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Forensic Analysis of Inorganic Anions from Post-Blast Pyrotechnic Residues

Umi Kalthom Ahmad[a*], Choon Yoong Liew[a], Mohamad Afiq Mohamed Huri[a], Shaikh Abdul Adzis Shaikh Abdullah[b]

[a]*Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor Darul Ta'zim, Malaysia*
[b]*Makmal Forensik JSJ, Polis Diraja Malaysia, Bt. 8 ½, Jalan Cheras, 43200 Cheras, Selangor*

*Corresponding author: umi@kimia.fs.utm.my

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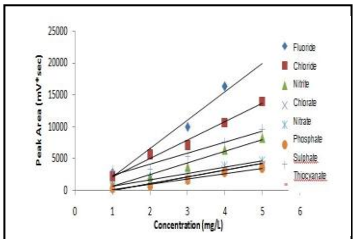
Graphical abstract



Abstract

Increase bombing activities in recent years have raised much awareness amongst forensic scientists of the importance of post-blast investigation. Analysis of post blast bomb residues is useful in identification of explosives and establishing link to its origin. The use of pyrotechnic in homemade explosives has emerged as a new threat to society. In this study, pre and post-blast inorganic anions from pyrotechnic residues were analyzed using ion chromatography with conductivity detection. Inorganic anions were separated using Metrosep A SUPP 5 anion column with $NaHCO_3$ - Na_2CO_3 eluent. Eight anions (fluoride, chloride, nitrite, chlorate, nitrate, phosphate, sulfate and thiocyanate) were successfully separated within 40 min. Good linearity of calibration graph and LOD ranged from 4.8 to 21.0 ppb were achieved. Chemical anionic constituents of the fireworks were found to differ from each other. However, they were found to be common in nitrate and chlorate as oxidizer. Ratio of oxidizer was also found to be much higher than other anions. Post-blast samples showed drastic reduction in oxidizer concentration.

Keywords: Pyrotechnic; ion chromatography; homemade explosives;, inorganic anions; post-blast

Abstrak

Peningkatan aktiviti pengeboman dalam tahun-tahun kebelakangan ini telah banyak menimbulkan kesedaran di kalangan saintis forensik tentang kepentingan penyiasatan pasca letupan. Analisis sisa-sisa bom pasca letupan adalah berguna dalam mengenal pasti bahan letupan dan mewujudkan pautan kepada asal-usulnya. Penggunaan piroteknik dalam bahan letupan buatan sendiri telah muncul sebagai ancaman baru kepada masyarakat. Dalam kajian ini, anion letupan pra dan pasca organik daripada sisa piroteknik dianalisis menggunakan kromatografi ion dengan pengesanan kekonduksian. Anion tak organik telah dipisahkan dengan turus anion Metrosep A SUPP 5 menggunakan eluen $NaHCO_3$ - Na_2CO_3. Lapan anion (fluorida, klorida, nitrit, klorat, nitrat, fosfat, sulfat dan tiosianat) telah berjaya dipisahkan dalam masa 40 min. Kelinearan graf penentukuran yang baik dan pelbagai LOD 4.8-21.0 ppb telah dicapai. Juzuk kimia anionik bunga api didapati berbeza daripada satu sama lain. Walau bagaimanapun, sampel didapati mengandungi nitrat dan klorat sebagai pengoksida. Nisbah pengoksida telah juga didapati lebih tinggi berbanding anion lain. Sampel pasca letupan menunjukkan pengurangan drastik dalam kepekatan pengoksida.

Kata kunci: Piroteknik; Kromatografi ion; letupan buatan sendiri; anion tak organic; pasca letupan

■1.0 INTRODUCTION

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 pyrotechnics have been used by terrorists to increase the damage of explosion. Increasing cases involving pyrotechnic mixed homemade explosives in international[1] and local[2] media have raised the awareness of law enforcers to study pyrotechnic components in depth.

Pyrotechnic material can be defined as a mixture of chemical elements and compounds of a self-contained and self-sustained exothermic chemical reaction, for the production of light, heat, gas, smoke or sound[3,4]. Pyrotechnics are generally composed of finely powdered fuels and oxidizers together with other additives depending on the requirement. Energy generated during reaction is then used to produce a glow (matchstick), or smoke and light (fireworks), or large quantities of gas (fireworks rockets). Pyrotechnic compositions are also used in heat-generating devices, delay and igniter compositions as well[5].

There are two special features of pyrotechnics: firstly, pyrotechnic compositions are mixture of different chemicals, mostly inorganic chemicals. These compositions only burn when ignited and do not detonate. However, some compositions can be detonated under confined environment or initiated by over stimulus. Secondly, pyrotechnics are used to produce special effects which cannot be found in explosives and propellants. These special effects are classified base on their nature and applied for different purposes[6].

The earliest pyrotechnic fuels are charcoal and sulfur. Nowadays, there are variety choices of fuels ranging from metallic to non-metallic elements and binary compounds to carbonaceous materials. Examples of metal elements are: aluminum, chromium, iron, magnesium, titanium, tungsten, and zirconium. While the non-metals include: boron, carbon, silicon, sulfur, and phosphorus. Magnesium (Mg) and aluminum (Al) are the most frequently used elements to produce light and heat in pyrotechnics. Magnesium produces intense white light when burning and thus it is used as fuel for most illuminating and tracers formulation. Mixture with aluminum is more stable than Mg and has better storage life. Al is the main ingredient for photoflash and thermite formulations. Titanium has also been used in formulations for first fires, igniters and heat sources[5].

The oxidizer provides oxygen for reaction. Oxidizer is usually metallic and some non-metallic oxides, oxygenated salts and some halides. Examples of oxidizers are chlorates, peroxides, perchlorates, chromates and nitrates. The common oxidizers for pyrotechnics are sodium and potassium nitrate. Barium and strontium peroxides are used as well but to a lesser extent. Different oxidizers will give different colors of light during decomposition[5].

Other additives such as coolants, retardants, dyes and color intensifiers and moderators are added as well. Coolants are used to decrease the temperature during burning of compositions. Examples are carbonates of magnesium, sodium and other metals. Retardants are used to retard the rates of burning in pyrotechnics. Examples are organic salts such as oxalates, formats, citrates and calcium carbonate as well. Dyes and color intensifiers are used to produce color in smoke and light. Moderators are used to modify the color of the flame or to improve the smoothness and efficiency of combustion[5].

Inorganic explosives are widely encountered in improvised homemade explosives. Common inorganic explosives include propellant such as black powder, pyrotechnic mixtures, and improvised compositions. Often anions such as nitrate, chlorate, perchlorate, sulfate, thiosulfate and thiocyanate can be detected in post-blast residue which mainly comes from oxidizer and reaction products of explosives[7].

Ion chromatography (IC) is widely used in the identification and detection of inorganic ions because of its high sensitivity and selectivity. A wide range of ions can be detected by using different types of column and eluent. Capillary electrophoresis (CE) has been used as a complementary technique for peak confirmation in IC[8-10].

A more recent study on ion chromatographic analysis of homemade inorganic explosives post-blast residues was done by Johns *et al.*[11]. The cations and anions produced from the detonations of inorganic homemade explosives were identified and separated. IC with two Dionex ICS-2000 systems coupled together allowed anions and cations from the same sample to be analyzed simultaneously.

Pyrotechnic composition is often used in homemade explosives. The lack of an explosive database causes great difficulties to the Royal Malaysia Police (RMP) when investigating explosion cases in order to link the explosives to its origin. This study was therefore aimed to assist RMP in post-blast investigation. The objective of this study was to determine the inorganic anions present in post-blast pyrotechnic samples.

2.0 EXPERIMENTAL

Double distilled deionised water (DDDW) used for preparation of solvent and dilution was obtained from Milipore Simplicity 185 water system.

2.1 Apparatus and Chemicals

For IC, standard solution of inorganic anions (F^-, Cl^-, NO_2^-, SO_4^{2-}, PO_4^{2-}) were prepared from 1000 mg/L stock solution respectively from Merck (Germany). Anion standards (NO_3^-, SCN^-, ClO_3^-) were prepared from solid analytical grade potassium nitrate, potassium thiocyanate, and potassium chlorate from Merck (Germany). The eluent for anion analysis was prepared using analytical grade sodium bicarbonate and sodium hydrogen carbonate from Merck (Germany). Suppressor was prepared using analytical grade sulfuric acid solution (QRec, Switzerland).

2.2 Instrumentation

Ion chromatography used in this study was Metrohm Advanced IC system by Metrohm Ltd (Herisau, Switzerland). The IC system comprised of Methrohm 830 IC interface, 819 IC detector (conductivity detector), 820 column thermostat, 818 IC pump, separation column and Metrosep A SUPP 4/5 guard column. For anionic separation, the column used was Metrosep A SUPP 5, 150 x 4.0 mm with 5 µm particle size, and polyvinyl alcohol with quaternary ammonium groups as column packing material. The flow rate was set at 0.7 mL/min.

2.3 Preparation of Standard Solutions

A serial dilution containing mixture of ions (F^-, Cl^-, NO_2^-, ClO_3^-, NO_3^-, SO_4^{2-}, PO_4^{2-}, SCN^-) from 1 ppm to 5 ppm was prepared from 1000 ppm anionic standard solutions. Each solution was subjected to sonication, filtered through 0.45 µm disc syringe filter and degassed.

2.4 Preparation of Eluent and Suppressor

IC anion eluent comprising of 1.0 mmol/L $NaHCO_3$ and 3.2 mmol/L Na_2CO_3 was prepared using 0.17 g of Na_2CO_3 and 0.04 g of $NaHCO_3$ (Merck, Germany) and made up to volume with DDDW in a 500 mL volumetric flask. The eluent was sonicated for 15 minutes and filtered with a 0.45 µm pore size, 47 mm diameter Whatman filter paper. Subsequently, the eluent was degassed for 15 minutes before used.

0.1 M sulfuric acid was prepared by dissolving 5.56 mL of sulfuric acid in 1 L volumetric flask with DDDW. The solution was then filtered through a 0.45 µm nylon membrane filter.

2.5 Calibration Graph and Limits of Detection

Anion standard solution containing mixture of ions (F^-, Cl^-, NO_2^-, ClO_3^-, NO_3^-, PO_4^{2-}, SO_4^{2-}, SCN^-) was prepared in serial dilution from 1 ppm to 5 ppm. The standard solutions were injected into IC to obtain the analyte peak areas for the preparation of calibration graph. Limit of detection of each analyte was assessed from signal to noise ratio (S/N) of 3:1.

2.6 Sampling and Sample Extraction

Six different types of pyrotechnic samples (fireworks) were purchased from local shops in Skudai, Johor. The types of firework included Rockets, Aerials, Display Shell, Fountain and Roman Candle. A small amount of pyrotechnic content was taken from each sample before the firework was ignited. The content was prepared as pre-blast sample solution by dissolving 0.1 g in 100 mL DDDW. The solution was sonicated, filtered and degassed.

Sampling process was done at a remote designated place in UTM Skudai which was supervised by a laboratory technician and assisted by peers. The pyrotechnic samples were ignited on a piece of aluminum foil (8 cm x 8 cm). Pyrotechnic residues on the foil were collected by swabbing with a wet cotton butt. The cotton was then dipped into 10 mL DDDW filled screw-cap bottle. The solution was sonicated, filtered and degassed as well.

3.0 RESULTS AND DISCUSSION

3.1 Separation of Standard Anions

A solution containing mixture of eight anions were successfully separated using Metrosep A SUPP 5 column. The earliest peak was attributed to F^-, followed by Cl^-, NO_2^-, ClO_3^-, NO_3^-, PO_4^{2-}, SO_4^{2-} and finally SCN^-. All peaks were found to elute within 40 minutes (Figure 1). Significant band broadening was observed for the SCN^- anion peak.

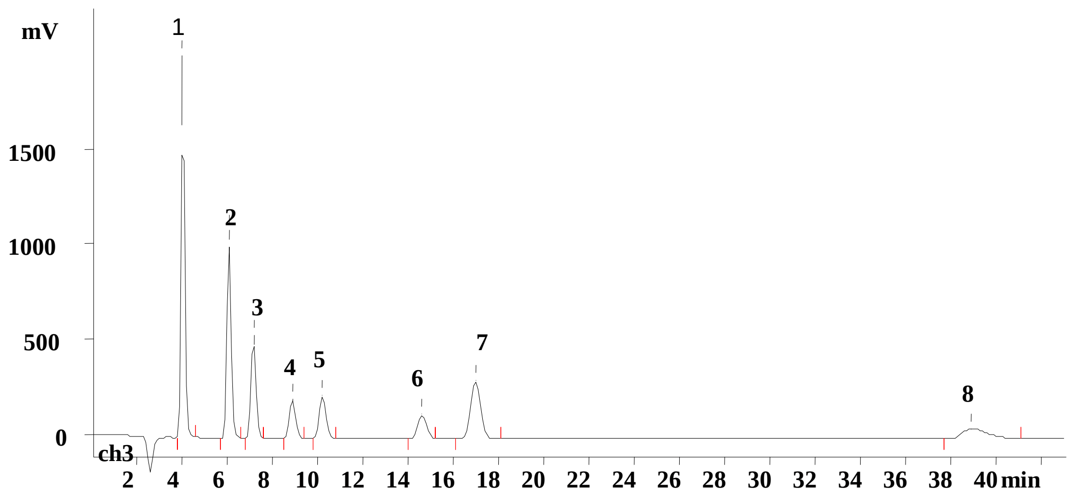


Figure 1 IC chromatogram of 4 mg/L standard anions. IC conditions: Metrosep A SUPP 5 column (150 x 4.0 mm I.D.) coated with polyvinyl alcohol with quaternary ammonium groups; 3.2 mM Na_2CO_3 and 1.0 mM $NaHCO_3$ eluent with flow rate of 0.7 mL/min; suppressed conductivity detection. Peak identities: (1) fluoride, (2) chloride, (3) nitrite, (4) chlorate, (5) nitrate, (6) phosphate, (7) sulphate and (8) thiocyanate

3.2 Calibration, Detection Limits and Repeatability

Calibration graph of standard anions is shown in Figure 2. All anions showed good linearity (r^2>0.95). LOD of standard anions range from 4.8 to 21.0 µg/L as listed in Table 1. The relative standard deviations for within-day retention time is less than 0.83% while for day-to-day is less than 2.36% as listed in Table 2.

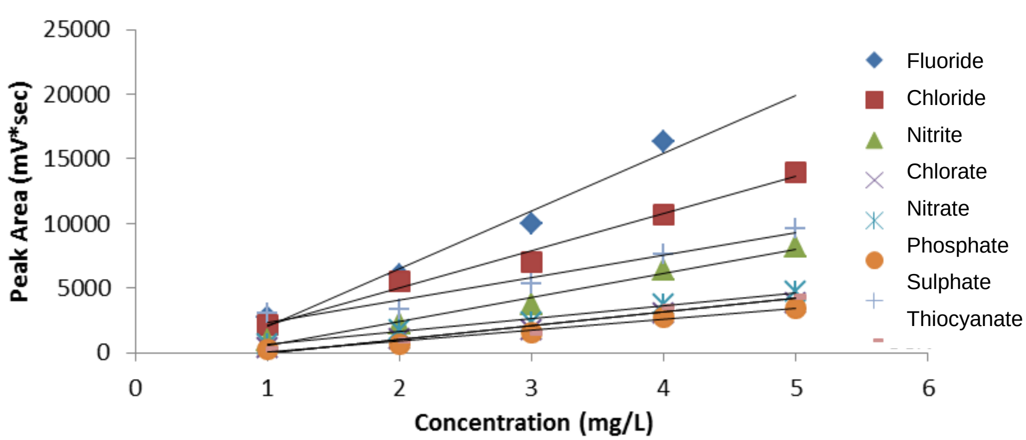


Figure 2 Calibration graph of anions standard

Table 1 Detection limit of standard anions

Analytes	Limit of Detection (µg/L)		Correlation coefficient (r^2)
	This study	Previous study*	
F^-	7.7	2.0	0.974
Cl^-	6.6	2.2	0.986
NO_2^-	7.5	4.4	0.982
ClO_3^-	7.1	7.2	0.983
NO_3^-	4.8	5.4	0.992
PO_4^{2-}	7.5	8.0	0.983
SO_4^{2-}	11.4	3.1	0.958
SCN^-	21.0	5.5	0.955

* John *et al*. [11]

Table 2 Evaluation of repeatability of IC results for within-day and day-to-day variation of the retention time and relative standard deviations of anions

Analytes	Within-day (n=3)		Day-to-day (n=6)	
	Mean Retention Time (min)	RSD (%)	Mean Retention Time (min)	RSD (%)
F^-	3.98	0.15	3.95	0.47
Cl^-	6.03	0.10	5.99	0.46
NO_2^-	7.12	0.14	7.07	0.51
ClO_3^-	8.87	0.24	8.79	0.50
NO_3^-	10.13	0.47	10.10	2.36
PO_4^{2-}	14.46	0.45	14.38	0.53
SO_4^{2-}	16.93	0.03	16.87	0.24
SCN^-	39.88	0.83	38.96	1.06

3.3 Profile of Pyrotechnic Samples

The firework samples obtained were manufactured mainly from China. Most of the samples were not labeled with the address of the manufacturer. The samples were all classified by US Department of Transportation under Class 1.4G which indicated as minor explosion confined to package (pyrotechnic). The types of fireworks were named by their effect when ignited. In this study, only 6 types of firework were selected. The details of the samples are shown in Table 3. These details are useful in tracing the source of the samples especially during post-blast investigation.

Table 3 Details of pyrotechnic samples

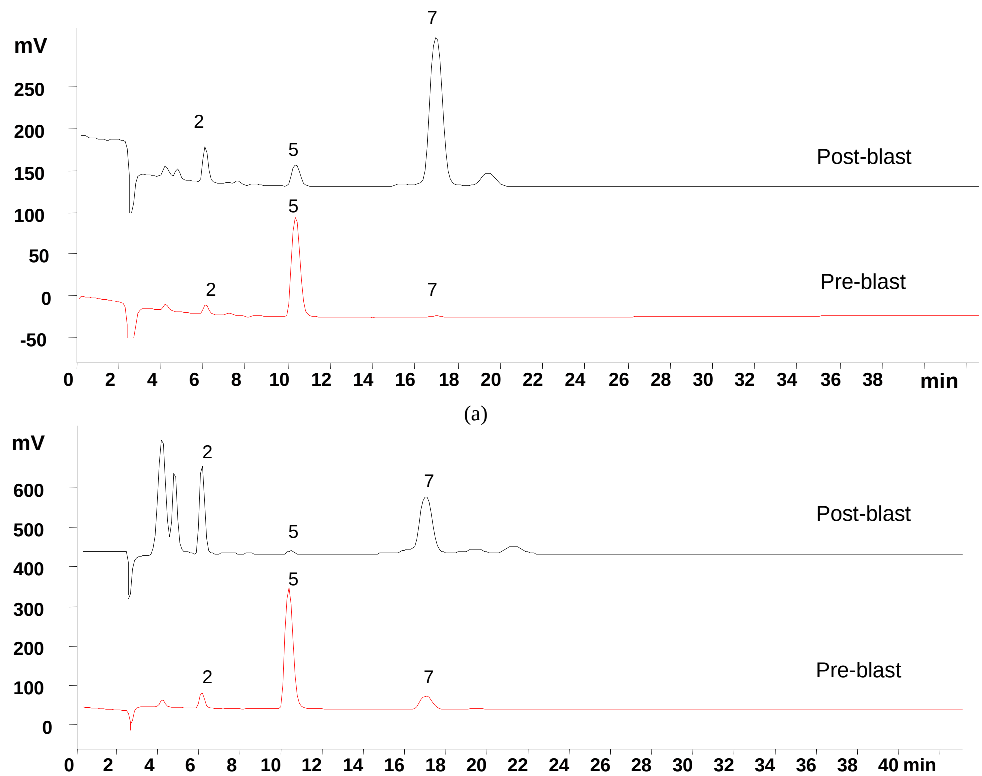
Samples	Label	Types	Manufacturer	Classification
WM	Whistling Moon Traveller With Report (No. 0445)	Rockets	China	UN 0336 1.4G Consumer Fireworks
FB	Plane flying at night fireworks (No.W522)	Aerials	China	UN 0336 1.4G Consumer Fireworks
BC	Unknown	Display shell	China	UN 0336 1.4G Consumer Fireworks
SM	Saturn Missiles Battery 25 Shots (No. K1130C_7)	Rockets	China	UN 0336 1.4G Consumer Fireworks
7C	KK999	Fountain	China	UN 0336 1.4G Consumer Fireworks
MS	15 Magic Shots (No. T6237)	Roman Candle	Liuyang Spring Fireworks Co., Ltd (China)	UN 0336 1.4G Consumer Fireworks

3.4 Ratio of Anions in Pre-blast and Post-blast Samples

The chemical constituent of each types of firework is very much different from each other. Most of the pyrotechnic samples used nitrate and chlorate as oxidizer. The critical changes of anions ratio was observed between pre-blast and post-blast sample. As shown in Table 4, nitrate and chlorate anions showed drastic reduction in post-blast samples. While increase in sulfate anions was observed in certain samples such as BC and MS. The concentration changes in nitrate and sulfate suggested the presence of black powder in the sample. Black powder consists of potassium nitrate, sulfur and charcoal. Oxidation of black powder will result in a decrease in nitrate and increase in sulfate (Equation 1).

$$10\ KNO_3 + 3S + 8C \rightarrow 2K_2CO_3 + 3K_2SO_4 + 6CO_2 + 5N_2 \qquad (1)$$

Besides that, increase of chloride is also observed in some of the samples. Increased in chloride suggests the end product of chlorate after chemical reduction[8]. The concentration of oxidizer in samples is also determined by the type and size of the fireworks. Higher concentration of oxidizer can be found in display shell and fountain type fireworks. These fireworks are made larger in size in order to burn a longer period of time in order to produce its effect. IC chromatogram of pre and post blast sample gave a unique profile as shown in Figure 3. These IC profiles can ultimately be used to reveal the identity of the exact type of explosive in a sample[10].



(b)

Figure 3 IC anionic profile of samples (a) MS and (b) 7C. IC conditions as in Figure 1

Table 4 Ratio of anions in pre-blast and post-blast pyrotechnic samples

Samples	Pre-blast Anion Concentration Ratio								Post-blast Anion Concentration Ratio							
	F^-	Cl^-	NO_2^-	ClO_3^-	NO_3^-	PO_4^{2-}	SO_4^{2-}	SCN^-	F^-	Cl^-	NO_2^-	ClO_3^-	NO_3^-	PO_4^{2-}	SO_4^{2-}	SCN^-
WM	ND	2.4	1.2	0.8	3.6	ND	0.3	ND	ND	2.6	ND	ND	0.9	ND	0.8	ND
FB	ND	0.6	ND	ND	9.3	ND	0.2	ND	ND	0.5	ND	ND	0.7	ND	0.1	ND
BC	ND	0.7	1.7	1.3	24.7	ND	4.8	ND	ND	16.1	ND	ND	0.7	ND	18.1	ND
SM	ND	0.8	ND	ND	22.0	ND	0.2	ND	ND	6.9	ND	ND	1.4	ND	7.1	ND
7C	ND	1.2	ND	ND	27.6	ND	0.9	ND	ND	0.9	0.3	ND	0.3	ND	1.6	ND
MS	ND	0.7	1.2	ND	11.0	ND	0.1	ND	ND	1.2	1.1	ND	2.6	ND	11.6	ND

ND – Not Detected
Pre-blast samples were diluted 100X before injected into IC. Post-blast samples were taken from 10 mL aliquot of sample residues

4.0 CONCLUSIONS

Anionic constituents of pyrotechnic firework samples have been determined using IC. Eight anions namely fluoride, chloride, nitrite, chlorate, nitrate, phosphate, sulfate and thiocyanate have been successfully separated within 40 min using Metrosep anion exchange column. Good linearity of calibration graph and LOD range from 4.8 to 21.0 ppb were achieved. Chemical anionic constituents of the fireworks were found to differ from each other. However, they were found to be common in nitrate and chlorate as oxidizer. Ratio of oxidizer was also found to be much higher than other anions. Post-blast samples showed drastic reduction in oxidizer concentration. The results obtained in this study will hopefully serve as a reference for RMP during cases involving pyrotechnic explosives.

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References

[1] The Star. May 2, 2010. NY Police Defuse Car Bomb in Times Square Retrieved on March 26, 2012 from http://thestar.com.my/news/story.asp?file=/2010/5/2/worldupdates/2010-0502T1 2303 7Z_01_NOOTR_RTRMDNC__-481584-1&sec=Worldupdates.

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

[3] Tamiri, T. 2000. Explosives. *Encyclopedia of Forensic Sciences*. Elsevier.

[4] Kosanke, K. L., R. C. Dujay and B. J. Kosanke. 2006. *J. Forensic Sci*. 51 (2): 296–302.

[5] Akhavan, J. 2004. Classification of Explosive Materials. *The Chemistry of Explosives*. 3rd Ed. Cambridge: Royal Society of Chemistry.

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

[7] 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*.

[8] McCord, B. R., K. A Hargadon, K. E. Hall and S. G. Burmeister. 1994. *Anal. Chim. Acta*. 288: 43–56.

[9] Kuila, D. K., A. Chakrabortty, S. P. Sharma and S. C. Lahiri. 2005. *Forensic Sci. Int*. 159: 127–131.

[10] Dicinoski, G. W., R. A Shellie and P. R. Haddad. 2006. *Anal. Lett.* 39: 639–657.

[11] Johns, C., R. A Shellie, O. G Potter, J. W. O'Reilly, J. P Hutchinson, R. M. Guilt, M. C. Breadmore, E. F. Hilder, G. W. Dicinoski, and P. R. Haddad. 2008. *J. Chromatogr. A*. 1182: 205–214.