FORENSIC ANALYSIS OF EXPLOSIVES FROM WATER SAMPLES USING
SOLID PHASE MICROEXTRACTION – GAS CHROMATOGRAPHY

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FORENSIC ANALYSIS OF EXPLOSIVES FROM WATER SAMPLES USING
SOLID PHASE MICROEXTRACTION – GAS CHROMATOGRAPHY

KIU KEE HENG

A project report submitted in partial fulfilment of the
requirements for the award of the degree of
Master of Science (Chemistry)

Faculty of Science
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OCTOBER 2006

I declare that this project report entitled "*Forensic Analysis of Explosives from Water Samples Using Solid Phase Microextraction – Gas Chromatography*" is the result of my own research except as cited in the references. The project report has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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ABSTRACT

The forensic identification of bulk explosive and postexplosion residues is important in bombing investigation. The information can be used to determine the type of explosive, to link the suspect to the bombing case and ultimately to provide evidence in court. Many analytical techniques have been applied to the identification of explosives and explosive residues. In this study, a solid-phase microextraction (SPME) technique followed by gas chromatography (GC) was used to determine the explosive residues. Gas chromatography with electron capture detection (GC-ECD) is very sensitive towards post-blast residues and therefore useful for the determination of explosive molecules. Several parameters including adsorption time, desorption time and temperature, SPME fiber types, stirring effect and salting out effect were optimized to obtain reproducible data with good accuracy. Addition of 10 % w/v of NaCl in the aqueous medium and use of a Carboxen/Polydimethylsiloxane (CAR/PDMS) coating fiber led to optimal extraction efficiencies. LOD of studied explosive compounds for the optimized SPME method was quite low (0.02-0.10 ppm) except for PETN (0.67 ppm). SPME/GC-ECD was optimized and applied to the trace analysis of explosive residues in real pond water and water sample from collection trays. 2,6-DNT, TNT and PETN were successfully detected from water samples. For some sampling points, TNT and PETN were not detected due to the amount of explosives used and low concentration of the explosives in water samples. Direct Immersion SPME/GC-ECD was found to be applicable for qualitative and quantitative analysis of explosives in post blast water samples.

ABSTRAK

Pengenalpastian forensik tentang bahan letupan dan sisa letupan adalah sangat penting dalam penyiasatan kes letupan. Maklumat yang berkenaan boleh digunakan untuk menentukan jenis bahan letupan, mengaitkan suspek dengan kes pengeboman dan akhirnya memberi bukti di dalam mahkamah. Banyak teknik analisis telah digunakan untuk pengenalpastian bahan letupan dan sisa letupan. Dalam kajian ini, teknik pengekstrakan mikro fasa pepejal (SPME) bersama dengan kromatografi gas (GC) telah digunakan untuk menentukan sisa letupan. Kromatografi gas bersama pengesanan tangkapan elektron adalah peka terhadap sisa bahan letupan dan berguna untuk pengenalpastian molekul bahan letupan. Beberapa parameter termasuk masa penjerapan, masa dan suhu nyahjerapan, jenis gentian SPME, kesan pengadukan dan kesan garam telah dioptimumkan untuk mendapat data yang tepat. Penambahan 10 % w/v NaCl dalam medium akues dan penggunaan gentian Carboxen/Polydimethylsiloxane (CAR/PDMS) menghasilkan pengekstrakan yang paling effisien. Had pengesanan bagi bahan letupan yang dikaji dengan pengoptimuman SPME adalah rendah (0.02-0.10 ppm) kecuali bagi PETN (0.67 ppm). SPME/GC-ECD telah dioptimumkan dan digunakan untuk menganalisis sisa letupan dalam air kolam sebenar dan sampel air daripada dulang tadahan. 2,6-DNT, TNT dan PETN berjaya dikesan daripada sampel air. Bagi beberapa lokasi pengsampelan, TNT dan PETN tidak dikesan disebabkan oleh amaun bahan letupan yang digunakan dan kepekatan yang rendah dalam sampel air. SPME/GC-ECD secara rendaman terus didapati sesuai digunakan untuk menganalisis bahan letupan dalam sampel air selepas letupan secara kualitatif dan kuantitatif.

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LIST OF ABBREVIATIONS/SYMBOLS/TERMS

2,4-DNT	-	2,4-Dinitrotoluene
2,6-DNT	-	2,6-Dinitrotoluene
ACN	-	Acentonitrile
CAR/PDMS	-	Carboxen/polydimethylsiloxane
CW/DVB	-	Carbowax/Divinylbenzene
DI-SPME	-	Direct immersion solid-phase microextraction
DNT	-	Dinitrotoluene
ECD	-	Electron capture detector
EGDN	-	Ethylene glycol dinitrate
FID	-	Flame-ionization detector
GC	-	Gas chromatography
GC-ECD	-	Gas chromatography with electron capture detection
GC-MS	-	Gas chromatography-mass spectrometry
HMX	-	1,3,5,7-Tetranitro-1,3,5,7-tetrazacyclooctane
HPLC	-	High-performance liquid chromatography
HS-SPME	-	Headspace solid-phase microextraction
IC	-	Ion chromatography
IR	-	Infra-red
LC-MS	-	Liquid chromatography-mass spectrometry
LLE	-	Liquid-liquid extraction
LMNR	-	Lead mononitroresorcinate
LOD	-	Limit of detection
MECC	-	Micellar electrokinetic capillary chromatography
NaCl	-	Sodium chloride
NG	-	Nitroglycerine
NPD	-	Nitrogen-phosphorus detector

PA	-	Polyacrylate
PDMS	-	Polydimethylsiloxane
PDMS/DVB	-	Polydimethylsiloxane/divinyl-benzene
PETN	-	Pentaerythritol tetranitrate
R^2	-	Correlation coefficients
RDX	-	1,3,5-Trinitro-1,3,5-triazacyclohexane
RSD	-	Relative standard deviation
SDME	-	Single-drop microextraction
SFC	-	Supercritical fluid chromatography
SPE	-	Solid phase extraction
SPME	-	Solid-phase microextraction
TEA	-	Thermal energy analyzer
TLC	-	Thin layer chromatography
TNT	-	Trinitrotoluene
UV	-	Ultra-violet
UXO	-	Unexploded ordnance

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CHAPTER 1

INTRODUCTION

1.1   Preamble

The forensic identification of bulk explosive and post explosion residues is important in bombing investigation. The information can be used to determine the type of explosive, to link the suspect to the explosive and ultimately to provide evidence in court. Many analytical techniques have been applied to the identification of explosives and explosive residues (Grob and Barry, 2004).

The battles of World War 1 and 2 required huge amounts of explosives as fillings of bombs, mines, shells, torpedoes etc. The main raw materials for nitroaromatics benzene, phenol and toluene were not available in sufficient quantities and it became necessary to search for substitutes. These were found among other compounds in mononitronaphthalenes, dinitronaphthalenes and trinitronaphthalenes which still today can represent a hazard on former explosives production sites, shell filling stations and ammunition destruction facilities. Nitronaphthalenes were used during World War 1 and to a minor extent in World War 2 (Bausinger *et al*., 2004). After the end of the world war, many environmental problems were being discovered at many of these locations. Surrounding lands were found to be laden with explosive residues, the common being 2,4,6-trinitrotoluene (TNT) and nitroaromatic and nitramine impurities. The highly toxic nature of many of these substances, coupled with their persistence in the environment, requires thorough characterization of contaminated areas (Kleiböhmer *et al*., 1993).

The bombings that occurred in Bali on the 12th October 2002 were the most callous act of terrorism in Indonesian history. Two hundred and two people were killed and many hundreds more were injured. Tiny fragments of tartan fabric were recovered from sites surrounding the blast epicenter. Numerous pieces of metal were also found amongst the debris and these were found to match fragments recovered from living and deceased victims (Royds *et al*., 2005). Indonesian police investigated the devastating bombing of a night club have found traces of plastic explosive at the site of the attack. After investigation by police together with expert from the FBI, they concluded that C4 explosive was used – a type manufactured mainly in the United State and used widely by military forces around the world (BBC News, 2002). There was another bombing in Bali in October 2005. At least 25 people were killed in this explosion and around 120 people were injured. Bali police chief informed that there was evidence that the explosion materials were attached to the body of the bombers and the composition of the bombs included TNT and metal slugs (ABC News, 2005).

Terrorism bombings are an increasingly common form of terrorist violence worldwide. Thousand of people have been killed or injured from such bombing in several countries. Turkey has been one of the target countries frequently suffering from terrorist action. From the study of terrorist bombing which related deaths in Istanbul (Turkey) between 1976 and 2000, a total of 45,714 autopsy case reports from the Morgue Department of Council of Forensic Medicine. There were 120 deaths due to terrorist bombing and terrorist bombing related deaths were significantly higher during the years (Yavuz *et al*., 2004).

In spite of bombing cases that cause many environmental problem, wartime activities including dumping of ammunition and sinking of warships have also resulted in the undersea deposition of considerable amounts of unexploded ordnance (UXO). Most explosives are toxic, and the leaching from UXO is considered to be a potential source of contamination for surrounding water. Due to the lack of effective tools to survey underwater areas, rapid and sensitive techniques for environmental monitoring are thus needed (Monteil-Rivera *et al*., 2004).

1.2 Explosives

An explosive can be liquid, gaseous or solid. A chemical explosive is a compound of mixture or alone which upon initiation undergoes a rapid chemical reaction without participation of external reactants such as atmospheric oxygen, resulting in large amount of gaseous pressure. An explosive must be sensitive to initiation. This reaction can be initiated by mechanical means (impact or friction), by the action of heat (sparks) or by detonating shock (Blasting Cap) (Köhler and Meyer, 1993). Any explosive must contain its own oxygen to be defined as an explosive. It cannot draw its oxygen from the air, as wood does when it burns (Brodie, 1973).

1.2.1 Types of Explosives

Explosives are either made of pure compounds or mixture of compounds. Basically, explosives which are pure compounds can also be divided to two categories that are organic and inorganic. Figure 1.1 shows the types of explosives classified as either organic or inorganic (Cooper and Kurowski, 1996).
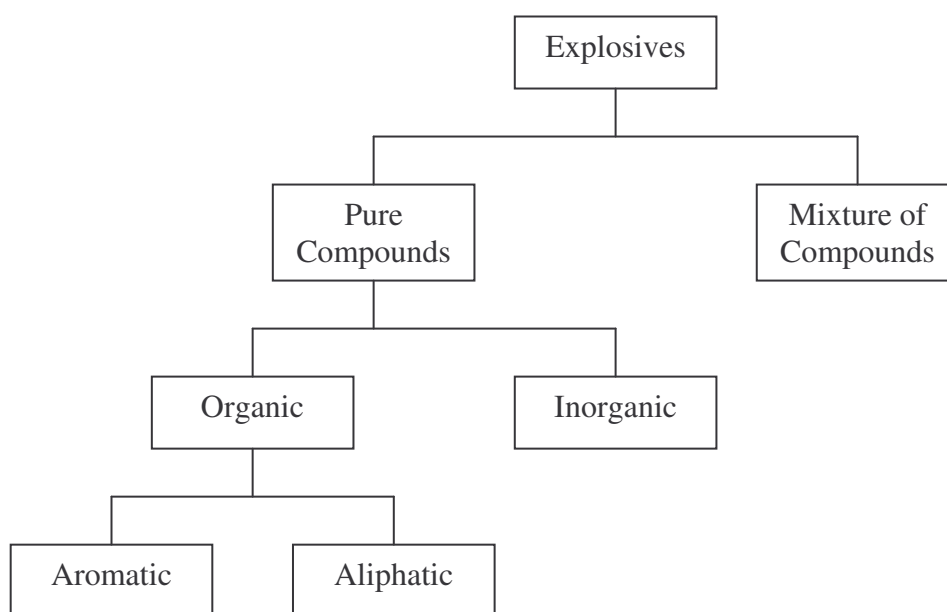
Figure 1.1: Types of Explosives

1.2.1.1 Organic Explosives

Almost all the explosive materials are organic compounds. An organic compound is built on a skeleton of carbon atoms. These skeletons fall into two major categories: aromatic and aliphatic. Explosives fall into both these categories (Cooper and Kurowski, 1996).

Aromatic explosives contain a benzene ring and in all these explosives, the benzene is nitrated. They are all solid crystalline materials. Trinitrotoluene (TNT) is the most common aromatic explosive (Figure 1.2a). TNT is stable, insensitive to shock and nontoxic. It is made from toluene, a petroleum byproduct. The nitro groups are added to it in steps, reacting the toluene in a mixture of concentrated nitric acid and with some sulfuric acid added. Disubstitution of toluene yields 2,4-dinitrotoluene (2,4-DNT) and 2,6-dinitrotoluene (2,6-DNT) (Figure 1.2b and 1.2c). 2,4-DNT and 2,6-DNT are priority pollutants generated during the synthesis of the explosive TNT, polyurethane foams, toluene, diiscocyanate and dyestuffs (Keenan *et al.*, 2005).

For aliphatic explosives, their compounds do not contain a benzene ring. These explosives were the first modern explosives to be mass produced. The most common aliphatic explosives are the nitrate esters. The nitrate esters comprise a large number of short-chain explosives that contain the nitrate group, $-ONO_2$. Some of them are oily liquids, insoluble in water, with moderate to high vapor pressures. They are very sensitive to impact. Usually, they are used in dynamites and in double-base propellants. Pentaerythritol tetranitrate (PETN) is a major aliphatic nitrate ester (Figure 1.2d). This white and powdered explosive is the major constituent in detonating cords. It is also used in many mixed and cast explosives.

1.2.1.2 Inorganic Explosives

Inorganic materials are not based upon a carbon skeleton. Most inorganic explosives are mixtures of fuels and oxidizers. Some examples of inorganic

explosives are ammonium nitrate, fulminates, silver fulminate and others. Ammonium nitrate, the most readily available and cheapest salt of HNO_3 is an odorless, white compound used as a solid oxidizer in explosive mixtures. Ammonium nitrate is also widely used as a fertilizer. It has a good chemical stability and a low sensitivity to friction and shock (Yinon and Zitrin, 1996).
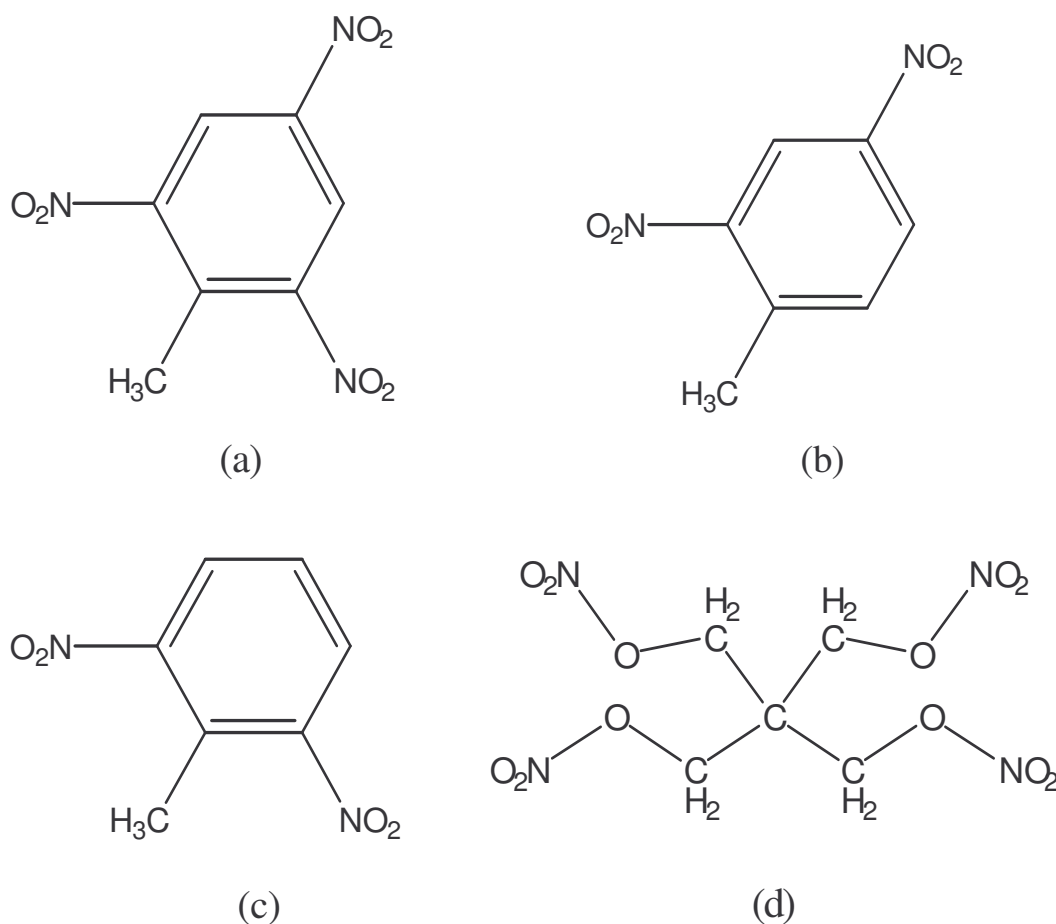
Figure 1.2: Chemical structure of (a) TNT; (b) 2,4-DNT; (c) 2,6-DNT and (d) PETN

1.2.1.3 High Order Explosives, Propellants and Pyrotechnics

Explosives can also be classified by their applications: high-order explosives, low-order explosives (propellants) and pyrotechnics, which are primarily differentiated by the burning rate and the manner of initiation.

High-order explosives are initiated by shock, usually through a booster charge or another explosive such as a blasting cap (Grob and Barry, 2004). It can be divided into two classes: primary explosives and secondary explosives. Primary explosives differ from secondary explosives in that they undergo a vary rapid transition from burning to detonation and have the ability to transmit the detonation to less sensitive explosives. Primary explosives will detonate when they are subjected to heat or shock. Primary explosives differ considerably in their sensitivity to the heat and in the amount of heat they produce on detonation. Their detonation velocities are in the range of 3500-5500 m/s (Akhavan, 1998). Typical primary explosives which are widely used are lead azide, lead styphnate, lead mononitroresorcinate (LMNR), potassium dinitrobenzofurozan and others.

For secondary explosives, they differ from primary explosives in that they cannot be detonated readily by heat or shock and are generally more powerful than primary explosives. They are less sensitive than primary explosives and can only be initiated to detonation by the shock produced by the explosion of primary explosives. Some secondary explosives are so stable that rifle bullets can be fired through them or they can be set on fire without detonating. The more stable explosives which detonate at very high velocities exert a much greater force during their detonation. Values of their detonation velocities are in the range of 5500-9000 m/s (Akhavan, 1998). Examples of high-order explosives are trinitrotoluene (TNT), tetryl, picric acid, nitrocellulose, nitroglycerine, 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX), pentaerythritol tetranitrate (PETN) and others.

Propellant is explosive material with low rate of combustion. It may be either solid or liquid (Köhler and Meyer, 1993). It is an explosive material which undergoes rapid and predictable combustion (without detonation) resulting in a large volume of hot gas. Propellants can be initiated by a flame or sparks and change from a solid to a gaseous state relatively slowly. A homogeneous propellant is where the fuel and oxidizer are in the same molecule, whereas a heterogeneous propellant has the fuel and oxidizer in separate compounds (Akhavan, 1998). Gun propellants are traditionally known to be homogeneous, whereas rocket propellants are heterogeneous. The compositions of gun propellants have traditionally been

fabricated from nitrocellulose-based material. Meanwhile for the rocket propellant, the composition is like gun propellant. The solid rocket propellant is manufactured in the form of geometrical shapes known as grains. Other examples of propellants are black powder, pyrodex, single-based and double-based smokeless powders and flash powders.

The name pyrotechnic is derived from the Greek words 'pyr' (fire) and 'techne' (an art), which describes the effect observed from a burning pyrotechnic composition (Akhavan, 1998). Pyrotechnics usually consist of a mixture of two ingredients: a fuel and an oxidizer, which is specifically formulated to produce a lot of energy. This energy is then used to produce a flame, or combined with other volatile substances to produce smoke and light like fireworks, or to produce large quantities of gas (firework rockets). Generally, the fuels are metals and the oxidizers are either salts or metal oxides. They differ from explosives in that the reaction is less than the bulk sound speed and the reaction rates are very low. There are five major productions of pyrotechnics: sound, color light, heat, smoke and delay. Usually different colors of smokes are produced due to the different material such as zinc, sulfur, phosphorous acid and other compounds used in pyrotechnic (Cooper and Kurowski, 1996). Figure 1.3 shows types of explosives and their applications (Köhler and Meyer, 1993).
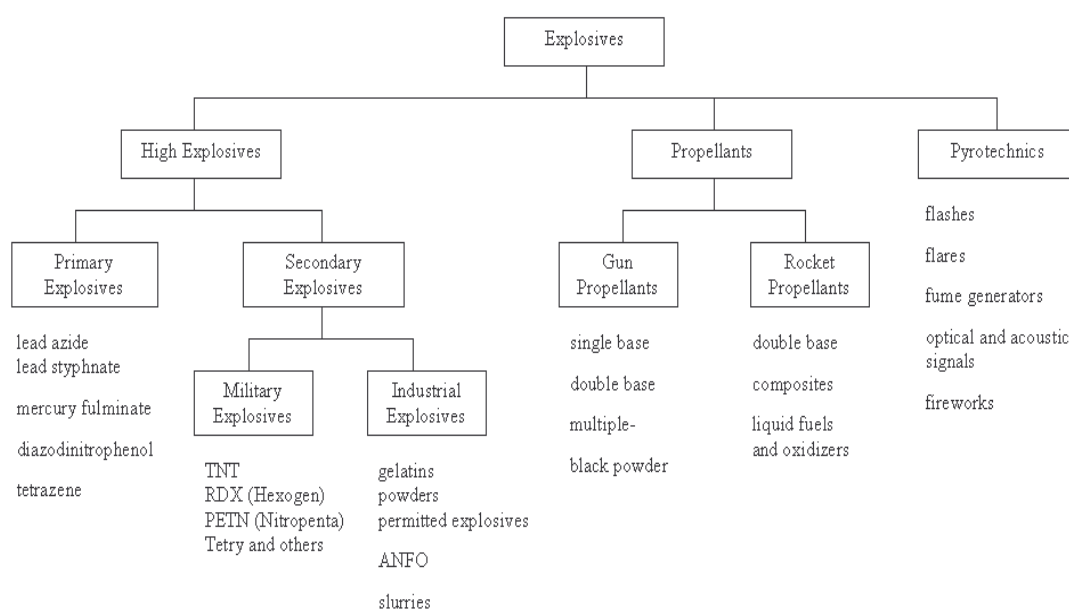

Figure 1.3: Types of Explosives and Their Applications

1.2.2   Properties of Explosives

A systematic approach to the relationship between the explosive properties of a molecule and its structure was proposed by van't Hoff in 1909 and Plets in 1953. According to Plets, the explosive properties of any substance depend upon the presence of definite structural groupings (Akhavan, 1998).

Hence, every explosive has its own properties such as melting point, energy of formation, color and others due to the structure and the functional groups present. For isomer of explosives (such as 2,4-DNT and 2,6-DNT), although they have the same empirical formula, they still have their own different properties that usually are physical properties such as melting point and density. Table 1.1 shows the properties of some explosives (Köhler and Meyer, 1993; Akhavan, 1998).

Table 1.1: Properties of Some Explosives

	2,4-DNT	2,6-DNT	TNT	PETN
Color	Yellow needle	Yellow needle	Pale yellow crystalline solid	Colorless crystalline solid
Empirical formula	$C_7H_6N_2O_4$	$C_7H_6N_2O_4$	$C_7H_5N_3O_6$	$C_5H_8N_4O_{12}$
Molecular weight	182.1	182.1	227.1	316.1
Melting point (^{o}C)	70.5	65.0	80.8	141.3
Density (g/cm^3)	1.521	1.538	1.654	1.76
Energy of formation (kJ/kg)	-298.8	-159.5	-184.8	-1509
Enthalpy of formation (kJ/kg)	-374.7	-241.2	-261.5	-1683
Solubility in water (mg/L)	270 @ 22°C	206 @ 25°C	130 @ 20°C	0.99

The thermodynamic concepts denote the energy which is bound during the formation of a given compound from its constituent elements at constant volume (energy of formation) or at constant pressure (enthalpy of formation, which includes the mechanical work preformed at the standard state, 25 °C = 77 °F and a pressure of 1 bar).

1.2.3   Extraction Techniques for Explosive Residues

1.2.3.1 Soxhlet

A Soxhlet extractor can be used to extract solutes from solids contained in a porous thimble, using any desired volatile solvent, which can be water-miscible or water-immiscible (Patnail, 2004). As the solvent is heated, the solvent will be vaporized. The distilled solvent drips into the porous thimble, immersing the solid sample. When the solvent is full, solvent is siphoned back into the solvent reservoir and redistilled (Grob and Barry, 2004). This process continues repeatedly as the solvent in the flask is vaporized and condensed.

If sample particles are hydrophilic, they may repel with organic solvent, reducing efficiency. Drying agents are often used to reduce this problem. A further disadvantage is that Soxhlet extraction is usually very slow, often requiring several hours. This is often pointed out when Soxhlet extraction is compared to other instrumental techniques such as supercritical fluid extraction or accelerated solvent extraction.

Soxhlet extraction of soil sample was performed in the study of Deuster *et al.* (1997). A 5 g soil was extracted for 8 h with 150 mL *n*-hexane. The concentrated extract was analyzed by high-performance liquid chromatography (HPLC). From the result, soxhlet extraction could be used to extract explosive residues from soil samples like other conventional extraction techniques.

1.2.3.2 Ultrasonic

During the sonication extraction, ultrasonic vibration energy is used to enhance the liquid-solid extraction. A converter, whose main component is a lead zirconate titanate piezoelectric crystal, translates this electrical energy into high frequency mechanical energy. The ultrasonic wave travelling through the solution consists of alternate compressions and rarefactions (Grob and Barry, 2004). This ultrasonic energy was found beneficial for the liquid-soil extraction of soils. The major benefit of applying ultrasonic to soil extractions is the disaggregation of soil particles, which occurs during the extraction procedure as the result of the sonic energy. This increases the surface area of the soil and allows the extractant to further penetrate the soil matrix.

In a study by Walsh (2001), soils were collected for traces of nitroaromatic, nitramine and nitrate ester explosives and analyzed by HPLC. The analytes were extracted from soils with acetonitrile by 18 hours of sonication in a cooled ultrasonic bath. This method gave detection limits around 1 μg kg^{-1} to 10 μg kg^{-1} for the di- and trinitroaromatics respectively. For RDX, HMX and nitrate esters (nitroglycerine, NG and PETN), detection limit were 3 μg kg^{-1}, 25 μg kg^{-1} and between 10-40 μg kg^{-1} respectively. Spike recovery studies revealed artifacts introduced when the mass of the soil spiked was large (25.0 g) in proportion to the volume of spike solution added (1.00 mL). Recoveries were excellent (around 100%) when 2 g soil samples were spiked with 1.00 mL of solution (Walsh, 2001).

1.2.3.3 Centrifugation

A centrifuge is a device that uses centrifugal force to separate two or more substances of different density such as two liquids or a liquid and a solid. Centrifuge devices are used in a variety of scientific and technical application by spinning carrier vessels (centrifuge tubes) at high rotation speeds and very high centrifugal force. The theoretical basis of this technique is the effect of gravity on particles in