

Direct Immersion Solid-Phase Microextraction for the Forensic Determination of Nitro Explosives in Post-Blast Water Samples

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ABSTRACT: The forensic identification of bulk explosives plays a significant role in bombing investigation. The type and composition of explosives can be used to link suspects to a bombing crime. In this study solid-phase microextraction (SPME) was employed for the recovery of seven selected nitro explosives from the aqueous samples using gas chromatography-electron capture detector (GC-ECD). SPME parameters including extraction time, desorption time, desorption temperature, and the concentration of sodium chloride (NaCl) for salting-out effect were optimized using Carboxen/polydimethylsiloxane (CAR/PDMS)-coated fiber. Addition of 10% (w/v) of NaCl in the aqueous compounds under study for the optimized SPME method was found to be within 2 to 10 ppb except for PETN (1.4 ppm). Solid-phase extraction (SPE) utilizing LiChrolut[®] EN sorbent was employed for an analyte preconcentration technique prior to SPME in post-blast water samples collected from sampling trays. Three water samples collected at two sampling points nearest to the explosion point were found to contain traces of PETN (0.020 – 0.039 ppm). SPE-SPME with direct immersion mode followed by GC-ECD analysis was found to be a viable method for the qualitative and quantitative analysis of explosive residues in post-blast water samples.

Keywords: Nitro explosive, solid-phase microextraction, gas chromatography-electron capture detector, Carboxen/polydimethylsiloxane fiber

“Bombing” is no longer a rare or unfamiliar term to us in this new millennium. Almost every year, we witness such acts of violation or terrorism in some parts of the world. Due to these inhumane acts, many innocent lives and properties were sacrificed. The forensic identification of explosives plays a significant role in bombing investigation. The type of explosive can be determined and thus, culprit to the crime can be linked to the crime scene and prosecuted under the law. Very often, the classical extraction techniques applied, such as liquid-liquid extraction (LLE) and salting-out liquid-liquid extraction (SOE) are time-consuming (Monteil-Rivera et al., 2004) and require large volume of samples. Additionally, with the introduction of environmental harmful organic solvents in the traditional techniques, analysts tend to be exposed to those toxic substances and consequently, severe health problem ensued. Realizing the numerous drawbacks existing in the conventional methods employed, the development of better methods, with the added advantages of speed,

small sample requirement and solvent-free, is ultimately needed. With this purpose, solid-phase microextraction (SPME) was chosen to be employed in this study.

SPME was first developed by Pawliszyn in 1990 (Koster and Jong 2000). It is known to be a powerful alternative to traditional techniques for the extraction of volatile or semi-volatile organic compounds from water samples (Bao et al., 1998). SPME is an environmentally friendly extraction method as it is a solvent-free technique (Zhang and Pawliszyn, 1993; Monteil-Rivera et al., 2004). In addition, SPME has an advantage in terms of speed (Furton et al., 2000; Psillakis and Kalogerakis, 2001). It has good sensitivity with very low limit of detection (Zhang and Pawliszyn, 1993; Furton et al., 2000; Calderara et al., 2003). Moreover, the small amount of samples required by SPME makes it a favourable method to be employed (Psillakis and Kalogerakis, 2001; Monteil-Rivera et al., 2005) especially in forensic casework.

Gas chromatography coupled with electron capture detector (GC-ECD) has often been used for the separation and detection method for explosives. ECD was the first detector to provide the selectivity and sensitivity necessary for detection of trace amounts of explosives (Tebbett, 1992). According to Walsh (2001), ECD is the most sensitive detector for the detection of nitroaromatic explosive compounds.

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In this study, SPME was employed for the recovery of seven selected nitro explosives, namely pentaerythritol tetranitrate (PETN), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitrobenzene (TNB), 2-amino-4,6-dinitrotoluene (2-ADNT) and 4-amino-2,6-dinitrotoluene (4-ADNT), from the aqueous samples using GC-ECD. Solid-phase extraction (SPE) utilizing LiChrolut® EN sorbent was employed as an analyte preconcentration technique prior to SPME in the analysis of post-blast water samples.

Materials and Methods

Chemicals, apparatus and instrumentation

Explosive standards employed in this study were 2,4-DNT, 2,6-DNT, TNT, TNB, PETN, 2-ADNT and 4-ADNT. Other chemicals used were analytical grade sodium chloride (NaCl) for salting-out effect, acetonitrile (ACN) as solvent for explosive standards, methanol (CH₃OH, HPLC grade), deionized water and double distilled water prepared in our analytical laboratory. A Supelco SPME fiber manual holder,

together with a 75 µm film thickness Carboxen™/polydimethylsiloxane (CAR/PDMS)-coated fiber was employed for SPME process. LiChrolut® EN from Merck (Germany) was used as the SPE cartridge.

A 10-port SPE Vacuum Manifold Processing Station (Agilent Technologies) was used for explosives extraction and a Perkin Elmer Autosystem XL GC-ECD was employed for the separation and detection of explosives. Software for data acquisition was Turbochrom Navigator Version 4.1.

Sampling of post-blast water samples

Sampling of post-blast water samples, a collaboration work between Universiti Teknologi Malaysia (UTM) Forensic Research Team and Forensic officers of Royal Malaysia Police (PDRM), was carried out at Baling Bom Firing Range of PDRM in Ulu Kinta, Perak, Malaysia on 21st December 2006. The position of the collection trays near sampling point P where 150 g of PETN was detonated is illustrated in **FIG. 1**. All samples were stored in the refrigerator at 4°C in the forensic room of UTM prior to analysis.

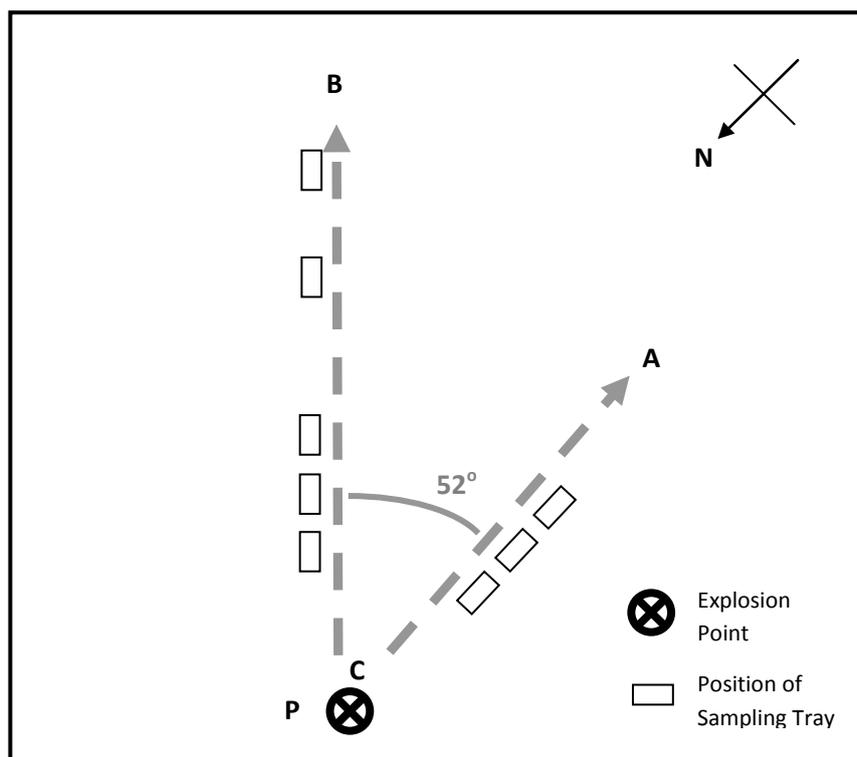


FIG. 1- Position of collection trays near sampling point P. Direction AC is the South of explosion point P, direction BC is the South-East of explosion point P whereas C is the point after explosion (Rajendran, 2006).

Direct immersion (DI)-SPME Procedure

In DI-SPME procedure, the fiber was exposed to 5 mL aqueous samples in a 10 mL vial sealed with a rubber septum prior to thermal desorption in GC injection port. The SPME parameters to be optimized in this study were extraction time, desorption time, desorption temperature and salting-out effect.

Calibration graph and Limit of Detection for SPME

In the preparation of calibration graphs for all analytes, the standard mixture containing 10 ppm each of 2,6-DNT, 2,4-DNT, TNT, TNB, 2-ADNT and 4-ADNT was prepared at 0.1-5.0% v/v whereas standard solution of 100 ppm PETN was prepared from 1.5 to 10% v/v. For limit of detection (LOD) determination, the volume of standard stock solution containing all analytes of known concentration was decreased until a GC response of analyte peak areas being equal to three times that of the baseline signal. The concentration of respective explosive standard was then calculated to determine LOD.

Analysis of water samples

SPE-DI-SPME technique was employed for the analysis of post-blast water samples. 600 mL of each water samples were gravity filtered to separate the soil and other unwanted solids prior to SPE. The SPE eluates (3 mL) were added with a certain amount of

distilled water for the optimization of DI-SPME method.

GC Conditions

GC separations employed Ultra 2 fused silica capillary column (25 m x 0.20 mm ID x 0.11 μ m film thickness) using helium as the carrier gas at a flow rate of 1 mL/min and nitrogen as the make-up gas for ECD at a flow rate of 30 mL/min. The injector and detector temperature were set at 230°C and 300°C, respectively. The initial oven temperature was set at 100°C for 3 min then ramped to 280°C at 15°C/min and finally held at 280°C for 1 min.

Results and discussion*GC Separation of Target Compounds*

GC-ECD was employed in this study for the chromatographic separation and detection of a mixture of target compounds, namely PETN, 2,4-DNT, 2,6-DNT, TNT, TNB, 2-ADNT and 4-ADNT. From the GC-ECD chromatogram obtained (**FIG. 2**), all of the explosive compounds were well separated within 15 min. PETN was found to be eluted first, followed by the dinitrotoluene isomers of 2,6-DNT, 2,4-DNT and TNB. TNT was found to be eluted next and followed by the aminodinitrotoluene isomers (4-ADNT and 2-ADNT).

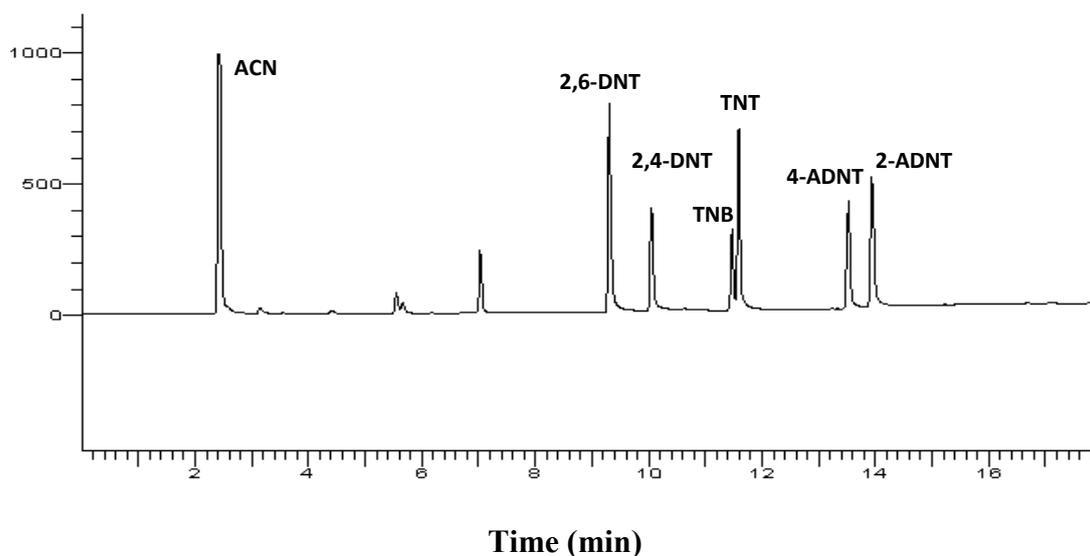


FIG. 2- GC-ECD chromatogram of explosive standard mixture on Ultra 2 fused silica capillary column. GC conditions: oven temperature initially at 100°C for 3 min then ramped to 280°C at 15°C/min and finally held at 280°C for 1 min; injector temperature at 230°C and detector temperature at 300°C.

Optimization of DI-SPME

Extraction Time Optimization

SPME sampling under equilibrium conditions is preferred for the quantitative analysis (Monteil-Rivera et al., 2004). The equilibrium period is limited by mass transfer of the analytes through a thin, static aqueous layer at the fiber-solution interface (Hornig and Huang, 1994). The amount of analyte adsorbed by the SPME fiber is a function of the distribution constant between the fiber and the solution, the analyte's diffusion coefficient and the thickness of the adsorbing phase. As all these parameters differ from one analyte to the other, the

equilibrium time should be measured for each analyte/fiber couple (Monteil-Rivera et al., 2005).

A SPME extraction time profile for all the explosives studied was attained by monitoring the ECD response as a function of duration of exposure (**FIG. 3**). Based on the results obtained, PETN, 2,6-DNT, 4-ADNT and 2-ADNT attained optimum average peak area at the extraction time of 30 min while 2,4-DNT, TNB and TNT showed optimum average peak area at 35 min. As the equilibrium condition was achieved at about 30 min for most of the explosives analyzed, 30 min extraction duration was therefore employed for all subsequent analyses.

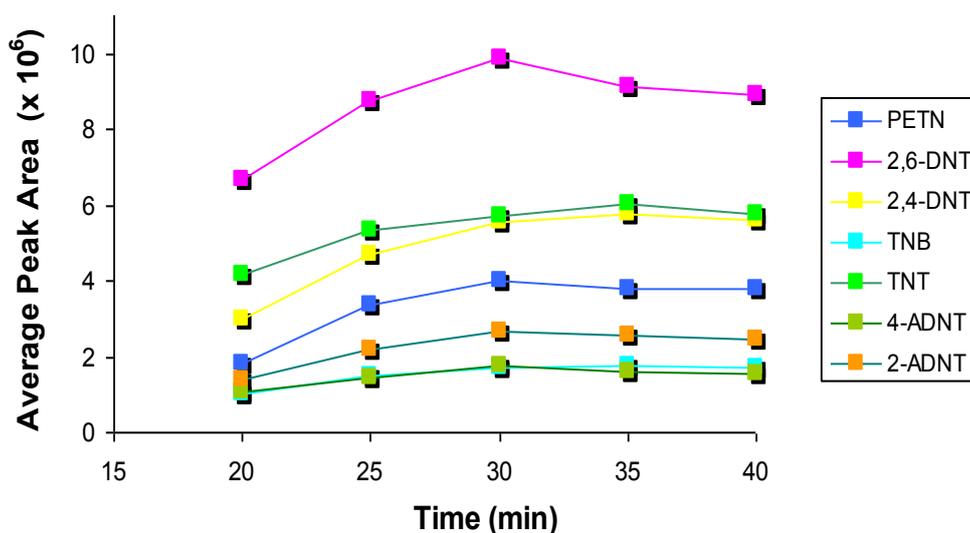


FIG. 3- Extraction time profile for PETN, 2,4-DNT, 2,6-DNT, TNT, TNB, 2-ADNT and 4-ADNT by DI-SPME/GC-ECD using CAR/PDMS fiber at room temperature.

Desorption Time Optimization

In the process of determining the optimum desorption time, the CAR/PDMS-coated fiber was immersed for 30 min in the aqueous solution of explosive (10% v/v) at room temperature. The fiber was then exposed in the GC injection port for various desorption time varying from 1 to 7 min (**FIG. 4**). From the results shown, the average peak areas increased gradually from 1 to 6 min and showed a slight drop after 6 min. This indicated that a complete desorption at desorption duration of 6 min was achieved for all explosives, except PETN for which in turn showed the optimum peak area at a longer duration (7 min). As majority of the analytes showed an optimum desorption time at 6 min, this duration was thus used as the optimum desorption time for the following experiments.

Desorption Temperature Optimization

When employing SPME/GC, desorption temperature can drastically affect the recovery of the analyte from the fiber. Temperature should be high enough to allow fast and quantitative desorption without decomposing the thermo-labile chemicals. Very often, the optimum desorption temperature of analyte depends on the fiber used; however, for most of the explosives, increasing desorption temperature too high will decrease the chromatographic response. This might be due to the fact that the explosives are by nature thermally unstable. The desorption temperature profile for all the explosives studied is presented in **FIG. 5a**. An enlarged desorption temperature profile for PETN, TNB, 2-ADNT and 4-ADNT is shown in **FIG. 5b** for clarity. Results obtained show that the average peak areas for PETN, 2,6-DNT, 2,4-DNT, 4-ADNT and 2-ADNT increased with temperature from 210 to 230°C,

however, they decreased after 230°C. This may be due to the fact that explosives are by nature thermally unstable at higher desorption temperature as aforementioned. For TNB and TNT, the optimum peak areas are obtained at 240°C and 220°C, respectively. As majority of the analytes studied showed optimum desorption at 230°C, this temperature was thus selected as the best compromise between a sufficient response and a limited degradation of analytes.

Effect of Sodium Chloride Concentration on Analyte Extraction

Several researchers have reported that salting-out effect increases the ionic strength of the aqueous solution and in this way, could decrease the solubility of the organic analytes; thereby, favouring their extraction by the fiber (Monteil-Rivera et al., 2005; Polo et al., 2006). However, high salt concentrations will degrade the fiber, thus limiting its lifetime and introducing imprecision in the measurements (Psillakis and Kalogerakis, 2001). Owing to this reason, the investigation on the effect of salt on analyte extraction in this study was only conducted by varying the percentage of salt from 0 to 30% w/v. The effect of salt concentration on extraction efficiency of all analytes tested employing CAR/PDMS-coated fiber is presented in **FIG. 6a**. An enlarged salting-out effect profile for PETN is shown in **FIG. 6b**.

Based on **FIG. 6**, it can be clearly seen that the addition of salt did not significantly affect the chromatographic response of 2,6-DNT and 2,4-DNT, however, it enhanced the GC response of PETN, TNB, TNT, 4-ADNT and 2-ADNT. **FIG. 6a** shows that the extraction efficiency of TNB, TNT and 2-

ADNT was enhanced at 10% w/v while PETN and 4-ADNT gave optimum extraction at 30% w/v and 20% w/v, respectively. The improvement in the efficiency of the extraction in the presence of salt is due to the enhancement of the ionic strength of the aqueous solution and thus, reducing the solubility of the target compounds and eventually favoring the transfer of analytes from the liquid medium to the fiber exposed.

It is worth noting that, at a higher salt concentration exceeding 10% w/v, a diminution in the average peak areas for most of the analytes studied was observed. A probable explanation for this is that the high salt concentration increases the viscosity of the sample and thus, slowing down the diffusion of the analytes to the fiber (Canosa et al., 2006), resulting in a decrease in extraction capability. Given the extraction enhancement caused by the addition of salt for several analytes, NaCl (10% w/v) was employed throughout the subsequent study to ensure the maximal extraction of most of the explosives under study was attained.

Evaluation of DI-SPME/GC-ECD method performance

Preparation of SPME Calibration Graph

Linearity ranges, equation parameters and correlation coefficients resulting from linear regression are provided in **TABLE 1**. A good linearity was observed with the CAR/PDMS fiber for all the analytes under investigation. Good correlation coefficients were obtained, with values greater than 0.984 in all cases.

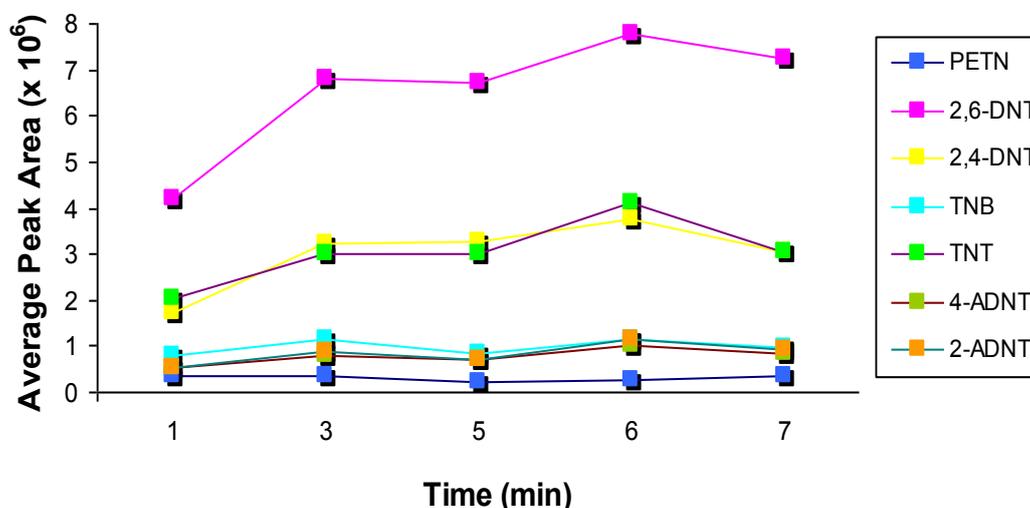


FIG. 4- Desorption time profile for PETN, 2,4-DNT, 2,6-DNT, TNT, TNB, 2-ADNT and 4-ADNT by DI-SPME/GC-ECD using CAR/PDMS fiber at room temperature with an extraction time of 30 min.

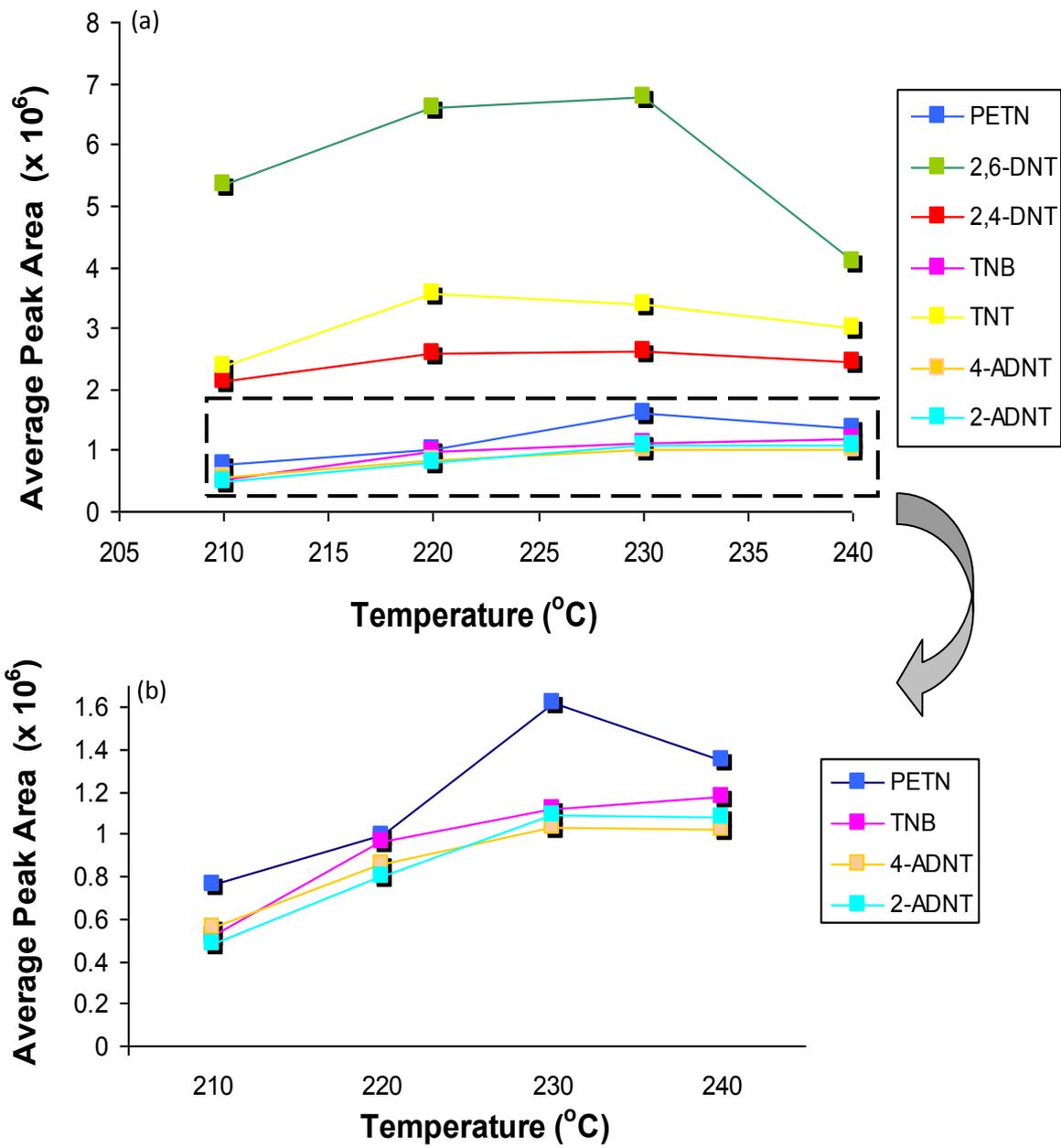


FIG. 5- Desorption temperature profile for (a) all explosives studied and (b) enlarged profile for PETN, TNB, 2-ADNT and 4-ADNT by DI-SPME/GC-ECD using CAR/PDMS fiber at room temperature. Fiber was immersed for 30 min in the aqueous solution and desorbed for 6 min in GC injection port.

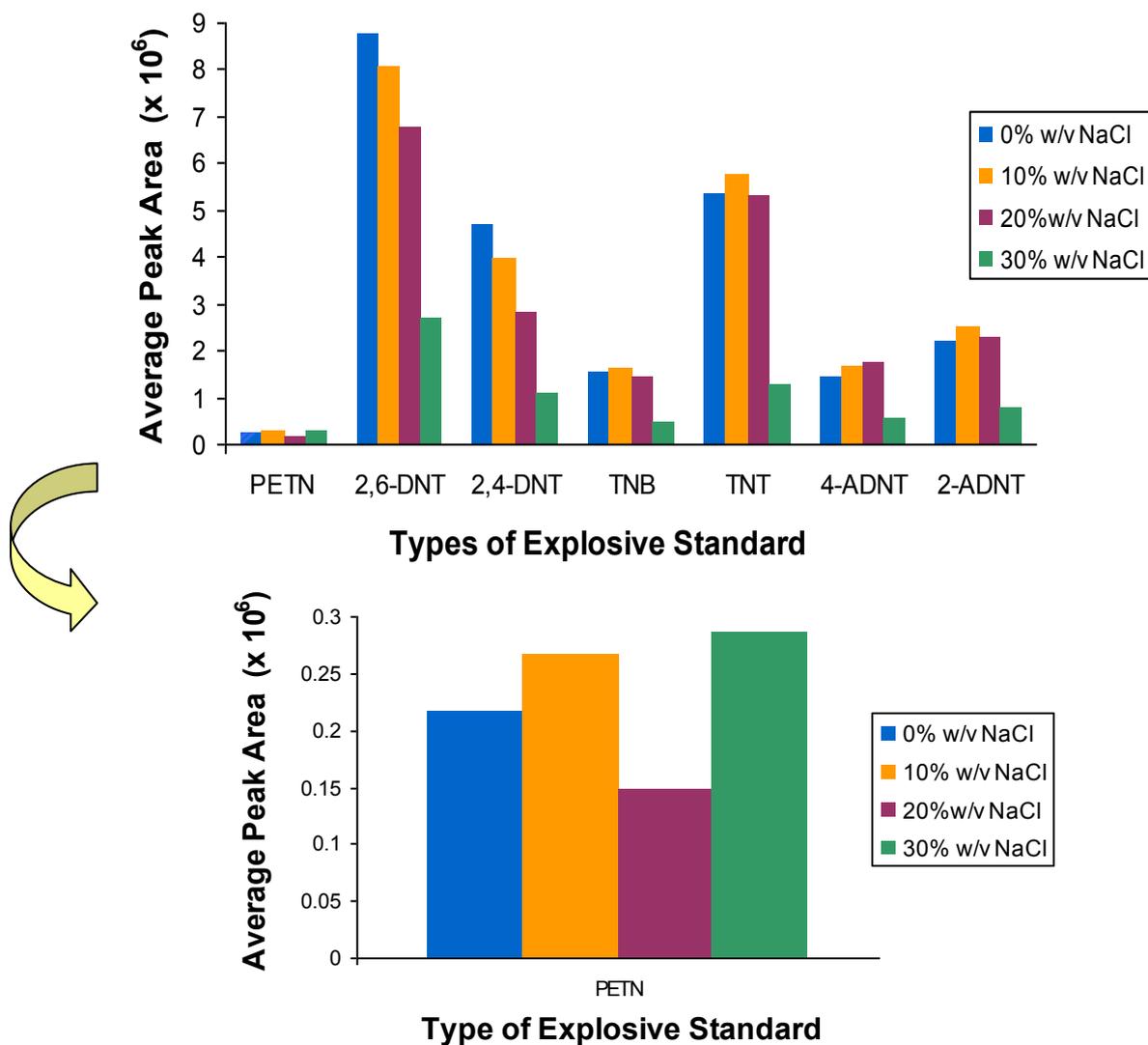


FIG. 6- Influence of various concentration of NaCl on DI-SPME for (a) all explosives studied and (b) PETN only; using CAR/PDMS fiber at room temperature. Fiber was immersed for 30 min in the aqueous solution and desorbed for 6 min at 230°C in GC injection port.

TABLE 1- Linearity and correlation of analytes by DI-SPME/GC-ECD using CAR/PDMS fiber

Analyte	Linearity Range (ppm)	Linear Equation	Correlation Coefficients (R ²)
PETN	1.5-10.0	y = 0.0686x	0.984
2,6-DNT	0.01-0.50	y = 12.607x + 0.6490	0.993
2,4-DNT	0.01-0.50	y = 6.1267x + 0.1875	0.996
TNB	0.01-0.50	y = 1.6787x + 0.0975	0.989
TNT	0.01-0.50	y = 8.6079x + 0.2817	0.992
4-ADNT	0.01-0.50	y = 2.6492x + 0.1220	0.993
2-ADNT	0.01-0.50	y = 2.9003x + 0.1805	0.998

Repeatability of SPME

The repeatability or expressed as relative standard deviation (RSD) values of the triplicate SPME extractions obtained in this study and the comparison of these values with that achieved by other researchers are summarized in **TABLE 2**. Results obtained revealed that the repeatability calculated with three replicates varies between 3.2 and 18.8%, which were satisfactory for the determination of

explosives in water samples. Similar or higher RSD values have been attained by Monteil-Rivera et al. (2005) on analysis of explosives using a different fiber coating. However, in the study of Kiu (2006) who employed the same type of fiber coating, similar or lower RSD values were reported. This may be attributed to the different type of GC column (HP-5 MS column) and GC system employed as different GC-ECD system and column could contribute to the efficiency of the result.

TABLE 2- Repeatability for optimized DI-SPME method of each analyte using CAR/PDMS-coated fiber and comparison of RSD obtained with other studies

Analyte	SPME/GC-ECD (Using CAR/PDMS)		SPME/GC-ECD (Using CW/DVB)
	RSD (%) (This Study)	RSD (%) (Kiu, 2006)	RSD (%) (Monteil-Rivera <i>et al.</i> , 2005)
PETN	18.74	7.28	NR
2,6-DNT	8.98	1.51	6.4
2,4-DNT	9.01	7.47	6.6
TNB	3.23	NR	9.4
TNT	5.12	5.35	22.3
4-ADNT	7.44	NR	13.3
2-ADNT	14.02	NR	19.0

Detection limit of SPME

TABLE 3 summarizes the LOD of individual standard compounds for the optimized DI-SPME method using CAR/PDMS fiber and the comparison of these values with that achieved by Psillakis et al. (2000). From the results obtained, detection limits for all the target analytes were found in the low ppb range (2 to 10 ppb), except for PETN which showed the highest LOD at 1400 ppb. The high LOD for PETN may be due to the fact that the CAR/PDMS-coated fiber employed in this study might not be really suitable for PETN extraction. PDMS/DVB- and PA-coated fiber showed better extraction efficiency for PETN compared to CAR/PDMS (Calderara et al., 2003).

Note that the detection limits obtained by Psillakis et al. (2000) were significantly different from that achieved in this study except for 2,6-DNT which was almost comparable. The possible explanation for this could be due to the different type of fiber and detector used.

Application to Water Samples

As the LODs of DI-SPME/GC-ECD using CAR/PDMS-coated fiber for several explosive compounds (PETN, 2,4-DNT, 2,6-DNT and TNT) reported in the study of Kiu (2006) have not achieved the satisfactory level, therefore it was of interest to apply preconcentration technique such as SPE (Ahmad and Rajendran, 2007) in order to reach the LODs demanded for explosive residues in post-blast water samples for forensic analysis. In this study, SPE utilizing LiChrolut® EN cartridges were employed prior to SPME for the determination of several simulated post-blast water samples obtained from Ulu Kinta, Perak. These water samples were collected from a number of collection trays, which were placed in two different directions (Point A and Point B), on the ground. The post-blast water sample obtained from point C was collected directly at the explosion point of PETN. The concentration of PETN residues in post-blast water samples from collection trays using SPE-DI-SPME/GC-ECD is shown in **TABLE 4**.

TABLE 3- Detection limit data of each analyte using the CAR/PDMS fiber and comparison of LOD obtained with other study

Analyte	Detection Limit (ppb)	
	SPME/GC-ECD (This Study)	SPME/GC-MS (Psilakis <i>et al.</i> , 2000)
PETN	1400	NR
2,6-DNT	2	2.5
2,4-DNT	8	2.5
TNB	8	25
TNT	3	15
4-ADNT	10	5
2-ADNT	10	5

TABLE 4- Concentration of PETN in water samples from collection trays using SPE-DI-SPME/GC-ECD

Sample	Distance from Explosion Point (m)	Concentration of PETN (ppm)
PA1	3	0.020
PA2	4	ND
PA3	5	ND
PB1	3	0.039
PB2	4	0.023
PB3	5	ND
PB4	10	ND
PB5	13	ND
PC	0	ND

*ND: Not detected

As can be interpreted from **TABLE 4**, the distance of the point of explosion to the sample collection tray did not show specific relationship with the concentration of the explosives. The concentration of water sample PB1 was the highest among those three samples. It was followed by PB2 and lastly, PA1, leaving zero concentration of PETN in PC. This phenomenon may be attributed to the explosive distribution pattern in which the soil containing explosive residues would randomly spread from the explosion point during explosion. Most of the mass of the explosive compounds resided in big pieces, resulting in a non-symmetrical and non-uniform distribution of explosive residues (Jenkins *et al.*, 2000). In addition to the explosive distribution pattern, the direction of the wind during simulated blasting of PETN also played an important role in this study. There could be a change in the direction of the wind during explosion which might blow the soil or debris to other places. Therefore, the residues collected in these sampling trays were very limited, even reaching an undetectable level or less than the detection limit of PETN in this study. These two factors could be the probable explanations for the failure in detecting traces of PETN residues in water samples PA2, PA3, PB3, PB4, PB5 and PC. Another

plausible explanation might be the degradation of PETN to other compounds due to the long storage period of sample before the samples were analyzed. Furthermore, for water samples at PB4 and PB5, the distance of these points were too far away for PETN to reach during explosion as the weight of the explosive employed in this simulated explosion was only 150 g.

Conclusion

DI-SPME technique utilizing CAR/PDMS fiber on the recovery of seven nitro explosives was performed. An extraction time of 30 min, desorption time of 6 min and desorption temperature of 230°C were found to be optimal for the extraction of explosive compounds. Addition of salt (NaCl) at the concentration of 10% w/v in the aqueous medium has proven to increase the extraction efficiency. Calibration graphs for all analytes gave good linearities with correlation coefficients greater than 0.984 for all the analytes investigated. The linearity ranges for PETN and all the other analytes under study were 1.5-10 ppm and 0.01-0.50 ppm, respectively. Repeatability for all analytes was fairly

good, with RSD ranging from 3.2 to 18.8%. Detection limits for 2,6-DNT, 2,4-DNT, TNB, TNT, 4-ADNT and 2-ADNT using DI-SPME/GC-ECD were found to be in the low ppb range (2-10 ppb) for all the analytes studied, except for PETN at 1400 ppb. The developed SPE-SPME method was applied to the qualitative and quantitative analyses of several post-blast water samples. Three water samples collected at sampling points A and B nearest to the explosion point were found to contain traces of PETN. In conclusion, SPE-SPME with direct immersion mode followed by GC-ECD analysis was found to be a viable method for the analysis of explosives under study.

Acknowledgements

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