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ANALYSIS OF C4 EXPLOSIVE RESIDUES ON POST BLAST HAIR SAMPLES

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Abstract. The occurrence of crimes involving high explosives in Malaysia in recent years has warrant the need for the analysis of high explosives in post blast samples, particularly residues that could be found on hairs of victims. This study reports on the detection of post blast residues of C4 explosives on human head hairs. Prior to a simulated explosion, a bundle of hair (200 strands) was tightly bound to a metal hook at each point of several pre-determined distances from the bomb seat. Hair samples containing post blast residues were extracted by ultrasonication using acetonitrile. Two analytes of interest, cyclotrimethylenetrinitramine (RDX) and pentaerythritol tetranitrate (PETN) were successfully separated using gas chromatography with electron capture detector (GC-ECD) on an HP5-MS capillary column. It was found that the amount of explosive residues decreased with increasing distance from the point of blast. At the nearest specified distance of 2.5m, the amount of PETN residues deposited on hair was much less compared to that of RDX residues.

Keywords: C4 explosive, post blast residues, hair samples, gas chromatography with electron capture detector

Abstrak. Terjadinya kes-kes jenayah yang melibatkan bahan letupan berkuasa tinggi di Malaysia telah membuka ruang kajian terhadap sampel pasca letupan, terutamanya residu yang boleh dijumpai pada rambut mangsa. Kajian ini melaporkan pengesanan residu letupan bagi bahan letupan C4 pada rambut manusia. Sebelum letupan simulasi, sejumlah rambut (200 helai) telah diikat pada mata kail logam bagi setiap jarak berdasarkan pada kedudukan yang berbeza dari pusat letupan. Bahan letupan C4 yang terdapat pada rambut telah diekstrak secara ultrasonik dengan menggunakan asetonitril. Dua analit kajian, iaitu siklotrimetilenatrinitramina (RDX) dan pentaeritritol tetranitrat (PETN) telah berjaya dipisahkan menggunakan kromatografi gas dengan pengesan tangkapan elektron (GC-ECD) menggunakan turus rerambut HP5-MS. Kajian mendapati bahawa amaun residu bahan letupan berkurangan dengan pertambahan jarak daripada

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pusat letupan. Bagi jarak dekat tertentu iaitu pada 2.5 m, amaun residu PETN yang terdapat pada rambut adalah amat kurang berbanding residu RDX.

Kata kunci: Bahan letupan C4, residu pasca letupan, sampel rambut, kromatografi gas dengan pengesan tangkapan elektron

1.0 INTRODUCTION

The ability of human head hair to provide evidence of chemical exposure has been extensively conducted by scientists. Hair testing has the advantages of being non-invasive, having the ability to provide a historical record of exposure, being resistant to countermeasures and frequently offering a wider window of detection rather than analysis on body fluids [1]. Other than the ability to 'tell-tale' the chemical that it is made up of, the human head hair also provides the adhering surface for residues from its surrounding environment (outside of the human body). Post blast residues of explosives are invisible to the naked eyes, especially when the residues are deposited together within layers of debris. The human head hair which provides the deposition surface for residues may therefore be an essential matrix from which residues could be extracted from. After an explosion, the vicinity around the blast seat is often strewed with post blast fragments containing explosive residues. Other than garments and other fragments found at the explosion vicinity, human head hair could also be a vital piece of evidence collected in crimes scene in order to determine the type and quantity of explosives used in the blast. Human head hairs of victims or spectators are also most likely to be deposited with unreacted or remaining explosive that were used for the explosion.

Human head hairs that are obtained from crime scenes most commonly serve as important evidence. It also has been shown to be one of key physical evidence in a wide variety of crimes. A review of the forensic aspects of hair examination must start with the observation that it is often difficult to individualize a human hair to a single head or body [4]. Besides deoxyribonucleic acid (DNA) analysis from hairs, the identification of the origin of the hair also can also be performed. It is possible to determine whether the hairs belong to human or animal via microscopic examination. The medullary index is required to differentiate between human hair and animal hair. If the medullary index has value less than

1/3 it is categorize as human hair while for animal the index value is 1/2 or greater [7].

The history of explosives and propellants, also known generally as energetic materials, began with a material known as gunpowder or black powder. The physical state of an explosive may be gaseous, liquid or solid. The chemical composition of explosives however, is either organic or inorganic in nature [1]. Generally, organic explosives are classified as high explosives while inorganic explosives as low explosives. C4 is one of the most frequent plastic explosives used by the military. C4 is 1.34 times more powerful than trinitrotolouene (TNT) [5]. The explosive material in C4 is cyclotrimethylenetrinitramine or known as RDX together with pentaerythritol tetranitrate (PETN) which is commonly used as a booster charger in C4.

RDX (Figure 1a) makes up about 91% of the total mass of C4 while plastic binder, plasticizer, chemical binders and PETN (Figure 1b), make up the rest of the explosive.

(a) (b)

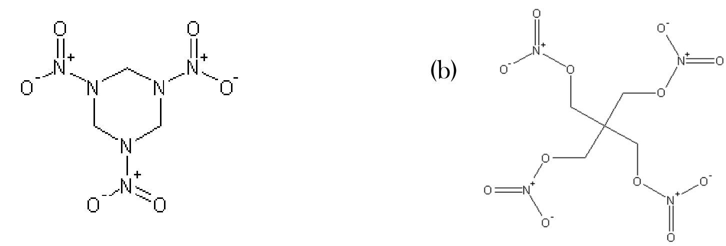

Figure 1 Chemical structure of (a) RDX and (b) PETN

Oxley *et al.* [2] have shown that hair can serve as a good template for binding a variety of explosives. The hair samples were exposed to several explosives namely TNT, PETN, RDX, EGDN, and TATP. The study examined the relationship of the explosive's vapour pressure to the amount of explosives deposited on the hair samples. PETN and RDX, both with extremely low vapor pressure were found to contain the minimum level of residue deposition on hair.

In Malaysia, human head hairs have been encountered as post blast samples in a high profile case. It was therefore of interest to undertake a study for the analysis of high explosive residues such as C4 in human hair.

2.0 EXPERIMENTAL

2.1 Chemicals and Materials

Extraction solvent of acetonitrile was obtained from Merck (Darmstadt, Germany). Explosive standards of RDX and PETN (military grade) were kindly donated by the Royal Malaysia Police. Samples of black, human head hairs were collected from a hair salon in Taman Universiti, Johor.

2.2 Instrumentation

A Perkin Elmer XL Autosystem gas chromatograph with electron capture detector (ECD) was utilized for the detection of RDX and PETN. The capillary column used was a HP5-MS (30 m x 0.25 mm x 0.25 μm). A temperature program was employed using an initial oven temperature of 100°C for 3 min, then ramped to 280°C at 15°C/min and finally held at 280°C for 1 min. Injector temperature was set at 230°C and detector temperature at 300°C. Carrier gas was helium at a flow rate of 1 mL/min and make up gas for ECD was nitrogen at a flow rate of 30 mL/min.

2.3 Explosive Sampling

Explosive sampling was performed at Lapang Sasar Kem Jugra, Banting, Selangor on 20th July 2011in collaboration with the Forensic Laboratory of Royal Malaysian Police (RMP). Prior to explosion, hair samples (approximately 200 strands of hair) were bound to a metal hook which was then placed at predetermined distances of 2.5 m, 5.0 m and 7.5 m from the point of blast. A 50 g of C4 explosive spherical shape putty material with attached with detonating cord was exploded by the RMP personnel. The hair samples were collected after the explosion, placed into individual plastic containers, sealed and labeled before being brought back to the laboratory for further examination.

2.4 Sample Extraction

For sample extraction, 0.1 g of hair samples was placed in a clean beaker containing 5 mL acetonitrile. The mixture was then subjected to sonication for 20 minutes. The mixture was later left overnight on a mechanical shaker (Vibromix 314 EVT from Tehtnica) configured for 86 shakes per min.

2.5 Preparation of Calibration Curves

The calibration curves of standard compounds were made in order to assess the concentration of unknown sample. For PETN, a series of standard concentrations ranging from 10 - 50 ppm were prepared. While for RDX, standard concentrations of 100 – 500 ppm were used. An aliquot of 1 µL of each standard concentration was injected into the GC-ECD in triplicates. Graphs of concentration against peak areas of analytes were constructed using Microsoft Excel.

3.0 RESULTS AND DISCUSSION

3.1 GC Profile of Standard Mixture

GC-ECD separation of a standard mixture of PETN and RDX gave two resolved peaks that eluted within 10.0 mins. Based on the chromatogram (Figure 2), PETN eluted earlier than RDX with retention times of 7.5 and 8.0 min. respectively. GC conditions used in this study was as suggested by Calderara *et al.* [6] but with slight modifications. ECD response for RDX (500 pm) was found to be much lower than PETN (50 pm) as reflected by their peak areas. Thus, a mixture of test compounds were prepared using unequal concentrations of each analyte.

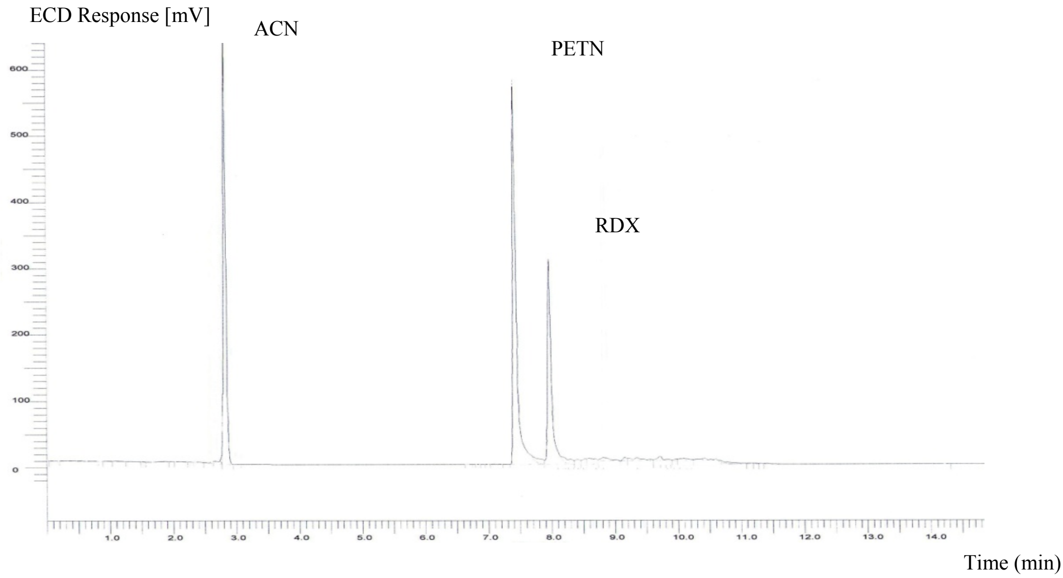

Figure 2 GC chromatogram for standard explosive of PETN (50 ppm) and RDX (500 ppm). GC conditions: HP5-MS (30 m x 0.25 mm x 0.25 µm) capillary column. Initial oven temperature of 100°C for 3 min, then ramped to 280°C at 15°C/min and finally held at 280°C for 1min. Injector temperature at 230°C and detector temperature at 300°C. Helium as carrier gas at flow rate of 1 mL/min and nitrogen as make-up gas at flow rate of 30 mL/min

3.2 Quantitation of Explosive Residues

The explosives residues extracted from post blast hair samples were then quantified using the standard curve obtained by linear regression. Figure 3 shows the calibration curves for PETN and RDX.

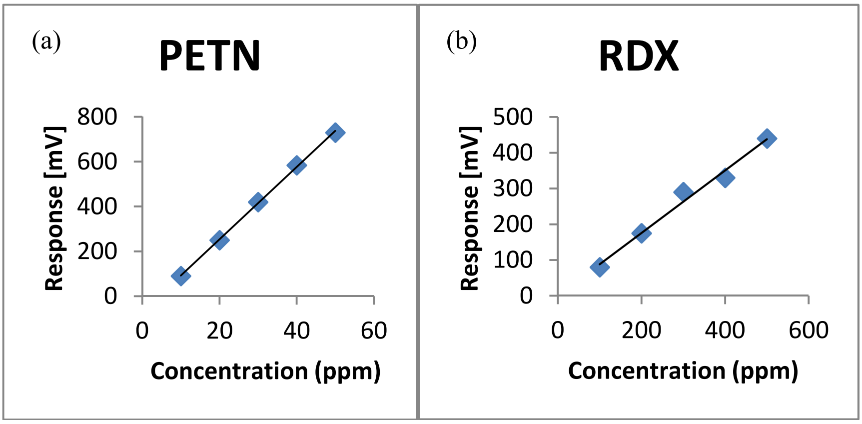

Figure 3 Calibration curves of (a) PETN and (b) RDX

Linear calibration graphs were obtained for both PETN and RDX. Both analytes gave good correlation coefficient of 0.9994 for PETN and 0.9843 for RDX. Limits of detection (LOD) of PETN and RDX, as assessed from signal to noise ratio of 3:1, were 0.2 ng and 20 ng respectively. The amount of explosive residues recovered from each predetermined distance is shown in Table 1. For a 50 g C4 explosive charge, the concentration of each analyte was found to decrease with increasing distance at 2.5 m interval from the point of blast. Sample H-1 which was situated closest to the bomb seat (2.5 m) showed the highest concentration of both explosive residues. RDX was found at higher concentration than PETN, consistent to the fact that C4 explosive contained RDX as the main ingredient and PETN as a minor constituent [5]. On other hand, sample H-2 located further away (5.0 m) recorded lesser amount of explosive residues than sample H-1. Sample H-3 which was placed at a further distance of 7.5 m revealed only the presence of minor amounts of PETN. However, RDX was not detected on sample H-3. Although initially present as minor constituent of the original explosive, PETN could still be detected further away than RDX possibly because of the vapour pressure of each analyte. Previous research [2] has shown that PETN residues has higher tendency to be absorbed into human head hair in comparison to RDX residues. This is due to the fact that PETN has higher vapor pressure and lower molecular weight than RDX. Location beyond 7.5 m was not investigated since it was anticipated that both analytes would not be detected. Factors of weather and wind conditions may also have an effect on the amount of explosive residues obtained in this study. Generally, the results showed a trend of decreasing concentration of residue deposited on hair with distance from the bomb seat.

Table 1 Concentration of analytes detected in hair samples

Sample label (distance from blast point)	**Range of concentration*(μg/g)**	
	PETN	**RDX**
H-1 (2.5 m)	0.20 – 0.26	1.66 – 1.76
H-2 (5.0 m)	0.04 – 0.14	0.03 – 0.17
H-3 (7.5 m)	0.04 – 0.06	nd

nd: Not detected
* Mean of triplicate analyses

4.0 CONCLUSIONS

Analysis of C4 explosive residues on hair samples have been developed using GC-ECD. Two constituents of C4, namely RDX and PETN were successfully separated on an HP5-MS capillary column within 10 mins. LODs of analytes were 20 ng for RDX and 0.2 ng for PETN. For a 50 g explosive used, RDX could only be detected in hair samples up to 5.0 m away compared to PETN which was detected up to 7.5 m away from the bomb seat. The study demonstrated the viability of human head hairs surface from which explosive traces can be recovered. The method developed in this research may be a great aid in the determination of explosive residues in human head hair. Furthermore, the distance at which the victim was most likely to be at the time of explosion which in turn could be used to locate the center of explosion could also be established via this method. To the best of our knowledge, there have been no reports on the detection of explosive residues on human head hairs. The results obtained from this initial study may hopefully serve useful as a guideline when dealing with real cases involving C4 explosives.

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