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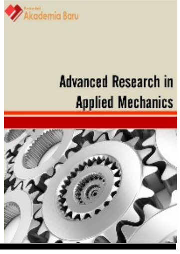

Chemical profiling of selected explosives using high performance liquid chromatography and ion chromatography

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ABSTRACT

Liquid chromatographic techniques have frequently been used for the analysis of explosives. In this study, high performance liquid chromatography with UV detection (HPLC-UV) was used for profiling of the organic components of explosive compound. Ion chromatography (IC) was used to analyze the inorganic components of explosive compound. Four samples of high explosive and three samples of low explosive were detonated in a sampling exercise performed in collaboration with Royal Malaysia Police. A tri-mixture of HPLC mobile phase system consisting of methanol: acetonitrile: water (50:10:40) was used in HPLC-UV separation and cotton swabbing technique was employed for sample extraction of post-blast explosive residues. Thirteen selected organic explosive compounds namely HMX, 4-nitrobenzonitrite, RDX, nitroglycerin, TNT, 2,6-DNT, 2,4-DNT, PETN, n-nitrosodiphenylamine, 4-nitrodiphenylamine, diphenylamine, 2-nitrodiphenylamine and ethyl centralite were successfully separated by using HPLC-UV within 60 minutes. For IC analysis, six cations (Li^+, Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}) and eight anions (F^-, Cl^-, NO_2^-, ClO_3^- , NO_3^-, PO_4^-, SO_4^{2-}, ClO_4^-) were analyzed as possible inorganic ions that could be found in post-blast residues. Based on the study, every sample showed different chemical profile due to each type of explosive.

Keywords:
Explosive, High Performance Liquid Chromatography, Ion Chromatography, post-blast residues, cotton swabbing techniques

1. Introduction

Bombing terrorism that have occurred in the past few years have increased awareness amongst forensic scientists and law enforcers regarding the need of advanced analytical techniques on explosive analysis [1]. The fatalities from bombing explosion may reach from single person to

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hundreds of peoples. As an example, the Bali bombing that occurred on October 2002 had caused the killing of more than 200 people at the explosion scene [2].

Improvised explosive devices or home-made explosive devices are frequently used in terrorist attacks. Homemade explosive devices used by terrorists are usually based on inorganic salts or peroxides since these materials are readily available in low cost and can often be purchased legally without any suspicion to the sellers [3].

The swabbing technique is commonly used for collecting residue from solid surfaces such as metal, plastics, human skin, and cloth. The efficiency of swabbing technique not only depends on the area being swabbed but also other factors such as the type of solvent used, interval of time between explosion and analysis and the nature of the target sample [4-7].

Ion chromatography (IC) technique has been frequently used to analyze inorganic anions and cations found in post blast residues from home-made inorganic explosives used frequently in terrorist attacks [8]. High Performance Liquid Chromatography (HPLC) is often used for analysis of explosives because it is amendable for the analysis of compounds that have low volatility, high sensitive to heat and high molecular weight. This will overcome the problem for detection of explosives that are thermally unstable and may result in decomposition products in the vapours. Furthermore, the wide range of HPLC detection between 190-800 nm provides a good range of separation [9].

Determining the nature of an explosion can be a significant challenge to the forensic investigator. The remaining residue are commonly mixed with surrounding physical materials such as water, soil, rubble and debris and the amount of residue recovered may be limited [10, 11]. Proper investigation and analysis must be carried out because from the evidence collected at crime scene, the scientist can determine the type of explosive after the sample has been analyzed and can be used as evidence in court to link the suspect with the crime [12, 13]. This study was therefore undertaken to employ HPLC-UV for profiling the organic components while IC was used to analyze the inorganic components of explosive compound.

2. Experimental

2.1. Chemicals and Materials

For organic solvents, acetonitrile and methanol used were of HPLC grade (Merck, Germany) and analytical grade (Merck) respectively. 2,4,6-TNT and HMX were acquired commercially as 1000 ppm individual solution in acetonitrile from Supelco (Bellefonte, USA). Explosive standards of RDX, PETN, 2,6-dinitrotoluene (2,6-DNT), 2,4-dinitrotoluene (2,4-DNT), N-nitrosodiphenylamine (N-NDP), 4-nitrodiphenylamine (4-NDP), diphenylamine (DP), ethyl centralite (EC), 2-nitrodiphenylamine (2-NDP), and 4–nitrobenzonitrile (4-NTB) (1000 ppm solution in acetonitrile) were obtained as gifts from Science and Technology Research Institute for Defense (STRIDE), Batu Arang, Selangor. Nitroglycerin was obtained in the form of medicinal tablet (Nitrostat) from UTM Health Centre.

The ionic analytes used for identification of explosives in this study comprised of several anions (chlorate, chloride, chlorite, fluoride, nitrate, nitrite, perchlorate, phosphate, sulfate and perchlorate) and cations (ammonium, calcium (II), magnesium (II), potassium (I), sodium (I), and lithium (I). For IC, standard solution of inorganic anions and cations (F^-, Cl^-, NO_2^-, ClO_3^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, ClO_4^-, Li^+, Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}) were prepared from 1000 mg/L stock solution respectively from Merck (Germany).

2.2. Instrumentation

Analytical instruments used in this study included high performance liquid chromatography (HPLC) and ion chromatography (IC). The HPLC used in this study was Agilent 1100 series HPLC that was equipped with a variable wavelength detector (VWD), degasser, quaternary pump and computerized data acquisition employing HPLC Chemstation Software g2170AA. The analytical column used was Supelco Ascentis C18 (4.6 x 250 mm, 3.5 µm). Mobile phase consisted of a mixture of deionized water, methanol and acetonitrile. An aliquot of 20 µL sample was introduced into the system via a Rheodyne six port injection valve fitted with a 20 µL sample loop.

IC used in this study was Metrohm Advanced IC system by Metrohm Ltd (Herisau, Switzerland). IC comprised of Methrohm 830 IC interface, 819 IC detector (conductivity detector), 820 column thermostat, 818 IC pump, separation column and guard column. For anionic separation, the column used was Metrosep A SUPP 4(250 x 4.0 mm with 5 µm particle size) and polyvinyl alcohol with quanternary ammonium groups as column packing material. Metrosep A SUPP 4/5 Guard was used as a guard column. For cationic separation, the column used was Metrosep C 4 (250 x 4.0 mm with 5 µm particle size), and silica gel with carboxyl group as packing material.

2.3. Sampling exercise

The sampling exercise was done in collaboration with Royal Malaysia Police (RMP) from RMP Technical College in Bakri, Muar (Johor). The sampling was performed on 6th May 2015 at a firing range field of Police Training Centre in Segamat, Johor. The field is located about 1 km from the main road. Explosives comprising of low explosive and military explosive material were used by the police officers for this sampling exercise (Table 1). All materials, except detonating cord of PETN were prepared at the scene and packed into commercial pepper bottles (Figure 1).

Table 1
List of explosive material used in the sampling exercise

Explosive Type	Sample Code	Description of Composition Material
Military Explosive		
Plastic Explosive PP01	S01	Shape of moldable form and orange in color
CE Primer	S02	Shape of solid form and yellow in color
Detonating Cord PETN	S03	Shape of fine powder form and white in color
Charging Linear Cutter	S04	Shape of fine powder form and white in color
Low Explosive		
ANFO + Emulate	S05	Shape of solid form and grey in color
Urea + Diesel + Emulate (booster)	S06	Shape of granular form and white in color
Urea + Icing Sugar + Gun Powder (booster)	S07	Shape of granular form and white in color

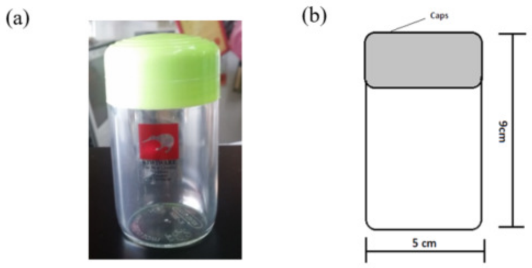

Fig. 1. Figures showing (a) Photograph of pepper bottle container and (b) dimensions of the bottle used as the bomb container

Each bomb container was placed on a sheet of aluminium foil surrounded by sandbags. For every explosion, fifteen sandbags and two sheets of aluminium foil were needed. An aluminium foil was placed at the bottom and 12 sandbags were placed in a rectangular multilevel layout before another aluminium sheet and three sandbags were placed at the top (Figure 2).

The seat of explosion was set up and relocated each time after detonation and collection of the samples. This was to contain the explosion and to avoid contamination as much as possible. A long cable was used in order to connect with the detonation wire of the explosive. For safety precautions, the seat of explosion was situated 100 m from the sheltered area. The explosive was fired off by RMP officer using electrical discharge from a special electrical device. All bombs prepared were successfully detonated without failure. All post-blast residues including soil and aluminum debris were collected and placed in ziplock-plastic bags, sealed and placed in an ice cooled cooler box.

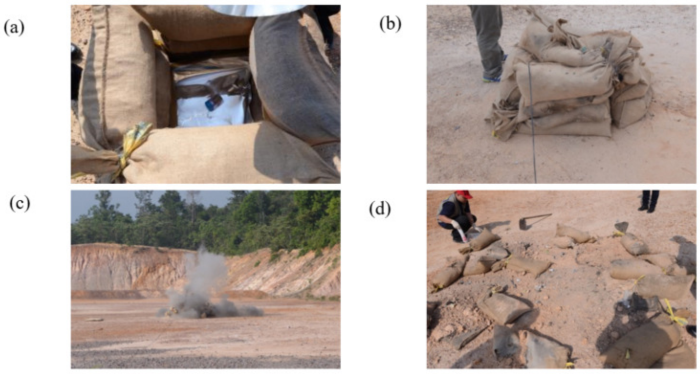

Fig. 2. Photographs showing (a) Arrangement of home-made bomb surrounded by sandbags, (b) Sandbag used to cover the bomb from above, (c) Scene immediately after the explosion, and (d) Debris from the seat of explosion ready for collection

2.4. Sample swabbing and extraction

Cotton balls were subjected to pre-cleaning by soaking the cotton balls overnight in acetone before being left to air-dry [14]. For the swabbing process of the residue, the cotton ball was added with 1 mL acetonitrile by using a micropipette in order to moisten the cotton ball. By using a tweezer, the moistened cotton ball was rubbed thoroughly on the surface of the post-blast sample in order to collect the explosive residue. The swabbed cotton ball was then inserted into the vial and 5-10 mL acetonitrile was added before the vial was submitted for vortex process for 1 minute. The sample extract was subsequently filtered by using a 0.45 µm nylon membrane disc syringe filter. The extract was later dried under a gently stream of nitrogen gas before acetonitrile was finally added to bring the extract volume to 1 mL.

3. Results and discussion

3.1. HPLC-UV analysis

3.1.1 Optimization of UV wavelengths

For UV wavelength optimization, all samples were analyzed individually at detection wavelengths of 220 nm, 240 nm, 254 nm, 270 nm and 290 nm (Figure 6.1). Seven analytes namely HMX, 4-NTB, NG, PETN, 2-NDP, DP and EC showed best detection at 220 nm. At 290 nm, all analytes showed weak absorption of UV wavelength except for 4-NDP. TNT, 2,4-DNT and 2,6-DNT displayed best absorption at 240 nm. NG and PETN could not be detected at any other wavelengths except at 220 nm. Meanwhile RDX showed best UV absorption at 254 nm, which is the common UV absorbing wavelength. Hence, UV absorption of 220 nm was chosen as the overall best UV wavelength of target analytes for further experiments (Figure 3).

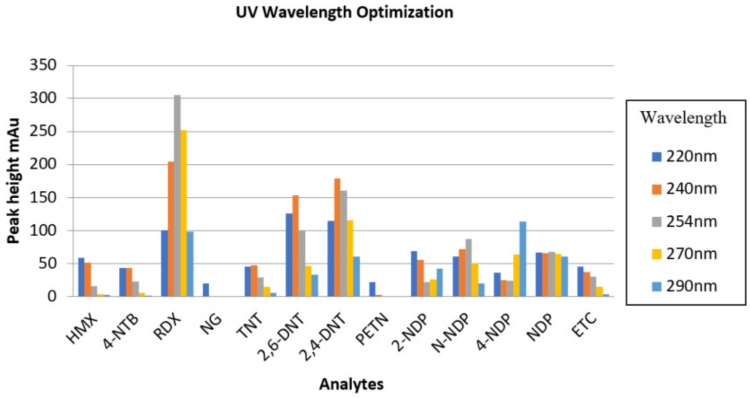

Fig. 3. Graph of UV wavelength comparison of target analytes

3.1.2 Tri-mixture mobile phase system optimization

Dual mobile phase system is a common and conventional practice for reversed-phase HPLC method. However, there are other systems such as multicomponent mobile phase system being used in HPLC separation [15]. This method has been applied to pharmaceutical [16] and food [17] analysis. However, there was only one report on analysis of explosive using a multicomponent mobile phase system by Jenkins et al., [18] who reported the separation of four organic explosives namely HMX, RDX, TNT, and 2,4-DNT.

This study was therefore undertaken to seek the feasibility of using such multicomponent mobile phase systems for separation of standard mixture using different composition ratio of tri-mixture of methanol-acetonitrile-water (Figure 4). Figure 4 (a) shows separation of standard mixture using methanol-acetonitrile-water with composition ratio of 40:20:40. All analytes was successfully separated except for TNT, 2,6-DNT and 2,4-DNT (peaks no 5, 6, and 7). At composition ratio of 30:30:40 (Figure 6.4 (b)), peak no 4-7 (NG, TNT, 2,6-DNT and 2,4-DNT) and peaks no 12-13 (DP and EC), were found to coelute.

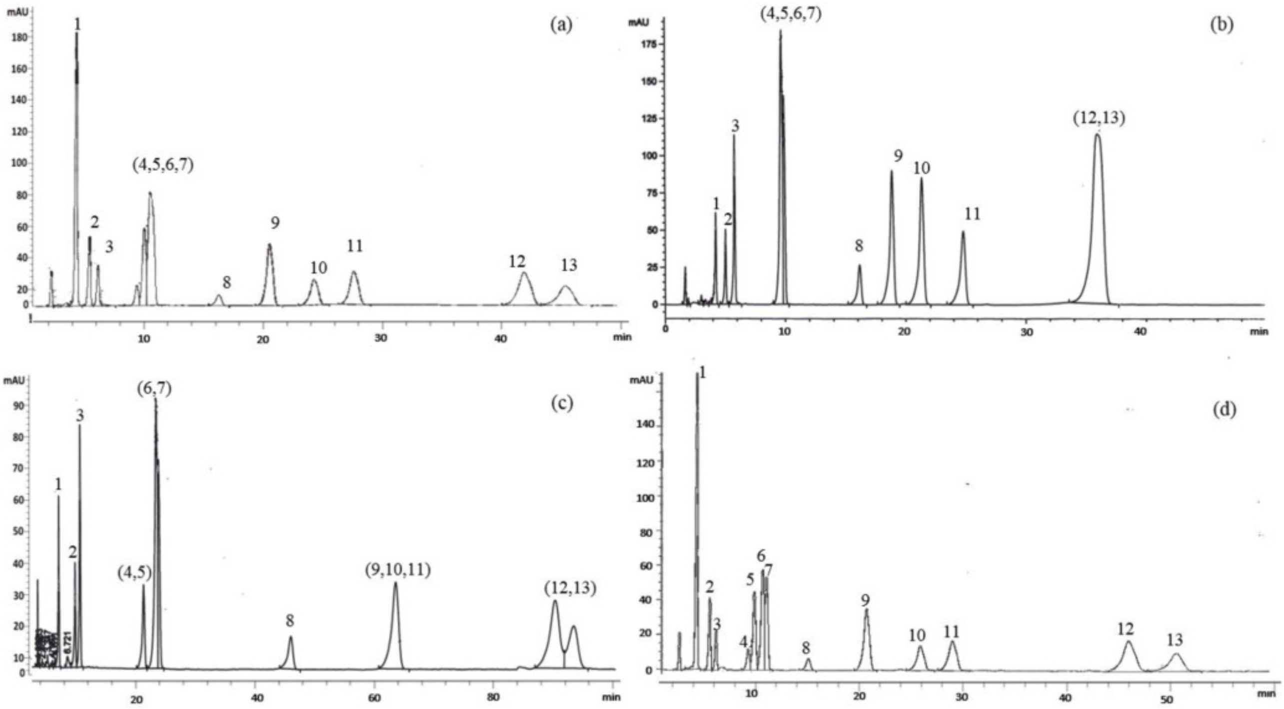

Fig. 4. Separation of explosive standard mixture on Supelco Ascentis C18 (4.6 x 250 mm, 3.5 µm) column, flow rate: 1.0 mL/min; injection volumn: 20 µL, analyte detection at 220 nm, Eluent: methanol-acetonitrile-water; at various mobile phase composition of (a) 40:20:40, (b) 30:30:40, (c) 40:10:50, (d) 50:10:40. Peak identity: (1) HMX, (2) 4-NTB, (3) RDX, (4) nitroglycerin, (5) TNT, (6) 2,6-DNT, (7) 2,4-DNT, (8) PETN, (9) 2-NDP, (10) N-NDP, (11) 4-NDP, (12) DP, and (13) EC

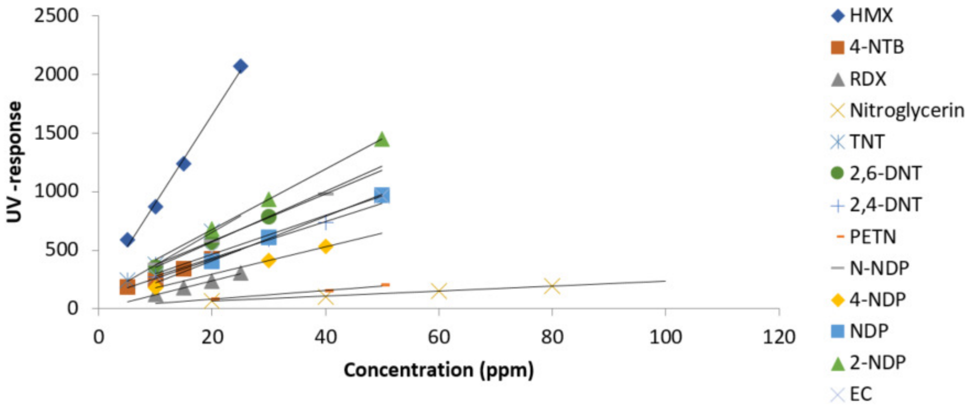

Fig. 5. Calibration graph of thirteen organic explosive analytes

Similar situation also occurred at mobile phase composition ratio of 40:10:50 (Figure 4 (c)). Peaks 4 and 5 (NG and TNT) as well as peaks 6 and 7 (2,4-DNT and 2,6-DNT) were found to coelute. In this mobile phase composition ratio, HPLC profile showed that peaks no 12 and 13 (DP and EC) were separated with inadequate baseline resolution.

Mobile phase composition ratio of 50:10:40 gave an adequate HPLC separation of target analytes as compared to the three eluents system analyzed (Figure 4 (d)). All analytes were successfully separated. However, separation between four analytes (NG, TNT, 2,4-DNT and 2,6-DNT) gave very poor baseline resolution. The separation was difficult especially for 2,4-DNT, 2,6-DNT and TNT because these three analytes have almost similar structure with 2,4-DNT and 2,6-DNT as a pair of isomers. Therefore, tri-mixture mobile phase methanol-acetonitrile-water with composition ratio of 50:10:40 was chosen as the mobile phase system for subsequent HPLC separation.

3.1.3 Calibration graph and detection limits

Calibration graphs were plotted using various concentration ratio of mixed standard solutions. For HMX, 4-NTB, RDX, and TNT the concentration mixture ranged from 5 to 25 mg/L, NG from 20 to 100 mg/L, and all other explosives analytes (2,6-DNT, 2,4-DNT, PETN, N-NDP, 4-NDP, DP, 2-NDP, and EC) ranged from 10 to 50 mg/mL (Figure 5). Linear calibration graphs were obtained with good correlation coefficients (0.986-0.999). Detection limit and correlation coefficients are summarized as in Table 2.

Table 2
Limits of detection and correlation coefficient of target analytes

Analytes	**Limit of Detection (ppm)**	**Equation**	**Correlation coefficient (r^2)**
HMX	0.55	y = 75.081x + 159.91	0.994
4-Nitrobenzonitrite	0.87	y = 16.248x + 95.843	0.986
RDX	0.84	y = 12.143x - 1.0702	0.991
Nitroglycerin	3.56	y = 2.1444x + 22.021	0.999
TNT	0.11	y = 27.827x + 100.22	0.999
2,6-DNT	0.97	y = 21.476x + 140.15	0.999
2,4-DNT	1.98	y = 15.542x + 120.95	0.999
PETN	5.47	y = 3.8197x + 5.9705	0.994
N-Nitrosodiphenylamine	0.29	y = 20.088x + 174.04	0.999
4-Nitrodiphenylamine	0.53	y = 11.641x + 65.235	0.999
Diphenylamine	1.69	y = 18.727x + 37.479	0.999
2-Nitrodiphenylamine	0.30	y = 25.743x + 164.65	0.999
Ethyl centralite	3.84	y = 16.652x + 133.07	0.998

3.1.4 Reproducibility and repeatability

Reproducibility and repeatability play important role in determining the accuracy and precision of data analysis including retention time and peak area under same condition. Relative standard deviation, RSD, was calculated to determine the precision of the method (Table 3). In order to determine the reproducibility and repeatability of the HPLC technique, one standard mixture was injected three times per day and also in three consecutive days.

All analytes showed good reproducibility and repeatability of the retention time for within-day and day-today with low RSD (Within day: 1.455-4.347 %, Day-to-day: 0.670-2.250 %). For the peak area, the RSD of all analytes within-day was in a good range below than 10 % except for 2,4-DNT which is 11.877 %. For RSD of peak area for day-to-day, almost all analytes exceeded more than 10 % but below than 17 % (9.627-16.138).

Table 3
Percentage relative standard deviation of retention time and peak area for each analyte within-day and day-to-day variation

Analytes	**Within-day RSD % (n=3)**		**Day-to-day RSD % (n=3)**	
	Retention Time	Peak Area	Retention Time	Peak Area
HMX	1.455	3.561	0.705	9.627
4-Nitrobenzonitrite	2.111	5.910	0.765	12.916
RDX	2.157	5.418	0.670	12.213
Nitroglycerin	3.722	7.916	0.972	14.021
TNT	2.539	7.340	1.010	12.222
2, 6-DNT	2.544	7.761	0.244	15.815
2, 4-DNT	2.487	11.877	0.983	15.629
PETN	1.854	7.478	1.070	16.138
N-Nitrosodiphenylamine	3.230	3.524	1.259	10.275
4-Nitrodiphenylamine	2.961	9.771	2.250	14.579
Diphenylamine	3.161	6.996	1.632	11.755
2-Nitrodiphenylamine	3.603	8.105	2.085	14.416
Ethyl centralite	4.347	7.774	2.103	12.603

3.1.5 Post-blast sample analysis

The samples were divided into military explosives and low explosives. Four types of military explosives (SO1-S04) and three low explosives (S05-S07) were detonated and analyzed using HPLC-UV. For the military explosives (Figure 6), all samples give different chromatogram profiling. Explosive analytes PETN could be seen on both pre-blast explosive of S01 and S03.

However, only trace amounts of PETN could be detected in post-blast sample of S03. For sample S02, TNT could be detected on both pre-blast and post-blast samples of S02. Excellent profiling also can be observed for RDX in both pre-blast and post-blast samples of S04. For the low explosives samples, only one peak due to non-retain compounds was observed for each sample of S05, S06, and S07 (Figure 7).

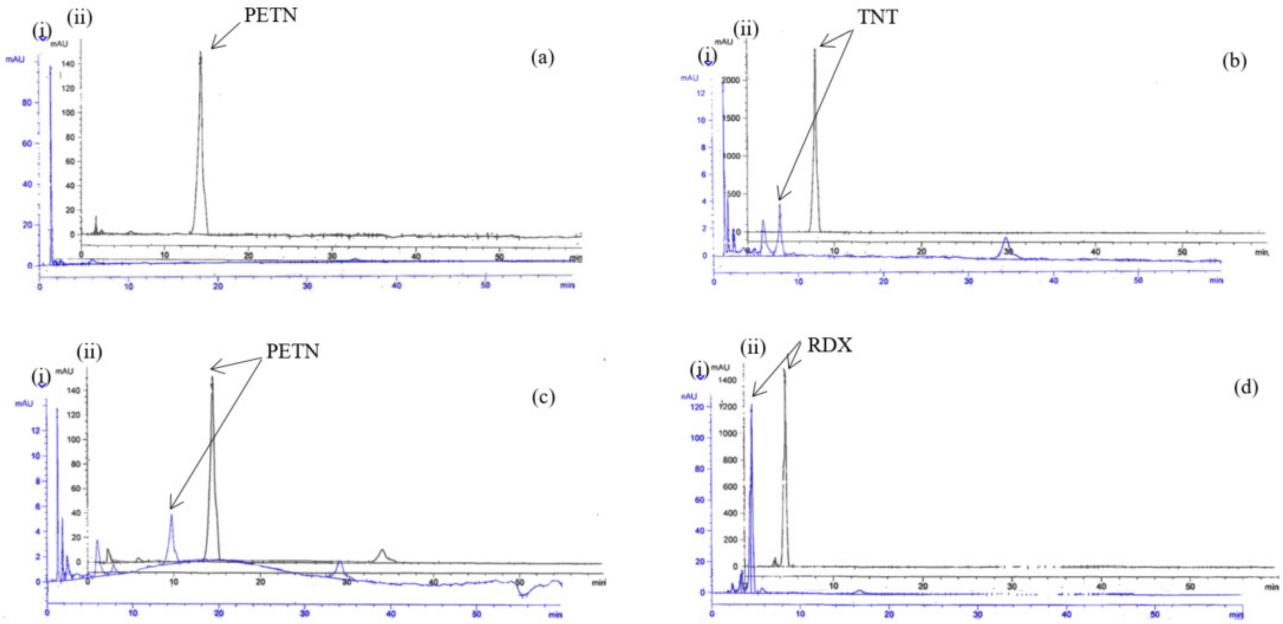

Fig. 6. HPLC chromatograms of (i) post-blast and (ii) pre-blast military explosive samples of (a) S01, (b) S02, (c) S03 and (d) S04

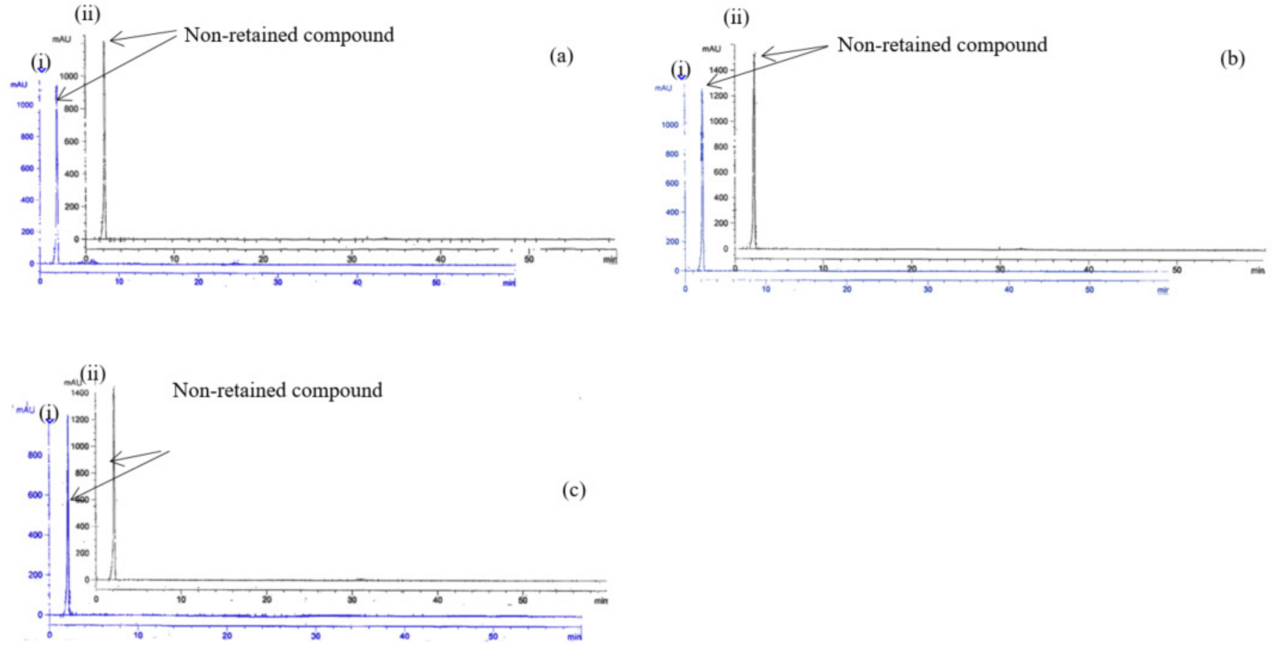

Fig. 7. HPLC chromatograms of (i) post-blast and (ii) pre-blast low explosive samples of (a) S05, (b) S06, and (c) S07

3.2. Ion chromatography analysis

3.2.1 Separation of inorganic anions and cations

For anionic analysis, Metrosep A Supp 4 was employed as the column. Using a mixture of Na_2CO_3 and $NaHCO_3$ as the eluent at a flow rate of 1.0 mL/min, all the target anions were successfully separated within 50 minutes (Figure 8). Most anions were found to elute closely within 16 minutes except for perchlorate that eluted at a much later retention time at around 50 minutes. Peak broadening could be seen on perchlorate because of van Deemter's effect that may arise from eddy diffusion, mass transfer or longitudinal diffusion.

For cationic separation, all target cations were successfully separated within 20 minutes on a Metrosep C4 column. 5-Sulfosalicylic acid dehydrate and 2% acetonitrile was chosen as the eluent. Figure 9 shows the IC chromatogram of standard cation separation. Broader peaks were obtained for calcium and magnesium ions that eluted later in the chromatogram. Peak broadening can be seen on calcium and magnesium due to van Deemter's effect.

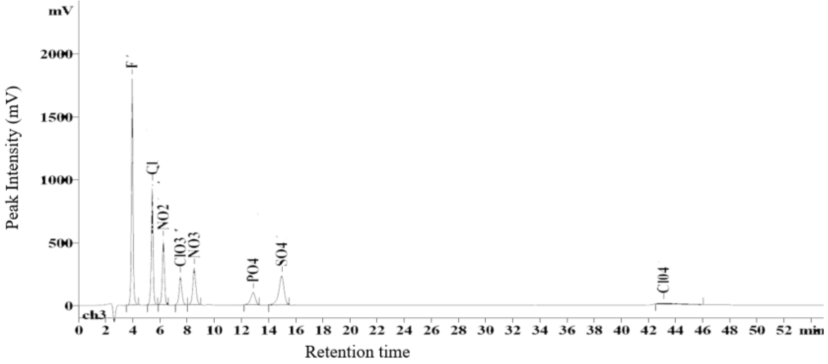

Fig. 8. Separation of standard anions (3 mg/L) on Metrosep A Supp 4 column. Eluent: 1.8 mmol/L Na2CO3 and 1.7 mmol/L NaHCO3; flow rate: 1.0 mL/min; suppressed conductivity detection; injection volume: 20 µL; temperature: 30oC; eluting sequence: 1. F- (3.96 min), 2. Cl- (5.42 min), 3. NO2- (6.25 min), 4. ClO3- (7.50 min), 5. NO3- (8.52 min), 6. PO4- (12.87 min), 7. SO42- (14.97 min), 8. ClO4- (43.13 min)

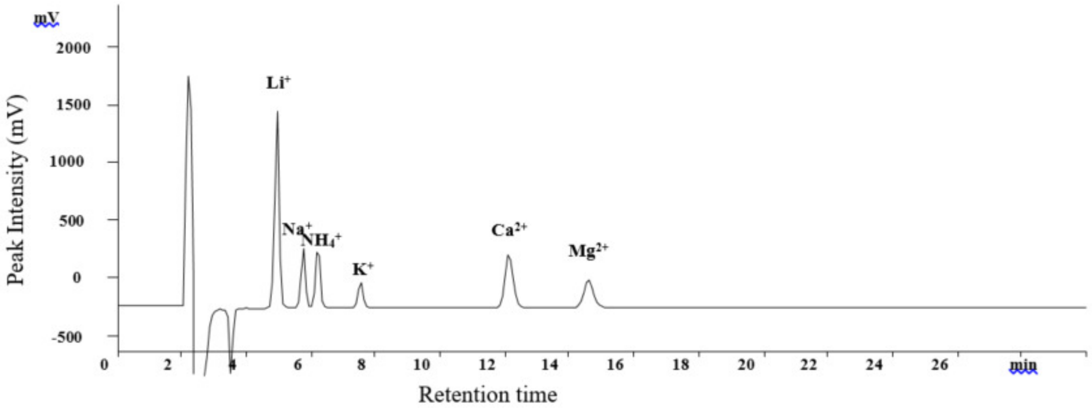

Fig. 9. Separation of standard cations (3 mg/L) on Metrosep C4 column. Eluent: 2.5 mmol/L 5-Sulfosalicylic acid dehydrate and 2% acetonitrile; flow rate: 1.0 mL/min; conductivity detection; injection volume: 20 µL; eluting sequence: 1. Li+ (4.98 min), 2. Na+ (5.78 min), 3. NH4+ (6.23 min), 4. K+ (7.55 min), 5. Ca2+ (12.12 min), and 6. Mg2+ (14.58 min)

3.2.2 Calibration graph and detection limits

Calibration graphs of anions were plotted using various concentrations of mixed standard solution from 1 mg/L to 5 mg/L (Figure 10a). Linear calibration graphs were obtained with good correlation coefficients (0.985-0.999). Meanwhile for cation calibration, a serial mixed standard solution (1 mg/L to 3 mg/L) was injected to obtain chromatograms, which were used to plot calibration graphs (Figure 10b). Good correlation coefficients were also obtained in cationic analysis (0.992-0.999).

Table 4
Detection limit data of each analyte and comparison LOD obtained with other study

Analytes	**Limit of Detection (ppm)**		**Equation**	**Correlation coefficient (r^2)**
	This study	*Meng *et al.*		
Anions				
F^-	0.22	-	y = 2727.9x + 546.99	0.998
Cl^-	0.17	0.12	y = 1420.5x + 415.06	0.995
NO_2^-	0.25	0.30	y = 743.14x + 35.978	0.998
ClO_3^-	0.26	0.30	y = 493.39x + 61.616	0.995
NO_3^-	0.20	0.05	y = 928.52x + 317.71	0.995
PO_4^{2-}	0.07	-	y = 380.27x + 134.98	0.998
SO_4^{2-}	0.08	0.07	y = 999.27x + 426.32	0.997
ClO_4^-	0.20	-	y = 380.27x + 134.98	0.992
Cations				
Li^+	0.13	-	y = 5533.9x - 208.63	0.998
Na^+	0.28	0.03	y = 1534.1x + 28.896	0.995
NH_4^+	0.20	0.15	y = 1692.9x + 133.73	0.995
K^+	0.13	0.30	y = 753.31x + 49.518	0.998
Ca^{2+}	0.19	-	y = 2712.5x - 86.117	0.999
Mg^{2+}	0.08	-	= 1575.6x + 58.39	0.998

*Meng, HB., Wang, TR., Guo, BY., Hashi, Y., Guo, CX., Lin JM. (2008). Simultaneous determination of inorganic anions and cations in explosive residues by ion chromatography. Talanta. 76(2). 241-245.

Detection limit in this study was comparable to previous work by Meng et al. (2008) that used ion chromatography as their instrumental technique [19]. Limit of detection and correlation coefficient (r2) of each analyte in this study are summarized as in Table 4.

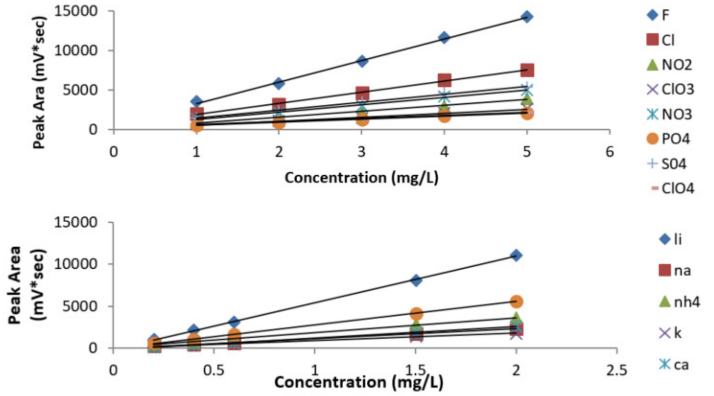

Fig. 10. Calibration graph of (a) nine anions and (b) six cations

3.2.3 Reproducibility and repeatability

In order to determine the reproducibility and repeatability of the IC technique, 3 mg/L of standard anions and 1 mg/L standard cations were injected three times per day and also in three consecutive days. Perchlorate ion shows high RSD because the stability was less compared to the other ions. Table 5 shows the excellent reproducibility of retention time and peak area in IC separation of both anions and cations.

3.2.4 Post-blast sample analysis

Chemical compositions of each types of the sample are different from another. However most of the samples contain nitrate, sulfate, chlorate or perchlorate as their main oxidizers. Some critical changes can be observed between comparison of unexploded explosive and post-blast residues sample. As shown from IC chromatogram profile of the military explosive, only sulphate ion was detected at high intensity for both sample S01 and sample S02 (Figure 11). No significant cations can be shown for cationic profile of IC analysis for military explosives (Figure 12).

However for low explosives, as shown in IC chromatogram in Figure 11, most of the nitrate anion showed drastic reduction in post-blast samples analysis. Saferstein [20] suggested the combustion of black powder will result in a decrease in nitrate and increase in sulfate (Eq. 1).

$$10KNO3 + 3S + 8C \rightarrow 2K2CO3 + 3K2SO4 + 6CO2 + 5N2 \qquad (1)$$

In post-blast residue analysis, significant changes in the chloride ion were observed. Although the increase of ion may come from contamination of surrounding including soil and dust, according to McCord *et al*. [21], the increase of chloride is a result of chemical reduction of other oxidizers including ClO4- and ClO3- (Eq. 2).

$$ClO4- \rightarrow ClO3- \rightarrow Cl- \qquad (2)$$

The presence of calcium and magnesium ions in post blast analysis indicated that the cations were used as additives to intensify the deflagration process (Figure 13 and 14). IC chromatogram of each sample gave unique finger print that could expose the identity of each type of explosive sample.

Table 5
Relative standard deviation of retention time for each analyte within-day and day-to-day variation

Analytes	**Within-day RSD % (n=3)**		**Day-to-day RSD % (n=3)**	
	Retention Time (min)	Peak Area (Abs unit)	Retention Time (min)	Peak Area (Abs unit)
Anions				
F^-	0.001	0.069	0.001	0.047
Cl^-	0.002	0.065	0.012	0.049
NO_2^-	0.002	0.064	0.012	0.005
ClO_3^-	0.002	0.049	0.012	0.147
NO_3^-	0.002	0.066	0.011	0.071
PO_4^{2-}	0.007	0.095	0.039	0.037
SO_4^{2-}	0.008	0.095	0.044	0.063
ClO_4^-	0.003	0.047	0.007	0.159
Cations				
Li^+	0.001	0.001	0.005	0.021
Na^+	0.001	0.001	0.006	0.025
NH_4^+	0.001	0.003	0.006	0.044
K^+	0.001	0.005	0.010	0.029
Ca^{2+}	0.001	0.001	0.010	0.027
Mg^{2+}	0.001	0.003	0.011	0.012

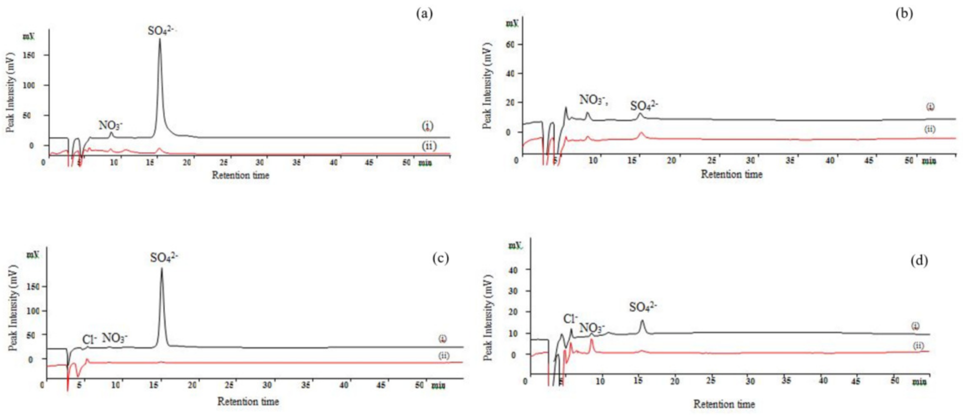

Fig. 11. Anionic IC chromatograms of (i) post-blast and (ii) pre-blast military explosive samples; a. S01, b. S02, c. S03 d. S04

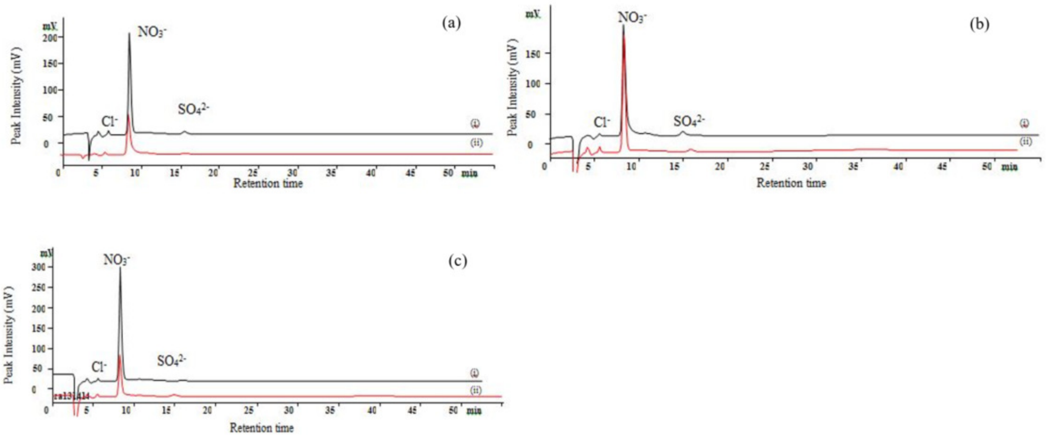

Fig. 12. Anionic IC chromatograms of (i) post-blast and (ii) pre-blast low explosive samples; a. S05, b. S06, c. S07

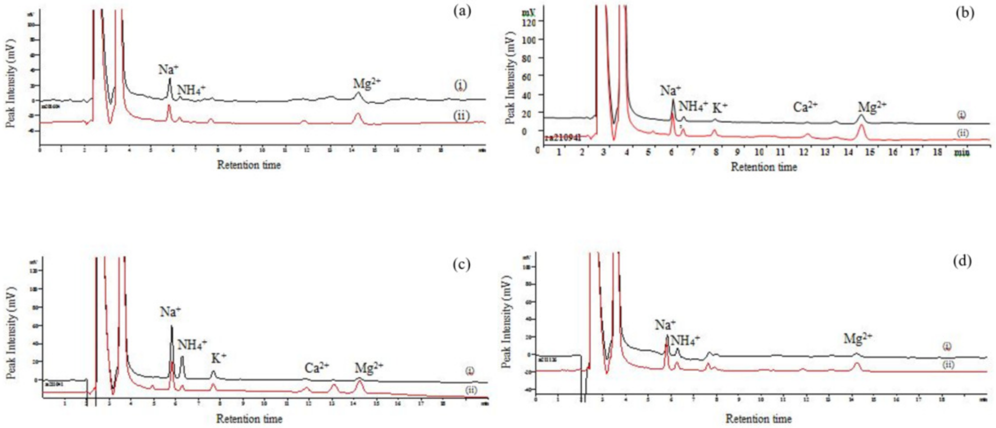

Fig. 13. Cationic IC chromatograms of (i) post-blast and (ii) pre-blast military explosive samples; a. S01, b. S02, c. S03 d. S04

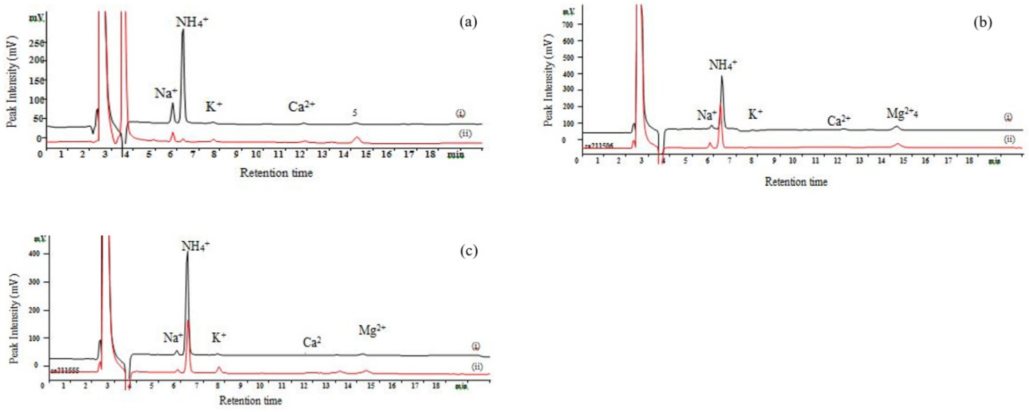

Fig. 14. Anionic IC chromatograms of (i) post-blast and (ii) pre-blast low explosive samples; a. S05, b. S06, c. S07

4. Conclusion

A tri-mixture mobile phase system consisting of methanol:acetonitrile:water (50:10:40) was successfully used for HPLC-UV separation and cotton swabbing technique was employed for sample extraction from post-blast explosive residues. Thirteen selected organic explosive compounds namely HMX, 4-nitrobenzonitrite, RDX, nitroglycerin, TNT, 2,6-DNT, 2,4-DNT, PETN, n-nitrosodiphenylamine, 4-nitrodiphenylamine, diphenylamine, 2-nitrodiphenylamine and ethyl centralite were successfully separated by using reversed phase HPLC-UV within 60 minutes.

Composition profiles of low explosive compounds were successfully determined by using ion chromatography. All target anions (F^-, Cl^-, NO_2^-, ClO_3^-, SO_4^{2-}, PO_4^{3-}, ClO_4^-) were successfully separated within 60 minutes using Metrosep A Supp 4 column with of 1.7 mmol/L of $NaHCO_3$ and 1.8 mmol/L of Na_2CO_3 as the eluent. For cation analysis, all cations (Li^+, Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}) was successfully separated within 20 minutes by using Metrosep C4 as column and mixtures of 2.5 mmol/L 5-sulfosalicylic acid dehydrate and 2% acetonitrile as eluent. Each type of explosives gave different composition profile of analytes. Contamination from surrounding area should be taken into account as significant amounts of analytes present such as chloride ion and existence of certain ions as possible contaminants were detected in post-blast samples.

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