used to produce a desired outcome (Murray, 2000). The detonator and booster then produce energy that is sufficient to initiate the ANFO, the main charge (Murray, 2000).

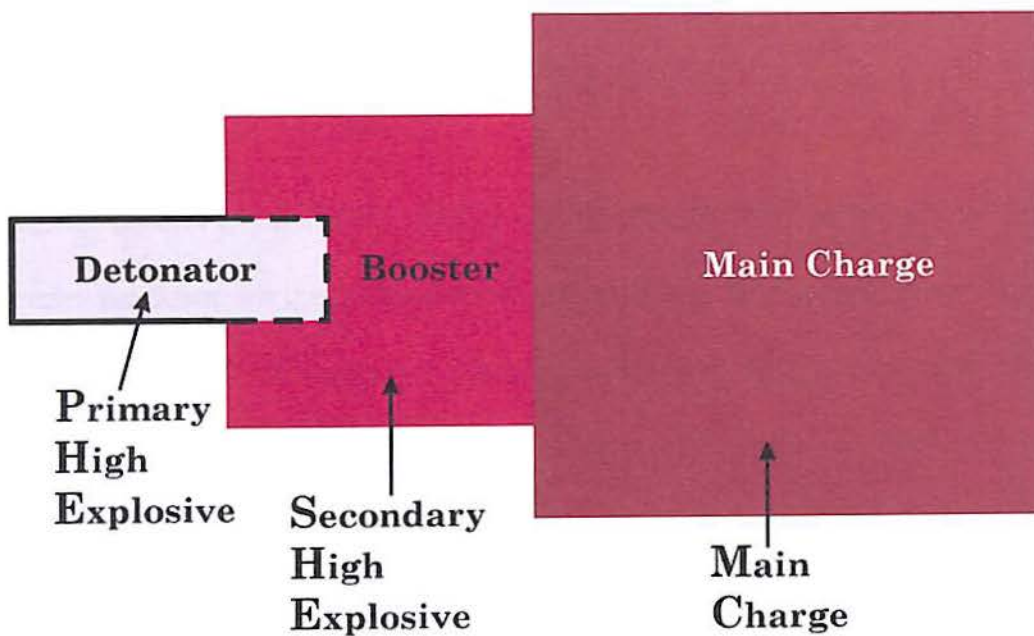


Figure 1.1. Three-step explosive train.

(Source: retrieved from <http://www.tracefireandsafety.com>)

1.2 Problem statement

In the field of forensic sciences, identification of explosives is an important task for forensic scientists (Dicinoski *et al.*, 2006). Identification of an explosive that has been used in a bombing by using chemical analysis on the debris collected at the site of an explosion poses a greater challenge (Dicinoski *et al.*, 2006). Lahoda *et al.* (2008) stated that it is important to ensure that analytical data from swabs taken at the scene of the explosion provide unambiguous results when post-blast explosives residue examinations are performed. Home-made or improvised devices that cover wide range of different chemical compositions are always being employed in terrorist attacks (Lahoda *et al.*, 2008). Thus, a forensic scientist must have an ideal technique and tools that enable the qualitative and quantitative analysis of the evidence collected in the explosion scene (Lahoda *et al.*, 2008). Otherwise, matrix interferences can be ambiguous or confuse the presence of residue from the blast (Dicinoski *et al.*, 2006).

According to Lahoda *et al.* (2008), matrix interferences can be addressed by collecting samples near the scene for comparison to determine the environmental factors that might affect the interpretation of analytical results. Examples of the samples near the scene include non-absorbent and absorbent materials. Over the past few years, the issue of background interferences has become more convincing particularly in the forensic analysis of huge and complex crime scenes such as the World Trade Centre (WTC) in 1993, bombing and the Pan Am crash in Lockerbie, Scotland (Lahoda *et al.*, 2008). The primary ingredients of explosives are fuels and oxidizers (Dicinoski *et al.*, 2006). Fuels commonly found in commercial explosives include diesel fuel, carbon, PETN, TNT, smokeless powder, monomethylammonium nitrate, and monoethanolammonium nitrate (Dicinoski *et*

al., 2006). The most common oxidizer used is AN, and sometimes sodium nitrate and calcium nitrate may also be used in explosion (Dicinoski *et al.*, 2006).

1.3 Scope of the study

ANFO is widely used by terrorists as explosive and it is often mixed at different ratio by a non-standard user during explosion. Therefore, the aim of this project is to serve as a preliminary study to investigate how far ANFO in different mixing ratio can travel after the blasts.

Chapter 2

Literature Review

2.1 History of ANFO

According to Graham (2002), the ANFO explosion was started since 16th of April 1947. A French cargo ship loaded with 2380 tons of AN (NH_4NO_3) fertilizer was anchored off at Texas City. The fire was raged out of control due to failure of crews in extinguishing fire (Graham, 2002). The AN was suddenly exploded and cause the 7200 tons loaded ship fly 20 feet in air (Graham, 2002). Burning debris reached surrounding oil refineries and chemical plants (Graham, 2002). In addition, 15 feet tidal wave caused collision of two other ships which anchored in the harbour (Graham, 2002). One of impacted vessels also contained AN (Graham, 2002). By the time the last flame had been distinguished, this tragedy had caused death of 576 people and put Texas City in ruin (Graham, 2002).

By analyzing the area surrounding the Texas tragedy, chemists analyzed the power and potential of AN-based explosives (Graham, 2002). An effective, relatively safe, and inexpensive explosive mixture called ANFO was developed on 1957 (Graham, 2002). There were no risky transport problems (Graham, 2002). AN and FO were transported in separate partition and then mixed at the blasting site, thus transport of AN and FO is not risky (Graham, 2002).

A strong oxidative and explosive properties of AN have led to a long history of major accidents including mass explosions in large storage units and mass explosions in ships (Marlair & Kordek, 2005). Hence, the safety issues associated with the storage of AN-based fertilizer are considered on low storage capacity premises (Marlair & Kordek, 2005). Low-capacity storage of any given commercial products is generally more imperative than large dedicated warehouses (Marlair & Kordek, 2005). Proper handling on safety and security issues in those facilities remains a challenge when dealt with hazardous products like AN-based fertilizer (Marlair & Kordek, 2005).

In the review of shock initiation on AN explosive, the initiation process of shock detonation is investigated experimentally in a charge of heterogeneous explosive that is loaded by the pressure pulse generated by a detonator (Cudzilo *et al.* 1995). The explosive test was mixtures of AN with TNT and aluminium (Al) (Cudzilo *et al.* 1995). The mean velocity of explosion propagation is measured at different depths in an explosive charge (Cudzilo *et al.* 1995). The coarser TNT in the AN/TNT mixture results in an increase of the run distance to detonation and a decrease of the detonation velocity whereas the aluminized AN explosives tested have the same detonation velocity, regardless of the type of Al admixture (Cudzilo *et al.* 1995). However, the reactive flow is building slowly towards detonation for coarser Al in the explosive mixture (Cudzilo *et al.* 1995).

2.2 Physical and chemical properties of AN and Diesel Fuel

The physical and chemical properties of AN as indicated by Oommen & Jain in 1999.

These properties are summarized and shown in Table 2.1.

Table 2.1. Physical and chemical properties of AN.

Property	Value
Molecular formula	NH ₄ NO ₃
Molecular weight	80
Heat of combustion	346 cal/g
Heat of formation	1098 cal/g
Heat of explosion	346 cal/g
Heat of fusion	18.23 cal/g
Density	1.725 g/cm ³
Colour	Colourless
Melting point	169.6 °C
Specific volume	0.580 cm ³ /g
Solubility in water at 20 °C	66 g/100 g
Oxygen content	60%
Available oxygen	20%
Estimated flame temperature	1500 °C
Detonation velocity	1250-4650 m/s
Coefficient of thermal expansion at 20 °C	9.82 x 10 ⁻⁴ %/ °C
Specific heat from 0 to 31 °C	1.72 J/mol
Vapour pressure at 205 °C	7.4 mmHg

Source: Oommen & Jain (1999)

According to material safety data sheet of HESS (2006), the physical and chemical properties of diesel fuel as summarized and shown in Table 2.2.

Table 2.2. Physical and chemical properties of diesel fuel.

Property	Value
Appearance	Clear, straw-yellow liquid
Odour	Mild, petroleum distillate odour
Boiling range	160 - 366 °C
Autoignition point	257 °C
Vapour pressure	21 °C
Vapour density	0.865
Specific gravity	16 °C
Density	0.832 kg/L
Solubility in water	Insoluble
Evaporation rate	Slow, varies with conditions
Percent volatiles	100 %

Source: HESS Material Safety Data Sheet, MSDS No. 9909 (2006)

However, the physical and chemical properties of AN and FO (diesel fuel) as stated in Table 2.1 and Table 2.2 must be investigated when mixed at different ratios.

2.3 Theory of energy output of ANFO

According to the theory of energy output of ANFO, Hustrulid (1999) stated that energy output of ANFO mixture was influenced by the percentages of FO added to AN. The effect on the energy output for different percentages of FO added to AN was shown in Figure 2.1. Different mixing ratio of ANFO will produce different energy output (Hustrulid, 1999).

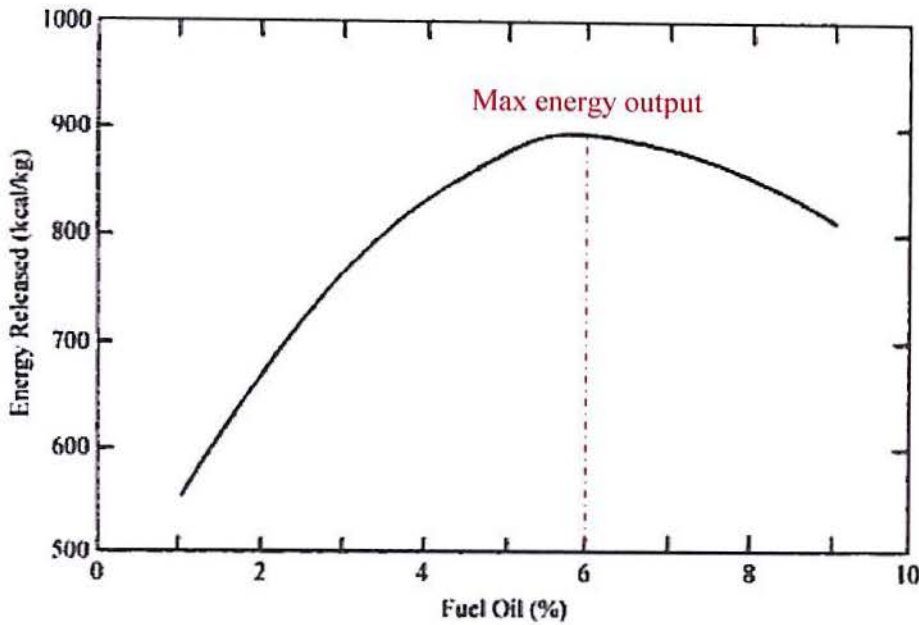
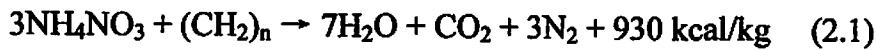


Figure 2.1. Relative ANFO energy as a function of the percent fuel oil used (Hustrulid, 1999).

Figure 2.1 showing the maximum energy output is obtained when the oxygen balanced mix of approximately 94 % of AN to 6 % FO (Hustrulid, 1999). On both sides of the oxygen balance mixture, there is a fall off in energy output because of excess or deficiency of FO added to AN. The values for the energy release when ANFO detonates can vary rather widely (Hustrulid, 1999). The energy output can be calculated for different ratios of

ANFO (Kennedy, 1990). The basic chemical reaction for ANFO in mixing ratio of 94:6 by weight is



In the commonly written chemical reaction (2.1), the symbol CH_2 is used to represent the FO (Kennedy, 1990). In practice the actual organic compound is much more complicated (Kennedy, 1990). Instead one finds values for organic compounds made up of multiples of CH_2 such as C_6H_{12} and C_7H_{14} , etc (Kennedy, 1990).

Maximum energy output occurs when the excess oxygen is used by the FO to give only carbon dioxide, steam and nitrogen and this is called zero oxygen balanced mixture (Kennedy, 1990). For ANFO mixtures with fuel oil content of more than 6 percent creates a deficiency of oxygen. As in other combustion reactions, the energy drops rapidly due to deficiency of oxygen and carbon monoxide is formed when too much fuel oil is added (Hustrulid, 1999). On the other hand, the energy also decreases due to excess of oxygen and formation of nitrous oxides when too little fuel oil is added (Hustrulid, 1999). The basic chemical reaction for ANFO in mixing ratio of 90:10 by weight is



In the chemical reaction (2.2), the energy output (810 kcal/kg) in mixing ratio of 90:10 is decrease due to the deficiency of oxygen compared to the energy output (930 kcal/kg) in mixing ratio of 94:6.

2.4 Instrumental analysis of explosives

Kolla (1994) investigated the effectiveness of instruments such as gas chromatography (GC), high-performance liquid chromatography (HPLC) and ion chromatography (IC) to identify the trace of explosives. This study was described by optimizing combinations of chromatographic methods with selective detection techniques for the analysis of trace explosives (Kolla, 1994). As a result, GC with chemiluminescence (CL) detector was effective and preferred in the determination of organic constituents in explosives (Kolla, 1994). HPLC in combination with selective detection can be used as alternative method to ensure accuracy of result gained from GC (Kolla, 1994). HPLC and Thin Layer Chromatography are useful in trace analysis of explosives with the disadvantage of lower resolving power and lower sensitivity than GC (Kolla, 1994). IC was used for the determination of the inorganic constituents of explosives (Kolla, 1994).

The detection of explosive using CL detection system was studied. Jimenez & Navas (2003) stated that most of the explosive compounds contain both nitro or nitrate groups which make then possible to detect and quantified using detection systems based on CL reactions. CL is specifically used in trace detection of explosives with combination of chromatographic techniques such as GC-thermal energy analyzer (TEA) (Jimenez & Navas, 2003). In the view of analytical chemistry, application of CL brings numerous advantages including high sensitivity, wide linear range, simple, inexpensive instrumentation, and considerable reduction in the background noise (Jimenez & Navas, 2003). In contrast, the lack of selectivity is one of the disadvantage (Jimenez & Navas, 2003). It is introduced as an alternative when TEA responds specifically to nitro and nitroso compounds (Jimenez & Navas, 2003). Other GC detectors with lower selectivity

such as the electron-capture detector (ECD) only can be used if the matrix is relatively clean (Jimenez & Navas, 2003).

The analysis and characterisation of nitroglycerine based explosives were studied by Burns & Lewis (1994). This study has illustrated the use of GC-MS in making it possible to attribute a degree of characterisation to commercial nitroglycerine based explosives by identifying and subsequently quantifying the nitroaromatic compounds inherent in the explosive types examined (Burns & Lewis, 1994). This study was conducted to develop a procedure based on GC-MS to characterise types of nitroglycerine based explosive types and determine what, if any, batch to batch variation occurs in their overall chemical make-up (Burns & Lewis, 1994). As a result, the GC-MS method outlined allows the unequivocal identification of the nitroesters and the various nitroaromatic compounds associated with nitroglycerine based explosives produced (Burns & Lewis, 1994). Variation in the individual dinitrotoluene isomer amounts and the presence or absence of *o*-nitrotoluene and isomers of dinitroethylbenzene allows degree of batch characterisation (Burns & Lewis, 1994).

Furthermore, Burns & Lewis have investigated the variation of the isomer content within the nitroaromatic component in nitroglycerine based explosives by using GC accompanied with flame ionisation detection (GC-FID) in 1995. It has been studied the use of GC-FID to identify patterns within the nitroaromatic isomer content of nitroglycerine based explosives and hence to associate explosives from similar batch types (Burns & Lewis, 1995). The result showed that the total percentage of nitroaromatic compounds is not a reliable guide to the particular explosive type (Burns & Lewis, 1995). This probably due to

the anomalies are poor mixing during the manufacturing stage or subsequent segregation, which leave small areas of high or low concentrations of nitroaromatic compounds within the bulk, and accidentally located in the sub-sampling procedure which caused bias to the overall content (Burns & Lewis, 1995).

Waddell *et al.* (2005) had conducted a study on determination of nitroaromatic and nitramine explosives from a Polytetrafluoroethylene (PTFE) wipe using thermal desorption-gas chromatography (TD-GC) with ECD. Since a wipe taken from a contaminated surface, TD analysis is an ideal dry sampling method that can be analyzed directly, eliminating sample preparation steps and thus increasing sample throughput (Waddell *et al.*, 2005). However, the wipe sampling method used in the field is a source of considerable variation, dependent upon factors such as the pressure applied during sampling, the sampling time, and the surface area covered (Waddell *et al.*, 2005). The result showed that the explosives were desorbed from a PTFE wipe with precision and desorption efficiencies that were considered acceptable for a field-deployable method; with a dual column, dual detector configuration, and simultaneous confirmation analysis was possible (Waddell *et al.*, 2005). This configuration not only offer improvement in term of sensitivity compared to MS, but also eliminates the vacuum system requirements associated with MS (Waddell *et al.*, 2005).

The study of a new concentrative extraction procedure for analysis of low-level explosive in soils was presented by Felt *et al.* (2008). The capability of detecting explosive-based contaminants at the level of environmental interest enables precise assessment of the transport pathways and treatment options for explosives contamination. An analytical method with lower detection limits for explosive compounds is required to assess explosive concentrations in soil accurately (Felt *et al.*, 2008). In this study, the new method of concentrative extraction procedure was compared with the traditional soil-dilution method (Felt *et al.*, 2008). Means of extraction and concentration of explosives from a soil matrix had been developed and reflected to produce result that are statistically significant and feasible for potentially low-level or heterogeneous contamination (Felt *et al.*, 2008). The new concentrative extraction procedure was proved to detect explosives in freshly amended and weathered soils at lower detection levels and with higher repeatability than the traditional soil-dilution method (Felt *et al.*, 2008).

2.5 GC-MS

GC-MS is used to identify and quantify the volatile and semi-volatile organic compounds in complex mixtures (Mathis, 2004). The apparatus used for GC generally consists of sample inlet system at one end of a capillary column packed with substrate material and a detector at the other end of the column (Mathis, 2004). A carrier gas propels the sample down the column (Mathis, 2004). Flow meters and pressure gauges are set to maintain a constant gas flow (Mathis, 2004). Carrier gases used is usually helium and its property that does not react with the sample or column which is essential for reliable results (Mathis, 2004).

Normally, the sample is injected into the sample inlet system with a syringe capable of measuring the specimen amount (Mathis, 2004). The GC oven was maintained at a temperature which the sample vaporizes immediately (Mathis, 2004). Ideally, the sample found spread equally along the cross section of the column and a plug is formed (Mathis, 2004). As the sample moved through the column, the different molecular characteristics on each substance in the sample determine the interaction with the column surface and packing (Mathis, 2004). Partition of various substances is allowed in the column (Mathis, 2004).

Mass Spectrometry (MS) detector is used to identify the substances by electrically charging the specimen molecules, accelerating them through a magnetic field, breaking the molecules into charged fragments and detecting the different charges (Mathis, 2004). A spectral plot is displayed the mass of each fragment and compound's mass spectrum is used for qualitative identification (Mathis, 2004). From the molecular mass and the mass of the fragments, reference data is compared to determine the identity of the specimen (Mathis, 2004).

Objectives of the Study

The objective of this study is:

1. to identify the oil residues on non-absorbent surfaces in a site of ANFO blasts.
2. to study the extent of FO residue travels from the crater mark after the blast.
3. to study ANFO blasting using different AN and FO proportions.

Chapter 3

Materials and Methods

3.1 ANFO blasting exercises

3.1.1 Preparation of non-absorbent surfaces

In present study, six types of non-absorbent surfaces with each 50 sets were prepared before conducting the blasting exercises. Different types of non-absorbent surfaces were chosen and used in order to figure out the presence of oil residue through blasting exercises. Furthermore, they are waterproof materials that commonly found in explosion scene. These six types of non-absorbent surfaces and quantity used are summarized in Table 3.1.

Table 3.1. Non-absorbent surfaces and the quantities used.

Code	Quantity	Non-Absorbent Surfaces
A	50	Aluminum sheets
B	50	Polyvinyl chloride (PVC) sheets
C	50	Glass plates
D	50	Rubber sheets
E	50	Plastic sheets
F	50	Ceramic tiles

PVC, rubber and plastic sheets were included as they are common materials found in an explosion scene. These materials are likely to cause interference to FO, however, GCMS may be able to subtract these interference by selecting appropriate ions during data interpretation.

3.1.2 Preparation of ANFO and firing devices

Since ANFO is a secondary high explosive, three-step explosive train was required to conduct these blasting exercises. In this study, three-step explosive train consists of electrical detonator, emulsion explosive (water-base) and ANFO mixture. Instant electric detonators with No. 8 cap and Emulex[®] 150 (25x200 mm, 0.120 kg) as emulsion explosive were used in this blasting exercise as shown in Figure 3.1. Furthermore, ANFO mixture comprises of explosive-based AN prills and commercial diesel fuel with varying proportions. Other devices used in this exercises were digital ohmmeter, blasting machine and connecting wires. All firing devices and ANFO mixture were provided by Tenaga Kimia Sdn Bhd (TKSB) Factory, and the mixing proportions were designed by the supervisor, Mr T. Nataraja Moorthy.

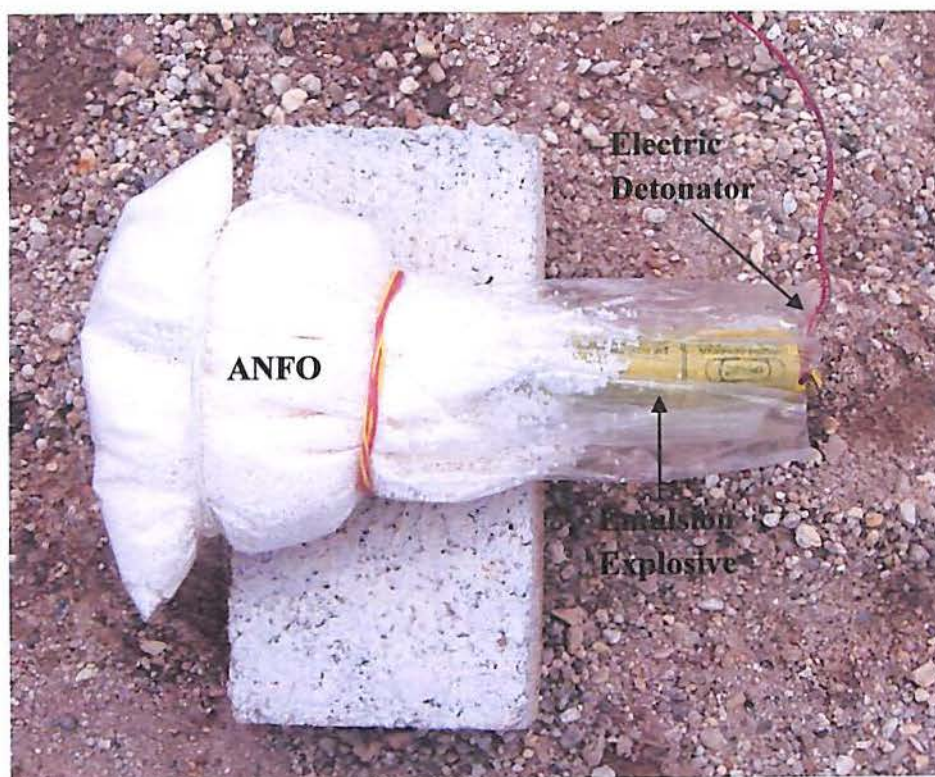


Figure 3.1. Three-step explosive train used in the blasting exercises.

In this study, 10 blasting exercises with varying proportions of AN and FO were conducted as shown in Table 3.2. The explosion was conducted by the licensed shotfirer from TKSB under the supervision of Mr T. Nataraja Moorthy. Table 3.2 shows the varying proportions of AN (by weight, kilogram) and FO (by volume, milliliter) for the blasting exercises.

Table 3.2. Varying proportions of AN and FO.

No.	Ratio of ANFO (by weight)	AN (kg)	FO (ml) (Diesel fuel)
1	94:6 (standard)	0.5	38.35
2	90:10	0.5	66.78
3	80:20	0.5	150.24
4	60:40	0.5	400.60
5	50:50	0.5	600.96

**** Density of FO (Diesel) = 0.832 kg/L**

The reason of ANFO in mixing ratio of 60:40 and 50:50 by weight used was to see the worst-case scenario when AN could have been mixed with excessive FO by an non-chemist as could be seen in a terrorist bombings.

3.1.3 Materials used in blasting site

The materials used in the preparation of the blasting site:

- i. Bricks
- ii. Polypropylene (PP) plastic bags
- iii. Rubber band
- iv. Measuring tape
- v. 100 mL Measuring cylinder
- vi. 500 mL Beaker
- vii. Balance
- viii. Rope

3.1.4 Materials used for sample collection

The materials used for sample collection are listed below:

- i. Polyethylene (PE) plastic bags
- ii. Rubber bands
- iii. Gloves
- iv. Marker pens
- v. Small mattock

3.1.5 Conducting blasting exercises

In this study, these blasting exercises were conducted by licensed shotfirer from TKS B and blasted at TKS B factory campus, Rawang, Selangor, as shown in Figure 3.2.



Figure 3.2. Location of blasting exercises.

These blasting exercises were conducted with different distances from seat of blast (5m, 7m and 9m) using different proportions (94:6, 90:10, 80:20, 60:40 and 50:50) of AN and FO. The schematic illustration of the blasting exercises as shown in Figure 3.3:

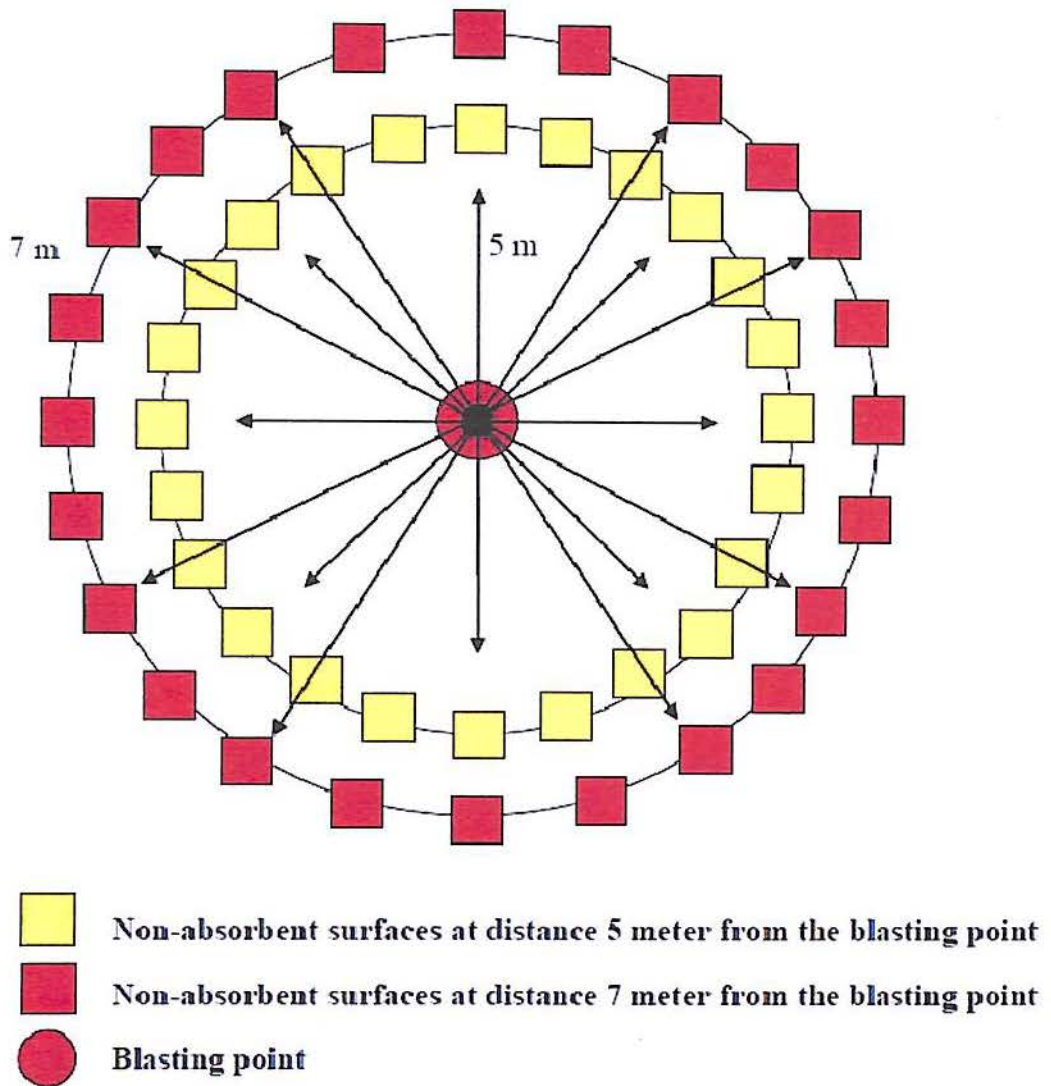


Figure 3.3. Blasting design at distances of 5 m and 7 m radius from the blasting point.