



A REVIEW OF EXPLOSIVE RESIDUE DETECTION FROM FORENSIC CHEMISTRY PERSPECTIVE

(Satu Ulasan Pengesanan Residu Letupan dari Sudut Pandangan Kimia Forensik)

Mohamad Afiq Mohamed Huri^{1*}, Umi Kalthom Ahmad¹, Roliana Ibrahim², Mustafa Omar³

¹Department of Chemistry, Faculty of Science

²Department of Computing, Faculty of Science Computer and Information System
Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

³Science & Technology Research Institute of Defense (STRIDE),
48100 Batu Arang, Selangor, Malaysia

*Corresponding author: afiqhuri91@gmail.com

Received: 10 August 2016; Accepted: 19 January 2017

Abstract

The growing threat of terrorism activities has caused an urgent need of improved forensic explosive analysis. Complex matrices, limited samples, and ambiguous interpretations serve as challenges for a forensic chemist in order to link the evidence to the perpetrator of the crime. This review focuses on three aspects namely screening techniques, extraction techniques, and instrumental techniques. For the screening techniques, this review focuses on fast detection based on chemical respond for pre- and post-explosion residues. Different types of extraction methods including swabbing technique, solid phase extraction, and solid phase microextraction were discussed. Instrumental techniques covered in this review included gas chromatography, high performance liquid chromatography, ion chromatography and capillary electrophoresis.

Keywords: explosive residue, forensic chemistry, screening techniques, extraction techniques, instrumental techniques

Abstrak

Peningkatan ancaman aktiviti keganasan telah membawa kesedaran akan perlunya penambahbaikan dalam analisis forensik. Pengeboman keganasan telah mengingatkan kepada penyelidik forensik dan penguatkuasa undang-undang akan pentingnya teknik analisis forensik dalam mengatasi aktiviti keganasan. Matriks sampel yang kompleks, terhad dan penafsiran yang tidak jelas menjadi satu cabaran dalam bidang kimia forensik untuk mengaitkan antara bahan bukti dan pelaku jenayah. Ulasan ini akan memberi tumpuan kepada tiga bahagian iaitu teknik saringan, teknik pengekstrakan dan teknik instrumental. Untuk kaedah saringan, kajian ini akan memberi tumpuan kepada pengesanan pantas residu letupan berdasarkan tindak balas kimia untuk sebelum dan selepas letupan. Pelbagai jenis kaedah pengekstrakan dinincangkan termasuk teknik sapuan, pengekstrakan fasa pepejal, dan pengekstrakan fasa pepejal mikro. Teknik peralatan yang akan dibincangkan dalam ulasan ini pula melibatkan kromatografi gas, kromatografi cecair berprestasi tinggi, kromatografi ion dan kapilari elektroforesis.

Kata kunci: residu letupan, kimia forensik, teknik saringan, teknik pengekstrakan, teknik instrumentasi

Introduction

Terrorism is often portrayed as unlawful acts of violence, disregarding the safety of civilians with intent to create fear for their senseless ideology [1]. Terrorism brings harm not only to structural or physical injury, but the victims will sustain the damage from the aspect of psychological, economic and social damage [2]. Based on Global Terrorism Database (GTD) from the year 2000 until 2010, 57% of terrorism method (Figure 1) used by terrorists is

from bombing terrorism [3] The distribution comprises of armed assault (31%), hostage taking (9%) and, unknown (2%), unarmed assault (1%) and hijacking (<1%).

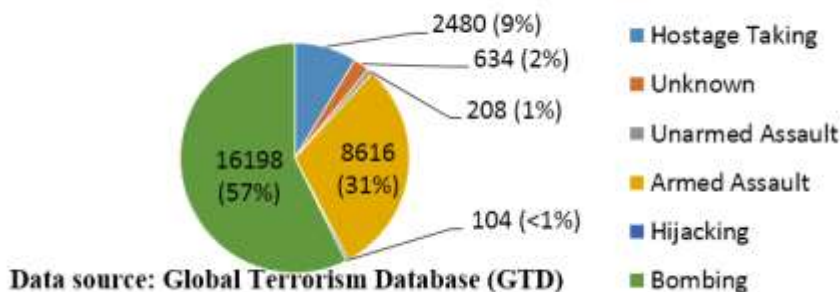


Figure 1. Distribution of terrorism method used by terrorist (2000 – 2010)

Bombing served as the preferred method of terrorism and this callous act of terrorism often happens in public spaces and cost innocent lives to be taken in their target [4-6]. Yavuz et al. [7] in their study on the terrorist bombing in Istanbul reported that 85% of deaths occurred at public spaces such as in the street, school, post-office, hotel lobby, university or campus and many others that involved non-combatant civilians. According to Bosnar et al. [8], suicidal deaths involving explosives have always been connected to terrorism instead of the unusual method of committing suicide.

The expanding threat, unlawful behavior and illicit activities utilizing energetic explosive materials for criminal and terrorism activities have urged the need for a reliable, rapid but also an accurate investigation technique for analyzing crucial puzzles left at the scene of the crime. Analysis of explosive residues become more difficult since the residues of origin material from post-blast samples usually trapped and fused into surrounding. To identify unknown explosive samples, it demands a competency technique to determine an extensive number of organic and inorganic explosive material. It is of great importance for the explosive and their post-blast residues analysis to assist forensic scientist in determining the origin of explosive material used in the bombing and eventually help the law enforcement in narrowing down the investigation. Therefore, the review emphasizes on steps to track traces of evidence, method of extraction and the use of analytical instrumentation for explosive residue analysis.

Sample collection

The forensic scientist needs to analyze and gather information on the physical evidence collected to link the crime scene with the crime perpetrator. The results of laboratory analysis are important to deter terrorist activities and to reduce the occurrences of crime [9-12]. There are many challenges faced by investigating officers and forensic scientist before the results can be taken to court for the prosecution [13].

Numerous studies were reported regarding explosive by performing fields experiments to investigate the properties of explosive, pattern of post-blast sample distribution, or potential source of evidence. Chemical explosive is classified as low or high explosives according to their rates of decomposition [14]. Varga and Ubrich studied the chemical properties of high explosive dynamite via gas chromatography with electron capture detector (GC-ECD) and ion chromatography (IC), by using solid phase extraction (SPE) as the extraction method [15]. Their study revealed that other than dinitrotoluene (DNT) and ethylene glycol dinitrate (EGDN), inorganic components of post-explosion products (Na^+ , NH_4^+ , and NO_3^-) were also found in dynamite post-blast residues.

The knowledge on explosive residue distribution is important for comparison analysis with real samples. Various approaches were made on the study of explosive residues distribution by using trays [16, 17] or witness plates [18-20] placed at different distances from the epicenter of the explosion. The impact from the detonation process resulting in the fragment or residue from the explosive device will be ejected outward from the epicenter of the

explosion. However, almost all studies showed no clear relationship between the amount of explosive detected with the distance from the detonation or amount of explosive used for the detonation process [21, 22]. Many factors contribute to this lack of correlation between the explosive residues distribution with the amount of explosive detected from post-blast explosive residues including efficiency of the detonation, non-homogenous fragment residual dispersal, and influence of wind direction during detonation process.

Determining potential source of evidence is a very crucial step to track traces the explosive residues. Numerous efforts have been made by the researchers to study on variety possible source of evidence so that it can become references for the future cases. These sources can exist in the form of solid [23] or porous material [24]. Since the bombing terrorism cases always involve human either as the perpetrator or as the casualty, human skin and hair having a potential becoming a reliable source for retrieving explosive residues [25-28]. Clothes also have a potential becoming a positive source of evidence since clothes are always intact with the human body [29]. Considering bombing incident also happens in open areas, the possibilities of explosive residues seep into the ground and make the soil become a potential source to track the explosive residues [30, 31]. Since the properties of water as a universal solvent to contain explosive residues, numerous of studies were also done to detect the explosive in water [32-34].

Numerous challenges are often confronted during the process of collecting and analyzing the physical evidence. At the crime scene explosion, the evidence tends to blend into the background thus making the collection process difficult. The fraction, residue or unexploded material that usually blend with surrounding include soil, water, rubble, debris, fabric or any physical material involved in the explosion and the amount of material remains from the devices were usually of limited quantity [33, 35-37]. Shankill Road explosion incident in 1993 is an example when the evidence were mixed with 15 tons of rubble and needed painstaking examination before the remains of the explosive device were discovered among the rubbles [35]. The perpetrator in this incident used short relay electronic explosive device using high explosion as the main component.

Massive explosions usually leave traces when compared to small explosions. Because of that reason, it is not extraordinary if only a small fraction of the samples remains after detonation and combustion processes. For example, the Bali bombing on 12 October 2002 involved three explosions at three different places with different explosion damage [4]. The first explosion took place at Paddy's Bar before the second and the largest explosion exploded a moment later outside the Sari nightclub. Approximately 45 seconds after the blast at Sari nightclub, a third bomb exploded 10 km away near to the United States and Australian Consulates. Compared to the second and largest explosion that used vehicle-borne improvised explosive device (VBIED), the third and the smallest explosion outside the consulate provided more promising physical evidence as compared to the other two explosions.

The blast location or center of the blast must be discovered and approached with extreme steps of precaution. If any portion of the device is visible to the naked eyes during approaching the seat of the explosion most likely to contain, it must be packaged and labeled because it will make an excellent source of recovering. In Boston marathon bombing in 2013, the remaining pieces from a pressure cooker bomb were successfully discovered at the scene of explosion [38]. The explosion killed three peoples and injured more than 200 people.

Post blast samples collected are often placed in a sealed container, with the appropriate size. Soil or soft material in the form of powder can be stored in ziplock plastic. Metal, debris or any sharp object should be wrapped with protective material to prevent the samples from piercing the container. Other good sources of explosive residues are soil or any solid object that could be penetrated such as wood, insulation, plastics and metals [9]. Physical evidence that is attached to the victims or deceases must be taken into account and recovered in steps and precautions. The Bali bombing in 2005, the bearing and electrical connectors were recovered from wounded victims and TNT explosive compound was successfully identified [39].

Screening: On-site detection of explosive devices and residues

Screening test for explosive trace residues in a post-blast forensic investigation is one of the important strategies for the on-site detection of explosives [40, 41]. The sensing methodology of optical and non-optical methods has been

widely applied by law enforcement and transportation security [42-46]. Trained canine team, metal detector, X-ray imaging, ion mobility spectrometry, and portable gas chromatography mass spectrometry (GC-MS) are among the examples of non-optical sensing methods. Spot test kit and thin layer chromatography are examples of preliminary colour tests often employed in laboratory screening of explosive residues.

Trained canine team, is a common and effective method for detection of explosives by training the dog to identify the explosives through vapour sniffing [9]. This approach is still widely practiced in airports or in crime scenes to locate evidence or any prohibited items including drugs and explosives. The abilities between humans and dogs were differentiated by the effectiveness of the olfactory system of the dog that can sniff the vapour much better when compared to human [47, 48]. However, the disadvantages of the canine teams are high maintenance, tendency for environmental distraction, physiological boredom and only the trainer can handle the sniffer dog limit the method for every operation [11].

X-ray imaging are widely used in security post, airports or border control to detect any prohibited items from passing the security line [49-51]. The recent system of the dual-view system is replacing a single view system which allows the image to be viewed at 360° and in pseudo-colors [49]. However, it has some weaknesses because the x-ray cannot penetrate high-density material such as a machine. Various items jumbled in the baggage, including organic materials, bottles, battery, electronic device together with cables and wire, increases the complexity of the image thus causing the possibilities of overlooking the existence of the explosive device.

Numerous reports were made on the development of spectroscopic sensors for detection of explosives [11, 52-55]. The principle of spectroscopy is the interaction between matter and the electromagnetic radiation, whereby samples from the explosive vapour are drawn from the surface or air into the drift region [56]. The ionized samples are then separated through the electric field, according to the mobility of ions or mass to charge ratio before being detected by the spectrometer detector. A few separation techniques combined with mass spectrometry have been developed for real-time detection of explosives (Table 1). Ion mobility spectrometry (IMS) [57] is an example of spectroscopic method that has been used on the field for detection of explosives [58-61]. The method has high selectivity and sensitivities, but until now, numerous efforts were made for miniaturization of the instruments and each instrument itself is very expensive.

Table 1. Example of explosive detection via spectrometry method

Spectrometry Method	Explosive Analytes	Detection Limit	References
AFT-MS	PETN ¹ , tetryl, RDX ² , NG ³	10 ppq	[62]
DBDI-MS	RDX, TNT ⁴ , PETN	0.01-0.1 ng	[59]
ESI-IMS	TNT, 2,4-DNT ⁵ , 2-ADNT ⁶ , 4-NT ⁷ , TNB ⁸ , RDX, HMX ⁹ , EGDN ¹⁰ , NG	0.015-0.190 ppm	[60]
NCD-IMS	RDX, TNT, PETN	0.07-0.3 ng	[61]

¹PETN: pentaerythritol tetranitrate

²RDX: cyclo-1,3,5-trimethylene-2,4,6-trinitramine

³NG: nitroglycerin

⁴TNT: trinitrotoluene

⁵2,4-DNT: 2,4-dinitrotoluene

⁶2-ADNT: 2-amino-4,6-dinitrotoluene

⁷4-NT: 4-nitrotoluene

⁸TNB: trinitrobenzene

⁹HMX: cyclo-tetramethylene-tetranitramine

¹⁰EGDN: dinitro-ethyleneglycol

Most portable kits utilized classical screening tests based on optical and colorimetric analyzes. They are usually high in portability, low in price, and provide rapid and reliable explosives detection. Fisco, in 1975 developed a portable thin layer chromatography (TLC) analysis for the detection of explosives [44]. The kit requires 20-30 minutes for the TLC development prior to visualization using portable UV lamp at 254 nm. Longer analysis time,

the need to prepare various amounts of chemical reagent in the developer chamber, and low portability were major weaknesses of this method. Another approach for detection of explosive is from colorimetric reaction via spot test analysis named as ELIT [40], *Detection Kit Detex* [43], and *FORANEX* [63] spot test kit were among the rapid and reliable colorimetric analytical methods for detection of explosives. However, the techniques needed subsequent instrumental analysis in order to confirm the presence of certain components of the explosive. Recent advanced techniques utilized the capabilities of hexaazamacrocyclic-capped [64]. Mohan and Chand reported on the rapid colour formation from red to blue with a detection limit at femtomolar (10^{-15} mol/dm³) concentration level. Table 2 shows the specific chemical reagents for the detection of certain explosives based on their respective color formation.

Table 2. References reagent for detection of explosive via colorimetric reaction [4, 37, 43, 63, 65]

Reagent	Composition	Explosive Analytes	Color Formation
Griess reagents	alphanaphthylamine and sulfanilic in acetic acid with zinc dust as reducing agent	RDX, PETN, Nitrate ion	Pink color
Nessler reagent	potassium iodide and mercury (II) chloride in deionized water	TNT, Ammonium ion	Red-orange color
Chloride reagent	concentrated silver nitrate in deionized water	Chloride ion	White precipitate
Sulfate reagent	10% barium chloride in deionized water	Sulfate ion	White precipitate
Perchlorate reagent	0.3% methylene blue in deionized water	Perchlorate ion	Purple color
Peroxides reagent	diphenylamine in concentrated sulphuric acid	Peroxides	Dark blue color

Sample extraction

Detection of explosive residues after a bombing incident is possible because not all the explosive materials are consumed during an explosion. Furthermore, characteristic by-products may be formed by the chemical reactions that take place during an explosion. Several methods of extraction techniques were employed to extract the explosive from the matrices, including swabbing technique solid phase extraction (SPE) and solid phase microextraction (SPME) [19, 25, 66]. The method of extraction is crucial to collect the analytes of interest effectively. Furthermore, a variety of the physical evidence will be recovered at the crime scene including soil, water, hair or debris need to be analyzed afterwards [24, 28, 33].

The swabbing technique is commonly used for collecting residues 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 [19, 26, 67, 68]. Song et al. in their study reported that polyester swabs were superior compared to the cotton swabs [68]. Their studies also indicated that dry swabbing was not an efficient technique as compared to wet swabbing. Wipes using alcohol was also found as a compromising solvent for its efficiency to transfer most of the target analyte from the surfaces to the polyester swab. However, the porosity, thickness and the nature of the surfaces may also reduce the effectiveness of swabbing technique [29].

The most challenging extraction process comes from matrices such as sand and soil. These matrices are found with many interferences from the surrounding such as fertilizers or waste product from home cleaning appliances that may be dissipated into the ground. Sample control from surrounding areas around the crime scene with the same physical properties of the soil at the seat of blast must be collected and taken to the laboratory before being analyzed

and compared with the questioned soil to remove the possibilities of background interferences. Most reported studies used EPA Method 8330 or a modified version of the EPA method to extract the target analytes from the soil [69, 70]. Halasz et al. [71] conducted their study on detection of explosives and degradation products in soil environment. Acetonitrile was used as the solvent to extract the analytes of interest. The sample was subjected to a sonication process for 18 hours prior to analysis by using HPLC-UV at 254 nm. Their study also revealed that from the training sites and former explosives manufacturing plants, the explosives compounds can be transferred from ground surfaces to groundwater and plant tissues.

Solid phase extraction (SPE) is a popular method for removing impurities and pre-concentration of target analytes [72]. This method mainly consists of four steps; conditioning, loading, washing and elution process. Warren et al. [73] applied a combined swab and SPE in their sample preparation. The sample was swabbed with a wetted ethanol cotton swab before the extract was passed through a Chromosorb-104 adsorbent column (washed with one-time acetone and three times of ethyl acetate). The loading sample was washed with ethanol/water fraction (50:50) for the collection of inorganic compound and the adsorbent was further washed using methyl tert-butyl ether/pentane before ethyl acetate fraction was used to elute the organic compound. The percentage recoveries of the selected inorganic ions (sodium, ammonium, potassium, magnesium, calcium, fluoride, chloride, nitrite, bromide, chlorate, nitrate, phosphate, sulphate, perchlorate, glucose, fructose and sucrose) were varied from 45.9% to 96.8%. However, it showed low percentage recoveries of selected organic explosive (nitroglycerin (NG), 2,4-dinitrotoluene (2,4 DNT), 2,6-dinitrotoluene (2,6 DNT), 3,4-dinitrotoluene (3,4 DNT), 2,4,6-trinitrotoluene (TNT), PETN and RDX) from 31.4% to 56%. Ahmad et al. [16] applied the SPE method on the post-blast water samples. For the optimization process, five nitro explosive compounds namely as HMX, 2,4 DNT, RDX, TNT and PETN was selected and undergoes pre-concentration process via SPE before being analyzed by using micellar electrokinetic chromatography (MEKC) and GC-ECD. They used LiChrolut EN SPE cartridges as their SPE adsorbent and used 10 mL of methanol followed by 20 mL distilled water for the conditioning process. The samples (200 mL) were allowed to pass through the SPE cartridge at the flow rate of 3 mL/min before the analytes were collected with three portions of 3 mL acetonitrile. From the optimization process, the SPE pre-concentration technique had succeeded to lower the detection limit by more than 1000 times and gave a good percentage recovery (>87%). From the post-blast water sampling, both RDX and PETN were detected in the range of 0.05 – 0.17 ppm and 0.0124 – 0.039 ppm respectively.

Solid phase microextraction (SPME) is an innovative approach of green technology to reduce the amount of solvent use for the extraction process, cutting the cost and chemical exposure to the human body [66]. Several factors affecting extraction process included the type of fiber use, nature of target analytes, the complexity of the matrices, temperature and desorption times. Studies of solid phase microextraction combined with GC-ECD has been made on organic explosive samples [74]. Four types of fiber namely, polydimethylsiloxane (PDMS), polydimethylsiloxane/divinylbenzene (PDMS/DVB), CarboxenTM/ polydimethylsiloxane (CAR/PDMS), and polyacrylate were used to study the relationship between the water solubility and the fibers. PDMS/DVB fiber with 30 minutes stirring showed a better result as compared to other fibers. Another study by Ahmad and Heng [75] demonstrated the effect of salting out procedure with 10% NaCl gave the best extraction of their target analytes of 2,6-dinitrotoluene (2,6-DNT), trinitrotoluene (TNT) and pentaerythritol tetranitrate (PETN).

Instrumental techniques

Instrumentation plays an important role in the detection of target compounds from various matrices. They are often combined with specific detectors for sensitive and selected detection of the explosive target compound (Figure 2).

An extensive review on instrumental techniques for the detection of explosive was reported by Kolla [76]. The review covers the instrumental techniques pertaining to organic and inorganic analytes. However, the review was limited to gas chromatography (GC), high performance liquid chromatography (LC), capillary electrophoresis (CE), and ion chromatography (IC) analysis of explosive residues up to 1994. For chromatographic separation, a survey was done on articles searched using the keywords of *explosive* and selected instruments, GC, HPLC, IC and CE (Figure 3). Analysis of explosive using GC appeared to be the most popular followed by HPLC, IC and CE. The interest of explosive study had significantly increased between 2003 to 2005, but display a decreasing trend from 2005 to 2007 before showing an increasing pattern from 2008 to 2015 (Figure 3). This trend was obtained following

media reports of series bombing terrorism attacks such as Bali Bombing (2002), Delhi Bombing 2008, Mumbai Bombing (2008) Jakarta Bombing (2009), Moscow Bombing (2010), Norways Attack (2011) and Boston Marathon Bombings (2013).

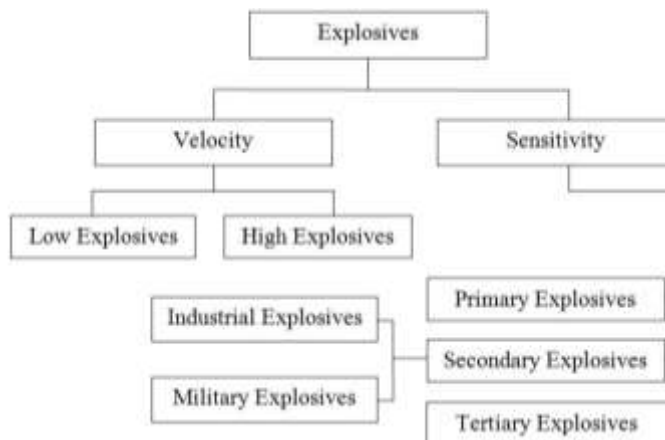


Figure 2. Classification of chemical explosives [14]

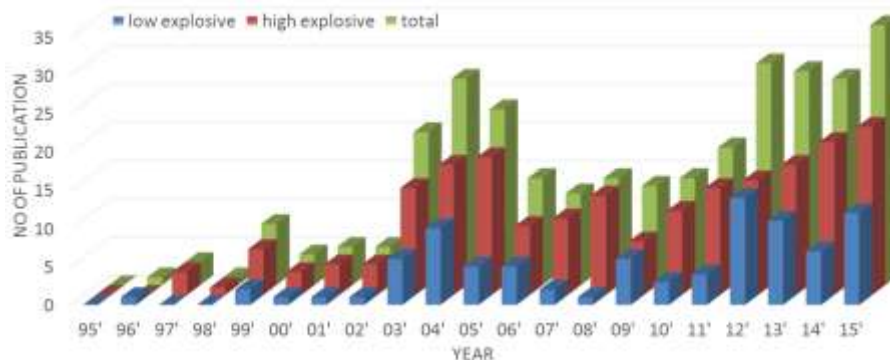


Figure 3. Distribution of journal publications on selected instrumentation based on SCOPUS database from year 2000 – 2015

Gas chromatography

Gas chromatography (GC) is frequently used for the identification of organic explosive compounds since the technique has high selectivity and sensitivity towards organic constituent analysis. However, the GC instruments prohibit non-volatile, mixture water samples and sparked samples to prevent the column from bearing the damage. Because of that, extra precaution on sample preparation is needed for every process. The detectors used combined with GC are electron capture detection (ECD) [30,74,77], thermal energy analyzer (TEA) [78,79], mass spectrometry (MS) [71, 80, 81], and tandem mass spectrometry (MS/MS) [82, 83]. Although ECD is less selective than TEA or MS, it is a sensitive means of detecting nitroaromatic base explosives [55]. ECD devices operate by passing a beam of electrons between two electrodes. When a sample elutes from the GC column, organic nitrate groups and the other electronegative moieties 'capture' these electrons, interrupting the current and thereby producing a signal. Varga and Ulbrich [15] successfully extracted TNT and PETN by using water as the medium of extraction and subsequent separation by using GC-ECD. However, nitrate ester based explosive compound such as ethylene glycol dinitrate (EGDN) and nitroglycerin (NG) were difficult to extract using water due to their hydrolysis

process. Ahmad et al. [27] had succeeded to detect both PETN and RDX from the C4 explosive residues on hair samples by using GC-ECD. Three hair samples were located at 2.5 m, 5.0 m, and 7.5 m from the point of the blast. Their studies concluded that the human head hair has the potential to become a reliable source for explosive residues to be deposited and the concentration of residue deposited on the hair decreased with distance.

Gas chromatography–tandem mass spectrometry (GC/MS/MS) become an alternative over gas chromatography-mass spectrometry (GC/MS). GC/MS/MS becoming an analytical tool of choices as the techniques are more superior on the selectivity and sensitivity besides its powerful capabilities for detecting compounds in complex matrices. Perr et al. [82] have developed a GC/MS/MS method by using positive chemical ionization (GC/PCI/MS/MS) approach to analyze organic high explosives of nitrobenzene, 2-nitrotoluene, 3-nitrotoluene, 4-nitrotoluene, 1,3-dinitrobenzene, 2,6-dinitrotoluene, 2,4-dinitrotoluene, 1,3,5-trinitrobenzene, 2,4,6-trinitrotoluene, RDX, 4-amino-2,6 dinitrotoluene, 2-amino-4,6-dinitrotoluene, tetryl and HMX with high range of LOD (0.0006-0.0414 ng/mL). This method successfully reduced sample preparation steps as the samples can be analyzed without any sample pre-concentration as well as reducing sample loss or sample contamination.

High performance liquid chromatography

High performance liquid chromatography is commonly used to detect the organic explosive compounds that are non-volatile. HPLC is often used as the instrument for analysis of explosives as it is amenable for the analysis compounds that have low volatility, high sensitive to heat and high molecular weight [55]. This will overcome the problem of detection of explosives that are thermally unstable and resulting in decomposition products in the vapors [76]. The common detector for HPLC is ultraviolet detector (HPLC-UV). The wide range of HPLC detection between 190-800 nm provides an excellent range of separation. Miller et al. [24] employed HPLC-UV for the identification of explosives from porous materials. By changing the temperature and methanol-water mobile phase ratio in HPLC system, separation of RDX, TNT and PETN was successfully achieved within 20 minutes. At a temperature of 30°C and methanol-water mixture of 50:50 was found as the optimum condition for the isocratic separation of target analytes. There was another study applying HPLC-UV for the analysis of organic high explosive on the analysis of nitroglycerin (NG) in post-blast samples [84]. By using reversed-phase c18 column employing acetonitrile-water (60:40) mixture and UV wavelength detection at 210 nm the LOD of NG detection obtained at very low concentration (20 ng)

Ultra-high performance liquid chromatography (UHPLC) has recently been a favorite among the researchers because of its effectiveness for compound separation. Makarov et al. used UHPLC equipped with photodiode array detector to study the hydrolysis kinetics of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12 hexaazaisowurtzitane (CL-20), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and hexahydro-1,3,5- trinitro-1,3,5-triazine (RDX) [85]. By using liophilic salts (KPF6) as mobile-phase additives, the study obtained a good range detection limit of CL-20, HMX and RDX at range of 0.04-0.05 mg/L. UHPLC, when combined with mass spectrometry (MS) or tandem mass spectrometry (MS/MS), makes the instrument a powerful tool regarding selectivity and sensitivity. Schramm et al. [86] developed a hyphenated method of ultra-high performance liquid chromatography-atmospheric pressure chemical ionization-tandem mass spectrometry (UHPLC-APCI-MS/MS). Fifteen nitro explosives were successfully detected at very low concentration (0.3-0.5 ppb) and their degradation products in environmental water samples.

Ion chromatography

Ion chromatography (IC) method was used to separate inorganic anions and cations found in post blast residues from homemade inorganic explosives as one of the types that was frequently used in terrorism attacks. Johns et al. [18] conducted an analysis of inorganic explosives on pipe bomb and soil samples via IC using suppressed IC on a Dionex column with potassium hydroxide as eluent for anions. For cations analysis, a Dionex SCS 1 column was employed using oxalic acid/acetonitrile as eluent for detection. Both anions (Cl^- , ClO_4^- , ClO_3^- , NO_3^{2-} and SO_4^{2-}) and cations (NH_4^+ , Na^+ and K^+) were successfully separated and detected.

Simultaneous determination of inorganic ions is very important to meet the need of real field determination. However, in most cases, anions and cations are usually determined separately using different separation systems with different types of columns and conditions. Meng et al. [87] developed a non-suppressed ion chromatographic method by connecting anion and cation exchange columns directly in series for the separation and determination of

five inorganic anions (Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , and ClO_3^-) and three cations (NH_4^+ , K^+ , and Na^+) simultaneously in explosive residues. The method was successfully applied to the analysis of the inorganic explosive residues samples from the explosion site with satisfactory results.

Capillary electrophoresis

In the explosive analysis, capillary electrophoresis (CE) serves as a complimentary technique to ion chromatography (IC) in the analysis of inorganic low explosives residues. CE components require narrow-bore capillary, a controllable high voltage power supply, two electrode, two buffer reservoirs and a detector. In CE, the targeted analytes eluted from one end of the capillary under the influence of electric field and the analytes were separated according to ionic mobility. The requirement of sample site is low and can be applied to both anions and cations. It gave shorter time of analysis but sacrificing the separation of analytes [88].

Hopper et al. [89] conducted simultaneous separation of anions and cations to analyze a variety of low explosives in post-blast residues. Both anions (Cl^- , NO_2^- , NO_3^- , SO_4^{2-} , ClO_4^- , SCN^- , ClO_3^- , and OCN^-) and cations (NH_4^+ , K^+ , Na^+ , Ca^{2+} , and Mg^{2+}) were successfully separated under 7 minutes. The major disadvantages of CE over IC are poor reproducibility and sensitivity. It gave lower sensitivity because of the low amount of analytes that could be injected resulting in tiny peak volumes [90]. Ahmad et al. [91] have developed a CE method by using 25 mM 2,6-pyridinedicarboxylic acid (PDC) as a background electrolyte (BGE) and the addition of 0.5 mM cetyltrimethylammonium hydroxide (CTAH) to reverse the direction of electroosmotic flow (EOF). This method successfully to determine four anions (Cl^- , NO_3^{2-} and SO_4^{2-} , and SCN^-) and three cations (Ca^{2+} , Fe^{2+} , and Fe^{3+}) simultaneously under 7 minutes at pH 4.7. This method was also successfully applied to the analysis of post-blast explosive residues of black powder and ammonium nitrate-fuel oil (ANFO).

Other techniques

There are other instrumental techniques, most of which were upgraded version of the conventional instrumental techniques for the analysis of explosive. Infrared spectroscopy was developed for detection of explosive in 1960. Pristera et al. [92] successfully compiled 68 infrared spectrograms including high explosive compound and other ingredients of explosive by using conventional dispersive IR spectroscopic method. Fourier transform infrared spectroscopy (FTIR) was discovered at the end of 1970. However, the application of FTIR on the explosive analysis began in 1990 with the analysis of HMX explosive compound [93]. Compared to conventional IR, FTIR gave more benefits in terms of speed of analysis and sensitivity. Primera-Pedrozo et al. [92] developed an advanced technique for qualitative and quantitative analysis of explosives on metallic surfaces using fibre optic coupled reflection/absorption infrared spectroscopy (RAIRS). Their study revealed low detection limit of 2,6 DNT (200 ng/cm³), TNT (160 ng/cm³), PETN (200 ng/cm³), HMX (400 ng/cm³), and Tetryl (200 ng/cm³). However, the study was only limited to highly reflective metallic surfaces.

X-ray powder diffraction (XRD) and X-ray fluorescence (XRF) are non-destructive methods for the composition analysis of the crystalline materials. Both of the methods are different but complementary to each other whereby XRD is used to analyze the phases or compounds meanwhile XRF is utilized for the analysis of the elemental composition of the crystalline material [95, 96]. The analysis of explosive using XRD begun in 1947 with 18 organic explosives were chosen to study their X-ray diffraction pattern [97]. O'Flynn et al. [98] developed a pixellated X-ray diffraction (PixD) system by combining both angular and energy dispersive X-ray diffraction into one system. By integrating principal component and discrimination analysis into the PixD system, a model was developed which can be used to identify explosive and inert samples.

There are many difficulties involved in the identification of materials and devices after an explosion. Thus, a wide range of analytical techniques or instrumentations are currently available and applicable for analysis of explosive residues. The choices of method used are dependent upon the type of sample collected and the types of analytes to be examined and studied. Table 3 shows some of the survey of explosive residue analysis with various instrumentation technique and types of explosive samples.

Table 3. Survey of explosive residue analysis

Analytes	Sample	Instrument	References
Urea nitrate (UN)	Post-blast debris	Gas chromatography mass spectrometry (GC/MS)	[99]
NB, 2-NT, 3-NT, 4-NT, 1,3-DNB, 2,6-DNT, 2,4-DNT, 3,4-DNT, 1,3,5-TNB, 2,4,6-TNT, AMDNT, Tetryl, HMX	-	Gas chromatography positive chemical ionization and tandem mass (GC/PCI/MS/MS) spectrometry	[82]
NG, 2,6-DNT, 2,4-DNT, TNT, PETN	Soil	Solvating gas chromatography with thermal energy analyzer (SGC/TEA)	[78]
TNT, DNT	TNT, dynamite	Gas chromatography with electron captured detector (GC/ECD) and Ion chromatography (IC)	[15]
PETN, RDX, TNT	Hair	Gas chromatography with electron captured detector (GC/ECD)	[28]
RDX, PETN	Semtex plastic explosive	Fourier transform-infrared spectroscopy (FTIR)	[14]
C-4, TNT, PETN	Improvised explosive devices (IED)	Fourier transform-infrared spectroscopy (FTIR)	[100]
HMX, RDX, TNT, DNT, PETN	Soil	High performance liquid chromatography (HPLC)	[101]
HMTD, TATP	Peroxide explosive	High Performance liquid chromatography-atmospheric Pressure chemical ionization-tandem mass spectrometry (HPLC-APCI-MS/MS)	[102]
HMX, RDX, TNB, DNB, NB, TNT, Tetryl, 2,4-DNT, 2,6-DNT, 2-NT, 4-NT, 3-NT, NG, PETN	Plastic explosive	Capillary electrophoresis (CE)	[103]
NH ₄ ⁺ , K ⁺ , Na ⁺ , Ca ²⁺ , Mg ²⁺ , HS ⁻ , Cl ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , ClO ₄ ⁻ , SCN ⁻ , ClO ₃ ⁻ , OCN ⁻	Pyrodex® RS, black powder, and smokeless powders.	Capillary electrophoresis (CE)	[89]
Cl ⁻ , NO ₂ ⁻ , HSO ₄ ⁻ , NO ₃ ⁻ , ClO ₃ ⁻ , benzoate, HS ₂ O ₃ ⁻	Black powder	Ion chromatography/mass spectrometry (IC/MS)	[104]

Table 3 (cont'd). Survey of explosive residue analysis

Analytes	Sample	Instrument	References
Cl ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , SCN ⁻	Soil	Ion chromatography (IC)	[69]
RDX	-	X-ray powder diffraction (XRD)	[105]
Lead and mercury	Detonator	X-ray fluorescence (XRF)	[106]
RDX, TNT, 4-AMDNT, TNB, DNB, 2,6-DNT, 2-NT, 4-NT, Tetryl, HMX, NB	Soil	Micellar electrokinetic capillary chromatography (MEKC) and high performance liquid chromatography (HPLC)	[107]
Arsine compound, TNT	gas shells	Micellar electrokinetic capillary chromatography (MEKC) and high performance liquid chromatography (HPLC)	[108]
TNT, RDX, PETN	-	Ion mobility spectrometry (IMS)	[61]
TNT, 2,4-DNT, 2-ADNT, 4-NT, HMX, EGDN, NG	-	explosives using electrospray ionization/ion mobility spectrometry (ESI-IMS)	[60]

Conclusion

The screening process from the usage of trained canine team to portable detection instrument either as sensors or a portable kit as an improvement on classical biological olfactory system shows the capabilities of new technology to be directly applied in fieldwork. Extraction process has evolved from year to year towards a green technology and has demonstrated a significant impact on the total cost, time consumption and decreased amount on chemical usage. Combined with the right instrumentation, research study allowed the constituent or element of interest to be analyzed with high selectivity and sensitivity. Simultaneous detection of anions and cations in inorganic explosive showed promise for the reduction of time and chemical consumption. Developments of SPME techniques has become a trending method when compared to the conventional liquid liquid extraction whereby consuming more chemicals and cause dangerous exposure to researcher's health. The development of database explosive in the future will become a great tool for researcher reference for lab-to-lab comparison.

Much research work can be improved in order to cope with the advancement in terrorism. For the sake of global security, other than enhancement of law enforcement and military strength, attention should be paid to the importance of research and development on the analysis of scientific evidence, particularly on explosive residue analysis.

Acknowledgement

Thanks are due to the Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, Johor, for research facilities as well as to Malaysian Ministry of Higher Education (MOHE) for financial assistance through FRGS grant no R.J130000.7826.4F200 (4F200). Collaboration assistance from Science & Technology Research Institute of Defense (STRIDE) is also greatly acknowledged.

References

1. Leistedt, S. J. (2013). Behavioural aspects of terrorism. *Forensic Science International*. 228(1–3): 21 – 27.
2. Miguel, E. and Roland, G. (2011). The long-run impact of bombing Vietnam. *Journal of Development Economics*, 96(1): 1 – 15.
3. Global Terrorism Database (2015) Available from: <http://www.start.umd.edu/gtd> [Date access 20 June 2015].
4. Royds, D., Lewis, S. W. and Taylor, A. M. (2005). A case study in forensic chemistry: The Bali bombings. *Talanta*, 67(2): 262 – 268.

5. Landman, A., Teich, J. M., Pruitt, P., Moore, S. E., Theriault, J., Dorisca, E., Harris, S., Crim, H., Lurie, N. and Goralnick, E. (2015). The Boston marathon bombings mass casualty incident: One emergency department's information systems challenges and opportunities. *Annals Emergency Medicine*, 66(1): 51 – 59.
6. Hicks, M. H., Dardagan, H., Bagnall, P. M., Spagat, M., and Sloboda, J. A. (2011). Casualties in civilians and coalition soldiers from suicide bombings in Iraq, 2003 – 2010: A descriptive study. *Lancet*, 378(9794): 906 – 914.
7. Yavuz, M. S., Asirdizer, M., Cetin, G., Yavuz, M. F. Cansunar, F. N. and Kolusayin, R. O. (2004). Deaths due to terrorist bombings in Istanbul (Turkey). *Journal Clinical Forensic Medicine*, 11(6): 308 – 315.
8. Bosnar, A., Stemberga, V., Coklo, M., Grgurevic, E., Zamolo, G., Cucic, T. and di Nunno, N. (2006). War and suicidal deaths by explosives in southwestern Croatia. *Archives of Medical Research*, 37(3): 392 – 394.
9. Yinon, J. and Zitrin, S. (1981). The analysis of explosives. 1st ed. England: Pergamon press. pp. 59 –118.
10. Lahoda, K. G., Collin, O. L., Mathis, J. A., LeClair, H. E., Wise, S. H. and McCord, B. R. (2008). A survey of background levels of explosives and related compounds in the environment. *Journal of Forensic Sciences*, 53(4): 802 – 806.
11. Singh, S. (2007). Sensors – An effective approach for the detection of explosives. *Journal of Hazardous Materials*, 144(1–2): 15 – 28.
12. Yinon, J. and Zitrin, S. (1996). Modern methods and applications in analysis of explosives. 1st ed. England: John Wiley & Sons. pp. 2 – 213.
13. Adams, D. E., Mabry, J. P., McCoy, M. R. and Lord, W. D. (2013). Challenges for forensic science: New demands in today's world. *Australian Journal of Forensic Sciences*, 45(4): 347 – 355.
14. Akhavan, J. (1991). Analysis of high-explosive samples by fourier transform raman spectroscopy. *Spectrochimica Acta Part A: Molecular Spectroscopy*. 47(9–10): 1247 – 1250.
15. Varga, R. and Ulbrich, P. (2004). Some experience with trace analysis of post-explosion residues. *Academic and Applied Research in Public Management Science*. 3(4): 633 – 646.
16. Ahmad, U. K., Rajendran, S., Ling L. W. and Hooi, Y. C. Hooi, (2008). Forensic analysis of high explosives residues in post-blast water samples employing solid phase extraction for analyte pre-concentration. *Malaysian Journal of Analytical Sciences*, 12(2): 367 – 374.
17. Taylor, S., Hewitt, A., Lever, J., Hayes, C., Perovich, L., Thorne, P. and Daghlion, C. (2004). TNT particle size distributions from detonated 155-mm howitzer rounds. *Chemosphere*, 55(3): 357 – 367.
18. Johns, C., Shellie, R. A., Potter, O. G., O'Reilly, J. W., Hutchinson, J. P., Guijt, R. M., Breadmore, M. C., Hilder, E. F., Dicinoski, G. W. and Haddad, P. R. (2008). Identification of homemade inorganic explosives by ion chromatographic analysis of post-blast residues. *Journal of Chromatography A*, 1182(2): 205 –214.
19. Thompson, R. Q., Fetterolf, D. D., Miller, M. L. and Mothershead R. F. (1999). Aqueous recovery from cotton swabs of organic explosives residue followed by solid phase extraction. *Journal of Forensic Sciences*, 44(4): 795 – 804.
20. Hutchinson, J. P., Evenhuis, C. J., Johns, C., Kazarian, A. A., Breadmore, M. C., Macka, M., Hilder, E. F. and Haddad, P. R. (2007). Identification of inorganic improvised explosive devices by analysis of postblast residues using portable capillary electrophoresis instrumentation and indirect photometric detection with a light-emitting diode. *Analytical Chemistry*, 79(18): 7005 – 7013.
21. Borusiewicz, R., Zadora, G. and Zieba-Palus, J. (2013). Chemical analysis of post explosion samples obtained as a result of model field experiments. *Talanta*, 116: 630 – 636.
22. Abdul-Karim, N., Blackman, C. S., Gill, P. P., Wingstedt, E. M. M. and Reif, B. A. F. (2014). Post-blast explosive residue-a review of formation and dispersion theories and experimental research. *RSC Advances*, 4(97): 54354 – 54371.
23. Song-im, N., Benson, S. and Lennard, C. (2013). Stability of explosive residues in methanol/water extracts, on alcohol wipes and on a glass surface. *Forensic Science International*. 226(1–3): 244 – 253.
24. Miller, C. J., Elias, G., Schmitt, N. S. and Rae, C. (2010). Identification of explosives from porous materials: Applications using reverse phase high performance liquid chromatography and gas chromatography. *Sensing and Imaging: An International Journal*, 11(2): 61 – 75.
25. Ahmad, U. K., Rajendran, S. and Hassan, S. A. (2008). Forensic analysis of explosive residues from hand swabs. *Malaysian Journal of Analytical Sciences*, 12(1): 213 – 226.
26. Twibell, J. D., Turner, S. L., Smalldon, K. W. and Higgs, D. G. (1984). The persistence of military explosives on hands. *Journal of Forensic Sciences*, 29(1): 284 – 290.

27. Ahmad, U. K., Bakar, N. H. A. and Abdullah, S. A. A. S. (2012). Analysis of C4 explosive residues on post blast hair samples. *Jurnal Teknologi*, 57(1): 163 – 171.
28. Oxley, J. C., Smith, J. L., Bernier, E., Moran, J. S. and Luongo, J. (2009). Hair as forensic evidence of explosive handling. *Propellants, Explosives, Pyrotechnics*, 34(4): 307 – 314.
29. Huri, M. A. M. and Ahmad, U. K. (2014). Forensic analysis of high explosive residues from selected cloth. *Malaysian Journal of Analytical Sciences*, 18(1): 68 – 77.
30. Walsh, M. E. (2001). Determination of nitroaromatic, nitramine, and nitrate ester explosives in soil by gas chromatography and an electron capture detector. *Talanta*, 54(3): 427 – 438.
31. Bausinger, T., Dehner, U. and Preub, J. (2004). Determination of mono-, di- and trinitronaphthalenes in soil samples contaminated by explosives. *Chemosphere*, 57(8): 821 – 829.
32. Babaei, S. and Beiraghi, A. (2010). Micellar extraction and high performance liquid chromatography-ultra violet determination of some explosives in water samples. *Analytica Chimica Acta*, 662(1): 9 – 13.
33. Kamysny, A., Magdassi, S., Avissar, Y. and Almog, J. (2003). Water-soaked evidence: Detectability of explosive traces after immersion in water. *Journal of Forensic Sciences*, 48(2): 312 – 317.
34. Monteil-Rivera, F., Beaulieu, C., Deschamps, S., Paquet, L. and Hawari, J. (2004). Determination of explosives in environmental water samples by solid-phase microextraction-liquid chromatography. *Journal of Chromatography A*, 1048(2): 213 – 221.
35. McCorkell, W. J. and Griffin, R. M. (1998). An overview of the scientific examinations performed after an explosion on the Shankill road. *Science and Justice*, 38(2): 75 – 79.
36. Hawthorne, S. B., Lagadec, A. J. M., Kalderis, D., Lilke, A. V. and Miller, D. J. (2000). Pilot-scale destruction of TNT, RDX, and HMX on contaminated soils using subcritical water. *Environmental Science and Technology*, 34(15): 3224 – 3228.
37. Hoffman, C. M. and Byall, E. B. (1974). Identification of explosive residues in bomb scene investigations. *Journal of Forensic Sciences*, 19(1): 54 – 63.
38. Sara, M. and Ellen. O. L. (2015). Timeline of Boston marathon bombing events. Available from: <http://www.boston.com/news/local/massachusetts/2015/01/05/timeline-boston-marathon-bombing-events/qiYJmANm6DYxqsusVq66yK/story.html>. [Date access 25 November 2015].
39. Oam, D. R. (2013). A ten year retrospective of the bombing campaign in Indonesia by terrorists, 2002–2006. *Australian Journal of Forensic Sciences*, 45(2): 123 – 146.
40. Reynolds, J., Nunes, P., Whipple, R. and Alcaraz, A. (2006). On-site analysis of explosives in various matrices. *NATO Security through Science Series C: Environmental Security*. Springer: pp. 27 – 32.
41. Yinon, J. (2002). Field detection and monitoring of explosives. *TrAC Trends in Analytical Chemistry*, 21(4): 292 – 301.
42. Germain, M. E. and Knapp, M. J. (2009). Optical explosives detection: From color changes to fluorescence turn-on. *Chemical Society Reviews*, 38(9): 2543 – 2555.
43. Stancl, M. and Kyncl, M. (2008). Some detection procedures for liquid explosives, in Detection of liquid explosives and flammable agents in connection with terrorism, H. Schubert and A. Kuznetsov, Editors, Springer Netherlands. pp. 79 – 96.
44. Fisco, W. (1975). A portable explosives identification kit for field use. *Journal of Forensic Science*, 20(1): 141 – 148.
45. Johns, S. H., Wist, A. A., and Najam, A. R. (1979). Spot tests: A color chart reference for forensic chemists. *Journal of Forensic Sciences*, 24(3): 631 – 649.
46. Nambayah, M. and Quickenden, T. I. (2004). A quantitative assessment of chemical techniques for detecting traces of explosives at counter-terrorist portals. *Talanta*, 63(2): 461 – 467.
47. Furton, K. G. and Myers, L. J. (2001). The scientific foundation and efficacy of the use of canines as chemical detectors for explosives. *Talanta*, 54(3): 487 – 500.
48. Quignon, P., Kirkness, E., Cadieu, E., Touleimat, N., Guyon, R., Renier, C., Hitte, C., Andre, C., Fraser, C., and Galibert, F. (2003). Comparison of the canine and human olfactory receptor gene repertoires. *Genome Biology*, 4(12): R80.
49. Wetter, O. E. (2013). Imaging in airport security: Past, present, future, and the link to forensic and clinical radiology. *International Journal of Industrial Ergonomics*, 1(4): 152 – 160.
50. Wells, K. and Bradley, D. A. (2012). A review of X-ray explosives detection techniques for checked baggage. *Applied Radiation and Isotopes*, 70(8): 1729 – 1746.

51. Michel, S., Mendes, M., de Ruiter, J. C., Koomen, G. C. M. and Schwaninger, A. (2014). Increasing X-ray image interpretation competency of cargo security screeners. *International Journal of Industrial Ergonomics*, 44(4): 551 – 560.
52. Moore, D. S. (2007). Recent advances in trace explosives detection instrumentation. *Sensing and Imaging: An International Journal*, 8(1): 9 – 38.
53. Yinon, K. (2007). Counterterrorist detection techniques of explosives. 1st ed. Uk: Elsevier: pp. 1 – 440.
54. Caygill, J. S., Davis, F. and Higson, S. P. J. (2012). Current trends in explosive detection techniques. *Talanta*, 88: 14 – 29.
55. Mäkinen, M., Nousiainen, M. and Sillanpää, M. (2011). Ion spectrometric detection technologies for ultra-traces of explosives: A review. *Mass Spectrometry Reviews*, 30(5): 940 – 973.
56. Ewing, R. G., Waltman, M. J., Atkinson, D. A., Grate, J. W., and Hotchkiss, P. J. (2013). The vapor pressures of explosives. *TrAC Trends in Analytical Chemistry*, 42(1): 35 – 48.
57. Ewing, R. G., Atkinson, D. A., Eiceman, G. A. and Ewing, G. J. (2001). A critical review of ion mobility spectrometry for the detection of explosives and explosive related compounds. *Talanta*, 54(3): 515 – 529.
58. Voyksner, R. D. and Yinon, J. (1986). Trace analysis of explosives by thermospray high-performance liquid chromatography – mass spectrometry. *Journal of Chromatography A*, 354: 393 – 405.
59. Na, N., C. Zhang, M. Zhao, S. Zhang, C. Yang, X. Fang, and X. Zhang, (2007). Direct detection of explosives on solid surfaces by mass spectrometry with an ambient ion source based on dielectric barrier discharge. *Journal of Mass Spectrometry*, 42(8): 1079 – 1085.
60. Reid A. G., Klasmeier, J. and Hill Jr, H. H. (2000). Analysis of explosives using electrospray ionization/ion mobility spectrometry (ESI/IMS). *Talanta*. 50(6): 1291 – 1298.
61. Khayamian, T., Tabrizchi, M. and Jafari, M. T. (2003). Analysis of 2,4,6-trinitrotoluene, pentaerythritol tetranitrate and cyclo-1,3,5-trimethylene-2,4,6-trinitramine using negative corona discharge ion mobility spectrometry. *Talanta*, 59(2): 327 – 333.
62. Ewing, R. G., Clowers, B. H. and Atkinson, D. A. (2013). Direct real-time detection of vapors from explosive compounds. *Analytical Chemistry*, 85(22): 10977 – 10983.
63. Ruslan, N. N. (2009). A spot test kit for the field detection of selected explosives, Universiti Teknologi Malaysia. Thesis Bachelor of Science (Industrial Chemistry).
64. Mohan, M. and Chand, D. K. (2014). Visual colorimetric detection of TNT and 2,4-DNT using as-prepared hexaazamacrocyclic-capped gold nanoparticles. *Analytical Methods*, 6(1): 276 – 281.
65. Feigl, F. and Anger, V. (1972). Spot tests in inorganic analysis: Elsevier Publishing Company.
66. Furtton, K.G., Almirall, J. R., Bi, M., Wang, J. and Wu, L. (2000). Application of solid-phase microextraction to the recovery of explosives and ignitable liquid residues from forensic specimens. *Journal of Chromatography A*, 885(1-2): 419 – 432.
67. DeTata, D. A., Collins, P. A., and McKinley, A. J. (2013). A comparison of common swabbing materials for the recovery of organic and inorganic explosive residues. *Journal of Forensic Sciences*. 58(3): 757 – 763.
68. Song-im, N., Benson, S. and Lennard, C. (2012). Evaluation of different sampling media for their potential use as a combined swab for the collection of both organic and inorganic explosive residues. *Forensic Science International*, 222(1-3): 102 – 110.
69. Ahmad, U. K., Tze, O. S., Ghazali, M. F., Hooi, Y. C., and Abdullah, M. K. (2011). Analysis of anionic post-blast residues of low explosives from soil samples of forensic interest. *Malaysian Journal of Analytical Sciences*. 15(2): 213 – 226.
70. Williford, C.W. and Mark, B. R. (1999). Extraction of tnt from aggregate soil fractions. *Journal of Hazardous Materials*, 66(1-2): 1 – 13.
71. Halasz, A., Groom, C., Zhou, E., Paquet, L., Beaulieu, C., Deschamps, S., Corriveau, A., Thiboutot, S., Ampleman, G., Dubois, C. and Hawari, J. (2002). Detection of explosives and their degradation products in soil environments. *Journal of Chromatography A*, 963(1): 411 – 418.
72. Abd-Talib, N., Mohd-Setapar, S. H. and Khamis, A. K. (2014). The benefits and limitations of methods development in solid phase extraction: Mini review. *Jurnal Teknologi (Sciences and Engineering)*, 69(4): 69 – 72.
73. Warren, D., Hiley, R. W., Phillips, S. A. and Ritchie, K. (1999). Novel technique for the combined recovery, extraction and clean-up of forensic organic and inorganic trace explosives samples. *Science and Justice*. 39(1): 11 – 18.

74. Calderara, S., Gardebas, D. and Martinez, F. (2003). Solid phase micro extraction coupled with on-column GC/ECD for the post-blast analysis of organic explosives. *Forensic Science International*, 137(1): 6 – 12.
75. Ahmad, U. K. and Heng, K. K. (2007). Solid phase microextraction-gas chromatography for the analysis of explosives in post blast water samples. *Jurnal Teknologi*, 46: 59 – 74.
76. Kolla, P. (1994). Gas-chromatography, liquid-chromatography and ion chromatography adapted to the trace analysis of explosives. *Journal of Chromatography A*, 674(1-2): 309 – 318.
77. Pan, X., Zhang, B. and Cobb, G. P. (2005). Extraction and analysis of trace amounts of cyclonite (RDX) and its nitroso-metabolites in animal liver tissue using gas chromatography with electron capture detection (GC-ECD). *Talanta*, 67(4): 816 – 823.
78. Bowerbank, C. R., Smith, P. A., Fetterolf, D. D. and Lee, M. L. (2000). Solvating gas chromatography with chemiluminescence detection of nitroglycerine and other explosives. *Journal of Chromatography A*, 902(2): 413 – 419.
79. Jiménez, A. M. and Navas, M. J. (2004). Chemiluminescence detection systems for the analysis of explosives. *Journal of Hazardous Materials*, 106(1): 1 – 8.
80. Chakraborty, A., Bagchi, S. and Chandra L. S. (2015). Studies of fire debris from bomb blasts using ion chromatography, gas chromatography-mass spectrometry and fluorescence measurements – evidence of ammonium nitrate, wax-based explosives and identification of a biomarker. *Australian Journal of Forensic Sciences*, 47(1): 83 – 94.
81. Fan, W. and Almirall, J. (2014). High-efficiency headspace sampling of volatile organic compounds in explosives using capillary microextraction of volatiles (CMV) coupled to gas chromatography-mass spectrometry (GC-MS) microextraction techniques. *Analytical and Bioanalytical Chemistry*, 406(8): 2189 – 2195.
82. Perr, J. M., Furton, K. G., and Almirall, J. R. (2005). Gas chromatography positive chemical ionization and tandem mass spectrometry for the analysis of organic high explosives. *Talanta*, 67(2): 430 – 436.
83. Kozole, J., Levine, L. A., Tomlinson-Phillips, J. and Stairs, J. R. (2015). Gas phase ion chemistry of an ion mobility spectrometry based explosive trace detector elucidated by tandem mass spectrometry. *Talanta*, 140: 10 – 19.
84. Ahmad, U. K., Harun S. N., and Hooi, Y. C. (2011). Forensic analysis of nitroglycerin in post blast samples. *3rd International Conferences and Workshops on Basic and Applied Sciences*: pp. 1 – 7.
85. Makarov, A., LoBrutto, R., Christodoulatos, C. and Jerkovich, A. (2009). The use of ultra high-performance liquid chromatography for studying hydrolysis kinetics of CL-20 and related energetic compounds. *Journal of Hazardous Materials*, 162(2-3): 1034 – 1040.
86. Schramm, S., Léonço, D., Hubert, C., Tabet, J.-C., and Bridoux, M. (2015). Development and validation of an isotope dilution ultra-high performance liquid chromatography tandem mass spectrometry method for the reliable quantification of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and 14 other explosives and their degradation products in environmental water samples. *Talanta*, 143: 271 – 278.
87. Meng, H. B., Wang, T. R., Guo, B. Y., Hashi, Y., Guo, C. X. and Lin, J. M. (2008). Simultaneous determination of inorganic anions and cations in explosive residues by ion chromatography. *Talanta*, 76(2): 241 – 245.
88. Hargadon, K. A. and McCord, B. R. (1992). Explosive residue analysis by capillary electrophoresis and ion chromatography. *Journal of Chromatography A*, 602(1-2): 241 – 247.
89. Hopper, K. G., LeClair, H. and McCord, B. R. (2005). A novel method for analysis of explosives residue by simultaneous detection of anions and cations via capillary zone electrophoresis. *Talanta*, 67(2): 304 – 312.
90. Cruces-Blanco, C., Gamiz-Gracia, L. and Garcia-Campana, A. M. (2007). Applications of capillary electrophoresis in forensic analytical chemistry. *TrAC Trends in Analytical Chemistry*, 26(3): 215 – 226.
91. Ahmad, U. K., Jamari, N. L. and Nagayah, S. (2012). Simultaneous determination of inorganic ions in post-blast residues using capillary electrophoresis. *Malaysian Journal of Analytical Sciences*, 12(1): 25 – 31.
92. Pristera, F., Halik, M., Castelli, A. and Fredericks, W. (1960). Analysis of explosives using infrared spectroscopy. *Analytical Chemistry*, 32(4): 495 – 508.
93. Achuthan, C. P. and Jose, C. I. (1990). Studies on octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) polymorphism. *Propellants, Explosives, Pyrotechnics*, 15(6): 271 – 275.

94. Primera-Pedrozo, O. M., Soto-Feliciano, Y. M., Pacheco-Londoño, L. C. and Hernández-Rivera, S. P. (2009). Detection of high explosives using reflection absorption infrared spectroscopy with fiber coupled grazing angle probe/FTIR. *Sensing and Imaging: An International Journal*, 10(1-2): 1 – 13.
95. Mantler, M. and Schreiner, M. (2011). X-ray analysis of objects of art and archaeology. *Journal of Radioanalytical and Nuclear Chemistry*, 247(3): 635 – 644.
96. Sánchez Ramos, S., Bosch Reig, F., Gimeno Adelantado, J., Yusá Marco, D. and Doménech Carbó, A. (2014). Application of XRF, XRD, thermal analysis, and voltammetric techniques to the study of ancient ceramics. *Analytical and Bioanalytical Chemistry*, 373(8): 893 – 900.
97. Soldate, A. M. and Noyes, R. M. (1947). X-ray diffraction patterns for the identification of crystalline constituents of explosives. *Industrial and Engineering Chemistry*, 19(7): 442 – 444.
98. O'Flynn, D., Reid, C. B., Christodoulou, C., Wilson, M. D., Veale, M. C., Seller, P., Hills, D. Desai, H., Wong, B. and Speller, R. (2013). Explosive detection using pixellated X-ray diffraction (PixD). *Journal of Instrumentation*, 8(3): 1 – 15.
99. Almog, J., Espino, D., Tamiri, T. and Sonenfeld, D. (2013). Trace analysis of urea nitrate in post-blast debris by GC/MS. *Forensic Science International*, 224(1-3): 80 – 83.
100. Banas, K., Banas, A., Moser, H. O., Bahou, M., Li, W., Yang, P., Cholewa, M. and Lim, S. K. (2010). Multivariate analysis techniques in the forensics investigation of the postblast residues by means of fourier transform-infrared spectroscopy. *Analytical Chemistry*, 82(7): 3038 – 3044.
101. Paull, B., C. Roux, M. Dawson, and P. Doble, (2004). Rapid screening of selected organic explosives by high performance liquid chromatography using reversed-phase monolithic columns. *Journal of Forensic Sciences*, 49(6): 1181 – 1186.
102. Xu, X., Van De Craats, A. M., Kok, E. M. and De Bruyn, P. C. A. M. (2004). Trace analysis of peroxide explosives by high performance liquid chromatography-atmospheric pressure chemical ionization-tandem mass spectrometry (HPLC-APCI-MS/MS) for forensic applications. *Journal of Forensic Sciences*, 49(6): 1230 – 1236.
103. Oehrlé, S. A., (1996). Analysis of nitramine and nitroaromatic explosives by capillary electrophoresis. *Journal of Chromatography A*, 745(1-2): 233 – 237.
104. Lang, G.-H. L. and Boyle, K. M. (2009). The analysis of black powder substitutes containing ascorbic acid by ion chromatography/mass spectrometry. *Journal of Forensic Sciences*, 54(6): 1315 – 1322.
105. Sun, J., Shu, X., Liu, Y., Zhang, H., Liu, X., Jiang, Y., Kang, B., Xue, C. and Song, G. (2011). Investigation on the thermal expansion and theoretical density of 1,3,5-trinitro-1,3,5-triazacyclohexane. *Propellants, Explosives, Pyrotechnics*, 36(4): 341 – 346.
106. Koudryashov, V. I., Serebryakov, A. S. and Smirnov, V. V. (2006). Investigation of possibility to detect the detonators of the explosive devices by means of EC XRF approach, in detection and disposal of improvised explosives, Schubert, H. and Kuznetsov, A. Editors, *Springer Netherlands*: pp. 223 – 226.
107. Kleiböhmer, W., K. Cammann, J. Robert, and Mussenbrock, E. (1993). Determination of explosives residues in soils by micellar electrokinetic capillary chromatography and high-performance liquid chromatography: A comparative study. *Journal of Chromatography A*, 638(2): 349 – 356.
108. Smedts, B. R., Baeyens, W. and De Bisschop, H. C. (2003). Separation of arsines and trinitrotoluene by reversed phase high performance liquid chromatography and micellar electrokinetic capillary chromatography. *Analytica Chimica Acta*, 495(1-2): 239 – 247.