DEVELOPMENT OF AN EXPLOSIVE INFORMATION SYSTEM FOR THE CHEMICAL COMPOSITION PROFILE OF EXPLOSIVES

MOHAMAD AFIQ BIN MOHAMED HURI

UNIVERSITI TEKNOLOGI MALAYSIA

DEVELOPMENT OF AN EXPLOSIVE INFORMATION SYSTEM FOR THE CHEMICAL COMPOSITION PROFILE OF EXPLOSIVES

MOHAMAD AFIQ BIN MOHAMED HURI

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy (Chemistry)

Faculty of Science
Universiti Teknologi Malaysia

.

MAY 2017

In the name of Allah, the Most Beneficent and the Most Merciful.

I dedicate this work to:

My late father
Mohamed Huri Bin Zakaria
He was my hero
Stronger than a Superman
Used to be there when I needed him
The best father a son could have

My mother
Hamidah Binti Saidin
She is my heroine
More amazing than a Wonder Woman
Who love me more than anyone else
The best mother a son could have

My siblings
Shamsul Syamuri, Hana Huri, Hazairin Huri, Aishah Huri and Hanis Huri
Bonds that can never be broken
The best family that I could have

Alhamdulillahilladzi bi ni'matihi tatimmussolihaat.

ACKNOWLEDGEMENT

Bismillahirrahmanirrahim,

Alhamdulillah, greatest thanks to Allah S.W.T for giving me strength, health and goodness while preparing and completing this study. First of all, I would like to express my deepest and warmest gratitude to my supervisor for this PhD project, Assoc. Prof. Dr. Umi Kalthom binti Ahmad for her motivation, critical reviews and enormous support and guidance in encouraging me to finish this project and writing my thesis. Because of her patient guidance, I am able to complete this task successfully. I have gained a lot of knowledge and experience during the course of this research.

My sincere thanks to Science & Technology Research Institute for Defense (STRIDE), Batu Arang, Selangor, especially to Brig. Gen. Mustafa Omar as my co-supervisor. For my database development, I also would like to give my sincere thanks to my another co-supervisor from Faculty of Computing UTM, Assoc. Prof. Dr Roliana bt Ibrahim.

I am greatly indebted to all staffs in Chemistry Department, Faculty of Science for their fruitful cooperation and helpful in completing this project. Last but not least, I wish to thank my beloved family for their great support and valuable advice. I would like to thank all my friends for their never ending support and willingness to give their support and sharing knowledge about this research. Thank you very much.

ABSTRACT

Analysis of post-blast residues collected from a crime scene is of great importance to forensic investigators in determining the nature of explosives used. The result of the analysis can be used as ultimate evidence in court to link a suspect with the crime. The traditional manual matching of explosive sample for case and control samples are often laborious and inefficient. The scarcity of standard explosives further aggravates the routine work of a forensic analyst. This study was therefore undertaken to develop a novel forensic explosive database information system for rapid and efficient data retrieval and matching. A total of 22 pre- and post-blast samples were collected including military explosives, improvised explosive devices and pyrotechnic explosive samples. All samples were subjected to spot test analysis prior to instrumental analysis. High performance liquid chromatography with diode array detector (HPLC-DAD) and gas chromatography tandem mass spectrometry (GC-MS/MS) were used for chemical profiling of high explosives with limits of detection (LOD) in the range of 0.02-4.35 mg/L and 0.30-10.89 ng/L, respectively. Ion chromatography (IC) was employed for chemical profiling of anionic (LOD: 0.07-0.26 mg/L) and cationic (LOD: 0.08-0.28 mg/L) content of inorganic low explosives. This study revealed that each sample displayed different chromatographic profile that could discriminate from one to another. Nitroexplosive compounds of PETN and tetryl were detected in GC-MS/MS analysis via the presence of degradation products of 1,3-propanediol,2,2-dimethyl-,dinitrate and 2,4,6-trinitro-*N*-methyl-aniline, respectively. Methods developed for IC, HPLC and GC-MS/MS were proposed as standard methods for the generation of results to be incorporated in the explosive database. A total of 52 data information was stored in the database using Microsoft SQL Server. MyForensic Explosive Database (MyFED) graphical user interface was developed using Microsoft Visual Studio. The database incorporated details of the explosives, results of spot test analysis, retention factor and chromatographic profile of each analyte for data searching, retrieval and matching with unknown explosive samples. The user interface involved spot test analysis comparison, followed by chromatogram searching with retention factor comparison. The administrator page allowed access only to the administrator for viewing, inserting, editing and deleting information. The developed MyFED information system supported easy matching of unknown explosive samples with known samples stored in the database. Although the database contained a limited number of explosives data, its capability of easily upgradable to handle more explosive information renders MyFED an attractive and promising start of a Malaysian database system available for use to forensic investigators in Malaysia as well as in the Asian region.

ABSTRAK

Analisis sisa pasca-letupan yang dikumpul daripada tempat kejadian jenayah adalah sangat penting kepada penyiasat forensik dalam menentukan jenis bahan letupan yang digunakan. Hasil analisis boleh digunakan di mahkamah sebagai bukti muktamad untuk mengaitkan suspek dengan jenayah. Pemadanan tradisional secara manual sampel bahan letupan bagi kes dan sampel kawalan sering payah dan tidak cekap. Kesukaran mendapatkan bahan letupan piawai memburukkan lagi kerja rutin penganalisis forensik. Oleh itu, kajian ini dilaksanakan untuk membangunkan satu sistem pangkalan data bahan letupan forensik yang baharu untuk mendapatkan dan memadankan data secara cepat dan cekap. Sebanyak 22 sampel pra- dan pasca-letupan telah dikumpul, termasuklah sampel bahan letupan ketenteraan, peranti letupan improvisasi dan sampel bahan letupan piroteknik. Semua sampel telah menjalani analisis ujian titik sebelum analisis berinstrumen. Kromatografi cecair berprestasi tinggi dengan pengesan susunatur diod (HPLC-DAD) dan kromatografi gas spektrometri jisim seiring (GC-MS/MS) telah digunakan untuk pemprofilan kimia bahan letupan tahap tinggi dengan had pengesanan (LOD) masing-masing dalam julat 0.02-4.35 mg/L dan 0.30-10.89 ng/L. Kromatografi ion (IC) telah digunakan untuk pemprofilan kimia kandungan anion (LOD: 0.07-0.26 mg/L) dan kation (LOD: 0.08-0.28 mg/L) bahan letupan tahap rendah tak organik. Kajian ini mendedahkan bahawa setiap sampel letupan menunjukkan profil kromatografi berlainan yang dapat mendiskriminasi daripada satu dengan yang lain. Sebatian bahan letupan nitro PETN dan tetril masing-masing dikesan dalam analisis GC-MS/MS melalui kehadiran produk degradasi 1,3-propandiol,2,2-dimetil-,dinitrat dan 2,4,6-trinitro-*N*-metil-anilina. Kaedah yang dibangunkan untuk IC, HPLC dan GC-MS/MS dicadangkan sebagai kaedah piawai bagi penghasilan keputusan yang perlu digabungkan ke dalam pangkalan data bahan letupan. Sejumlah 52 maklumat data disimpan di dalam pangkalan data menggunakan Microsoft SQL Server. Antaramuka laman grafik pengguna MyForensic Explosive Database (MyFED) dibangunkan menggunakan Microsoft Visual Studio. Pangkalan data ini menggabungkan butiran bahan letupan, keputusan analisis ujian titik, faktor penahanan dan profil kromatografi bagi setiap analit untuk pencarian data, dapatan semula dan pemadanan sampel bahan letupan yang tidak diketahui. Antara muka laman pengguna melibatkan pemadanan analisis ujian titik, dan pemadanan kromatogram dengan perbandingan faktor penahanan. Laman pentadbir hanya membenarkan hanya pentadbir untuk melihat, memasukkan, menyunting dan memadam data. Sistem informasi MyFED yang dibangunkan membantu memudahkan pemadanan sampel tidak diketahui dengan sampel yang diketahui yang disimpan dalam pangkalan data. Walaupun sistem mengandungi data bahan letupan yang terhad, keupayaannya yang mudah dinaiktaraf bagi mengendalikan lebih banyak data bahan letupan manjadikan MyFED suatu permulaan yang menarik dan menjanjikan bagi sistem pangkalan data Malaysia yang tersedia bagi kegunaan penyiasat forensik di Malaysia mahupun di rantau Asia.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

HPLC	-	High Performance Liquid Chromatography
DAD	-	Diode Array Detector
IC	-	Ion Chromatography
GC	-	Gas Chromatography
MS	-	Mass Spectrometry
MS/MS	-	Tandem Mass Spectrometry
ECD	-	Electron Capture Detector
DDW	-	Double Distilled Deionized Water
IED	-	Improvised Explosive Device
ND	-	Not Detected
RSD	-	Relative Standard Deviation
RMP	-	Royal Malaysia Police
STRIDE	-	Science Technology Research Institute for Defense
PDRM	-	Polis Diraja Malaysia
SPE	-	Solid Phase Extraction
SPME	-	Solid Phase Microextraction
MyFED	-	MyForensic Explosive Database
FOREHILEX	-	Forensic Reagent for Low and High Explosive
GTD	-	Global Terrorism Database
HMX	-	Cyclotetramethylenetetranitramine

4-NBN	-	4-nitrobenzonitirle
RDX	-	Cyclotrimethylenetrinitramine
NG	-	Nitroglycerin
TNT	-	2,4,6-trinitrotoluene
2,6-DNT	-	2,6-dinitrotoluene
2,4-DNT	-	2,4-dinitrotoluene
PETN	-	Pentaerythritoltetranitrate
N-NDP	-	N-nitrosodiphenylamine
4-NDP	-	4-nitrodiphenylamine
DP	-	Diphenylamine
2-NDP	-	2-nitrodiphenylamine
EC	-	Ethyl centralite
EGDN	-	Ethyleneglycoldinitrate
ANFO	-	Ammonium Nitrate Fuel Oil
UN	-	United Nations
TLC	-	Thin Layer Chromatography
VBIED	-	Vehicle-Borne Improvised Explosive Device
EPA	-	Environmental Protection Agency
UV	-	Ultraviolet
MEKC	-	Micellar Electrokinetic Chromatography
PDMS/DVB	-	Polydimethylsiloxane/divinylbenzene
CAR/PDMS	-	CarboxenTM/ polydimethylsiloxane
TEA	-	Thermal Energy Analyzer
PCI	-	Positive Chemical Ionization
XRD	-	X-ray Powder Diffraction
XF	-	X-ray fluorescence
IMS	-	Ion Mobility Spectrometry

ESI	-	Electrospray Ionization
DBMS	-	Database Management System
SQL	-	Structured Query Language
RDBMS	-	Rational Database Management System
VB	-	Visual Basic
GUI	-	Graphic User Interface
IDE	-	integrated development environment
IR	-	Infrared
IBIS	-	Integrated Ballistic Identification System
PDQ	-	Paint Data Query
k	-	Capacity Factor/Retention Factor
IAFIS	-	Integrated Automated Fingerprint Identification System

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

An explosion may result from a criminal act and can also occur by accident, for example from an ignition's spark of a leak of domestic gas**.** In recent years, terrorists have used improvised explosives devices (IED) for the purpose of increasing damage of explosion. Growing number of cases involving improvised explosives devices in local and international media have raised the awareness of forensic researchers and law enforcers to study explosives components in details (Ahmad *et al.*, 2011). Bombing activities that occurred in the past few years such as the Bali bombing in 2002, the Altantuyaa murder in October 2006 and the Jakarta bombing in July 2009 have all involved improvised explosives devices that were made from both low and high explosive materials (Oam and Royds, 2013).

According to Malaysian Corrosive and Explosive Substances and Offensive Weapons Act 1958, the term "explosive substance" include “materials for making any explosive substance and any bomb, grenade, apparatus, machine, implement, or material used or intended to be used or adapted for causing or aiding in causing any explosion in or with any explosive substance and any part of such bomb, grenade, apparatus, machine or implement”. Explosives can exist in the form of solid, liquid or gases. It is made of either mixtures or pure compounds (Akhavan, 2011). Pure

explosive compounds be can further divided into organic and inorganic explosives. Furthermore, explosive can also be classified as low explosive and high explosive based on their impact of bombardment. Improvised explosives devices are usually made from low explosive materials since the materials are commonly used and easily obtained in the local market. It arises as a potential menace to public safety as pyrotechnics such as crackers and fireworks can be conveniently purchased either legally or illegally from local market (Yoong, 2013).

In a case of Boston marathon bombing in 2013, an improvised explosive device with pressure cooker as the container was detonated close to the marathon finish line (Sara and Ellen, 2015). The perpetrator used low explosive materials believed to be from firework and increased the explosion damage by adding shrapnel in their explosive device (Dezenski, 2013; Singh *et al.*, 2014). However, the criminals at international level often used high explosive material in their explosive device because of its capability to increase the damage tremendously. In the Bali bombing of 2002, high explosive material identified as trinitrotoluene (TNT), had been used as the main charge for all three explosions that were detonated almost at the same time (Royds *et al.*, 2005).

Determining the nature of an explosion can be a significant challenge to the forensic investigator. High level of contamination, small amount of device fragment or minimal amount of post-blast residue found at the crime scene are among the challenges that need to be faced by each forensic investigator. Proper investigation and analysis must be carried out because from the evidence collected at crime scene, the researcher can determine the type of explosive after the sample has been analysed and can be used as evidence in court to link the suspect with the crime (Ahmad and Heng, 2007; Ladham *et al.*, 2005; Sharma *et al.*, 2010; Varga and Ulbrich, 2004).

1.2 Statement of Problem

The expanding threat, unlawful behaviour and illicit activities utilising energetic explosive materials for criminal and terrorism activities have urged the need for a reliable, rapid but also an accurate investigation technique for analysing crucial puzzles left at the scene of the crime. Analysis of explosive residues become more difficult since the residues of origin material from post-blast samples usually trapped and fused into surrounding. To identify unknown explosive samples, it demanding a competency technique to determine an extensive number of organic and inorganic explosive material. It is a great importance for the analysis of explosive and their post-blast residues analysis to assist forensic scientist in determining the origin of explosive material used in the bombing and eventually help the law enforcement in narrowing down the investigation.

However, the lack of an explosive database has caused great difficulties for the law enforcement when investigating explosion cases in connecting the explosives to their source of origin. Thus, a research to develop an explosive database is important in order to assist the bombing investigators. This research is therefore undertaken to answer the following questions; what are the techniques suitable to analyse explosive residues? What database information system can be used to facilitate in finding a link of post-blast residues to the source of origin and ultimately to the perpetrator of crime?

1.3 Objective of Study

The objectives of this study are divided into two phases which are experimental and computational part.

Phase 1

In the experimental part, the objectives are focused on the chemical reaction and instrument optimization.

i. To develop a portable explosive spot test kit as a screening technique for the field detection of organic high explosive and inorganic low explosives.
ii. To analyse inorganic low explosives by using ion chromatography.
iii. To determine organic high explosives by using high performance liquid chromatography
iv. To apply gas chromatography tandem mass spectrometry for analysis of high explosive.
v. To propose suitable chromatographic methods for analysis of low and high explosives.

Phase 2

In the second phase, the objectives are focused on computational work aim to develop an information system for explosives by using the experimental data from the first phase. The novelty of this research lies in the building a database information system. The database information system is focused on recognition system and the user may use the program to identify the profiling of the real sample with data that has been stored in the database. Two more objectives are listed as follows:

vi. To develop an explosive database information system for the profiling of explosives.
vii. To apply the developed explosive database information system for the comparison of unknown samples of explosive with database of known sample.

1.4 Scope of Study

The scope of this study involved the analysis of both high and low explosives. Colour spot tests were employed to screen for target analytes that were recovered onsite. The samples were analysed using ion chromatography, high performance liquid chromatography, and gas chromatography tandem mass spectrometry. Standards and post-blast residues were collected with the collaboration of Royal Malaysia Police (RMP), and Science Technology Research Institute for Defense (STRIDE). A database information system of the chemical composition profile of explosives named as MYForensic Explosive Database was developed by using Microsoft SQL server and Microsoft visual studio. This database was intended to serve a great support in order to determine the source or types of explosive of unknown samples with known samples stored in the database. The flexibility of database system also allowed administrator the capability of viewing, inserting, editing and deleting data from the database.

1.5 Significance of Study

Results of this study will be particularly useful to forensic investigators especially those working at Jabatan Kimia Malaysia in handling such evidence of explosion cases to determine the nature of the explosive and to profile its origin. Identification of the nature of the explosives may lead to the perpetrator of the crime. Therefore, this study will be able to assist other institutions like Royal Malaysia Police or any private agencies to further their investigation in establishing links to the suspects once the nature of the explosives used is positively identified.

1.6 Thesis Outline

This thesis is divided into nine chapters. Chapter 2 presence the literature review. Chapter 3 describes the general experimental work and chapter 4 describes the development of a spot test kit. Analysis of explosives using IC, HPLC and GC-MS/MS are described in chapter 5, 6 and 7 respectively. Chapter 8 deals with the development of explosive database system. The final chapter 9 concludes the experimental results and opens up the world of future research in explosives.