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ANALYSIS OF ANIONIC POST-BLAST RESIDUES OF LOW EXPLOSIVES FROM SOIL SAMPLES OF FORENSIC INTEREST

(Analisis Residu Pasca Letupan Anion Bagi Bahan Letupan Rendah Daripada Sampel Forensik Tanah)

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Abstract

The growing threats and terrorist activities in recent years have urged the need for rapid and accurate forensic investigation on post-blast samples. The analysis of explosives and their degradation products in soils are important to enable forensic scientist to identify the explosives used in the bombing and establish possible links to their likely origin. Anions of interest for post-blast identification of low explosives were detected and identified using ion chromatography (IC). IC separations of five anions (Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, SCN^-) employed a Metrosep Anion Dual 2 column with carbonate eluent. The anions were separated within 17 minutes. Sampling of post blast residues was carried out in Rompin, Pahang. The post-blast explosive residues were extracted from soil samples collected at the seat of three simulated explosion points. The homemade explosives comprised of black powder of various amounts (100 g, 150 g and 200 g) packed in small plastic sauce bottles. In black powder standard, three anions (Cl^-, NO_3^-, SO_4^{2-}) were identified. However, low amounts of nitrite (NO_2^-) were found present in post-blast soil samples. The amounts of anions were generally found to be decreased with decreasing amount of black powder explosive used. The anions analysis was indicative that nitrates were being used as one of the black powder explosive ingredients.

Keywords: Anions, homemade low explosives, ion chromatography, black powder, post-blast soil samples

Abstrak

Ancaman dan aktiviti pengganas yang berleluasa sejak beberapa tahun kebelakangan ini telah membangkitkan keperluan untuk siasatan forensik yang segera dan tepat terhadap sampel sisa letupan. Analisis terhadap bahan letupan dan produk degradasi dalam tanah adalah penting untuk saintis forensik mengenalpasti bahan letupan yang telah digunakan dalam aktiviti letupan dan seterusnya mengaitkan hubungan yang mungkin terhadap sumber asalnya. Anion yang penting dalam pengenalpastian bahan letupan telah dikesan melalui ion kromatografi (IC). Pemisahan IC bagi lima jenis anion (Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, SCN^-) melibatkan penggunaan turus Metrosep Anion Dual 2 dengan eluen karbonat. Anion ini telah dipisahkan dalam masa 16 minit. Persampelan sisa bahan letupan telah dijalankan di Rompin, Pahang. Sisa bahan letupan ini telah diekstrak dari sampel tanah yang dikumpul daripada tempat letupan simulasi. Bahan letupan buatan sendiri terdiri daripada pelbagai amaun (100 g, 150 g dan 200 g) serbuk hitam yang dimampat dalam botol plastik sos yang kecil. Dalam serbuk hitam piawai, tiga anion (Cl^-, NO_3^-, SO_4^{2}) telah dikenalpasti. Namun, nitrit (NO_2^-) telah ditemui dalam sampel tanah pasca letupan. Kandungan ion didapati menurun dengan pengurangan amaun serbuk hitam yang diguna. Analisis anion ini menunjukkan bahawa nitrat telah digunakan sebagai salah satu ramuan dalam bahan letupan serbuk hitam.

Kata kunci: Anion, bahan letupan buatan sendiri, kromatografi ion, serbuk hitam, sampel tanah pasca letupan

Introduction

In the last decade, terrorism has emerged as an international disaster threat that can be widespread to any particular region within the world. The bombings that occurred in Bali on the 12 October 2002 have brought a great impact to the world especially towards the nation of Australia where two bombs exploded almost simultaneously in a night club district on the tourist island Kuta, killing 202 people, most of whom were Australians [1]. On 9 September 2004, another massive bomb took place in front of the Australian Embassy in Jakarta, Indonesia, resulting in ten dead victims and over 180 injured. The explosion was later identified as a car bomb, driven by a suicide bomber [2]. The subsequent bombing occurred on 7 July 2005 where a series of coordinated suicide bombs exploded on London’s public transport system, killing 56 people and 700 were injured [3]. A very recent terrorist attack took place in Jakarta, Indonesia on 17 July 2009 where high explosive bombs exploded in two luxury hotels, resulting in the death of nine people and approximately 40 wounded [4]. In Malaysia, only a few cases relating to homemade explosive bombings have been reported. Two thieves attempted to break open an automated teller machine (ATM) in CIMB bank in Puchong with a homemade explosive device made of fireworks. The ATM machine and part of the ceiling were damaged but they did not get the money [5].

Explosions often present complex and difficult circumstances to investigate. Normally, these incidents are committed at the convenience of a perpetrator who has thoroughly planned the criminal act and has left the crime scene long before any official investigation is launched. Furthermore, proving commission of the offense is more difficult because of the extensive destruction that frequently dominates the crime scene. The contribution of a forensic scientist is only one aspect of a comprehensive and difficult investigative process that must establish a motive, the modus operandi, and a suspect [6].

In general, explosives are classified as high and low explosives, according to the type and velocity of the reaction involved. High explosives as detonating charges, are subdivided into two groups, primary and secondary explosives, according to their function in the explosion. The primary explosives, which include lead azide and lead styphnate, are used to start the explosion as in the blasting cap [7]. Secondary explosives, which include nitroaromatics and nitramines are common at military sites than primary explosives. If the explosive decomposition reaction moves through the charge faster than the speed of sound in the unreacted medium, it is termed as detonation. However, if it moves slower, it is termed as deflagration [8]. All high explosives and blasting agents detonate when properly initiated, whereas low explosives or black powder deflagrate. Low explosives are normally known as propellants as they undergo deflagration slowly at rate of 1000 feet per second [6]. Gun powder or black powder and smokeless powder are some of the typical low explosives known. There are many compositions of black powder with the common form containing a mechanical mixture of potassium or sodium nitrate with sulphur and finely ground charcoal [9].

Ion chromatographic (IC) analysis is an important tool for forensic explosives investigation. A large proportion of improvised explosive devices used in bombing incidents in the United States used low explosives such as black powder or homemade mixtures. These types of bombs leave significant amount of inorganic residues upon deflagration [10].

The growing threat, unlawful intention and sophisticated criminal or terrorism activities committed using energetic materials in recent years have generated the need for fast and accurate investigation techniques for evaluating vital clues left at the crime scene. The post-blast analysis of trace amounts of explosives is particularly difficult because traces are usually trapped in or deposited on various debris materials. Identifying unknown explosives requires the ability to quantitatively determine a large number of inorganic and organic materials. Thus, analysis of explosives and their post-blast residues in soil is of great important to enable the forensic scientist to identify the explosives that were used in the bombing and eventually help to find links to their likely origin. Knowing the explosive compounds and materials subsequently leads to tracing and identifying the perpetrators involved in the bombing activities. Limited studies have reported on the analysis of post-blast residues using several analytical techniques [10-16].The objective of the study was to analyze selected anions of interest in post-blast residues using IC.

Experimental

Apparatus and Chemicals

Standard solutions of inorganic anions Cl^-, NO_2^- and SO_4^{2-} were purchased as 1000 ppm stock solutions (Merck, Darmstadt, Germany) and were diluted as required using deionized water. The remaining inorganic anion standard solutions (NO_3^- and SCN^-) were prepared from potassium nitrate and potassium thiocyanate (Fisher Scientific, Malaysia). For the bicarbonate eluent used for anionic analysis, the chemicals were solid analytical grade sodium bicarbonate and sodium hydrogen carbonate (Merck, Darmstadt). Water treated with Barnstead Nanopure ultrapure water purification system was used to prepare standard solutions and eluent.

Sampling

The sampling exercise was conducted at the sea shore of Pantai Wecando, Kampung Jawa, Rompin in collaboration with Post Blast Investigation (PBI) team of Forensic Laboratory from Royal Malaysia Police. To imitate real post-blast conditions, three black powder explosives of different amount (100 g, 150 g and 200 g) placed in separate document bags were deflagrated under controlled conditions. The explosives were loaded in three separate ketchup sauce plastic containers of the same size and thickness. Each plastic container was then inserted into a nylon document bag (25.0 × 38.0 × 8.0 cm) filled with polystyrene foam.

Three points on the ground were set as the point of explosion of the homemade bomb. The blast points were labeled as Point A, B and C respectively and the direction was determined using a compass. Each point was subdivided into four grids and labeled as A1 to A4, B1 to B4 and C1 to C4 respectively. The sampling grid was marked with red masking tape at every 5 m with a metal tag positioned on the ground to produce an area size of 25 m^2 in each grid. Figure 1 illustrates the schematic diagram of the sampling grid and the blast points. The distance from Point A to B and C was 11.18 m respectively.

The soil collection method in the study was performed as reported by Radtke *et al*. [17] with slight modification. The soil control samples from each point of explosion were collected before each explosion. At each grid, a stainless steel spade was used to collect 100 g samples from the top 1 inch of soil. Each detonation point was sampled four times, once from each grid. The samples from each point of detonation were placed into three separate snap-seal plastic bags and homogenized by hands.

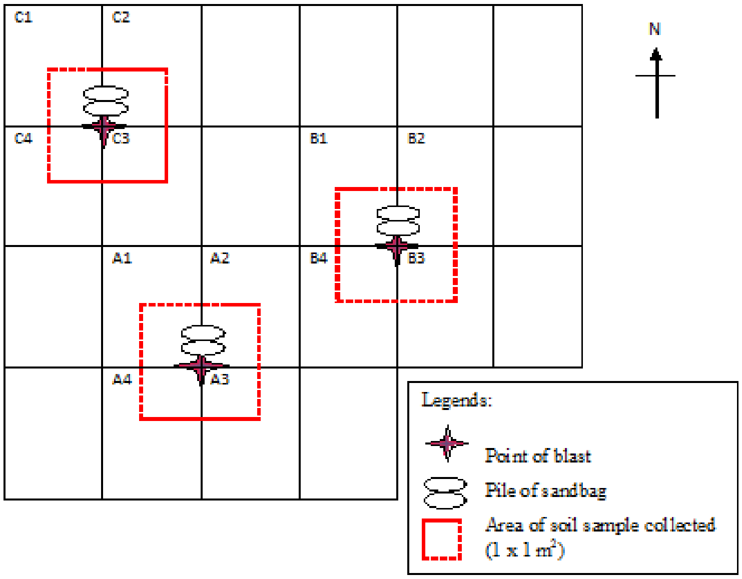


Figure 1**:** Schematic diagram of the sampling grid and the points of blast.

The homemade bombs and explosion exercise were prepared and conducted by PBI team. After each blast, all the fragments found were first tagged with red flags. The document bag and plastic container fragments as well as the cotton and polystyrene foams were then photographed and collected. Four moderately contaminated areas within each point of detonation were selected based on visible soil discoloration. The soil samples were collected within an area size of 1 m^2 and to the depth of 1 to 2 inches using stainless steel spade and stored into snap-seal plastic bags and labeled accordingly. The pH of the soil samples collected was measured on-site using universal pH indicator strips (Merck, Darmstadt). The samples collected were taken to the laboratory for chemical analysis.

Soil Extraction

The soil sample extraction was performed using Johns *et al.* [11] method. All soils were air dried at room temperature prior for extraction. The samples were not exposed to direct sunlight. A 0.8 g sample of soil was added to 8 mL of deionized water in a 15 mL Falcon tube. The mixture was gently shaken, sonicated for 40 mins and centrifuged at 3500 rpm for 5 mins. The supernatant produced was passed through a cleaned 0.45 µm disc syringe filter. The extraction procedures were repeated three times for each sample of soil to produce three batches of soil extracts. The extracted solutions were diluted 500X using deionized water. The control soil samples from Point A, B and C were labeled as A-CS, B-CS and C-CS respectively. The soil samples containing post-blast residues from Point A, B and C were labeled as A-PBS, B-PBS and C-PBS respectively. The extracted samples were kept under refrigeration at 4°C.

Analysis of Black Powder Standard

The black powder control sample used in the study was provided by PBI team. The unexploded control sample was observed and examined microscopically under low magnification and then weighed. The sample was ground into fine powdered form using mortar and pestle. A 0.1 g of black powder was added to 10 mL of deionized water. The mixture was vortexed, filtered and diluted 600 × using deionized water. The diluted standard solution was kept under refrigeration at 4°C.

Instrumentation

The IC analyses were conducted using a Metrohm Advance IC system (Metrohm Ltd, Herisau, Switzerland) equipped with a modular system comprising of the eluent 11 system, 830 interface, 819 detector, 820 separation center, 818 pump, 833 liquid handling unit. For anionic separation, the column used was Metrosep Anion Dual 2 with dimension of 75 mm × 4.6 mm I.D. and particle size of 6.0 µm. The guard column used was Metrosep C2 Guard for anion exchanger column. The pump was operated at a flow rate of 0.8 mL/min. The eluent used was 1.3 mM Na_2CO_3 and 2.0 mM $NaHCO_3$.

Preparation and Separation of Standard Solutions

A single stock standard solution (100 ppm) containing a mixture of all ions of interest (Cl^-, NO_2^-, NO_3^-, SO_4^{2-} and SCN^-) were prepared by adding 1 mL standard solution of each ion with 45 mL of deionized water. After sonication for 10 mins, 5 mL of the solution was then added to 45 mL deionized water to produce 10 ppm anionic standard solution. A serial dilution (1 - 5 ppm) was prepared from the 10 ppm standard solution. Each solution was sonicated, filtered through 0.45 µm disc syringe filter and degassed. All standard solutions were stored in screwed-top glass bottle and kept under refrigeration at 4°C. The anion mixed standard solutions of 1 – 5 ppm were separated by IC to reveal analyte peak areas that were used to produce an anion calibration graph.

Limits of Detection (LOD)

The LODs of each ion were evaluated by diluting 1 ppm standard solution of anions containing a mixture of all ions with deionized water and separated in IC method under Metrohm Anion Dual 2. The lowest detectable concentration for each ion was noted based on the signal-to-noise ratio of 2:1.

Results and Discussion

IC Separation of Standards

In this study, inorganic homemade explosive device containing black powder was used to conduct a simulated explosion. The ionic species originated from the fuel and oxidizer of the explosive material was deposited at the surface of blast seat as a result of chemical reaction occurred during the explosion. Thus, some of the typical components of black powder explosives and their probable decomposition products or by-products were identified as the ions of interest for the analyses of post-blast residues from soil sample extracts.

A set of target analytes comprising five anions (Cl^-, NO_2^-, NO_3^-, SO_4^{2-} and SCN^-) was selected as the indicator ions for identification of the homemade inorganic explosive. In the IC separation, two different flow rates were tested in this study. By using a flow rate of 1.0 mL/min, only four peaks were obtained where by the NO_2^- and Cl^- were found to coelute. Therefore, acceptable separation was achieved at a flow rate of 0.8 mL/min in which the five ions of interest present in the standard solution were well separated within 16 minutes (Figure 2).

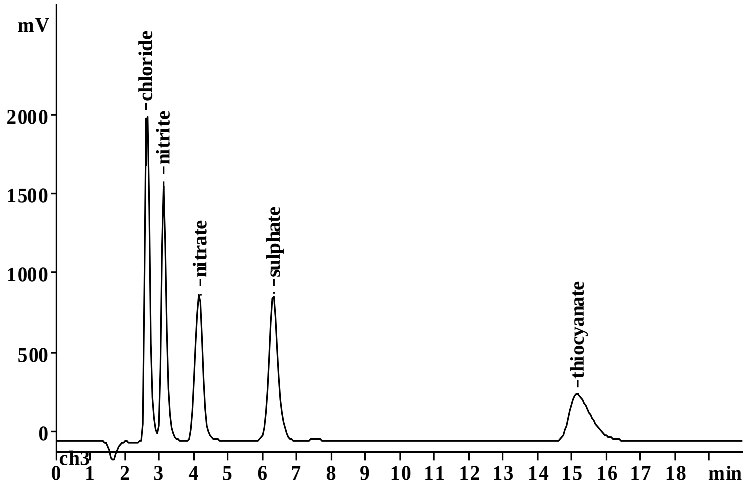


Figure 2: Separation of 5 ppm anion standard solution by IC. Conditions: a Metrohm Anion Dual 2 column (75 mm x 4.6 mm I.D.), flow rate of 0.8 mL/min, an injection volume of 20 µL, column temperature at 28 ºC, bicarbonate eluent, suppressed conductivity detection.

Method Validation and Repeatability

A calibration plot for anions was generated to determine the concentration of the analyte ions in the post-blast soil residues. Five different concentrations (1–5 ppm) of standard solutions were used under the same chromatographic condition. The correlation coefficients (r^2) and detection limits (LOD) are listed in Table 1. From the table, the $r^2 > 0.93$ proved good linearity of the present method. The LOD of each analyte ions were determined and compared against previous studies. The LOD for anionic species ranged from 0.1 – 100 ppb. The results reveal a reduction in LOD for Cl^- and NO_3^- compared to the study done by Johns *et al.* [11]. The differences in LOD obtained from the present study and the earlier study [9] may be due to variation in the IC system as well as the columns used.

Table 1: The detection limits (LODs) and correlation coefficient (r^2) of the anions obtained in the study.

Analyte	Limit of Detection (LOD) (ppb)		Correlation coefficient (r^2)
	This study	Previous study [a]	
Cl-	1.8	2.2	0.9831
NO2-	9.5	4.4	0.9926
NO3-	0.1	5.4	0.9326
SO_4^{2-}	27	3.1	0.9779
SCN-	100	5.5	0.9984

[a] The value was compared against the LOD from Johns *et al.* [9]

[b] NR- Not reported

A good chromatographic analysis of explosive residues should include reproducible retention time, minimal interferences and the ability to separate each ion present in the post-blast residues [12]. To determine the repeatability of the method, three replicate injections were performed using a standard mixture containing the anions of interest. Each sample was injected into the IC system three times consecutively and also at intervals of three days to examine the within-day and day-to-day variations of the retention time during the separation of analyte ions. The retention time, resolution and relative standard deviation (RSD) were summarized in Table 2. The results show that the RSD for retention time for the selected anions evaluated within-day were less than 0.25 % For day-to-day variation, the RSD were less than 2.86 %. Based on the data, the variation of retention time was larger for day-to-day compared to that of within-day. The resolution factor (R_s) of 1.0 or greater represents complete separation. In this study, the R_s of anions separation was evaluated and calculated in which all values are greater than 1.0. Therefore, the inorganic ions were completely separated by IC.

Table 2: The mean retention time, resolution and relative standard deviations of anions obtained using IC system for evaluation of within-day and day-to-day variations.

Analyte	Within-day (n=3)			Day-to-day (n=6)		
	Mean Retention Time (min)	$^*R_s$	RSD (%)	Mean Retention Time (min)	$^*R_s$	RSD (%)
Cl^-	2.6		0.00	2.7		1.49
NO_2^-	3.1	1.17	0.00	3.2	1.21	1.89
NO_3^-	4.1	1.88	0.25	4.2	1.89	0.96
SO_4^{2-}	6.3	2.73	0.00	6.4	2.82	2.86
SCN^-	15.4	7.81	0.13	16.1	7.97	2.85

$^*R_s$ - Resolution

Analysis of Black Powder Standard

The black powder standard was examined microscopically under low magnification. Figure 3a shows appearance of black powder under 20-fold magnification. The sample was observed to consist of a mixture of small crystal-like particles and grayish black irregular shape particles. Such observation was consistent with the raw material of black powder, which contains a mixture of nitrate salt as main compound and carbon source. When examined under 30-fold magnification, it was possible to see traces of fine powder (Figure 3b).

(a) (b)

Figure 3: Appearance of black powder at (a) 20 x magnification and (b) 30 x magnification.

The particles of the black powder standard observed under microscope were measured and tabulated in Table 3. For small crystal-like particles (nitrate salt), the mean grain size measured was 6.3 µm. As for the grayish black irregular shape particles (carbon), the mean grain size was 11.8 µm. The particle size of homemade black powder standard obtained in this study was compared with that of commercial black powder known as sulfurless fine grain gunpowder (SFG). The SFG was graded according to its grain size. For example, SFG 12 contains particles of size 1.40 mm. As the grading numerical increases, the gunpowder becomes finer by having smaller grains. In the work reported by Kosanke *et al.* [18], the carbon presented in commercial black powder was less than 20 µm. Under scanning electron microscope (SEM), the sizes of black powder particles fall in the range of 10 – 15 µm [19]. Thus, the grain size of homemade black powder measured in the present study was similar to that of commercial black powder.

Table 3: Particle sizes of homemade black powder standard.

Type of particle	Largest grain (µm)	Smallest grain (µm)	Ratio (Largest: smallest)
Crystal-like	9.50	3.10	3.06
Grayish-black	18.00	5.60	3.21

A study done by Brown and Rugunanan [20] reported the effect of particle sizes of KNO_3 and charcoal contain in black powder to the burning rates. By varying the sizes of both particles, a maximum burning rate (0.95 ± 0.01 cm/s) was observed at a mean charcoal particle size of approximately 25 µm and the burning rates generally decreased with increasing charcoal particle size. As for KNO_3, a maximum burning rate (0.83 ± 0.01 cm/s) occurred when particle-size ranged from 0 to 53 µm was tested. The results suggested that variation of the particle size of charcoal had a greater effect on the burning rate than that of varying the KNO_3 particle size.

The ground black powder was extracted using deionized water and separated by IC to identify the inorganic ions present in the explosives. Black powder which consists of KNO_3, charcoal and sulfur may produce anions such as NO_2-, NO_3^-, SO_4^{2-}, SCN^- on the aqueous extract [10]. Figure 4 shows the chromatogram of black powder standard where the anions were well separated by IC within 7 mins. NO_3^- constituted the major anion and small amounts of Cl^- and SO_4^{2-} were detected. From the IC separation of black powder, it was conclusive that nitrate salt was used as an important ingredient in the black powder explosive. The detection of Cl^- suggests that chloride salt may have been used as an additive in the explosive material.

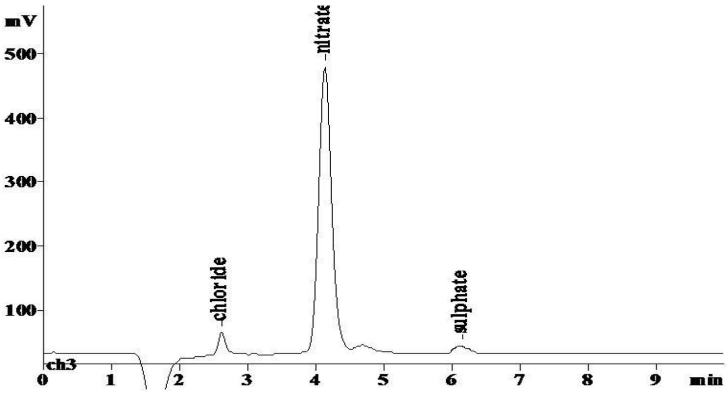


Figure 4: Anions separation of black powder standard. IC conditions as in Figure 2.

The 10 % aqueous extract of black powder (0.1 g/ 10.0 mL) were separated by IC and the concentrations of ions present in the raw material were calculate. Table 4 shows the concentration (µg/g) of ions detected in the black powder standard. The quantitative analysis of black powder standard gives assistance to the further analysis of post-blast residues in determining the nature and possible composition profile of the sample.

Table 4: The amount of ionic analytes detected in black powder standard.

Analyte	Mean concentration (µg/g)±SD	Percentage of ionic analyte composition (%)
Cl^-	6484.8±80.7	4.32
NO_2^-	ND	0
NO_3^-	139732.1±250.2	93.00
SO_4^{2-}	4020.1±59.6	2.68
SCN^-	ND	0

SD – Standard deviation based on triplicate extraction
ND – Not detected

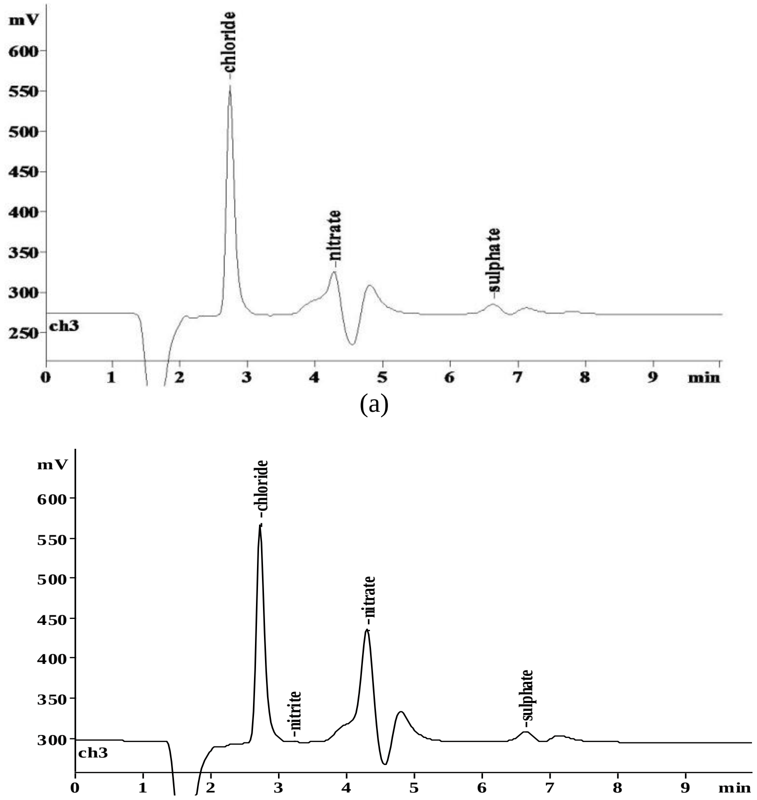
The typical composition of black powder is 75 % KNO_3, 15 % charcoal and 10 % sulfur. However, many variations to that ratio have been identified and reported, in which most of the differences are insignificant [18, 21]. In this study, the homemade black powder contained 93 – 95 % of nitrate salt and only 2.68 % of sulphate as the ionic analyte content. There were small amounts of Cl^- (4.32 %) present in the explosive which suggest the use of chloride salt as an additive. The percentage of analyte comprises the black powder standard varied to that of the typical composition of black powder. This may be due to the dissociation or decomposition of these ions in the aqueous extract which could not be recovered and detected using IC. Apart from that, the differences in percentage of analytes in black powder composition may be due to the homemade recipe in which additives and analyte substitutes were incorporated in the explosive mixture.

Analysis of Post-blast Residues

In this study, soil sample size of 0.8 g which showed the best extraction efficiency was applied to the identification of homemade inorganic explosives in the pre-blast and post-blast residues. The blank sample containing deionized water was separated by IC for each batch of sample. Any ions present in the blank were deducted in further analysis.

Soil Analysis at Explosion Point A

At point A explosion site, 200 g of homemade explosives were compacted in the plastic container placed in the document bag. The soil samples were collected before and after the explosion to determine the amount of explosive residues present in the samples. The 10% aqueous extract (0.8 g/8.0 mL) of blank soil collected before the explosion (A-CS) shows the presence of significant amount of Cl^- as well as NO_3^- and SO_4^{2-} (both in low amounts) as the background ions in the soil matrix (Figure 5a). After the explosion, the soil sample (A-PBS) surrounded within the blast seat at point A was collected and separated by IC. Figure 5b shows the chromatogram of the anions analysis of A-PBS. Cl^-, NO_2^-, NO_3^- and SO_4^{2-} were detected in the post-blast residues.



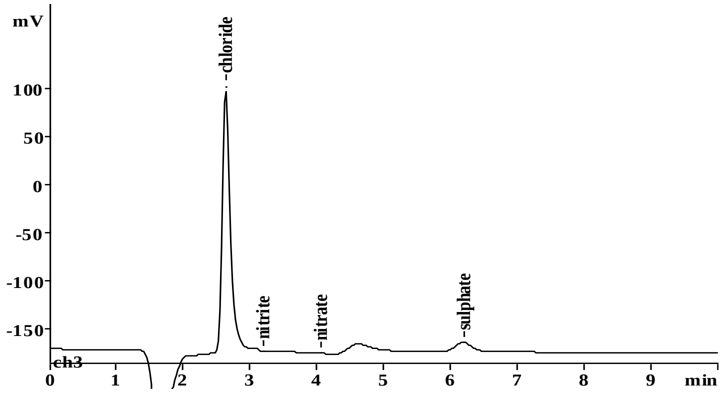
(a)

(b)

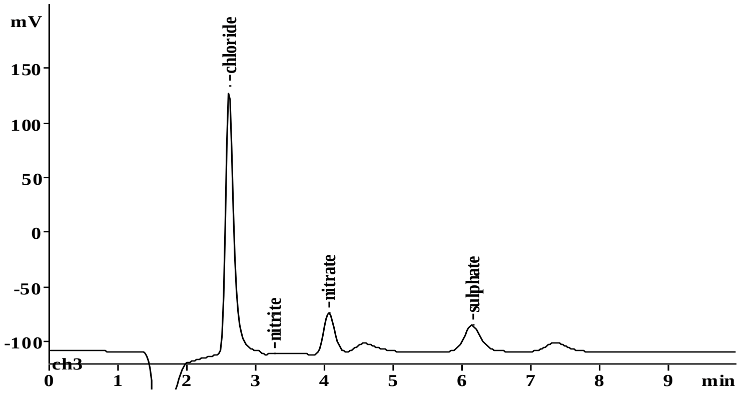
Figure 5: Anions separation of soils collected from blast seat A for (a) pre-blast soil extract and (b) post-blast soil extract. IC conditions as in Figure 2.

Soil Analysis at Explosion Point B

At point B explosion site, 150 g of homemade explosives were employed and deflagrated. As at explosion Point A, soil samples were collected before and after the explosion to determine the amount of explosive residues present in the soil sample. The aqueous extract of blank soil collected before the explosion (B-CS) revealed the presence of Cl^-, NO_2^-, NO_3^- and SO_4^{2-} as the background ions (Figure 6a). The analysis of post-blast soil (B-PBS) is illustrated in Figure 6b. Based on the chromatogram, Cl^-, NO_2^-, NO_3^- and SO_4^{2-} were detected in the post-blast residues.



(a)

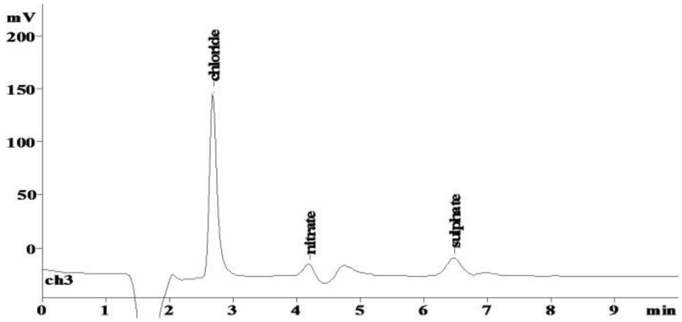


(b)

Figure 6: Anions separation of soils collected from blast seat B for (a) pre-blast soil extract and (b) post-blast soil extract. IC conditions as in Figure 2.

Soil Analysis at Explosion Point C

As explosion point C, 100 g of homemade low explosives was deflagrated. Similar to soil sampling at blast points A and B, the soil samples were collected before and after the explosion to determine the amount of explosive residues present in the soil sample. The background ions present in the pre-blast soil (C-CS) were identified by IC. From the anions chromatogram, Cl^-, NO_3^- and SO_4^{2-} were detected in the blank soil (Figure 7a). Figure 7b shows the anion analysis of post-blast soil (C-PBS) in which significant amount of Cl^-, NO_3^-, as well as low amounts of NO_2^- and SO_4^{2-} were detected in post-blast residues.



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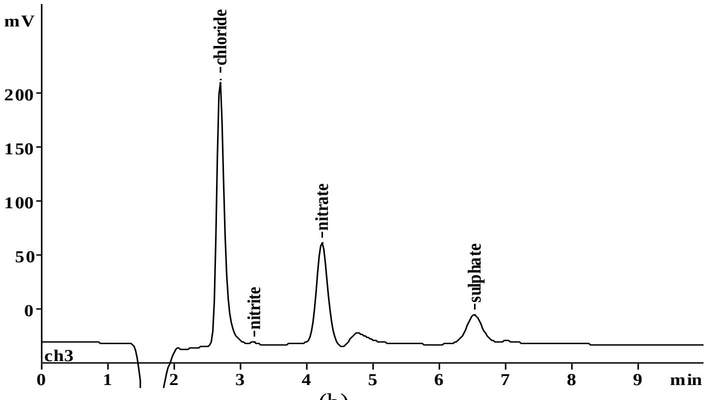

(b)

Figure 7: Anions separation of soils collected from blast seat C for (a) pre-blast soil extract and (b) post-blast soil extract. IC conditions as in Figure 2.

Post-Blast Identification of Homemade Inorganic Explosives

IC has been successfully applied to post-blast residues for identification of explosives-related ions [10-13]. The detection of explosives residue after a bombing may be possible as the explosive material is not completely consumed during an explosion. The relative concentration of the ions in the residues was different from their relative concentration in the unconsumed explosive. This complication has lead to the difficulty in interpretation of IC results for post-explosion samples. The productions of additional ions resulted from chemical reaction occurred during explosion further complicated the possibility in relating the composition profile of the original explosion used. Therefore, it was considered unsafe or inaccurate in the attempt of identifying the type or composition of the original explosive on the basis of IC results for the residues [17]. By considering the weaknesses and difficulties encountered in IC interpretation of explosive materials, a different approach was made in the present study to evaluate the percentage of explosives deposited and left behind at the bombing scene.

Table 5 shows the concentration of analyte ions detected in these samples. The amounts of ions detected in the post-blast residues were compared against the amount of ions present in the unburned black powder. Based on the study, percentage of these ions remained in post-blast soils were calculated. In all three samples, 86 – 99 % of Cl^- was detectable in post-explosion residues. Most of the NO_3^- were decomposed or dispersed away from the crater to the bombing fragments as only 11 – 16 % of the ions remained in the post-blast soils. By comparing the amount of SO_4^{2-} detected in unconsumed black powder, higher amount of the same ion was identified in the sample A. This trend was inconsistent for sample B and C as only 95 – 99 % of SO_4^{2-} was identified in the post-blast soils. The presence of SO_4^{2-} could have originated from sulfur fuel used as one of the ingredients in the homemade explosive.

The large amount of NO_3^- detected in the unconsumed black powder as well as the post-blast residue support the use of nitrate-containing explosive. However, large amount of Cl^- produced in the explosion could not serve as evidence for the original presence of chlorate-based mixture. This was due to the fact that large amount of Cl^- was found to be present in pre-blast soil samples, which may interfere the IC analysis or overload the chromatographic column [9]. In this study, the presence of Cl^- detected in unconsumed black powder may be originated from chloride salt which was used as an additive in the homemade explosive. In addition to Cl^-, NO_3^- and SO_4^{2-} which were originally present in black powder, NO_2^- formed in the combustion was also identified in the present study. The formation of NO_2^- in post-explosion residue was probably due to the reduction of nitrate incorporated in the original explosive (Equation 1). However, its amount varies depending on several factors such as burn rates and the heat of the blast [10].

$$KNO_3 \longrightarrow K^+ + NO_2^- + \tfrac{1}{2}\,O_2 \qquad (1)$$

In the second approach, a study was conducted to evaluate the correlation between the concentration of analyte ions detected and the amount of explosives used. A 3-dimensional (3-D) bar graph was drawn to illustrate the relationship between these variables (Figure 8). From the graph, the mean concentration of each analyte ions detected from the post-blast residues of soil samples show gradual decrease with the reduction in amount of explosives used in the simulated explosion.

Overall, the post-explosion residues showed the presence of chloride, nitrite, nitrate and sulphate in this study. These ions were consistent with the presence of nitrate salt oxidizer, carbon and sulfur fuel in the homemade inorganic explosive used. Besides, the partial identification of these ions can be related to the reactants and products of Equation 2 [10].

$$\begin{gathered}KNO_3 + KClO_4 + S + C + C_6H_5CO_2Na + NH_2C(NH)NHCN \longrightarrow \\ NO_2^- + Cl^- + SO_4^{2-} + HS^- + SCN^- + OCN^- + HCO_3^- + K^+ + Na^+ \end{gathered} \tag{2}$$

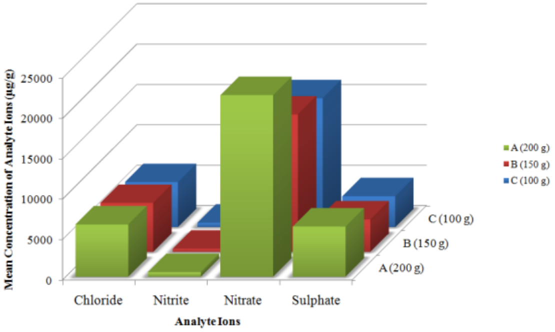

Figure 8: The relationship between the amount of explosives used and the mean concentration of analyte ions detected from post-blast residues of soil samples.

Table 5: Summarized data for the mean concentration of analyte ions calculated in relation to the amount of explosives used for the simulated explosion and percentage of analyte ions remained in post-blast residues.

Analyte	Black powder standard	Post-blast residues **A (200 g)**		
		Amount of analytes	Percentage resided in soil (%)	RSD (%)
Cl^-	6484.8±80.7	6477.6±615.5	99.89	11.68
NO_2^-	ND	576.5±41.5		
NO_3^-	139732.1±250.2	22498.2±1240.8	16.10	7.55
SO_4^{2-}	4020.1±59.6	3814.8±616.5	94.90	11.92

SD – Standard deviation based on triplicate extractions.
ND – Not detected

Analyte	Black powder standard	Post-blast residues **B (150 g)**		
		Amount of analytes	Percentage resided in soil (%)	RSD (%)
Cl^-	6484.8±80.7	6072.1±442.2	93.64	8.54
NO_2^-	ND	404.4±6.4		
NO_3^-	139732.1±250.2	17025.8±1080.0	12.18	8.73
SO_4^{2-}	4020.1±59.6	4017.1±393.8	99.92	11.77

SD – Standard deviation based on triplicate extractions.
ND – Not detected

		Post-blast residues **C (100 g)**		
		Amount of analytes	Percentage resided in soil (%)	RSD (%)
Cl^-	6484.8±80.7	5578.5±356.9	86.02	7.29
NO_2^-	ND	556.4±5.0		
NO_3^-	139732.1±250.2	15964.6±1888.5	11.43	16.46
SO_4^{2-}	4020.1±59.6	3828.2±150.5	95.23	3.46

SD – Standard deviation based on triplicate extractions.
ND – Not detected

Conclusion

IC has been successfully applied in post-blast identification of homemade inorganic explosives. In this study, IC analysis of soil collected at the seat of blast has successfully been carried out and strongly indicated that a low explosive containing KNO_3 has been employed in the explosion. By noting the presence of Cl^-, NO_2^-, NO_3^- and SO_4^{2-}, it can be concluded that the explosive contained nitrate salt, which is a strong evidence for the use of black powder explosive in the improvised explosive device.

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