PROFILING OF INORGANIC IONS IN SELECTED POST-BLAST PYROTECHNIC RESIDUES

LIEW CHOON YOONG

UNIVERSITI TEKNOLOGI MALAYSIA

PROFILLING OF INORGANIC IONS IN SELECTED POST-BLAST PYROTECHNIC RESIDUES

LIEW CHOON YOONG

A dissertation submitted in partial fulfillment of the requirements for the award of the degree of Master of Science (Forensic Science)

Faculty of Science
Universiti Teknologi Malaysia

JANUARY 2013

To my beloved father and mother

ACKNOWLEDGEMENT

In preparing this dissertation, I was in contact with many people, researchers, academicians, and practitioners. They have contributed towards my understanding and thoughts. In particular, I wish to express my sincere appreciation to my main dissertation supervisor, Associate Professor Dr. Umi Kalthom Ahmad, for her encouragement, guidance, critics and friendship. I am also thankful to my co-supervisor, Supt. Shaikh Abdul Adzis Shaikh Abdullah, for his suggestions and advices. Without their continued support and interest, this dissertation would not have been the same as presented here.

I am also indebted to Ministry of Higher Education for funding my Master study via MyBrain 15 scholarship. My sincere appreciation also extends to the laboratory assistants of Universiti Teknologi Malaysia (UTM), particularly Madam Mariam Hasan, Mr. Mat Yasin Sirin from analytical laboratory C19-410. Mr. Mohd Nazri Zainal and Miss Siti Rafezah Mat Emin from forensic analytical laboratory C19-319 for their help and guidance.

My fellow colleagues should also be recognized for their support and assistance at various occasions. Their views and tips were useful indeed. Unfortunately, it is not possible to list all of them in this limited space. I am grateful to all my family members.

ABSTRACT

Pyrotechnic homemade explosives have emerged as a new threat to society. Analysis of explosive residues is useful in identification of explosives and establishing link to the perpetrators. The objectives of this study were to detect the selected inorganic ions in firework samples followed by the determination of chemical profiles. Six different types of firework samples were analyzed in this study. Inorganic ions of pre-blast and post-blast samples were analyzed using ion chromatography with conductivity detection. All targeted anions (F^-, Cl^-, NO_2^-, NO_3^-, ClO_3^-, SO_4^{2-}, PO_4^{3-} and SCN^-) were successfully separated within 42 minutes using Metrosep A SUPP 5 column and $NaHCO_3$-Na_2CO_3 as the eluent. Calibration graph of targeted anions with good linearity (r^2>0.9796) were obtained with detection limits within range from 16 to120 µg/L. Besides that, all targeted cations (Li^+, Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}) were well separated within 24 minutes using Metrosep C 4 employing nitric acid-dipicolinic acid as the eluent. Good linearity (r^2>0.9948) of calibration graph was obtained and detection limits was 31-171 µg/L. Anions (Cl^-, NO_2^-, NO_3^-, ClO_3^- and SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}) were detected in pre-blast firework samples. Concentration of NO_3^-, ClO_3^- and K^+ were the highest among detected ions in pre-blast samples. Magnesium ion which is a common element in fireworks was detected in all samples. In post-blast residues, targeted ions presence in pre-blast samples can still be detected but in lower concentration. There was significant reduction in NO_3^- and ClO_3^- concentration in post-blast residues. Concentrations of SO_4^{2-} are relatively higher compared to other anions detected in post-blast residues. Identification of fireworks cannot be based solely on chemical profile of post-blast residues as it is not fully accurate. However, presence of Ca^{2+} and Mg^{2+} in post-blast residues strongly suggest the used of pyrotechnic fireworks.

ABSTRAK

Bahan letupan piroteknik buatan sendiri telah timbul sebagai ancaman yang baru kepada masyarakat. Analisis sisa-sisa letupan adalah berguna dalam pengenalpastian jenis bahan letupan serta menentukan suspek yang terlibat. Tujuan kajian ini adalah untuk mengesan kehadiran anion dan kation tertentu yang terdapat dalam sampel bunga api diikuti dengan penentuan profil kimianya. Sebanyak enam jenis bunga api telah dianalisis dalam kajian ini. Ion-ion tak organik dalam sampel sebelum dan selepas letupan telah dianalisis dengan menggunakan ion kromatografi dengan pengesanan konduktiviti. Semua anion yang terpilih (F^-, Cl^-, NO_2^-, NO_3^-, ClO_3^-, SO_4^{2-}, PO_4^{3-} dan SCN^-) telah berjaya diasingkan dalam masa 42 minit dengan menggunakan turus Metrosep A SUPP 5. Eluen yang digunakan ialah campuran $NaHCO_3$ dan Na_2CO_3. Graf penentukuran setiap ion mencapai garis lurus yang bagus (r^2>0.9796) dan had pengesanan adalah dalam lingkugan 16-120 µg/L. Selain itu, kation (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}) telah diasingkan dalam masa 24 minit dengan menggunakan Metrosep C 4, eluen nitric asid-dipikolinik asid. Garis lurus setiap ion dalam graf penentukuran mencapai r^2>0.9948 dan had pengesanan ialah 31-171 µg/L. Anion (Cl^-, NO_2^-, NO_3^-, ClO_3^- and SO_4^{2-}) dan kation (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}) telah dikesan dalam sampel sebelum letupan. Kepekatan ion NO_3^-, ClO_3^-, and K^+ adalah yang tertinggi di antara ion-ion yang dikesan dalam sampel bunga api sebelum letupan. Ion Mg^{2+} yang biasa terdapat dalam bunga api telah dikesan dalam semua sampel. Dalam analisis sisa-sisa letupan, ion-ion yang dikesan adalah sama seperti sampel sebelum letupan tetapi dengan kuantiti yang kurang dari asal. Kepekatan NO_3^- dan ClO_3^- berkurang dengan ketara dalam sisa letupan. Kepekatan relatif SO_4^{2-} adalah lebih tinggi berbanding dengan anion yang lain. Pengenalpastian jenis bahan letupan berdasarkan profil kimia sisa-sisa letupan sahaja adalah tidak tepat. Bagaimanapun, kehadiran Ca^{2+} dan Mg^{2+} dalam sisa letupan telah mencadangkan penggunaan piroteknik bunga api.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ATM	-	Automated Teller Machine
DDW	-	Distilled deionised water
CE	-	Capillary Electrophoresis
C-4	-	Composition-4
FRDM	-	Fire and Rescue Department of Malaysia
GC	-	Gas chromatography
HPLC	-	High performance liquid chromatography
HMX	-	High-velocity military explosive
IC	-	Ion chromatography
IMS	-	Ion Mobility Spectroscopy
ND	-	Not detected
MS	-	Mass spectrometer
MYR	-	Malaysia Ringgit
PDA	-	Photodiode array
PETN	-	Pentaerythritol tetranitrate
RDX	-	Research Department Explosive
RMP	-	Royal Malaysia Police

RSD	-	Relative standard deviation
SD	-	Standard deviation
SEM-EDA	-	Scanning electron microscope-Energy dispersive x-ray analyzer
TATP	-	Triacetone triperoxide
TEA	-	Thermal energy analyzer
TLC	-	Thin layer chromatography
TNT	-	Trinitrotoluene
UV	-	Ultraviolet
VAAR	-	Vinyl acetate alcohol resin

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Pyrotechnics mixed explosives are often used in making homemade explosives. It emerges as a potential threat to public security as pyrotechnics such as fireworks can be easily purchased either legally or illegally. In recent years, improvised explosives mixed with pyrotechnic have been used by terrorists to increase the damage of explosion. Increasing cases involving pyrotechnic mixed homemade explosives in international and local have raised the awareness of law enforcers to study pyrotechnics components in depth (Ahmad *et al*., 2011). According to Law of Malaysia Explosive Act 1958, explosive substance include any 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.

On 2nd of May 2010, a car bomb was found near the Times Square in New York. The car bomb was loaded with fireworks, fuel and fertilizer. The bomb was successfully defused and later a Pakistani suspect was arrested for investigation (The Star, 2010).

On 17th of April 2011, a bomb was detonated at a Nigeria hotel and wounded eight people during the presidential election. The bomb was later identified containing celebratory fireworks (The Star, 2011).

Homemade explosives cases have increased in Malaysia in recent years. In 2008, at Shah Alam and Puchong, three cases where explosives made from fireworks were used to blow up Automated Teller Machines (ATMs). Although the explosion caused damage to the machines, the thieves failed to get the cash. Among three attempts, only one successfully got away with MYR 30000 (The Star, 2008).

On 29th August 2010, a deadly firework explosive packed in a parcel was place in front of an apartment unit in Desa Tun Razak, Cheras. When a woman opened the parcel, it detonated. The woman was killed and another co-worker was badly injured. The explosive was identified as mixture of cannonball fireworks with kerosene (The Star, 2010).

Another case that happened on 9th January 2012, involved three homemade explosives that exploded in front of Jalan Duta court complex during an assembly by Datuk Seri Anwar Ibrahim's supporters. Four members of the public were injured while vehicles parked nearby suffered minor damage. The explosive was suspected of containing pyrotechnics and black powder (The Star, 2012).

1.2 Statement of Problem

Pyrotechnic composition is often used in homemade explosives. The lack of an explosive database hinders Royal Malaysian Police (RMP) when investigating explosion cases. RMP often faced difficulties when it comes to linking the explosives to its origin. Therefore, a research to develop explosive database is essential in order to fill the missing link for RMP investigation.

1.3 Objectives

This study embarks in the following objectives;

i. To detect the presence of anions and cations in pre and post blast pyrotechnic fireworks samples.

ii. To determine the chemical profile of pyrotechnic fireworks samples.

1.4 Scope of Study

This study focuses on the analysis of the constituent of pyrotechnic from pre blast and post blast source. Profiling of the pyrotechnic samples is based on the detecting of anions (F^-, Cl^-, NO_2^-, NO_3^-, ClO_3^-, SO_4^{2-}, PO_4^{3-} SCN^-) and cations (Li^+, Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}) studied using ion chromatography. Common inorganic explosives such as nitrate, chlorate, sulfate, ammonium, and potassium are part of the study.

1.5 Significance of Study

This study can be used to help Royal Malaysia Police (RMP) and Malaysian Fire and Rescue Department (FRDM) in determining the type of explosives used in a bombing attack. Analysis of the explosive residues will provide valuable information regarding the substances that been used in making the explosives. This will eventually establish a link between the explosive and its perpetrators.

REFERENCES

Agrawal, J. P. (2010). Pyrotechnics, in High Energy Materials: Propellants, Explosives and Pyrotechnics. Wiley-VCH Verlag GmbH & Co. Weinheim, Germany.

Ahmad, U. K., Jamari, N. LA., Nagayah, S. (2012). Simultaneous Determination of Inorganic Ions in Post-Blast Residues using Capillary Electropheresis. *Malay J. Forensic Sciences 2012 :* 16-25.

Ahmad, U. K., Ong, S. T., Ghazali, M. F., Yew, C. H., Abdullah, M. K. (2011). Analysis of Anionic Post-blast Residues of Low Explosives from Soil Sample of Forensic Interest. *Malays J. Anal. Sci.* 15 (2): 213-226.

Akhavan, J. (2004). Classification of Explosive Materials. *The Chemistry of Explosives*. (3th Ed). Royal Society of Chemistry. United Kingdom.

Borch, T., & Gerlach, R. (2004). Use of Reversed-Phase High-Performance Liquid Chromatography Diode Array Detection for Complete Separation of 2, 4, 6-trinitrotoluene Metabolites and EPA M8330 Explosives: Influence of Temperature and an Ion-Pair Reagent. *J. Chromatogr. A*, 1022, 83–94.

Bradley, C. (2008). Types of Fireworks. Retrieved on April 21, 2012 from http://www.pyrouniverse.com/consumer/types.htm.

Byall, E. B. (2001). Explosives Report 1998-2001 Detection and Characterization of Explosives and Explosive Residue: A Review. *13th INTERPOL Forensic Science Symposium, Lyon, France, October 16-19 2001*.

Caygill, J. S., Davis, F., Higson, S. P. J. (2012). Current Trends in Explosive Detection Techniques. *Talanta* 88: 14-29.

Conkling, J. A. and Mocella, C. J. (2010). *Chemistry of Pyrotechnics: Basic Principles and Theory*. CRC Press Taylor & Francis Group. United State.

Dicinoski, G. W., Shellie, R. A., Haddad, P. R. (2006). Forensic Identification of Inorganic Explosives by Ion Chromatography. *Anal. Lett*., 39: 639-657.

Dolan, J. W. (2003). Why Do Peaks Tail?LC troubleshooting. *LC.GC Europe September 2003*: 1-4.

Fritz, J. S. and Gjerde, D. T. (2009). *Ion Chromatography*. Weinheim: Wiley-VCH. Germany.

Gibbs, T. R., Baytos, J. F. (1980). *LASL Explosive Property Data*. University of California Press.

Girard, J. E. 2007. Criminalistics: Forensic Science and Crime. Jones & Bartlett Learning. United State.

Houck, M. M., Siegel, J. A. (2006). Fires and Explosions. *Fundamental of Forensic Science*. Elsevier.

Johns, C., Shellie, R. A., Potter, O. G., O'Reilly, J. W., Hutchinson, J. P., Guilt, R. M., Breadmore, M. C., Hilder, E. F., Dicinoski, G. W., Haddad, P. R. (2008). Identification of Homemade Inorganic Explosives by Ion Chromatographic Analysis of Post-Blast Residues. *J. Chromatogr. A*, 1182 205-214.

Kosanke, K. L., Dujay, R. C., Kosanke, B. J. (2006). Pyrotechnic Reaction Residue Particle Analysis. *J. Forensic Sci* 51, 296-302.

Krausa, M., Reznev, A. A. (2004). Vapour and trace detection of explosives for anti-terrorism purposes. *Volume 167 of NATO science series: Mathematics, physics, and chemistry Volume 167 of NATO Science Series*. Springer.

Kuila, D. K., Chakrabortty, A., Sharma, S. P., Lahiri, S. C. (2006). Composition profile of low explosives from cases in India. *Forensic Sci. Int*., 159 (2006) 127- 131.

Jamari, N. LA. (2012). Simultaneous Detection of Anions and Cations in Post-Blast Explosive Residues Using Capillary Electrophoresis. Master of Science Dissertation Report, Universiti Teknologi Malaysia, Skudai.

McCord, B. R., Hargadon, K. A., Hall, K. E. and Burmeister, S. G. (1994). Forensic Analysis of Explosives Using Ion Chromatographic Methods. *Anal. Chim. Acta*, 288: 43-56.

Miller, C. J., Elias G., Schmitt, N. C., Rae C. (2010). Identification of explosives from porous materials: Applications using reverse phase high performance liquid chromatography and gas chromatography. *Sens Imaging*, 11: 61-75.

Moore, D. S. (2007). Recent Advances in Trace Explosion Detection Instrument. *Sens Imaging* 8: 9-38.

Murray, S. G. (2000). Explosive: Military. *Encyclopedia of Forensic Sciences*. Elsevier United Kingdom. 764-767.

Pacakava, V., Stulik, K. (1997). Capillary electrophoresis of inorganic anions and its comparison with ion chromatography. *J. Chromatogr. A*, 789:169-180.

Russell, M. S. (2009). *The Chemistry of Fireworks*. Royal Society of Chemistry. United Kingdom.

Saferstein, R. (2007). *Criminalistics: An Introduction to Forensic Science*. (9th Ed). New Jersey: Pearson Prentice Hall, Englewood Cliffs.

Schafer, H., Laubli. M. and Dorig. R. (2003). *Ion Chromatography: Theory, Columns and Eluent*. Metrohm Monograph 8.014.5003. Metrohm AG, CH-9101 Herisau.

The Star. Bomb Experts to Assist Cops Over Jalan Duta Blasts (January 18, 2012). Retrieved on March 26, 2012 from http://thestar.com.my/news/story.asp?file=/2012/1/18/nation/20120118200527&sec=nation.

The Star. Bomb Goes Off at Nigerian Hotel After Vote, Eight Hurt (April 17, 2011). Retrieved on March 26, 2012 from http://thestar.com.my/news/story.asp?file=/2011/4/17/apworld /20110417211245&sec=apworld.

The Star. NY Police Defuse Car Bomb in Times Square (May 2, 2010). Retrieved on March 26, 2012 from http://thestar.com.my/news/story.asp?file=/2010/5/2/worldupdates/2010-05-02T123037Z_01_NOOTR_RTRMDNC_0_-481584-1&sec=Worldupdates.

The Star. Theives Blow Up ATM with Fireworks Bomb (October 14, 2008). Retrieved on March 26, 2012 from http://thestar.com.my/news/story.asp?file=/2008/10/14/nation/2270584& sec=nation.

The Star. Woman Dies After Parcel Bomb Explodes in Cheras Apartment Blast (Updated) (August 29, 2010). Retrieved on 26 March 2012 from http://thestar.com.my/news/story.asp?file=/2010/8/29/nation/20100829123325&sec=nation.

Tamiri, T. (2000). Explosives. *Encyclopedia of Forensic Sciences*. Elsevier. Jerusalem, Israel.

U.S. Department of Transportation. (2012). Explosives (EX) Approvals. *Regulatory Guidelines for Shipping and Transporting Fireworks*.

Vermeij, E., Duvalois, W., Webb, R., Koeberg, M. (2009). Morphology and composition of pyrotechnic residues formed at different levels of confinement. *Forensic Sci. Int.*, Volume 186, 68-74.

Windelspecht, M. (2003). *Groundbreaking Scientific Experiments, Inventions & Discoveries of The 19th Century*. Greenwood Press.

Yinon, J. (2000). Explosives. *Handbook of Analytical Separations Vol.2*: 603-616. Elsevier, Oxford, United Kingdom.

Yinon, J. and Zitrin, S. (1993). *Modern Methods and Applications in Analysis of Explosives*. Chichester: John Wiley and Son.

Zukas, J. A., Walters. W., Walters. W.P. (2002). *Explosive Effects and Applications*. Springer Berlin, Germany.