

**DETERMINATION OF THE POSTEXPLOSION RESIDUES OF
NITRO GROUP CONTAINING EXPLOSIVES IN SOIL WITH
GAS CHROMATOGRAPHY-MASS SPECTROMETRY
AND
GAS CHROMATOGRAPHY-THERMAL ENERGY ANALYSER**

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**DETERMINATION OF THE POSTEXPLOSION RESIDUES OF NITRO
GROUP CONTAINING EXPLOSIVES IN SOIL WITH GC-MS AND GC-TEA**

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ABSTRACT

DETERMINATION OF THE POSTEXPLOSION RESIDUES OF NITRO GROUP CONTAINING EXPLOSIVES IN SOIL WITH GC-MS AND GC-TEA

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There is an increase in bombing assaults in recent years in our country. Determining the explosive material used in these cases by the quick and correct analysis of the evidence obtained after the explosions, is an important starting point for the investigations which are done to reach the perpetrators. The forensic chemistry investigations have to be correct, exact and rapid in order to reach the right criminal. In this study, the Gas Chromatography-Mass Spectrometry (GC-MS) and Gas Chromatography-Thermal Energy Analyser (GC-TEA) methods which are being used for the determination of the explosive materials' residues used in bombing attacks are optimized with the standard solutions of 2,4,6-Trinitrotoluene (TNT) and 1,3,5-trinitro-1,3,5-triazocyclohexane (RDX) and standard mixture solution. The two methods were compared by analysing the postexplosion soil samples. Also an efficient and applicable sample preparation procedure was developed. The results showed that both methods are efficient and sensitive for the postexplosion investigations. It is seen that GC-TEA has lower detection limit and simple chromatograms due to its selectivity against only nitro group containing explosives. However it is concluded that there is a need for a reliable and sensitive method like GC-MS which provides identification and library search for the determination of the organic components which can not be identified with GC-TEA.

Key words: Explosive materials, GC-MS, GC-TEA, postexplosion investigations, forensic chemistry.

ÖZ

NİTRO GRUBU İÇEREN PATLAYICI MADDELERİN TOPRAK İÇERİSİNDEKİ PATLAMA SONRASI KALINTILARININ GC-MS VE GC-TEA YÖNTEMLERİ İLE TESPİTİ

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Son yıllarda ülkemizde bombalı saldırı olaylarında bir artış vardır. Bu olaylarda patlama sonrasında elde edilen bulguların doğru ve hızlı analiz edilerek kullanılan patlayıcı maddenin tespitinin yapılması; olayın faillerine ulaşılabilmesi için yapılan soruşturmalara önemli bir başlangıç noktası olmaktadır. Gerçek suçluya ulaşılabilmesi için yapılan adli kimya incelemeleri, hızlı, kesin ve doğru olmak zorundadır. Bu çalışmada bombalı saldırı olaylarında kullanılan patlayıcı madde kalıntılarının tespiti için kullanılan Gaz Kromatografi-Kütle Spektrometri (GC-MS) ve Gaz Kromatografi-Termal Enerji Analizörü (GC-TEA) yöntemleri standard 2,4,6-Trinitrotoluen (TNT) ve 1,3,5-trinitro-1,3,5-triazosiklohegzan (RDX) çözeltileri ile standard karışım çözeltisi kullanılarak optimize edildi. Patlamadan sonra patlama noktasından elde edilen toprak numuneleri analiz edilerek iki yöntem karşılaştırıldı. Aynı zamanda etkin ve uygulanabilir bir numune hazırlama yöntemi geliştirildi. Sonuçlar her iki yöntemin de patlama olayları sonrası incelemelerde etkin ve hassas olduğunu gösterdi. GC-TEA yönteminin yalnızca nitro gruplarına karşı seçici olması sebebiyle, daha düşük tayin limitine ve daha yalın kromatogramlara sahip olduğu görüldü. Bununla birlikte GC-TEA yöntemi ile tanımlanamayan diğer organik bileşenlerin belirlenmesinde tanımlama ve kütüphanesinde tarama yapma imkanı bulunan GC-MS gibi güvenilir ve hassas bir yöntem ihtiyacı duyulduğu sonucuna varıldı.

Anahtar Kelimeler: Patlayıcılar, GC-MS, GC-TEA, patlama sonrası incelemeler, adli kimya.

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CHAPTER 1

INTRODUCTION

1.1 DEFINITION OF AN EXPLOSIVE

An explosive is defined as a substance or mixture of substances which may be made to undergo a rapid chemical change without an outside supply of oxygen, with the liberation of large quantities of energy, generally accompanied by the evolution of hot gases. Many substances not ordinarily classed as explosives may do one or even two of these things. For example a mixture of nitrogen and oxygen can be made to react with great rapidity and yield the gaseous product nitric oxide; yet the mixture is not an explosive since it does not evolve heat, but rather absorbs heat (21).



For a chemical to be an explosive, it must exhibit all of the following:

- Formation of gases
- Evolution of heat
- Rapidity of reaction
- Initiation of reaction

1.1.1 Formation of Gases

Gases may be evolved from substances in a variety of ways. When wood or coal is burned in the atmosphere, the carbon and hydrogen in the fuel combine with the oxygen in the atmosphere to form carbon dioxide and steam (water), together with flame and smoke. When the wood or coal is pulverized, so that the total surface in contact with the oxygen is increased, and burned in a furnace or forge where more air

can be supplied, the burning can be made more rapid and the combustion more complete. When the wood or coal is immersed in liquid oxygen or suspended in air in the form of dust, the burning takes place with explosive violence. In each case, the same action occurs: a combustible burning forms a gas (21).

1.1.2 Evolution of Heat

The generation of heat in large quantities accompanies every explosive chemical reaction. It is this rapid liberation of heat that causes the gaseous products of reaction to expand and generate high pressures. This rapid generation of high pressures of the released gas constitutes the explosion. It should be noted that the liberation of heat with insufficient rapidity will not cause an explosion. For example, although a pound of coal yields five times as much heat as a pound of nitroglycerin, the coal cannot be used as an explosive because the rate at which it yields this heat is quite slow (21).

1.1.3 Rapidity of Reaction

Rapidity of reaction distinguishes the explosive reaction from an ordinary combustion reaction by the great speed with which it takes place. Unless the reaction occurs rapidly, the thermally expanded gases will be dissipated in the medium, and there will be no explosion. Again, consider a wood or coal fire. As the fire burns, there is the evolution of heat and the formation of gases, but neither is liberated rapidly enough to cause an explosion. This can be likened to the difference between the energy discharge of a battery, which is slow, and that of a flash capacitor like that in a camera flash, which releases its energy all at once (21).

1.1.4 Initiation of Reaction

A reaction must be capable of being initiated by the application of shock or heat to a small portion of the mass of the explosive material. A material in which the first three factors exist cannot be accepted as an explosive unless the reaction can be made to occur when desired (21).

1.2 THERMOCHEMISTRY OF EXPLOSIVES

Explosive reactions can be slow or fast, the former characterized by low rates of reaction (a few centimeters to a few meters/second) and the latter by very high rates (up to several kilometers/second). The reactivity of a chemical depends on its chemical structure. All explosive chemicals such as nitrate ($-\text{ONO}_2$), nitro ($-\text{NO}_2$), chlorate ($-\text{ClO}_3^-$) and perchlorate ($-\text{ClO}_4^-$) are characterized by low thermodynamic stability.

The chemical compositions of typical molecular explosives are shown in Figure 1.1. The oxygen attached to these structures breaks away easily to combine with other elements such as carbon, hydrogen, sulphur, etc. to form more stable compounds. There are also some explosive compounds which are either highly oxygen deficient (e.g. trinitrotoluene (TNT), Pentaerythritol tetranitrate (PETN)) or totally devoid of it (e.g. lead azide ($\text{Pb}(\text{N}_3)_2$)). But they are all unstable compounds and decompose rapidly by releasing heat and hot gases when desired.

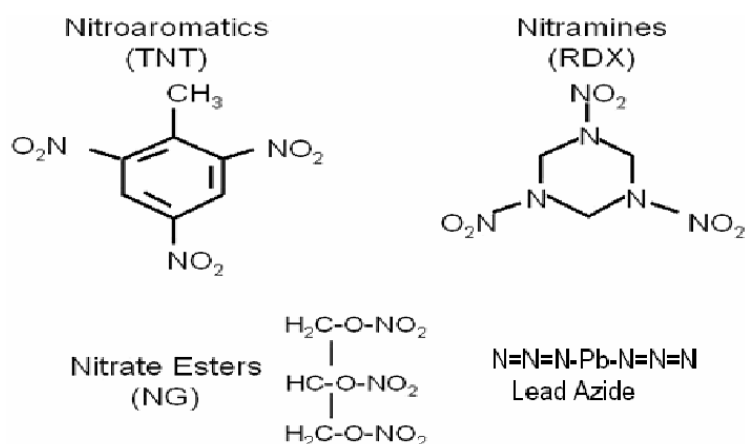
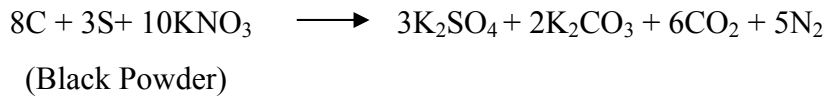
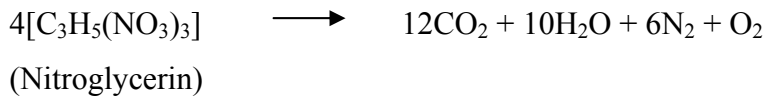
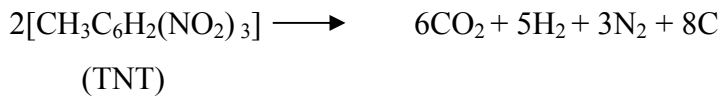


Figure 1.1 Structural formula of some explosives.

The major reactions in the explosion process are the following: C to carbon dioxide, H to steam and water, N to nitrogen gas, Al to aluminum oxide, S to gas or solid sulphates, ammonium nitrate to water, nitrogen and oxygen, and so on.



In each process, the unstable bond between nitrogen and oxygen is transformed into more stable compounds; nitrogen combining with itself, oxygen combining with carbon, hydrogen and sulphur. Actually the reactions at the high temperatures and pressures prevailing in the reaction zone are, of course, more complex, and it is difficult to determine these reaction schemes.

All explosive compounds can be considered to be composed of three components;

- Fuel,
- Oxidizer,
- Sensitizer.

Carbon, hydrogen, sulphur, etc. provide the essential fuel for the oxygen in the oxidizer. Incorporation of a chemical or physical sensitizer enhances the ease with which the explosive can be made to react by means of an initiator. The molecular explosives such as nitroglycerin (NG) or TNT which contain both fuel (C, N) and oxidizer (O) in their structure, do not require a sensitizer, whereas others may require such components in order to attain a degree of sensitivity.

The bulk of the commercial explosives are not molecular explosives but are made of mixtures of these three essential components. As a result they are considerably less sensitive than the molecular explosives. Initiation of these explosives is therefore much more difficult, and requires adequate boosting. The common form of initiators and boosters are detonators (1g of PETN), detonating cords (4 g/m to 40 g/m of PETN inside a thin plastic tube or plastic yarn), cast boosters (20 g to 1kg of Pentolite (PETN/TNT:50/50)), and cartridges (200 g to 500 g detonator-sensitive explosives) Figure 1.2 (1).



Figure 1.2 Cartridges and detonating cords.

1.3 HISTORICAL BACKGROUND OF EXPLOSIVES

It is difficult to speak of modern explosives without referring to black powder. The discovery of black powder probably precedes its actual use in a systematic fashion by several centuries. Its essential ingredients (potassium nitrate, charcoal and sulphur) have been essential since ancient times, and chance or deliberate ignition of a mixture of these ingredients may not have been so rare. However, its systematic use belongs to the Chinese, who packed these mixtures into bamboo tubes and used them as rockets for display and signalling purposes. It took several centuries before black powder became a standard military tool. Even then, the early 14th century cannons consisted simply of wooden tubes filled with black powder charge which expelled a stone projectile. The first use of the material in mining took place in Hungary in the early 17th century. Its use accelerated with the discovery of vast deposits of sodium nitrate in Chile in 1840.

Other related developments quickly followed. In 1846, reacting strong nitric acid with glycerol, a by-product of soap manufacture, resulted in an oily product called glyceryl trinitrate, which is more commonly known as nitroglycerin (NG). Practical use of NG was pioneered by the Nobel family in the years following 1859. Alfred Nobel is also inventor of the blasting cap in 1863, which revolutionized the mining industry. But the behaviour of the NG-based explosives still remained unpredictable, resulting in numerous accidents and fatalities.

After many years of work, Nobel finally discovered that kieselguhr, a diatomaceous earth, absorbed up to three times its own weight of NG to form a relatively dry, leak resistant paste, which came to be known as “dynamite”. The word was derived from the Greek word “dynamis”, which means power.

Other momentous advances in the explosives technology include the development of safety fuse (essentially black powder core inside a tough yarn) by William Bickford in 1831, invention of the detonating cord in 1908 in France and further refined by Ensign-Bickford Corporation in USA, and the chance discovery of ammonium nitrate as being a very powerful explosive in 1947, when the ship Grand Camp carrying fertilizer grade ammonium nitrate (AN) blew up at its dock in Texas City following a fire! The place of AN in explosive industry has since been secure. The other significant developments in the explosive industry were the introduction of the slurry explosives in the late 1950s, and shock tube based detonators (“Nonel”; a plastic tube with a wall coating of High Melting Explosive (HMX) and aluminum) in the early 1970s, and of water-in-oil emulsion explosives in the late 1970s (1).

1.4 TYPES OF EXPLOSIVES

Explosion events could originate from several sources. These include dust explosions, ignition of flammable gases and initiation of condensed phase chemicals such as propellants and explosives, and finally, detonation of nuclear devices.

The chemical explosives can be roughly grouped under two categories: military explosives and commercial explosives. There is however no sharp distinction except in their applications and their relative sensitivity to initiation.

The military explosives, as well as the so-called primary explosives used in the manufacture of detonators, are normally composed of molecular explosives which require no additional ingredients to make them explode. Examples are: lead azide, lead styphnate, TNT, PETN, RDX and various combinations of the latter three compositions such as “Semtex” (RDX/PETN). In general, the molecular explosives have higher sensitivity and higher reaction rates than composite explosives.

The development of commercial explosives preceded military explosives by several decades and continues to be an active area of research. Examples are: Nitroglycerin (NG)-based explosives (dynamites), explosives with alternate sensitizers such as TNT, RDX and perchlorates, slurry explosives, emulsions and dry blasting agents such as ANFO (ammonium nitrate+fuel oil). All explosives other than NG-based ones may contain varying amount of aluminum for extra energy. Although NG-based and slurry explosives still have a significant market share, dry blasting agents such as ANFO and emulsion explosives and their variants have become the mainstay of most blasting operations.

The emulsion explosives have several outstanding advantages over other explosives including: its simplified composition (saturated AN liquor with fuel oil and an appropriate emulsifier), intimate mixing of fuel and oxidizer (droplet size ranging from 1 μm to 5 μm), its relative waterproofness, its ease to manufacture and high velocity of detonation. Emulsion explosives can be sensitized, for small diameter applications, with either chemical or physical sensitizers (air bubbles or glass or plastic microballons), and can incorporate varying amounts of aluminum to give additional strength. It can be manufactured in a wide range of densities; lower densities for small diameter application and higher densities for large diameter application. The emulsion explosive can be used by itself or mixed with ANFO or AN pills, or it can be used as a filler of intergranular spaces in ANFO (1).

In addition to the classification according to use as military and commercial, explosives may be classified according to their chemical structure, their place in the detonation chain and their explosive properties.

1.4.1 Classification by Type of Explosion

Explosives are distinguished between high explosives, which detonate, and low explosives, which deflagrate;

- Low Explosives burn through deflagration rather than a detonation wave, are usually a mixture, are initiated by heat and require confinement to create an explosion.

- High Explosives explode in supersonic reactions and without confinement, are usually compounds, are initiated by shock or heat and give high brisance (the shattering effect of an explosion).

Some explosives fall into either category, according to how they are initiated. For example, nitrocellulose deflagrates if ignited, but detonates if initiated by a strong detonator. Gunpowder burns if uncontained, but will detonate if contained and fired (21).

1.4.2 Classification by Composition of the Material

Mixtures of an oxidizer and a fuel

Gunpowder: potassium nitrate, charcoal and sulfur

Ammonal: ammonium nitrate and aluminum powder.

ANFO: ammonium nitrate and fuel oil.

Cheddites: chlorates or perchlorates and oil.

Chemically pure compounds, often mixed with stabilizers

Dynamite: nitroglycerin mixed into a paste with powdered silica, which act as a stabilizer.

RDX, PETN, TNT: very strong explosives which can be used as pure.

C-4: plastic explosive, adhesive properties.

Acetone peroxide: simple to make using household items.

1.4.3 Classification by Sensitivity of the Material

Explosives are classified by their sensitivity, which is the amount of energy to initiate the reaction. This energy can be anything, from a shock, an impact, a friction, an electrical discharge, or the detonation of another explosive. There are two basic divisions on sensitivity:

Primary explosives

They are extremely sensitive and require a small quantity of energy to be initiated. They are mainly used in detonators to initiate secondary explosives. For example; tetryl, lead azide, mercury fulminate, lead styphnate, tetrazene, hexanitromannitol.

Secondary explosives

They are relatively insensitive and need a great amount of energy to initiate decomposition. They have much more power than primary explosives and are used in demolition. They require a detonator to explode. For example; TNT, RDX, PETN, HMX, ammonium nitrate, tetryl, picric acid, nitrocellulose. Some secondary explosives are insensitive enough that they can be lit with a match or a torch and will simply burn like wood; a detonation wave is never formed (21).

1.4.4 Classification by Chemical Structure

• Organic nitro explosives:

Nitroaromatic: 2,4-dinitrotoluene (2,4-DNT), 2,4,6-trinitrotoluene (TNT);

Nitrate esters: ethyleneglycol dinitrate (EGDN), glycerol trinitrate (NG), pentaerythritol tetranitrate (PETN), cellulose nitrate (NC);

Nitramines: 1,3,5-trinitro-1,3,5-triazocyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetrazocyclooctane (HMX);

• Organic peroxides:

3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxacyclononane (TATP), 3,4,8,9,12,13-hexaoxa-1,6-diazabicyclo [4,4,4] tetradecane (HMTD);

• Inorganic salts:

Ammonium nitrate (AN);

• Mixtures of oxidizing and reducing agents:

Black powder (potassium nitrate, sulfur and charcoal), potassium chlorate and sugar (19).

1.5 EXPLOSIVES USED IN THIS STUDY

1.5.1 TNT (2,4,6-Trinitrotoluene)

TNT is one of the most common bulk explosives. 2,4,6 Trinitrotoluene (TNT) is an explosive used in military munitions and in civilian mining and quarrying activities. TNT was first used on a wide scale during World War I and is still in use today. The United States military stopped production of TNT in the mid-1980s.

TNT is classified as a secondary explosive because it is less susceptible to initiation and requires a primary or initiating explosive to ignite it. TNT can be used as a booster or as a bursting charge for high-explosive shells and bombs. Also, TNT may be mixed with other explosives such as Royal Demolition Explosive (RDX) and High Melting Explosive (HMX) and it is a constituent of many explosives, such as amatol, pentolite, tetrytol, torpex, tritonal, picratol, ednatol, and “Composition B”; a mixture of 59.5 % RDX, 39.5 % TNT and 1 % wax.

TNT is a crystalline substance. The importance of TNT as a military explosive is based upon its low cost, safety in handling, fairly high explosive power, good chemical and thermal stability, compatibility with other explosives, a low melting point favorable for melt casting operations and moderate toxicity. Manufacturing yields are high and production relatively economical. The chemical names for TNT are trinitrotoluene and trinitrotol. Other (commercial) names are Trilite, Tolite, Trinol, Trotyl, Tritolol, Tritone, Trotol, and Triton. TNT is toxic, odorless, comparatively stable, nonhygroscopic, and relatively insensitive. When TNT is pure, it is known as grade-A TNT and varies from white to pale yellow. When the proportion of impurities is much greater, the color is darker, often brown, and the chemical is known as grade-B TNT. It maybe ignited by impact, friction, spark, shock, or heat. TNT does not form sensitive compounds with most metals. The melting point varies between 80.6 °C for grade-A and 76 °C for grade-B (crude TNT). TNT does not appear to be affected by acids but is affected by alkalies (lye, washing soda, and so on), becoming pink, red, or brown, and more sensitive.

TNT is highly soluble in acetone (132 g/100 g at 25 °C) but still soluble enough in water (10 mg/100 g at 25 °C). Its vapor pressure at 25 °C is 5.8×10^{-6} Torr. The velocity of detonation is approximately 6797.04 ms^{-1} (4, 24).

In order to detonate, TNT must be confined in a casing or shell and subjected to severe pressures and/or temperatures (502.2 °C) such as from a blasting cap or detonator. In fact, U.S. Army tests on pure TNT show that when struck by a rifle bullet TNT failed to detonate 96% of the time and when dropped from an altitude of 1220 m onto concrete, a TNT filled bomb failed to explode 92% of the time.

2,4,6-Trinitrotoluene (TNT) causes liver damage and aplastic anemia. Deaths from aplastic anemia and toxic hepatitis were reported in TNT workers prior to the 1950s. With improved industrial practices, there have been few reports of fatalities or serious health problems related to its use (4).

1.5.2 RDX [Cyclonite - 1,3,5-trinitro-1,3,5-triazocyclohexane]

RDX stands for Royal Demolition Explosive or Research Department Explosive. It is also known as cyclonite, cyclotrimethylenetrinitramine, or hexogen. RDX is currently the most important military high explosive in the USA. RDX is second in strength to nitroglycerin among common explosive substances. When compressed to a specific gravity of 1.70, it has a confined detonation velocity of about 8230 ms^{-1} . RDX is used as an explosive, usually in mixtures with other explosives, oils, or waxes. It has a high degree of stability in storage and is considered the most powerful and brisant of the military high explosives. RDX is used as a base charge in detonators and in blasting caps. RDX can be used alone or with other explosives, including PETN. RDX can be mixed with plasticizers to make C-4, and the most common explosive combining RDX and PETN is Semtex. RDX forms the base for the following common military explosives: Composition A, Composition B, Composition C, HBX, H-6 and Cyclotol. Composition A consists of RDX melted with wax; in Composition B, RDX is mixed with TNT; and Composition C contains RDX blended with a non-explosive plasticizer. Pure RDX is used in press-loaded projectiles.

RDX has both military and civilian applications. As a military explosive, RDX can be used alone as a base charge for detonators or mixed with another explosive such as TNT to form cyclotols, which produce a bursting charge for aerial bombs, mines, and torpedoes. Common military uses of RDX have been as an ingredient in plastic bonded explosives, or plastic explosives which have been used as explosive fill in almost all types of munition compounds. Civilian applications of RDX include use in fireworks, in demolition blocks, as a heating fuel for food rations, and as an occasional rodenticide (4).

RDX is an explosive nitramine compound. It is in the form of a white powder with a density of 1.806 g/cc. Nitrogen content of 37.84%. The chemical name for RDX is 1,3,5-trinitro-1,3,5-triazine. The chemical formula for RDX is $C_3H_6N_6O_6$ and the molecular weight is 222.117. Its melting point is 205 °C. It is most soluble in dimethyl sulfoxide (41 g/100 g at 25 °C), in dimethyl formamide (37 g/100 g at 25 °C), and in acetone (8.3 g/100 g at 25 °C), and it is slightly soluble in water (6 mg/100 g at 25 °C). Its vapor pressure at 25 °C is 4.6×10^{-9} Torr. RDX does not sorb to soil very strongly and can move into the groundwater from soil. It can be broken down in air and water in a few hours, but breaks down more slowly in soil (4-24).

Although RDX was first prepared in 1899, its explosive properties were not appreciated until 1920. RDX was used widely during World War II because petroleum was not needed as a raw ingredient. During and since World War II, RDX has become the second-most-widely used high explosive in the military, exceeded only by TNT.

Soldiers and other workers have been exposed to RDX during its manufacture, in the field, and through the contamination of the environment. The main occupational exposure to RDX during its manufacture is through the inhalation of fine dust particles. Ingestion may also be a possible route of exposure, but it is poorly absorbed through the dermis. The greatest potential for occupational exposure to RDX occurs at ammunition plants with load, assemble and pack (LAP) operations, where workers involved with melt-pouring and maintenance operations have the greatest potential for exposures.

RDX can cause seizures in humans and animals when large amounts are inhaled or ingested. Nausea and vomiting have also been observed. The effects of long-term (365 days or longer), low-level exposure on the nervous system are not known. No other significant health effects have been reported in humans. Rats and mice that ate RDX for 3 months or more had decreased body weights and had slight liver and kidney damage. It is not known whether RDX causes birth defects in humans. It did not cause birth defects in rabbits, but did result in smaller offspring in rats. The EPA has determined that RDX is a possible human carcinogen (Class C). In one study, RDX caused liver tumors in mice that were exposed to it in the diet. However carcinogenic effects were not noted in rat studies and no human data are available (4).

1.5.3 Composition C-4 / Comp C-4 Plastic Explosive

C-4 is made up of explosive, plastic binder, plasticizer and, usually, marker or taggant chemicals such as 2,3-dimethyl-2,3-dinitrobutane (DMDNB) to help detect the explosive and identify its source. As with many plastic explosives, the explosive material in C-4 is RDX which makes up around 91% of the C-4 by weight. The plasticizer is diethylhexyl or dioctyl sebacate (5.3%) and the binder usually is polyisobutylene (2.1%). Another plasticizer used is dioctyl adipate (DOA). A small amount of motor oil (1.6%) is also added. C-4 detonates with a velocity of about $8,040 \text{ ms}^{-1}$.

C-4 is manufactured by combining RDX slurry with binder dissolved in a solvent. The solvent is then evaporated and the mixture dried and filtered. The final material is an off-white solid with a feel similar to modeling clay. A major advantage of C-4 is that it can be molded into any desired shape. C-4 can be pressed into gaps, cracks and voids in buildings, bridges, equipment or machinery. Similarly, it can easily be inserted into empty shaped-charge cases of the type used by special forces. C-4 is well known for its durability, reliability, and safety. It will not explode if hit by a bullet, punched, cut, or thrown into a fire. The only reliable method for detonation is to apply both heat and pressure, e.g. with a detonator or blasting cap. C-4 does not expire and does not become inert over time.

When a military team or a commercial demolition company employs C-4 at a demolition site, typically 3 to 5 kg (8 to 10 pounds) of C-4 are used to destroy 20 cm square steel beams.

British Military plastic explosive is referred to as *PE4*. Like C-4, it is an off-white colored solid and its explosive characteristics are nearly identical to C-4. The only difference between C-4 and PE4 is the type and proportion of plasticizer used.

Because C-4 burns slowly when it is ignited with a flame rather than detonated with a primary explosive, soldiers would sometimes during the Vietnam War era use small amounts of C-4 as fuel for heating rations while on long patrols. While many soldiers used C-4 safely in this manner, there are several anecdotes about soldiers attempting to put out the fire by stamping on it — causing it to detonate.

Michael Herr in *Dispatches*, his famous book about the Vietnam War, relates that a soldier would occasionally ingest C-4 from a claymore mine in order to be sent on sick leave. The ploy often did not work; experienced commanders knew the trick and kept the man on board. It should well be noted that current forms of C-4 incorporate a highly toxic tracer chemical which causes death if ingested (22).

1.6 ANALYSIS OF THE EXPLOSIVES

Military and industrial explosives are routinely analyzed after their production for quality control. In this area, apart from qualitative analysis, the analysis usually includes quantitation of explosives, by-products and impurities in order to meet accepted specifications. Other areas which deal with the analysis of explosives are forensic science, environmental analysis and in certain cases, toxicology.

Forensic analysis of explosives deals with the identification of unreacted explosives as well as with postexplosion identification. The identification of an unexploded explosive is carried out to prove its possession or its intended use.

In postexplosion analysis the situation is different; when an explosion has already occurred, it is reasonable that an explosive was involved. It may seem unnecessary to perform postexplosion analysis, but such analyses have the highest priority in most forensic laboratories. The reason is that information about the explosives involved can be of great assistance to the investigation. Sometimes it is not unequivocally clear whether the explosion was initiated by a high explosive or by the ignition of a fuel–air mixture (“vapor explosion”). When an explosive is identified in residues it may strongly suggest that it caused the explosion. On the other hand if no explosive is identified it may suggest that no explosive was involved (e.g. ‘vapor explosion’) but it may also be that the analysis was unsuccessful. Sometimes the results of the analysis can direct the investigator as to whether the explosion was carried out by terrorists or by criminals unrelated to terrorist activity. Certain types of explosives have been typical to terrorist groups (e.g. ‘Semtex’, especially before the fall of the ‘iron curtain’). In rare cases the type of explosive may even hint to a certain organization. Another reason to pursue postexplosion analysis is the need for law-enforcement agencies to know what materials are used by criminals or terrorists. This information may help in connecting between different cases and also to realize that some materials are not as ‘innocent’ as they seem, but are starting materials for the preparation of these explosives (e.g. acetone and hydrogen peroxide for the preparation of triacetoneperoxide (TATP)).

Another very important type of work is the trace analysis of explosives on suspects' hands, and on items and premises which may be related to suspects. Although not a postexplosion situation, the procedures used in such analyses are similar to those used in postexplosion analysis. The analysis in these cases is difficult because it usually deals with trace amounts of unreacted explosive mixed with large amounts of contaminants. The ultimate goal of a forensic analyst is to provide an expert opinion for a court of law. Wrong results may lead to a gross injustice, where innocent people can be found guilty. This dictates the need to adhere to extremely strict criteria for the safe identification of explosives (19).

1.6.1 Analytical Procedures

Naturally, a procedure for postexplosion analysis is different from the analysis of intact explosives. In the latter case the analysis is based on a normal methodology for unknown samples. The procedure may include spot tests, chromatographic methods and spectrometric methods. It is essential for the forensic laboratory to have a library of spectral data of all common explosives and related compounds and preferably also standard samples of the explosives. The analysis usually includes identification of the sample but sometimes quantitation is also required (e.g. when a common origin of samples is suspected).

Procedures for postexplosion analysis are much more complicated, including recovery techniques as well as methods of identification. Recovery methods may include microscopic examination, headspace sampling, adsorption and extraction procedures. The identification, as in many areas in forensic analysis, may start with a screening method followed by a suitable confirmation method.

The methods in a procedure may also be derived from the properties of the explosives. Different explosives have different chemical and physical properties. Some explosives are highly volatile (e.g. EGDN), some undergo easy sublimation (e.g. TATP) and some are nonvolatile (e.g. HMX). Some explosives are thermally labile and decompose when heated. Knowing the properties of the different explosives is relevant to the choice of the most suitable method for the recovery and the analysis of specific explosives. For example, analytical methods which involve evaporation of compounds (e.g. GC or GC-MS) may be unsuitable for nonvolatile explosives. Finally and not less important, the procedures used in each laboratory are influenced by the financial ability to purchase sophisticated instrumentation and by the professional skill of the staff (19).

1.6.2 Analytical Methods, Advantages and Limitations

Various analytical methods have been used for the analysis of explosives: chemical tests (based on color reaction); chromatographic methods which are used in forensic

analysis of explosives, both for separation of mixtures and for preliminary identification, such as thin layer chromatography (TLC), column chromatography, gas chromatography (GC), high pressure liquid chromatography (HPLC), capillary electrophoresis (CE) and ion chromatography (IC); and spectral methods; infrared (IR), nuclear magnetic resonance (NMR), mass spectrometry (MS), scanning electron microscopy–energy dispersive X-ray spectrometry (SEM-EDX) and X-ray diffraction (XRD). Hyphenated methods, usually on-line combinations of chromatographic and spectrometric methods (e.g. GC-MS, GC-TEA, HPLC-MS) are powerful analytical techniques which have become widely used in forensic laboratories (19).

1.6.2.1 Chemical tests

Chemical tests, also referred to as spot tests or color tests, take advantage of a color produced by a reaction between a reagent and an analyte. Some well-known color reactions (sometimes in a modified version) are used in the analysis of explosives. These color reactions are widely used by many forensic laboratories as presumptive tests, for screening and for field tests.

Some widely used spot tests are described according to the classes of explosives. Di- and trinitroaromatic compounds develop colors with some basic solutions: TNT develops a purple–brown color whereas 2,4-DNT and 2,6-DNT develop a yellowish color when reacted with KOH in ethanol (e.g. 3%). The colors developed in the reaction between polynitroaromatic compounds and bases are sometimes attributed to the formation of the so called ‘Meisenheimer complexes’. The Griess reaction is a well-established, highly specific color reaction for the identification of nitrite ions. In this reaction, nitrite ion reacts with an aromatic amine, such as sulfanilamide, in an acidic medium to form a diazonium ion. This ion is then coupled with a suitable active aromatic compound, such as *N*-1-naphthylethylenediamine, to produce an azo compound, which has a characteristic purple color. Nitrate esters and nitramines produce NO_2^- ions by the action of an alkali whereas nitrate ions produce the nitrite ions by reduction (e.g. by zinc powder).

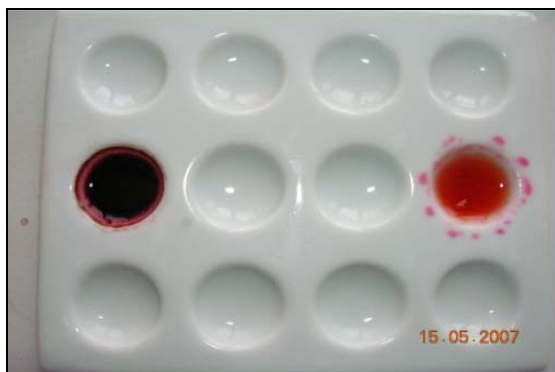


Figure 1.3 Colour tests for TNT and RDX.

Another type of spot test is based on the oxidation of a reagent by an explosive or an oxidizing constituent of an explosive mixture. Diphenylamine develops a blue color when reacted with TATP; aniline sulfate develops a blue color when reacted with chlorates in acidic medium.

In general, the sensitivity of many spot tests used in the analysis of explosives is in the microgram range. Spot tests are fast, inexpensive, simple, do not need instrumentation and may be performed by technicians in the field.

Spot tests cannot be the basis for reliable identification. At best they may strongly indicate that the analyte belongs to a certain class of compounds (e.g. nitroaromatic) (19).

1.6.2.2 Thin layer chromatography (TLC)

The sensitivity of TLC is generally in the microgram to submicrogram range depending on the type of visualization used. TLC is widely used for the analysis of explosives in forensic laboratories.

Although there are many reports describing different TLC systems for the separation of explosive compounds, no single system has been reported to separate all organic explosives. Therefore a combination of several systems is routinely used, such as: (1) 1,2 dichloroethane:acetonitrile (90:10,v/v); (2) trichloroethylene:acetone (80:20,v/v);

(3) petrol ether (b.p. 60–80):ethyl acetate (90:10, v/v), (4) toluene. A TLC plate, sprayed with the reagents deteriorates quickly; therefore it is recommended that documentation by camera or scanner is carried out immediately after spraying.

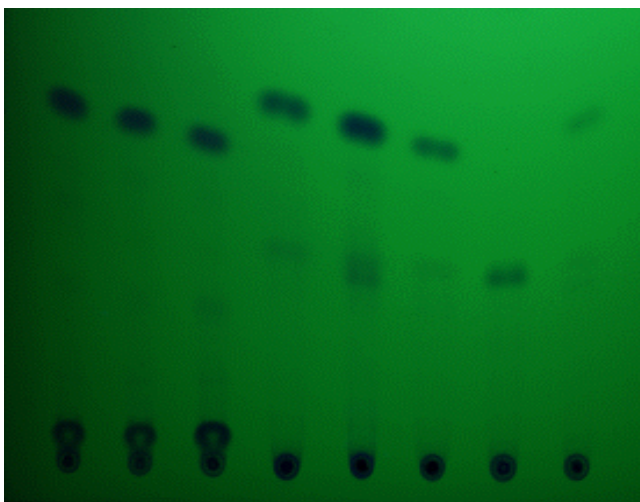


Figure 1.4 Some military explosives separated by a TLC system.

TLC is a simple, inexpensive and fast method allowing analysis of several samples in a single run. However, it is considered a low-resolution method and in addition, separation is susceptible to contaminants (when present in high amounts). It must be emphasized that identification cannot be based on TLC only and must be confirmed by other methods (19).

1.6.2.3 Gas chromatography (GC)

Modern GC utilizes capillary columns in which the stationary phase is chemically bonded to the fused silica wall. A sample, dissolved in a suitable solvent, is injected into a heated injection port. The compounds are evaporated and pushed along the coated column, usually at elevated temperatures, towards a detector by the flow of a mobile phase (carrier gas, e.g. helium). Different compounds, with different affinities to the stationary phase, are separated, usually with a good resolution. GC is also a suitable method to perform quantitative analysis.

A typical column used in the analysis of explosives is the nonpolar diphenyl (5%)–dimethylsiloxane (95%) copolymer (e.g. DB-5, HP-5, SP-5), 25 µm coating, 15 m long. Typical GC conditions are: injector temperature 170 °C, column temperature programmed from 50 °C to 250 °C at a rate of 25 °C min⁻¹. GC is a simple, high-speed and high-resolution method that is very suitable for the analysis of nitroaromatic explosives. Some loss in sensitivity is observed when analyzing thermally labile compounds (e.g. some nitrate esters and nitramines). Sometimes decomposition products are produced in the injector or in the column. Nonvolatile explosives (e.g. HMX, inorganic compounds) cannot be analyzed by GC. The organic peroxides TATP and HMTD can be analyzed by GC (19).

Several common detectors are used in GC, some of them are explained below.

Flame ionization detector (FID)

FID, a very common detector in GC used in forensic laboratories, is less common in the analysis of explosives. This is mainly due to a decreased sensitivity towards some explosives which have a high O/C and N/C ratios in their molecules (e.g. NG).

Electron capture detector (ECD)

In ECD the eluent from the GC column passes through a slow-electron beam. An analyte containing electronegative atoms such as nitrogen, ‘captures’ electrons from the constant electron current, producing a signal by decreasing this current. Sensitivity is usually in the picogram range. ECD is quite selective, as it is highly sensitive towards nitrogen-containing compounds but insensitive to hydrocarbons.

Chemiluminescence detector (thermal energy analyser (TEA))

It is a selective detector against nitro and nitroso compounds. Sensitivity is in the picogram range (19). (Detailed information is given in part 1.7.2.)

1.6.2.4 High performance (pressure) liquid chromatography (HPLC)

In HPLC the stationary phase is often a ‘reversed phase’ type, such as octadecylsiloxane. The mobile phase is a solvent or a mixture of solvents which is pumped into the column at relatively high pressure, usually at room temperature.

HPLC may be also used in a preparative mode by collecting the desired fraction and confirming its identity by other methods (19).

Different detectors can be used with HPLC like ultraviolet and diode array and electrochemical detectors. Selectivity is low for HPLC but sensitivity is rather high, in nanogram range.

1.6.2.5 Ion chromatography (IC)

This method utilizes ion-exchange resin as the stationary phase and a solution of salts as the mobile phase. The functional group attached to the stationary phase in anion analysis is usually a quaternary ammonium ion and in cation analysis the exchange function is usually a sulfonate ion.

Some instruments utilize a suppressor reaction which takes place in a second column (suppressor column) situated after the ion-exchange column. This enhances the sensitivity by lowering the background noise of the detector. Sensitivity is in the nanogram range. Most widely used detector systems for IC are; conductivity and UV/VIS (19).

1.6.2.6 Capillary electrophoresis (CE)

Chromatography is performed on a capillary column, immersed at its two ends in a buffer solution. Silanol (Si-OH) groups attached to the interior wall of the capillary are ionized to negatively charged silanoate (Si-O⁻) groups at pH values greater than three, leading to accumulation of solvated cations. Application of an electric field (e.g. 10–25 kV) on the capillary results in the migration of the solvated cations towards the cathode, generating electro-osmotic flow (EOF). Analytes introduced to the capillary column move in different directions and with different mobilities; negatively charged species move towards the anode, positively charged species move towards the cathode and neutral compounds move with the EOF. Since the EOF is usually faster than the migration velocity of the anions, all species are swept towards the detector which is usually situated near the cathode.

Compounds with different mobilities are usually separated with a high efficiency because the profile of the advancing mobile phase is flat, in contrast to its parabolic profile in other separation techniques (e.g. GC and HPLC). Detection is usually by UV where the capillary itself serves as the cell. In CE it is possible to analyze different classes of compounds: organic and inorganic, neutral and ionic. All these compounds can be analyzed by changing the buffer. Sensitivity is in the picogram range.

The most suitable method for the analysis of ions is capillary zone electrophoresis (CZE) which is applied in some laboratories as a confirmation method for results obtained in IC (19).

1.6.2.7 Infrared spectrometry (IR)

Molecules irradiated by infrared light (e.g. $4000\text{--}450\text{ cm}^{-1}$) absorb energy at certain wavelengths which correspond to intramolecular vibrations. Absorbing bands in the range $4000\text{--}1300\text{ cm}^{-1}$ are usually associated with specific functional groups whereas absorption bands below 1300 cm^{-1} are usually characteristic of the molecule as a whole. Therefore the region below 1300 cm^{-1} is sometimes called the 'fingerprint' region of the IR spectrum. Modern IR instruments, used by most laboratories are Fourier Transform IR (FTIR). IR may be used to identify a pure compound by comparing its spectrum to the spectrum of an authentic sample. Mixtures may require chemical separation of components before the analysis in order to obtain IR spectra of the pure components. Sensitivity is usually in the microgram range; detection limit may be lowered by using microscope FTIR ($10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$) (19). Some examples of standard explosives' IR spectra are given below.

Symmetric and asymmetric stretching vibrations of the NO_2 group give rise to two distinct absorption bands, which have a highly diagnostic value. In nitroaromatic compounds these bands appear at $1390\text{--}1320\text{ cm}^{-1}$ and $1590\text{--}1510\text{ cm}^{-1}$, respectively. They can be clearly observed in the IR spectrum of 2,4,6-TNT (Fig. 1.5). The spectra given below have been obtained by the analysis of pure explosives with a Perkin Elmer Spectrum 100 FTIR spectrometer.

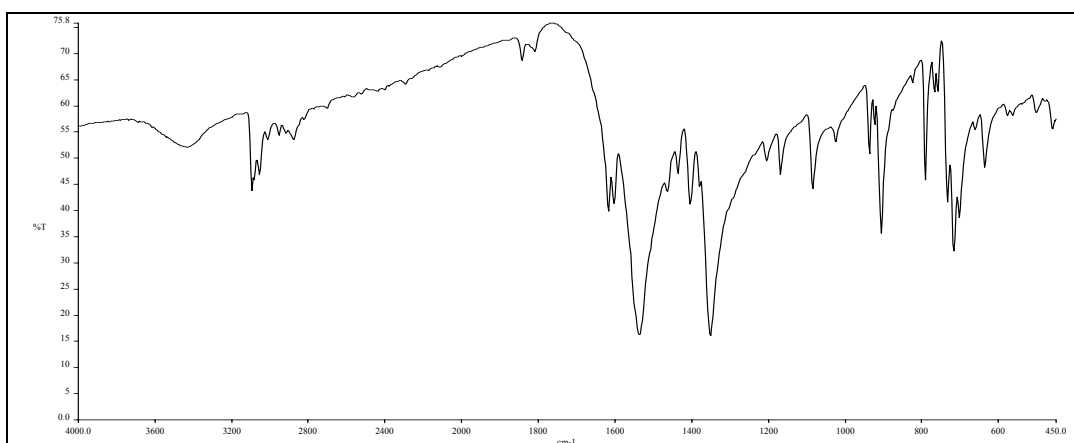


Figure 1.5 IR spectrum of 2,4,6 TNT.

The two NO_2 stretching vibrations in nitrate esters appear at $1285\text{--}1270\text{ cm}^{-1}$ and $1660\text{--}1640\text{ cm}^{-1}$, respectively, as can be seen in the IR spectrum of PETN (Fig. 1.6).

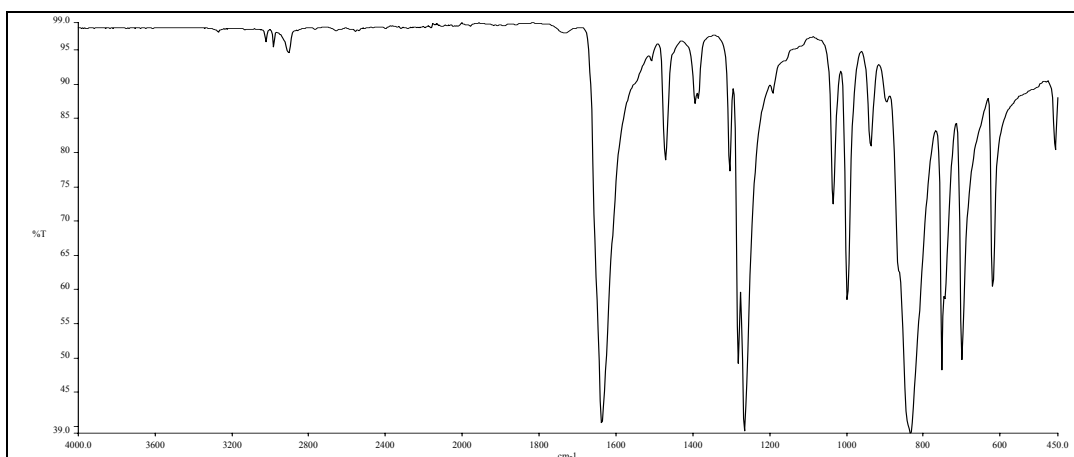


Figure 1.6 IR spectrum of PETN.

The two NO_2 stretching vibrations in nitramines appear at $1310\text{--}1270\text{ cm}^{-1}$ and $1590\text{--}1530\text{ cm}^{-1}$, respectively, as can be seen in the IR spectrum of RDX (Fig. 1.7).

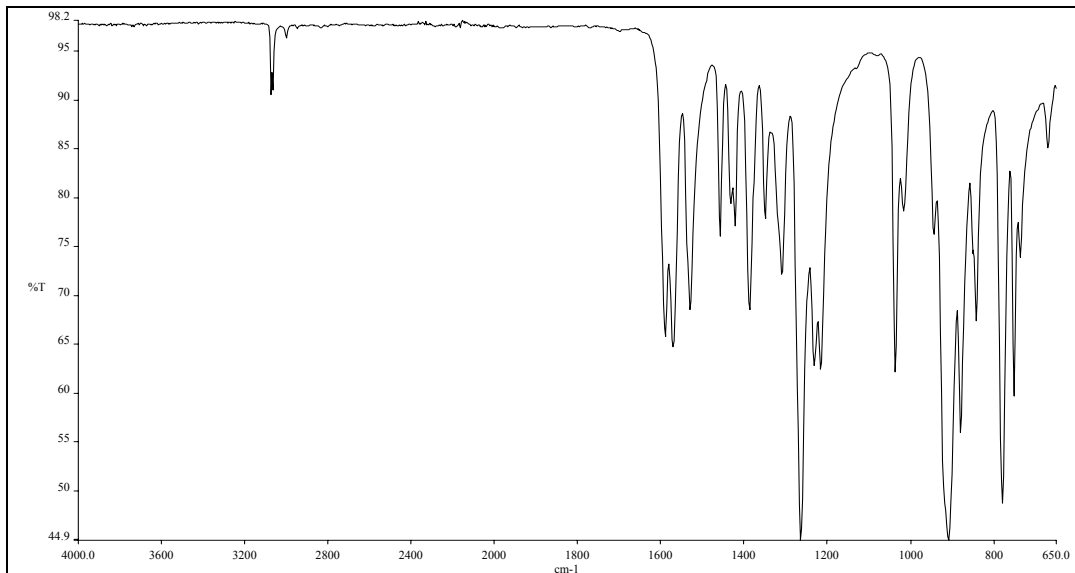


Figure 1.7 IR spectrum of RDX.

An IR spectrum of TATP (which lacks nitro groups) is shown in Fig. 1.8.

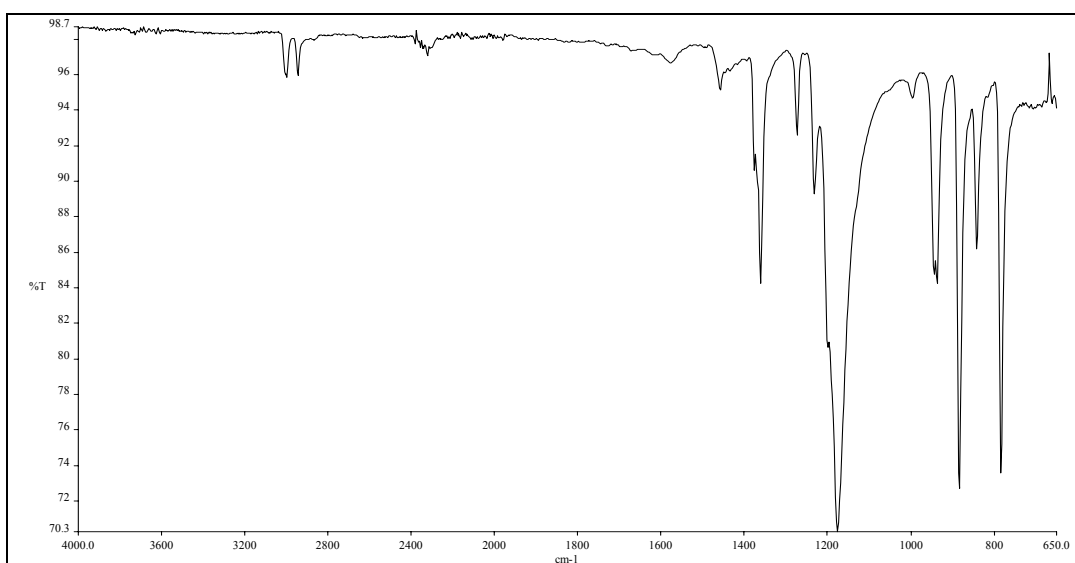


Figure 1.8 IR spectrum of TATP.

Inorganic anions related to explosives also have highly characteristic absorption bands. Chlorates absorb at $980\text{--}910\text{ cm}^{-1}$, $630\text{--}615\text{ cm}^{-1}$ and $510\text{--}480\text{ cm}^{-1}$ (Figure 1.9). Nitrate ions absorb at two bands: $1380\text{--}1350\text{ cm}^{-1}$ and $840\text{--}815\text{ cm}^{-1}$ (Figure 1.10).

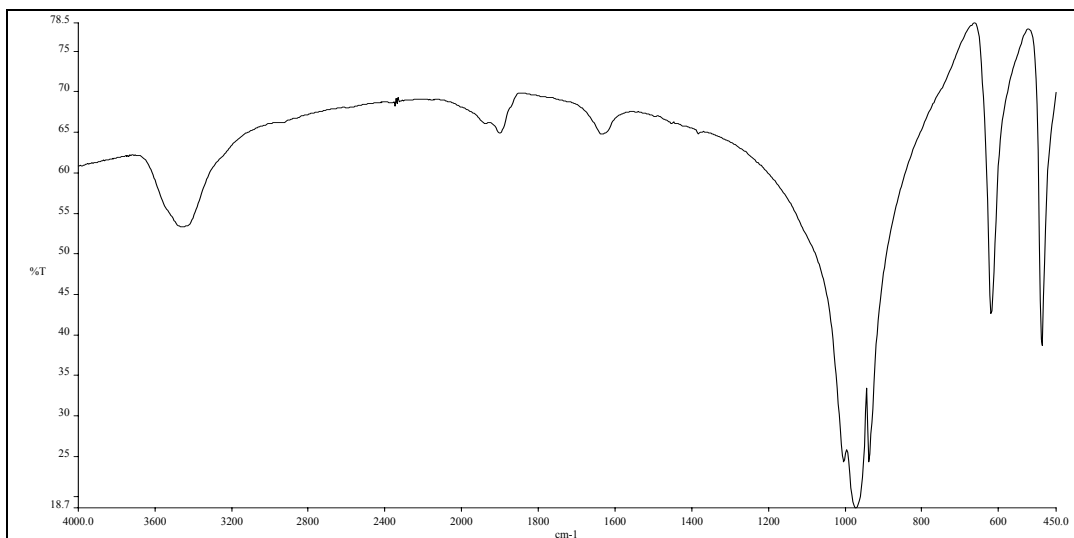


Figure 1.9 IR spectrum of KClO₄.

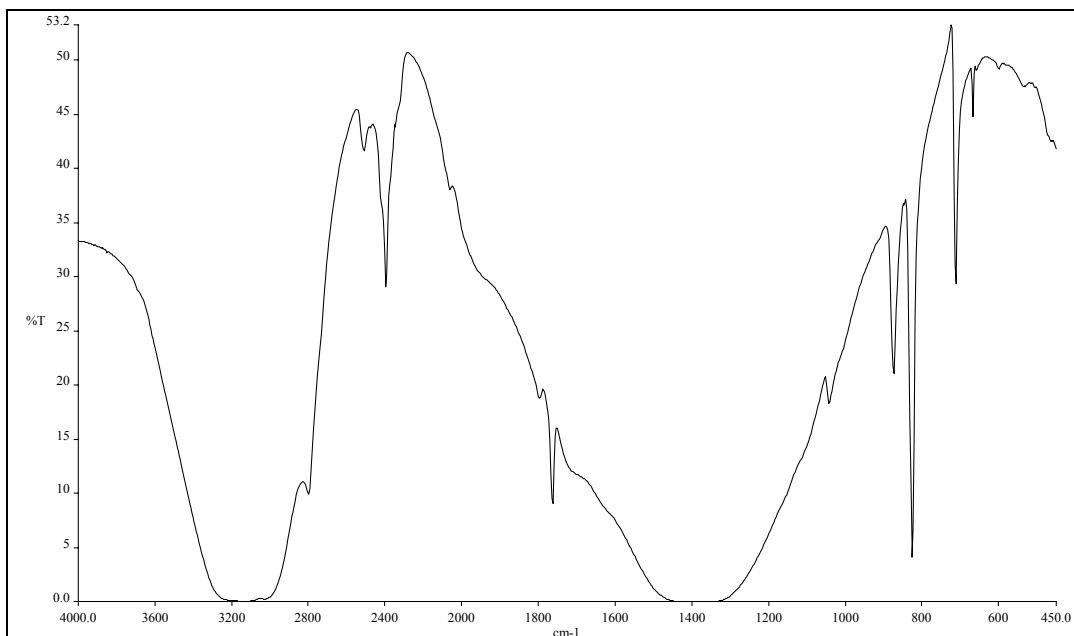


Figure 1.10 IR spectrum of NH₄NO₃.

1.6.2.8 Nuclear magnetic resonance (NMR)

Nuclei, whose nuclear spin is not zero (e.g. ^1H , ^{13}C , ^{14}N) behave as small magnets. When such nuclei are put in an external magnetic field they may align with the magnetic field, having a low-energy orientation, or against it, having a high-energy orientation. Transition between these two energy levels takes place by absorption of suitable radio frequency (RF) radiation called the resonance frequency.

The energy absorbed at such transition depends on the chemical environment of the nucleus; thus, various protons in a molecule resonate at different frequencies. The exact amount of energy absorbed by a specific proton is expressed by its 'chemical shift'. Different protons in the molecule usually have different chemical shifts. Scanning RF while keeping the magnetic field constant, or scanning the magnetic field while keeping the RF constant will result in an NMR spectrum. The NMR spectrum is highly characteristic and may be used for the identification of a compound by comparing its spectrum to that of an authentic sample. NMR is especially useful for structure elucidation of unknown samples even when no authentic sample is available. This is done by correctly interpreting the different signals in the spectrum, leading, often by combination with other methods, to a complete structure elucidation. Most work in NMR has been done on protons producing databases of chemical shifts and spectra. Sensitivity of NMR is usually in the micrograms to milligrams range. NMR has not been routinely used in the forensic analysis of explosives (19).

1.6.2.9 Mass spectrometry (MS)

In this technique a compound is introduced into an ion source where it is ionized to form molecular and fragment ions according to its structure. The ions pass through an analyzer (e.g. magnet, quadrupole or ion trap) which separates the ions according to their mass to charge ratio (m/z). The ions are detected and recorded, producing a mass spectrum. A mass spectrum often reflects the structure of a molecule. It is usually highly specific and is often referred to as a 'fingerprint' of the molecule. Identification of a compound by its mass spectrum is therefore highly reliable.

In addition, a mass spectrum can be used for structure elucidation of unknown compounds. As it is highly reliable as well as highly sensitive, it is considered to be an excellent method for the identification of organic compounds. Sensitivity usually lies in the picogram to nanogram range depending on the operation mode.

Introduction techniques include inlets for gases and liquids (usually based on needle valves or gold leaks) and direct insertion probe, also known as ‘solid probe’ for solids. Solid probe is usually used for the insertion of nonvolatile compounds, such as HMX, and is usually unsuitable for the analysis of mixtures. However, the most common introduction techniques are the on-line combination with GC (GC-MS) and HPLC (LC-MS). LC-MS requires an interface between high output of liquids and sometimes nonvolatile buffers, and the high vacuum of the MS. This enables analysis of nonvolatile compounds that cannot be analyzed by GC-MS (19).

The common ionization methods in MS are;

- Electron ionization (EI)
- Chemical ionization (CI)
- Negative ion mass spectrometry
- Thermospray ionization
- Electrospray ionization (ESI)

1.6.2.10 X-Ray diffraction spectrometry (XRD)

X-ray diffraction, or X-ray powder diffraction (XRPD), utilizes X-ray radiation on crystalline organic and inorganic samples. The rays are diffracted in a pattern determined by the position, arrangement and size of the constituents of the crystal. Scattered photons, which may undergo subsequent interference, lead to a characteristic diffraction pattern. The pattern is characteristic for a specific crystalline powder and may serve as a ‘fingerprint’ of this powder. Identification of a powder may be carried out by comparing its spectrum to a spectrum of an authentic sample. Data bases of diffractograms are commercially available and it is also possible to analyze and identify multiphase crystalline mixtures, qualitatively and

quantitatively. Sensitivity is usually in the microgram to milligram range. XRD is mainly used to analyze crystalline powders of inorganic explosives and explosive mixtures. The advantage of this method over IC or CE is the identification of a compound as a whole; in the latter methods anions and cations are identified separately. XRD instruments are expensive and require expert operators (19).

1.6.2.11 SEM/EDX

This technique enables examination and morphological characterization of surfaces of organic and inorganic samples. The sample is bombarded by a high-voltage (e.g. 25 kV) electron beam. An interaction between the sample and the electron beam causes emission of radiation in the X-ray range typical of an element. EDX permits high-speed qualitative and quantitative elemental analysis according to the intensity of the energy emitted by the sample. Elements with the atomic number 11 (sodium) and higher may be analyzed by this technique. Special light-element detectors enable the identification of elements with the atomic number 5 (boron) and higher. This has relevance to the identification of explosive compounds which often contain nitrogen atoms. SEM/EDX is suitable for the identification of metals present in primary explosives such as lead azide or mercury fulminate. SEM/EDX instruments are expensive and require expert operators (19).

Table 1.1 Advantages and limitations of the analytical methods used in the forensic analysis of explosives.

Method	Sensitivity	Advantages	Limitations	
Color Test	µg range	Fast, inexpensive, simple, no instrumentation.	Can not be the basis for reliable identification, only address to a certain chemical group.	
TLC	µg range	Simple, inexpensive, fast, analysis of several samples in a single run.	Low resolution, susceptible to contaminants, needs additional confirmation methods.	
	ECD	pg range	Quite selective, highly sensitive against nitrogen-containing compounds.	Insensitive to hydrocarbons.
	TEA	pg range	Highly selective against nitro and nitroso compounds.	Impossible to detect other than nitro/nitroso containing compounds.
HPLC	ng range (UV det.)	High sensitivity, analysis at room Temp., analysis of both organic and inorganic samples.	Low selectivity.	
IC	ng range	Determination of inorganic ions.	Not applicable to organics.	
CE	pg range	Possible to analyze organic and inorganic, neutral and ionic subs.	Needs buffer change for different groups of subs.	
IR	µg range	Gives finger print spectra.	Mixtures may require separation before analysis.	
NMR	µg - mg range	Highly characteristic spectrum, allows structure elucidation.	Not so common in forensic analysis.	
MS	pg - ng range	Highly reliable and sensitive, identification of organic compounds.	As it is widely used for different purposes contamination will occur.	
XRD	µg range	Fingerprint spectrum of a crystalline powder.	Limited to inorganic explosives, expensive.	
SEM/EDX		Identification of metals and elements in inorganic mixtures.	Only elemental analysis, expensive.	

1.7 METHODS USED IN THIS STUDY

1.7.1 GC-MS

The technical possibility of connecting a highly efficient separation method (GC) with a highly sensitive and reliable identification method (MS) was a breakthrough

in analytical chemistry. GC-MS enables the separation of highly complex mixtures with the subsequent rapid identification of each of the separated components. Therefore GC-MS is the method of choice in organic analysis in many forensic laboratories. In modern GC-MS instruments, the GC capillary column end is placed near the ion source without the need of an interface, thus enhancing instrument efficiency. As mentioned above some explosives are easily analyzed by GC (hence by GC-MS) whereas with others some difficulties are encountered (19).

1.7.2 GC-TEA

In this method the eluent from the GC column passes through a furnace which pyrolyzes the compounds at elevated temperatures (e.g. 500°–900°C). Nitro and nitroso compounds produce nitrogen oxide which is then allowed to react with ozone to produce nitrogen dioxide in an excited energy level. Decaying of the excited NO₂ to its ground state is accompanied by emission of light at the UV region which is monitored by a suitable detector. Sensitivity of a TEA detector is in the picogram range. Commercial Instruments e.g. ‘Thermal Energy Analyser (TEA)’ are available and are very sensitive and highly specific for the analysis of nitro-containing compounds (though there have been some reports of signals from compounds without nitro or nitroso groups).

GC-TEA is suitable for the analysis of postexplosion residues mainly because most contaminants having no nitro groups, are not observed. GC-TEA is therefore widely used in the forensic analysis of explosives. The identification and characterization of the explosives are done by comparing the retention time of an unknown sample with the standard explosives’ retention times. The TEA detector is expensive, and its use is limited to the analysis of nitro-containing explosives. (19)

GC-TEA that is used in this study is a modified one, in which the porcelain tubes in pyrolyser and interface were replaced with a quartz tube and capillary column passes directly inside this tube to the ozone reaction chamber. This was done to minimize the gas leaks at column conjunction points.

1.8 POSTEXPLOSION AND TRACE ANALYSIS OF EXPLOSIVES

Postexplosion analysis is normally based on the identification of the unreacted explosive which “survived” the explosion. Usually only trace amounts of the unexploded explosives are present. Therefore the crucial step in postexplosion and trace analysis of explosives is the sample preparation step. Much work has been done to establish a methodology for the collection of exhibits according to their distribution around the bomb site. Unfortunately, no such methodology has been proved to be efficient and it seems that luck plays an important role in collecting the “right” exhibit. Attempts to overcome this problem have been made by screening exhibits at the explosion scene, using kits based on color tests or “sniffing” devices. Sniffing instruments are usually based on chemiluminescence detection or ion mobility spectrometry (IMS). The results of these preliminary tests are of indicative value only and cannot be regarded as an identification.

A major problem in postexplosion work is the potential contamination which occurs either at the stage of collecting exhibits or during the subsequent laboratory analysis. Anyone collecting exhibits should also submit swabs of himself, taken before the sampling, to reveal the possibility of cross contamination. These swabs should be sent to the laboratory, considered as “blank samples”, and processed by the same procedures used for the exhibits (19).

1.8.1 Visual Examination

It is highly recommended that the analysis of an exhibit begins with visual examination. As is usual in routine forensic work, nondestructive methods should be used first in order to extract information that may be lost after the use of destructive methods. Such information may include the morphological appearance of a particle which may connect a suspect to the scene if an identical particle is found in a suspect's possession. The naked eye or a low-power stereoscope may be used for the physical separation of particles such as black powder, smokeless powder or material not consumed in the blast (19).

1.8.2 Vapor Analysis and Adsorption on Solid Phase

Volatile explosives such as TATP or NG may be detected in vapors of an exhibit by direct headspace analysis. Adsorption of explosives from the vapor phase may be carried out at the scene (or in the laboratory) by passing the vapors through a suitable adsorbent material such as Amberlite XAD-7[®] or Tenax[®]. Explosives adsorbed on such resins may be eluted by a suitable solvent and then analyzed (19).

1.8.3 Organic Extraction

Organic extraction is usually performed with acetone, which is the most commonly used solvent for explosive compounds. The solvent is then evaporated, under a stream of nitrogen rather than by heating, in order to minimize evaporation of volatile explosives. Acetone also dissolves nonexplosive materials from the debris such as oily compounds (e.g. hydrocarbons, fatty acids), plasticizers (e.g. phthalates) and some polar compounds. These materials may coelute with the explosives in chromatography and even change the t_R of the explosives. For example, contamination of the injection port, column and ion source in GC-MS results in decrease in sensitivity and resolution. To minimize extraction of oily compounds, ethanol/water mixtures rather than acetone may be used to swab exhibits (19).

1.8.4 Cleaning Procedures

In order to reduce the amounts of contaminants in the extract, cleaning procedures may be carried out prior to the analysis. They include liquid/liquid extraction, preparative TLC or HPLC, and solid phase extraction (SPE). SPE employs a suitable adsorbent packed in a column or in commercially-available cartridges. The extract is mounted on the adsorbent; starting with nonpolar eluting solvents (e.g. hexane), the hydrophobic compounds (e.g. hydrocarbons) are washed out first and the explosives are eluted later, when more polar solvents are used (19).

1.8.5 Analysis

Analysis of a completely unknown compound often starts with screening tests (e.g. TLC, HPLC) followed by a suitable confirmation method (e.g. MS). In addition to serving as a screening method, GC-TEA, being highly specific, may also serve as a confirmation method.

1.8.6 Aqueous Extraction and Analysis

Water is used to extract hydrophilic, water-soluble compounds. The dried extracts are then subjected to further analysis. Inorganic explosive-related anions may be detected by spot tests and confirmed by IC or CE. IR may also be used for the identification of these anions and other water-soluble compounds such as sugars. Unequivocal identification of some explosive-related inorganic anions may be carried out by GC-MS. Nitrate, nitrite, thiocyanate and sulfide anions are derivatized by a suitable reagent such as pentafluorobenzylbromide (PFBB), to produce volatile compounds which are easily analyzed by GC-MS (19).

1.9 LITERATURE SURVEY

The literature contains many books, journals and papers about the explosives and detection and identification of explosives. Also internet is an important source in these topics. As the explosives are compounds or mixtures of compounds many of the analytical systems can apply to the analysis of the explosives. Many examples of the application of analytical systems to the analysis of explosives exist in the literature.

The literature search has started with the theory of explosives and forensic analysis of explosives. There were a plenty of books, papers and internet sources about this subject in the literature. Some of them are used in the introduction part of this study. In addition to the introduction part of the study, the paper of Moore (2004) who prepared a review of the literature about the explosives and the instrumentation principles for the analysis of explosives [14], is a good source for a literature search.

Due to the large volume of the literature about the explosives it was needed to use certain terms related to this study to specify the search and make it's scope narrower. Firstly it was concentrated specifically on GC-MS and GC-TEA and related methods in forensic analysis of the explosives. Some of the results are given below. These studies were used in optimization of the method parameters in the study.

Jimenez et al. (2004) published a paper to provide a comprehensive review of explosive detection by chemiluminescence through a summary of the related literature for the years 1999-2004. In the study, properties of chemiluminescence in relation to explosives and a summary of related studies were given [7].

McAvoy et al. (1999) studied the analysis of explosives using packed-column supercritical fluid chromatography with atmospheric pressure chemical ionisation mass spectrometry. It was concluded that the system overcomes the thermal decomposition problem of explosives with GC, but it could not offer the low sensitivity of GC-TEA and GC-ECD with a sensitivity value of 100 ng [13].

Yinon (2003) studied the analysis of explosives by LC-MS with both Electrospray (ESI) and Atmospheric Pressure Chemical Ionization (APCI). It was found that ESI is the most suitable ionization mode for nitramine explosives (LOD; 0.04 µg/l) and APCI is better for nitroaromatic explosives (LOD; 5pg) [23].

Koyuncu et al. (2005) studied the examination of organic explosives using Ion Mobility Spectrometry (IMS). The study involved the analysis of standard explosives and postexplosion samples. IMS provided lower detection limits, lower injection volumes and shorter analysis times than GC-FID and GC-MS [11].

Kolla et al. (1993) studied the stability of explosives traces on different supports. Analysis were performed with LC-diode array detector and GC-TEA. They stated that in order to avoid the loss of explosive traces due to evaporation it is best to freeze the dry samples and perform the analysis as soon as possible, they also stated that UV irradiation did not effect the recovery of the explosives [10].

Kirchner et al. (2007) studied the analysis of high explosives with Fast GC-ECD and GC-MS. In the study optimization of the parameters like inlet temperature; which prevents thermal decomposition of the analytes and serves the highest response, column temperature program; that renders the best separation of the sample in the least time, and EI ionization voltage; which provides the best fragmentation of the analytes and the highest ion abundances, were performed. An LOD value of 0.19 µg/ml was observed in the study [8].

After searching for the methods it was searched for the determination of explosive residues in postexplosion samples and especially in soil samples. Soil was chosen because it is easy to handle and some organics exist in soil thus their peaks can be observed with GC-MS while analysing for explosive residues, which will permits the comparison of the selectivities of GC-MS and GC-TEA. Many examples of determination of the explosive residues in soil samples exist in the literature, some of them which have utilized in sample preparation step of the study are given below.

Byall (2001) prepared a report for Interpol Forensic Science Symposium, he gave a review of literature about detection and identification of explosive residues for the years 1998-2001 [3].

Kolla (1994) studied the application of HPLC, GC-TEA and IC to the trace analysis of explosives. He has optimized the injection temperature parameter and decided on the temperature 170 °C which is in the range between optimum evaporation and the beginning of decomposition for the most difficult explosives (PETN and RDX). He concluded that with high selectivity against nitro and nitroso compounds and high sensitivity GC-TEA is the method of choice for the analysis of organic explosives. Its selectivity makes it possible to study with contaminated samples.

On the other hand confirmation analysis are necessary for unidentified peaks. Also, he stated that HPLC has the advantage of ability of separation of dirty samples due to stability of its column and eluents. It is possible to analyse the explosives that can not be evaporated without decomposition such as HMX. Analysis can be done at room temperature without decomposition of the explosives. But it has low resolving

power and poorer sensitivity than TEA. The detection limit for an explosive oil with GC-TEA was given as 0.1 µg/ml [9].

Zitrin (1986) studied the postexplosion analysis of explosives by mass spectrometry. The study involved the application of LC-MS, GC-MS, MS-MS and NMR techniques to post explosion analysis and their comparison. Also the EI and CI modes are compared. An LOD value of 10 ng was observed with GC-MS and it was concluded that the days of “TLC only” for organic explosives was over [26].

Bowerbank et al. (2000) studied the detection of nitroglycerin and other explosives with solvating gas chromatography coupled to a TEA detector. Possibility of programming the pressure and the temperature of the mobile phase provides additional advantage of high solvating power. Study was performed with explosive containing soil samples. The explosives were extracted with acetonitrile after shaking the solvent-soil mixture in ultrasonic bath. SGC-TEA response was obtained in the low picogram range and that means higher sensitivity than SGC-FID [2].

Walsh (2001) studied the determination of nitro group containing explosives in soil by GC-ECD. 2 g of soil sample was mixed with 10 mL of acetonitrile and extracted for 18 h in a cooled sonic bath. Method detection limits were observed in the low µg/kg range. It was stated that GC-ECD offered the advantages of lower detection limits and improved chromatographic resolution over standard HPLC system [20].

Hewitt et al. (2001) studied the determination of explosives in soils with GC-Thermoionic detector system. The soil samples were extracted with different volumes of acetone by shaking the soil-acetone slurry for 30 seconds or longer manually. The observed data showed that the on-site GC-TID provided accurate results [6].

Sharma et al. (2005) studied the characterization and identification of explosives and explosive residues using GC-MS, FTIR Microscope and HPTLC. The explosives were identified and characterized with Microscope and GC-MS and quantitative analysis were performed using HPTLC [16].

Mayfield et al. (2006) studied the analysis of explosives in soil using Solid Phase Microextraction (SPME) and Gas Chromatography. The study exhibited the advantages of SPME technique as a sampling method [12].

Halasz et al. (2002) performed a study to describe the use of supercritical carbon dioxide (SC-CO₂), acetonitrile (MeCN) (US Environmental Protection Agency Method 8330) and solid-phase microextraction (SPME) for the extraction of explosives and their degradation products from various water, soil and plant tissue samples for subsequent analysis by either HPLC–UV, capillary electrophoresis (CE–UV) or GC–MS [5].

1.10 OBJECTIVES OF THIS STUDY

In recent years there is a serious increase in bombing attacks against police and military forces and also against the public places in Turkey. Forensic investigations of these cases are carried out by the Police and Gendarme Criminal Laboratories. Criminal Police Laboratories are using the highest technology instruments and techniques and also methods that FBI, English, French and German Forensic Laboratories are using.

Generally each terrorist group uses a certain group of explosives and a certain bombing style. These facts are known by intelligence services and the results of forensic laboratories are used by them to reach the criminals. Actually finding the explosive material does not mean finding the criminal, but it is a good starting point for investigations. Thus the results of forensic analysis play a crucial role in determining the criminal. Also these results affect the verdict in a court of law. For the right terrorist or the criminal to be arrested and punished, forensic analysis have to be correct and exact.

As mentioned above generally for post explosion cases the work is difficult in forensic analysis. Initially the correct portion of the evidence which has the probability of containing traces of the explosive, should be sent to the laboratory. Then experts at the laboratory have to apply the right procedure for the analysis.

They should prepare the samples to analyse with minimum loss in amount and with minimum contamination. As the residues composed of different organic and inorganic materials, usually it is difficult to get an extract that is free of contamination. Thus the instrumental techniques should be selective enough to minimize the effect of contaminants. So it is very important to use a well established method in such cases. As can be seen from the literature there are lots of different sample preparation procedures and also different instrumental methods. In this study these examples are used to remodel the previously used methods.

In this work the soil samples collected after an explosion were analysed in order to detect the traces of explosives used. Two most encountered nitro group containing explosive materials in bombing cases in Turkey, TNT which is mostly used in mines and C-4 which is composed of RDX (as explosive material) and some other plasticizers, were used for this study. The analysis were performed with GC-MS and GC-TEA which are regarded as the most reliable and sensitive methods. In literature there are many examples of related studies that has used both instruments. GC-MS is the most widely used instrument in forensic laboratories and GC-TEA is a highly selective instrument against nitro-nitroso group containing explosives.

This study was done to see the efficiency of analytical methods in analysing the explosion residues in order to detect the explosive material. After an explosion in soil, there will be many organic contaminants together with explosive traces. As a foresight these contaminants with the plasticizers in C-4 would cause some problems during analysis with GC-MS but not with GC-TEA. TNT as being a pure explosive would be easier to detect. This study was also done to compare the results that obtained at each instrument to see this fact. It was also thought that while doing optimizations for the instrumental analysis, some modifications and improvements can be done in sample preparation step and method parameters of the previously used methods with utilizing from the literature.

CHAPTER 2

EXPERIMENTAL

2.1 CHEMICALS AND SAMPLES

2.1.1 Standard Materials

- TNT and C-4, supplied from Mechanical and Chemical Industries Corporation (MKE), the quality control tests were performed and certified by MKE.
- Acetone (%99.8), supplied from Merck.
- All the other reagents used in this study are of analytical reagent grade.
- Double distilled water is used for cleaning.

2.1.2 Soil Samples

Soil samples used in the study were collected from the explosion points where 100 grams of TNT and C-4 were detonated by Bomb Disposal Experts. The circular areas ($r \approx 30$ cm) around the explosion points were divided into four parts and the soil samples were collected from these regions in 1 hour, 1 day, 1 week and 2 weeks times after detonations and weighed amount of these soils were used as the laboratory samples for analysis.

2.2 INSTRUMENTS

2.2.1 GC-MS

The GC-MS system was Agilent 6890 Gas Chromatograph coupled to Agilent 5975 Inert XL Mass Selective Detector (Fig. 2.1). The optimized method parameters are shown in Table 2.1.



Figure 2.1 The GC-MS System used in the study.

Table 2.1 Optimized GC-MS Parameters.

Column	15 m – 0.25 mm ID – 0.25 μ m (film thickness) (HP-5MS)
Inlet Type	Splitless
Injection Port T.	170 °C (250 °C for TNT)
Carrier gas	Helium
Column Parameters	Constant Pressure Front Detector (MS) Pressure: 10.00 psi Flow: 2.0 ml/min Speed: 73.6 cm/sec
Oven	Initial T: 80 °C Initial Time : 2 min Ramp: 15 °C/min Final T: 300 °C Hold: 1 min
Scanning range	40 – 400 amu
MS Transfer Line T	280 °C
MS Source T	230 °C
MS Quad T	150 °C
Solvent Delay	3.00 min
Injection Volume	1 μ l (Autosampling)
MS Voltage	70eV
Ionization Type	EI
Analyser	Quadrupole

2.2.2 GC-TEA

The GC-TEA system was Agilent 6890 Gas Chromatograph coupled to Thermo Orion TEA 610, TEA Analyzer Detector (Fig. 2.2). The optimized method parameters are given in Table 2.2.



Figure 2.2 The GC-TEA System used in the study.

Table 2.2 Optimized GC-TEA Parameters.

Column	15 m – 0.25 mm ID – 0.25 μ m (film thick.) (HP-5)
Inlet Type	Splitless
Injection Port T.	170 °C
Carrier gas	Helium
Column Parameters	Constant flow Front Detector (TEA) Pressure: 43.51 psi Flow: 14.0 ml/min Speed: 186 cm/sec
Oven	Initial T: 50 °C Initial Time : 1 min Ramp: 10 °C/min Final T: 200 °C Ramp: 25 °C/min Final T: 250 °C Hold: 1 min
Interface T- Pyrolyser T	250 °C – 800 °C
Injection Volume	1 μ l (Autosampling)

2.3 PROCEDURES

2.3.1 Method Optimization and Validation Studies

Method optimizations for GC-MS and GC-TEA were done by using standard solutions of TNT and C-4 by changing the inlet temperatures and column temperature programs of the previously used conventional methods and applying the values given in the literature. All the other parameters were held constant. Optimum method conditions are given above in tables 2.1 and 2.2.

After determining the minimum concentrations for observable peaks, standard solutions of TNT (MS; 3-9 $\mu\text{g/mL}$, TEA; 0.9-3 $\mu\text{g/mL}$) and C-4 (MS; 50-250 $\mu\text{g/mL}$, TEA; 5-30 $\mu\text{g/mL}$) in 5 different concentrations for each instrument were analysed to obtain calibration curves. For each method, limit of detection and limit of quantitation values were calculated by using the results of these analysis. The precisions of the methods were also determined. The detectable lowest two concentrations for each solutions were injected 10 times in order to determine the LOD and LOQ values, other three concentrations were injected five times due to the time problem.

Time is an important factor for analytical procedures. In this study after the extraction and filtration of the soil samples, the filtrates were concentrated to 1.0 mL before analysis. To decide about the optimum preconcentration procedure three dilute solutions of C-4 were prepared where three 1.0 mL (25 $\mu\text{g/mL}$) of stock standard TNT solutions were diluted to 3.0 mL. Then one of these solutions kept in room temperature, the second was put in 60 °C oven and the third one was concentrated at room temperature by passing N_2 through the solution, in order to evaporate the excess acetone. After concentrating each solution to 1.0 mL, these solutions and a 1.0 mL of stock C-4 solution were analysed with GC-TEA to determine the optimum preconcentration procedure which would be short and result minimum sample loss.

2.3.2 Sample Preparation

The soil samples collected from the explosion areas in 1 h, 1 day, 1 week and 2 weeks times, were dried and grinded before extraction. 10.0 g of each dried soil sample was put in a 25.0 mL glass vial and extracted with 10.0 mL of acetone by shaking the slurry for 1.0 min manually. Then the extracts were filtered through a filter paper and the filtrates were put in an oven at 60 °C for evaporation of excess acetone until decreasing the volume of the extracts to approximately 1.0 mL, in order to concentrate the solution. After decreasing to 1.0 mL, the solutions were analysed with each instrument. To avoid contamination of the column, solvent (acetone) was injected after every injection of the extract.

CHAPTER 3

RESULTS AND DISCUSSIONS

3.1 OPTIMIZATION OF METHOD PARAMETERS

3.1.1 Total Analysis Time

In order to optimize total analysis time, column temperature program of the previously used programs for each instrument was optimized in order to shorten the retention times of the analytes, which is the time that passes from injection of the sample to reach the detector. Also the best separation of the samples in the least time should be achieved with the optimized program. The differences obtained between previous and optimized column temperature programs for both methods are given in Figure 3.1 and Figure 3.2.

Previous GC-MS column temp. Program; Injection Port T.: 250 °C

Oven : Initial T: 80 °C Initial Time : 2 min
15 °C/min to 280 °C Hold: 10 min

By varying the column temperature programs, the total analysis time decreased from 25 min to 19 min with GC-MS and from 27 min to 19 min with GC-TEA systems.

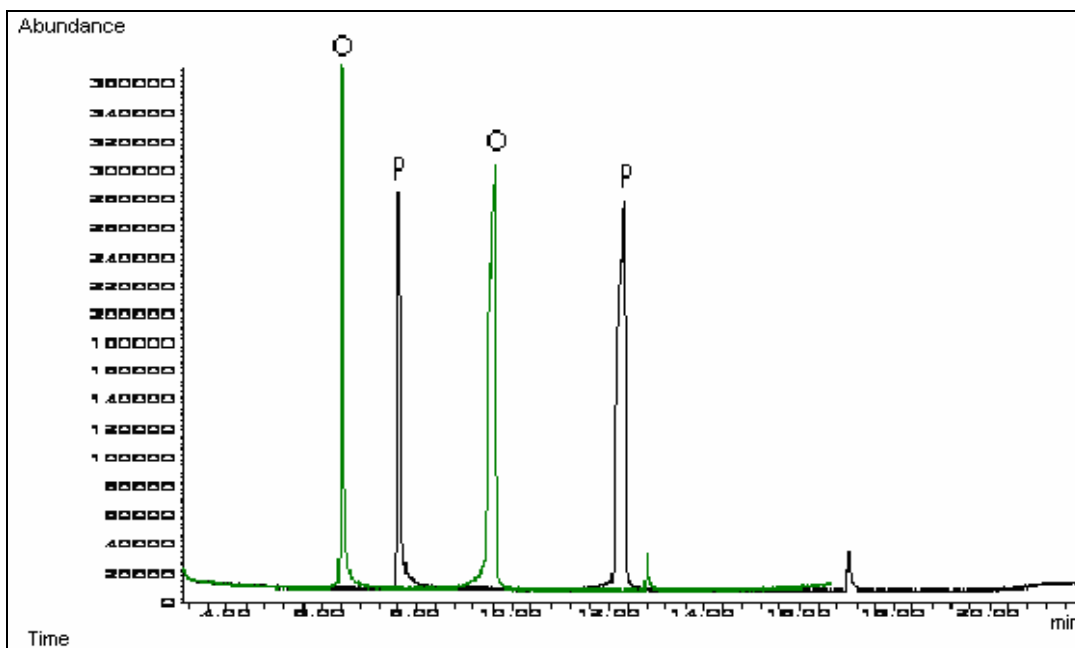


Figure 3.1 Optimization of total analysis time with GC-MS. (P; with previous program; initial time; 2 min, from 80 °C to 280 °C at a rate of 15 °C min⁻¹, final time; 10 min, inj. temp.; 250 °C. O; with optimized program given in Table 2.1.)

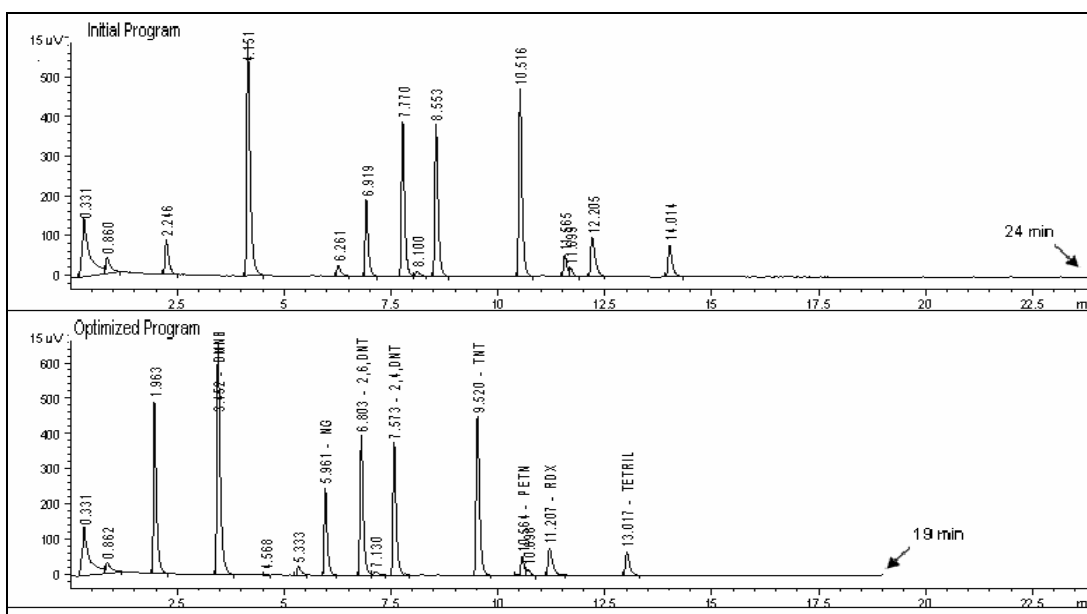


Figure 3.2 Optimization of total analysis time with GC-TEA. (Initial program; initial time; 2 min, from 50 °C to 270 °C at a rate of 10 °C min⁻¹, final time; 3 min, inj. temp.; 170 °C; Optimized program was given in Table 2.2.)

3.1.2 Inlet Temperature

In the literature Kolla (1994) has determined the optimum inlet temperature which prevents thermal decomposition of the samples and provides the highest response, as 170 °C for the analysis of explosives from the extracts with GC-TEA, this value was used with GC-TEA in this study. Effect of inlet temperature on the recovery of the explosives with GC-MS was checked by comparing this value with previously used value 250 °C and it was seen that sensitivity for TNT is higher at 250 °C than at 170 °C as shown in Figure 3.3 (Two total ion chromatograms that observed at two temperatures were given in the same figure). RDX recovery was not affected by the change of inlet temperature.

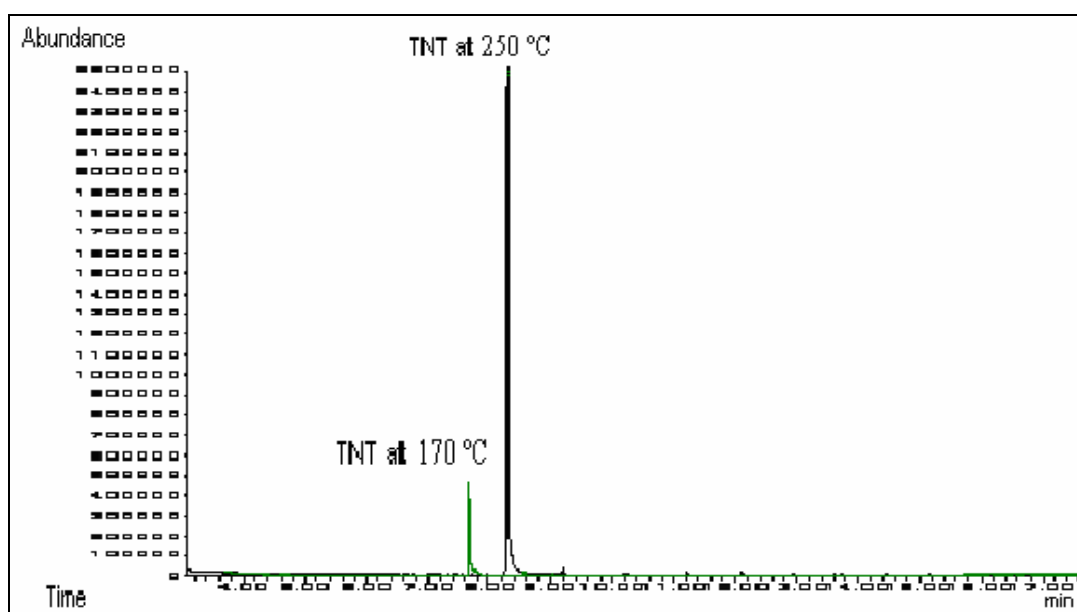


Figure 3.3 Effect of Inlet Temperature on recovery of TNT.

3.1.3 Preconcentration Procedure

It was seen that it took approximately 10 min to decrease the volume of a 3.0 mL dilute solution to 1.0 mL under N₂, approximately 20 min in an oven at 60 °C and more than 2 h at room temperature. After concentrating the dilute solutions to 1.0 mL

mL in three different ways, these solutions and a 1.0 mL standard solution were analysed with GC-TEA. When the peak heights of the solutions compared, it was seen that the peak height obtained after the analysis of the solution which was concentrated in oven, was the closest to the standard 1.0 mL solution's peak height (Fig. 3.4), hence the recovery was the highest when preconcentration was performed in oven than by passing N₂ and keeping the solution at room temperature, thus in the study preconcentration of the extract was performed in an oven at 60 °C. The N₂ flow should probably have forced the analyte to evaporate or leave the acetone solution. Results which are the averages of three injections are shown in Figure 3.4 and Table 3.1.

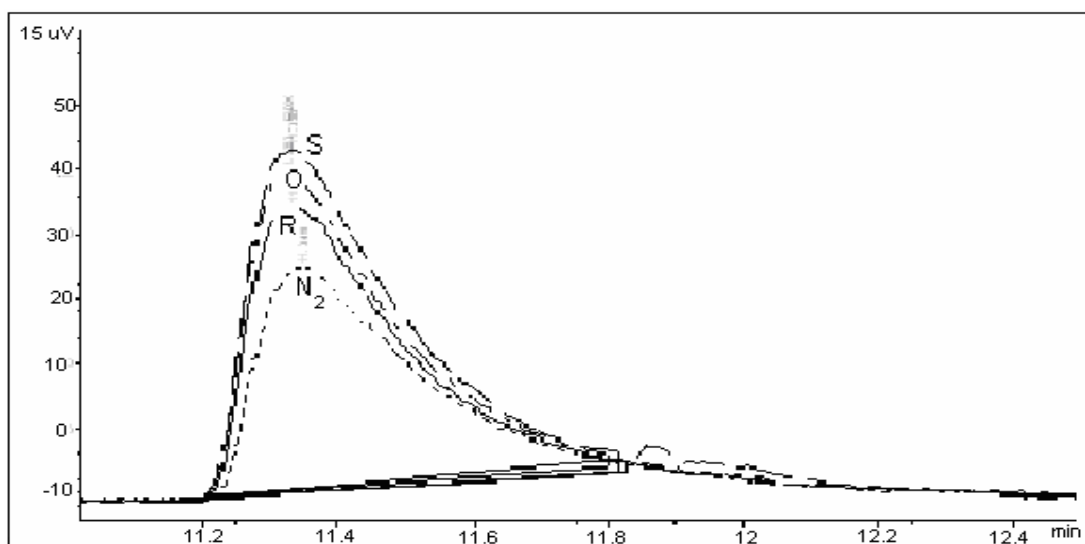


Figure 3.4 Effect of preconcentration procedure on sample recovery. (S; Stock solution, O; Oven, R; Room Temperature, N; N₂).

Table 3.1 Results of the Optimization of Preconcentration Procedure.

Concentrated Sample	Concentration time	Analysis Result (p. height)
1.0 ml stock soln. (25 µg/ml)	-	49.9
Under N ₂	10 min	32
60 °C oven	20 min	47.3
Room temperature	> 2 h	44.1

3.2 METHOD VALIDATION STUDIES

Before starting an instrumental analysis, the analyst should know the efficiency, sensitivity and ability, hence the validity of the method which is going to be used, in determining the target substance. For this study the efficiency of the GC-MS and GC-TEA methods were already known from the literature, but it was needed to determine the sensitivity of both methods and the precisions of the results that will be obtained in both instruments.

In order to calculate the limit of detection and limit of quantitation values and to determine the precisions of each methods, standard solutions of C-4 (MS; 50-250 µg/ml, TEA; 5-30 µg/ml) and TNT (MS; 3-9 µg/ml, TEA; 0.9-3 µg/ml) in five different concentrations for each instrument were analysed to obtain calibration curves. Chromatograms and GC-MS mass spectra for these analysis and the results which are obtained as peak heights are given below. Also the calibration tables and the analytical figures of merits are shown below.

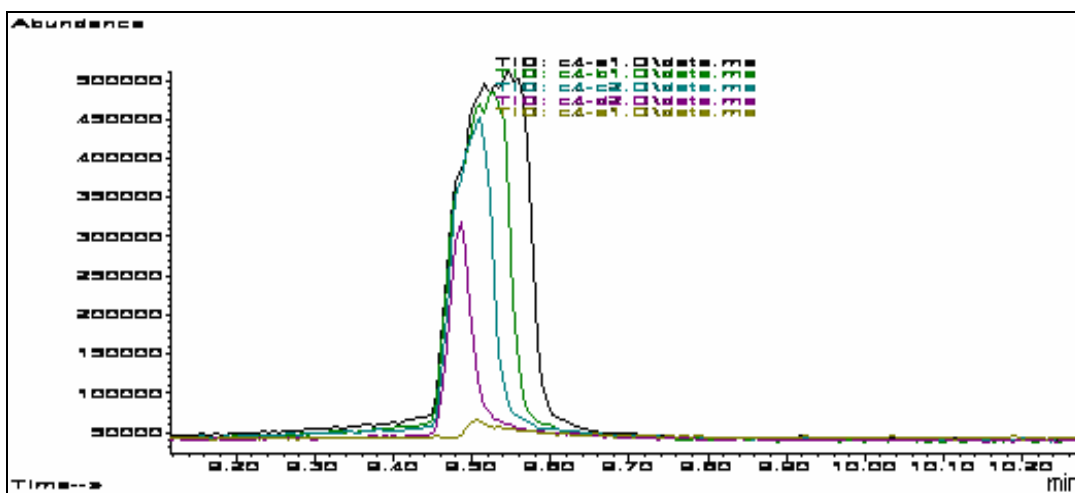


Figure 3.5 GC-MS total ion chromatograms for calibration solutions of C-4.

In addition to comparison of the retention time of the sample with a standard explosives', determining the mass spectrum of the sample is a way of identification of the analyte. EI mass spectrum of the RDX sample is given below (Fig. 3.6), which

can be easily obtained by a right click with the mouse of the computer, on the peak of the analyte whose retention time was determined by an analysis of standard RDX. Also analyst can check for the retention time or the peak of the target substance by entering the base peak values of the RDX (30, 46) to the related option of the software of a GC-MS system.

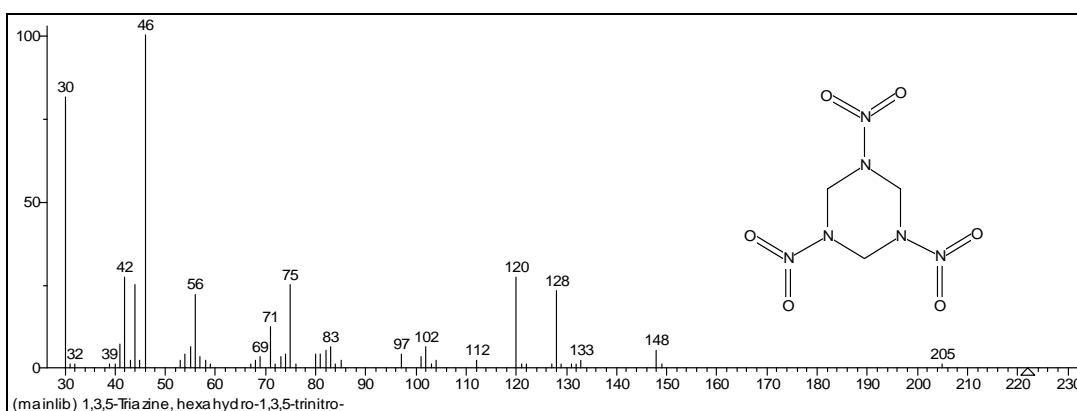


Figure 3.6 EI mass spectrum of RDX.

Table 3.2 GC-MS method calibration results (as peak heights) with C-4.

Concentration ($\mu\text{g/ml}$)	Degrees of freedom (N)	Average (\bar{X})	Stand. Dev. (σ)	%RSD	$\pm (t\sigma/\sqrt{N})$
50	10	16297.6	2812.3	17.2	± 1983.2
100	10	258177.8	10705.8	4.1	± 7549.2
150	5	396034.8	5519.3	1.4	± 6343.5
200	5	447021	13903.8	3.1	± 15980
250	5	463283.4	7873.5	1.7	± 7993

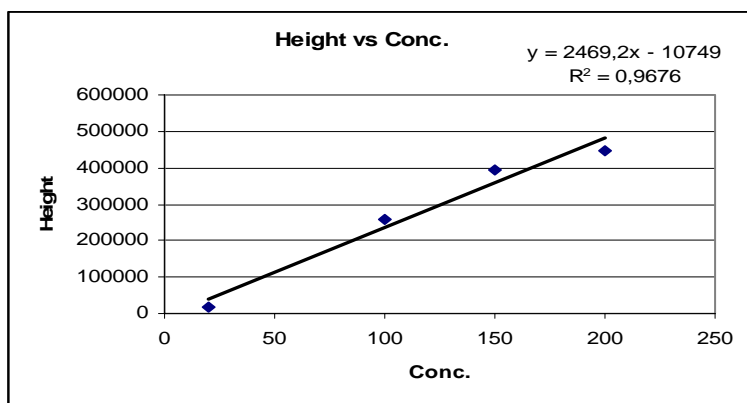


Figure 3.7 Calibration curve for C-4 standard samples analysed with GC-MS.

Reaction scheme in a GC-TEA system is given below in Figure 3.8. The radiation from the excited NO_2^* specie is characteristic for a compound that identification of a compound with GC-TEA is done by comparing the retention time of the analyte with the retention time of a standard explosive (11.23 min for RDX). In this study the instrument can automatically perform this comparison by using the standard explosives' chromatograms in its memory.

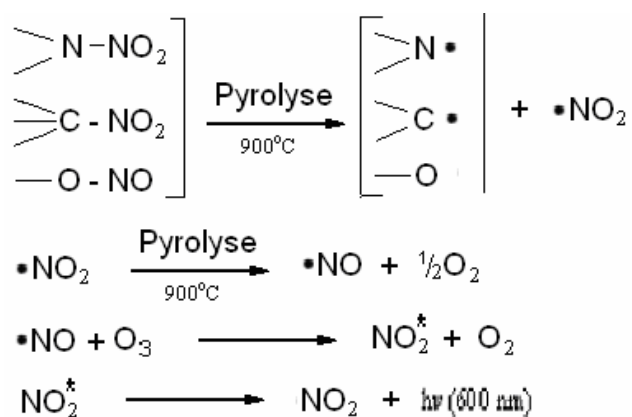


Figure 3.8 Schematic representation of reactions in a TEA system.

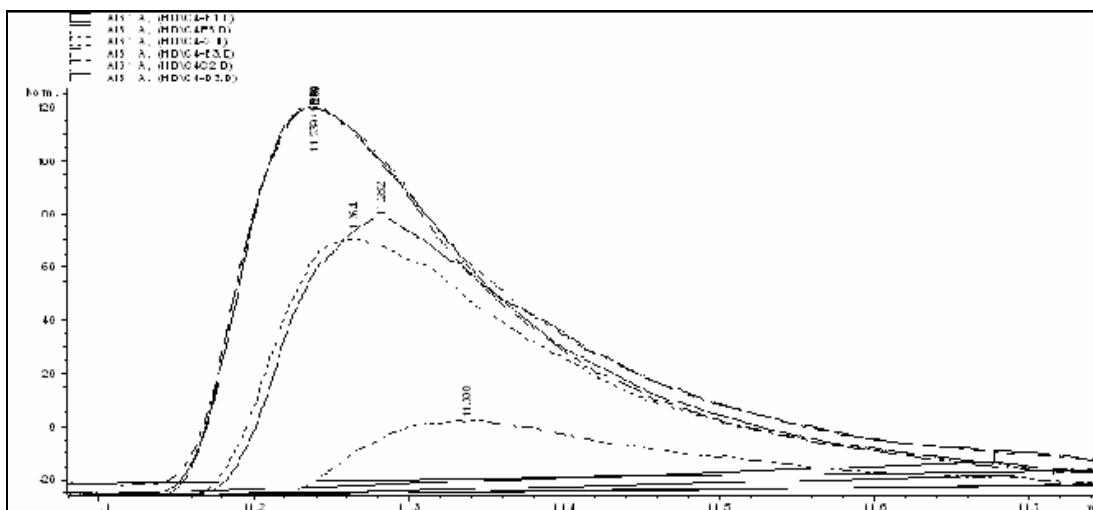


Figure 3.9 GC-TEA chromatograms for calibration solutions of C-4.

Table 3.3 GC-TEA method calibration results (as peak heights) with C-4.

Concentration (µg/ml)	Degrees of freedom (N)	Average (\bar{X})	Stand. Dev. (σ)	%RSD	$\pm (t\sigma/\sqrt{N})$
5	10	12.5	0.5	4.2	0.35
10	10	36.8	1.1	3.0	0.78
15	5	40.3	2.3	5.7	2.64
20	5	102.4	10.8	10.5	12.41
30	5	122.1	2.1	1.7	3.10

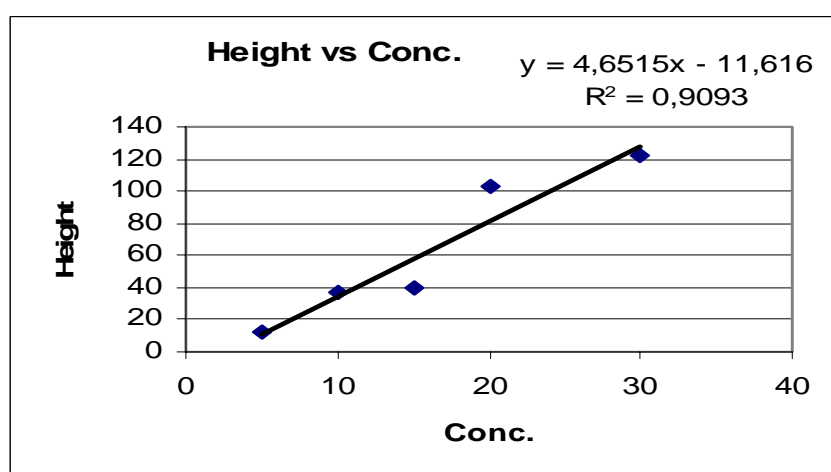


Figure 3.10 Calibration curve for standard C-4 samples analysed with GC-TEA.

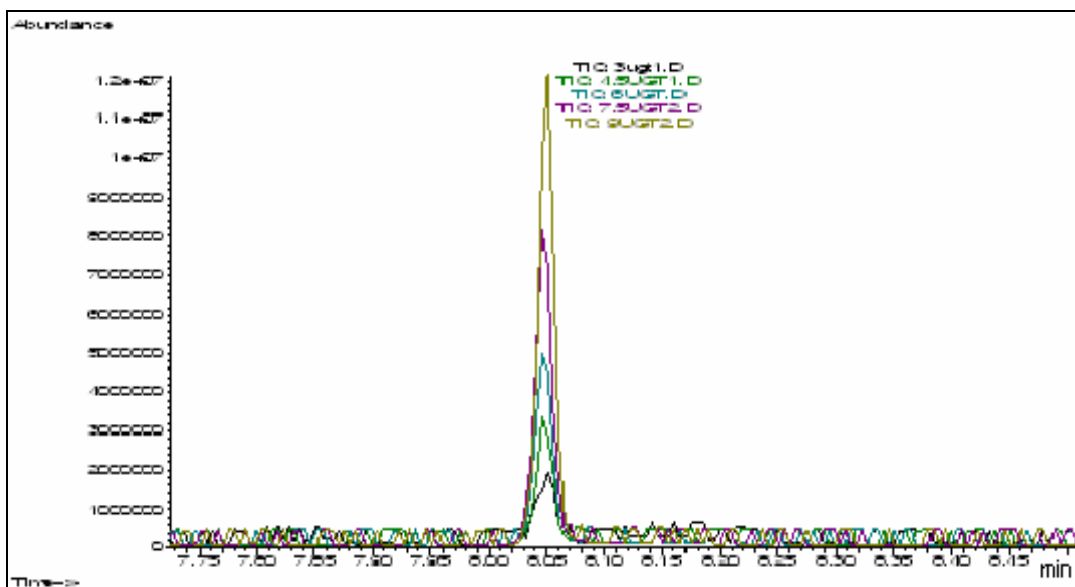


Figure 3.11 GC-MS total ion chromatograms for calibration solutions of TNT.

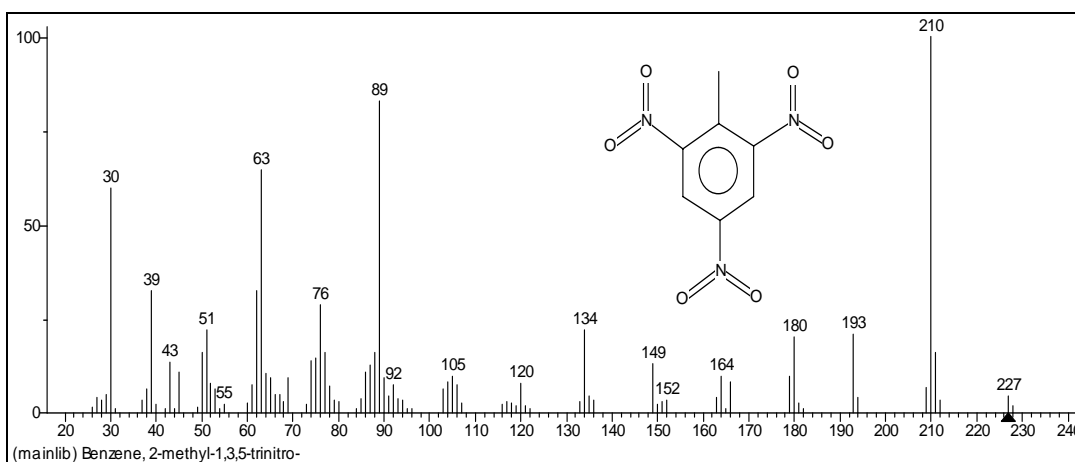


Figure 3.12 EI mass spectrum of 2,4,6 TNT. (Spectrum was taken from the NIST library of the instrument used in the study.)

The abundant ion (“base peak”) in the EI spectrum of 2,4,6-TNT (m/z 210) is attributed to an unusual loss of a hydroxyl group from the molecular ion. This loss also occurs in the EI spectrum of other nitroaromatic compounds with a nitro group in an ortho position to a hydrogen-containing moiety such as methyl (“ortho effect”). The molecular ion is not observed in the EI mass spectrum of TNT.

Table 3.4 GC-MS method calibration results (as peak heights) with TNT.

Concentration (µg/ml)	Degrees of freedom (N)	Average (\bar{X})	Stand. Dev. (σ)	%RSD	$\pm (t\sigma/\sqrt{N})$
3	10	1333075	161768.8	12.1	114077.4
4.5	10	3353968	316196.7	9.4	222977.6
6	5	5028540	363721.3	7.2	418039.1
7.5	5	7884205	564308.8	7.2	648582.1
9	5	11142814	776248.7	7.0	891172.9

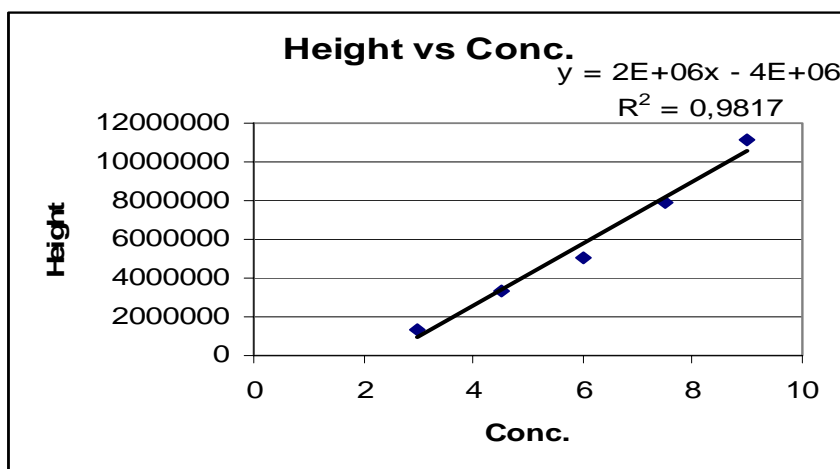


Figure 3.13 Calibration curve for standard TNT samples analysed with GC-MS.

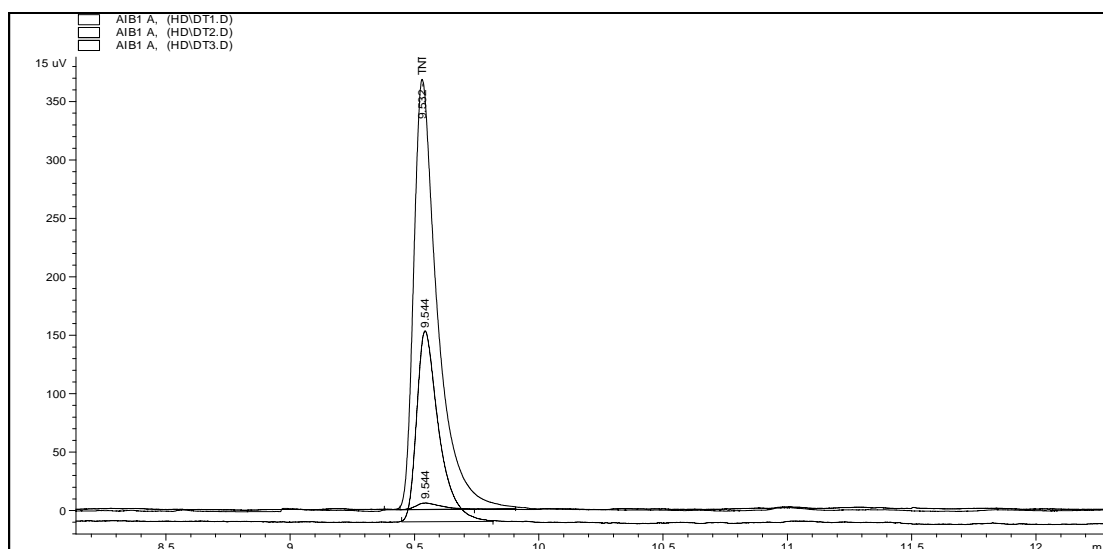


Figure 3.14 GC-TEA chromatograms for calibration solutions of TNT.

Table 3.5 GC-TEA method calibration results (as peak heights) with TNT.

Concentration (µg/ml)	Degrees of freedom (N)	Average (\bar{X})	Stand. Dev. (σ)	%RSD	$\pm (t\sigma/\sqrt{N})$
0.9	10	14.7	1.5	10.0	1.06
1.2	10	19.5	1.3	6.8	0.92
1.5	5	27.4	0.9	3.2	1.72
2.1	5	33.0	1.0	3	1.15
3	5	37.7	0.4	1.1	0.46

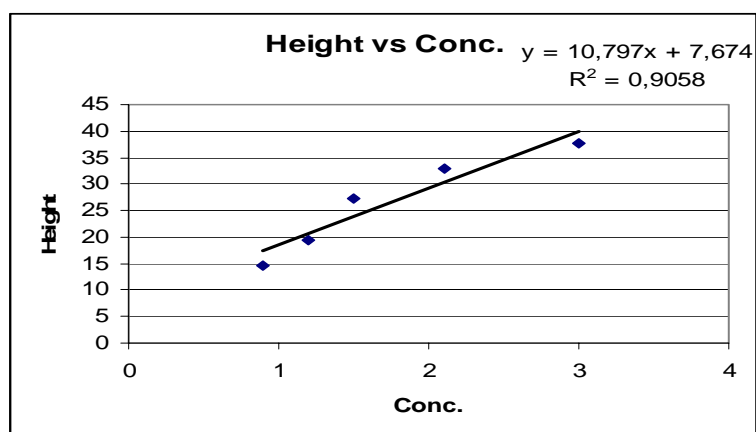


Figure 3.15 Calibration curve for standard TNT samples analysed with GC-TEA.

Table 3.6 Analytical figures of merits for method calibrations.

PARAMETER	GC-MS		GC-TEA	
	TNT	C-4	TNT	C-4
LOD (µg/ml)	2.2	7.7	0.1	2.8
LOQ (µg/ml)	6.7	23.0	0.3	8.4
r^2 (Corr. Coeff.)	0.9817	0.9676	0.9058	0.9092
% RSD	9.4	4.1	6.8	3.03

As can be seen from the table, GC-TEA has lower detection and quantitation limits than GC-MS. Also when we look at the chromatograms, the GC-MS system has higher noise and background values.

3.3 ANALYSIS OF POSTEXPLOSION SOIL SAMPLES

The chromatograms and mass spectra obtained for the analysis of the soil sample extracts are given below. The analysis results of each explosive with each instrument are given respectively that the differences in chromatograms with respect to time of collection of samples can be examined easier by this way. Decrease in peak heights of the explosives with time was observed, this makes the identification of the analyte peak more difficult, as expected. Also for the GC-MS isolation of the peak of explosive even became more difficult as the elapsed time after the explosions became longer than one day. To decide for the peak of the explosive in GC-MS total ion chromatogram; firstly the retention time of the analyte was determined by analysing a standard sample then the peak at that time in a chromatogram of soil sample was selected and the ion spectrum of that peak which observed by using the software of the GC-MS, was compared with the standard explosive's spectrum which exist in the library of the instrument. Also the software allows the analyst to check for the base peak values of the explosive in the chromatogram of an extract thus by this way you can determine the explosive if exist in the sample. To isolate and identify the peak of the analyte additional operations using the software of the instrument like background and spectrum subtraction were applied.

3.3.1 Analysis of Postexplosion TNT Samples

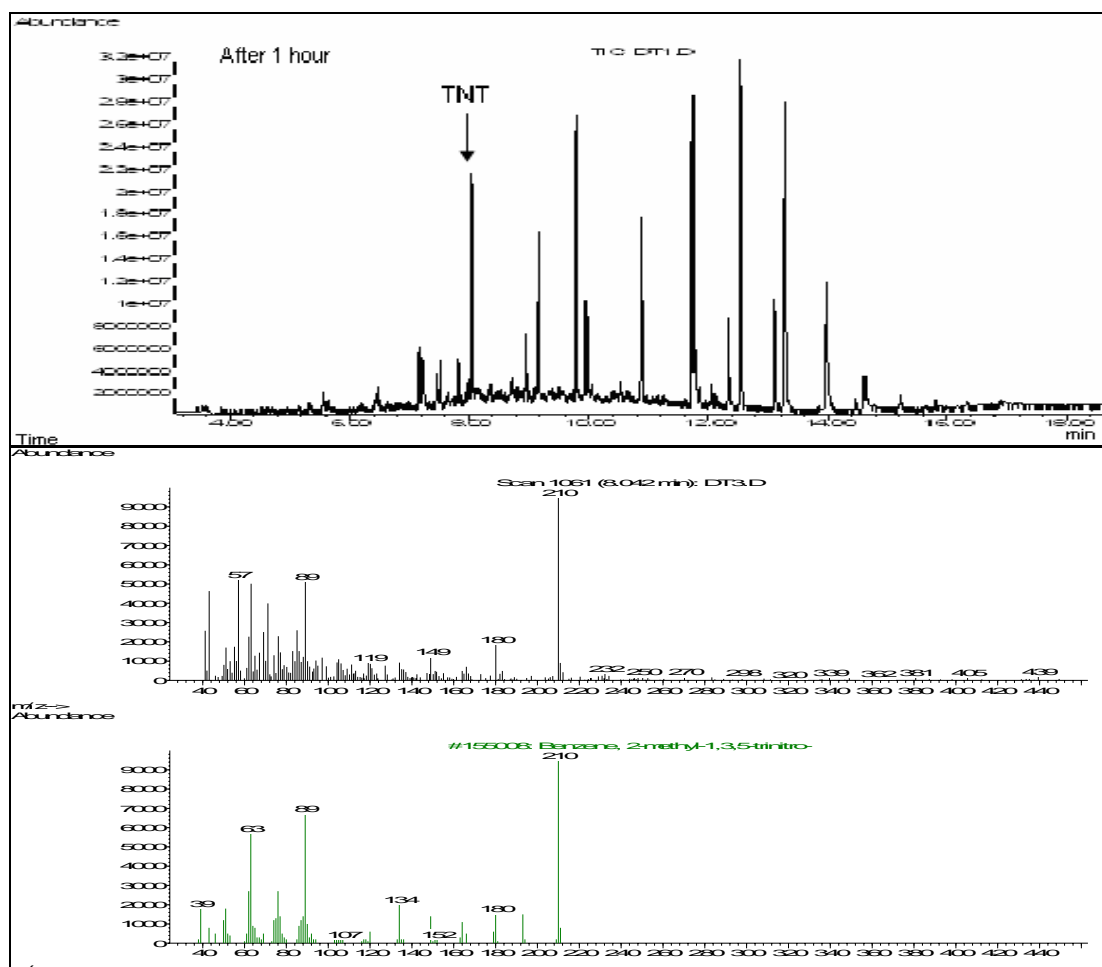


Figure 3.16 GC-MS total ion chromatogram and mass spectrum of postexplosion TNT sample after 1 h. The retention time of TNT peak is 8.05.

The peak of TNT in postexplosion soil sample after 1 hour from the explosion was very clear and had very high abundance value. Thus identification of TNT was so easy by determining the mass spectrum of the peak of TNT, whose retention time was determined in method validation studies by using standard TNT solutions. Instrument automatically compare the mass spectrum of the sample with standard substances' mass spectra and perform the identification of the analyte.

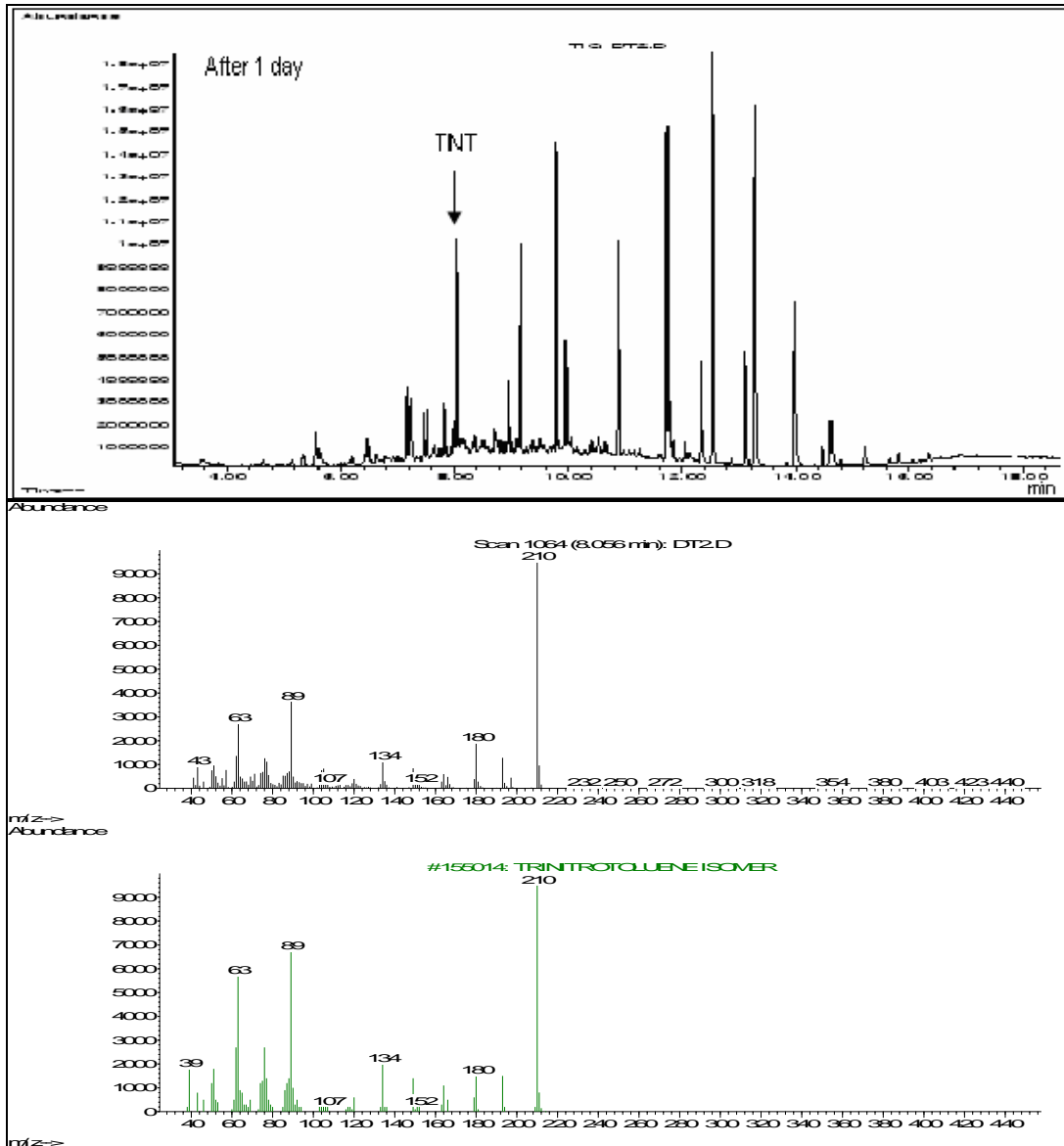


Figure 3.17 GC-MS total ion chromatogram and mass spectrum of postexplosion TNT sample after 1 day.

The peak of TNT in total ion chromatogram of postexplosion soil sample after 1 day was still obvious, so it was easy to determine the mass spectrum of it. The peak height dropped nearly to the half in 1 day time after the explosion.

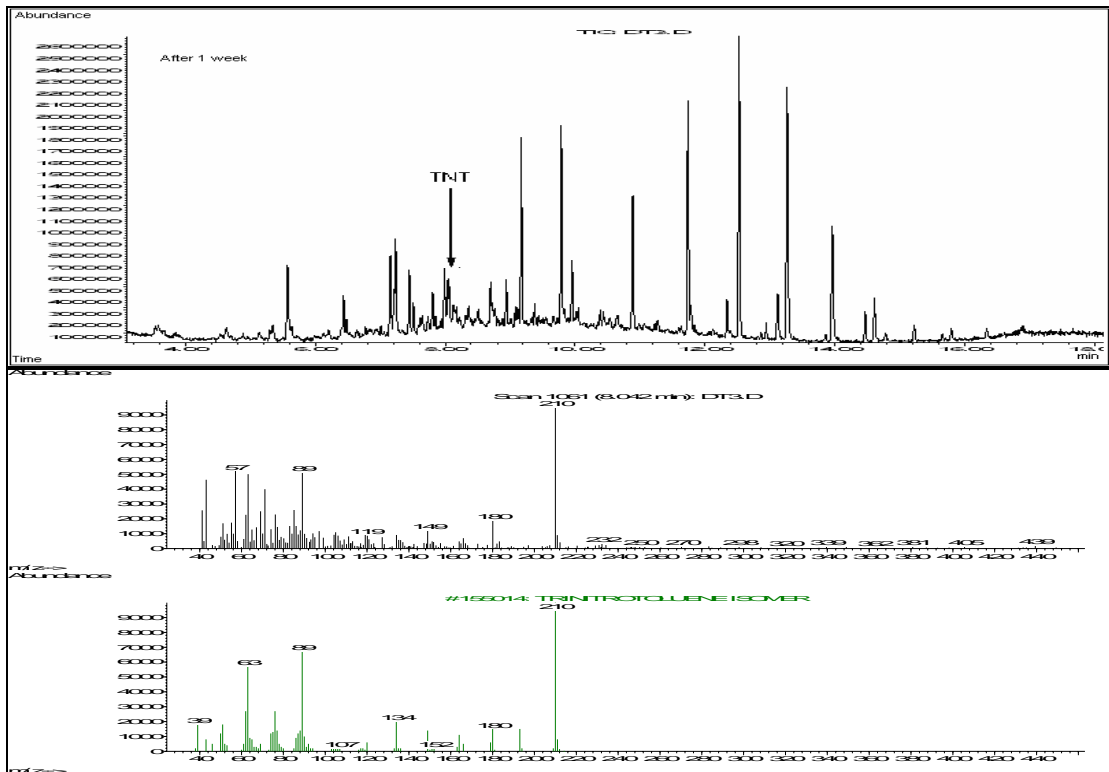


Figure 3.18 GC-MS total ion chromatogram and mass spectrum of postexplosion TNT sample after 1 week.

It was difficult to determine the peak of TNT after 1 week, thus software operations like background and chromatogram subtractions were applied to determine the peak of TNT and the mass spectrum of it.

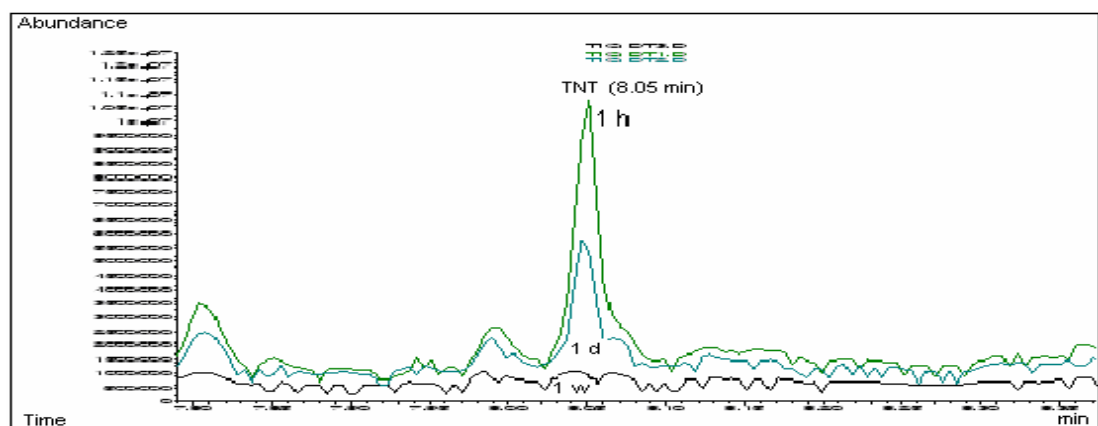


Figure 3.19 GC-MS total ion chromatograms of postexplosion TNT samples. (Three chromatograms were overlaid and maximized.)

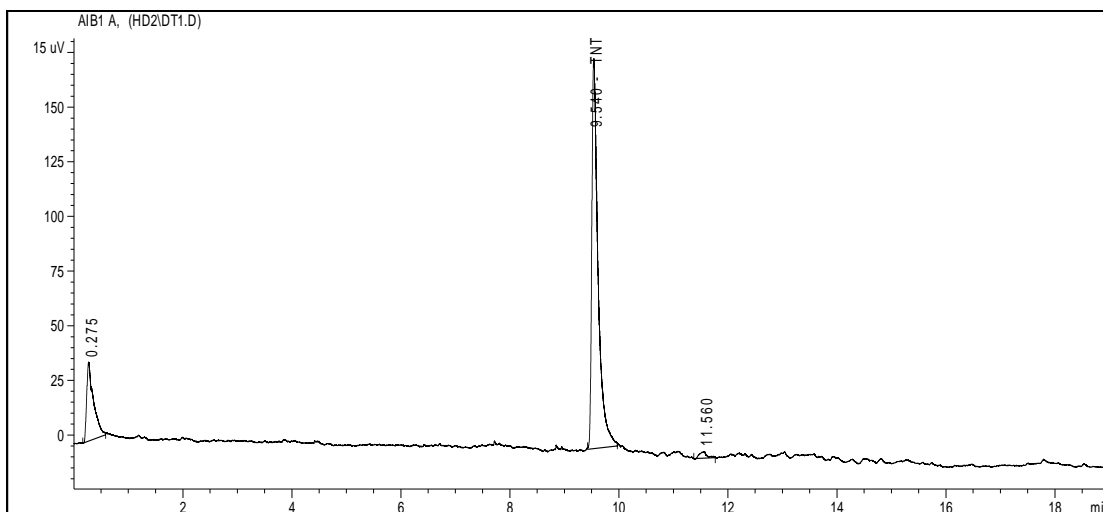


Figure 3.20 GC-TEA analysis result of postexplosion TNT sample after 1 h.

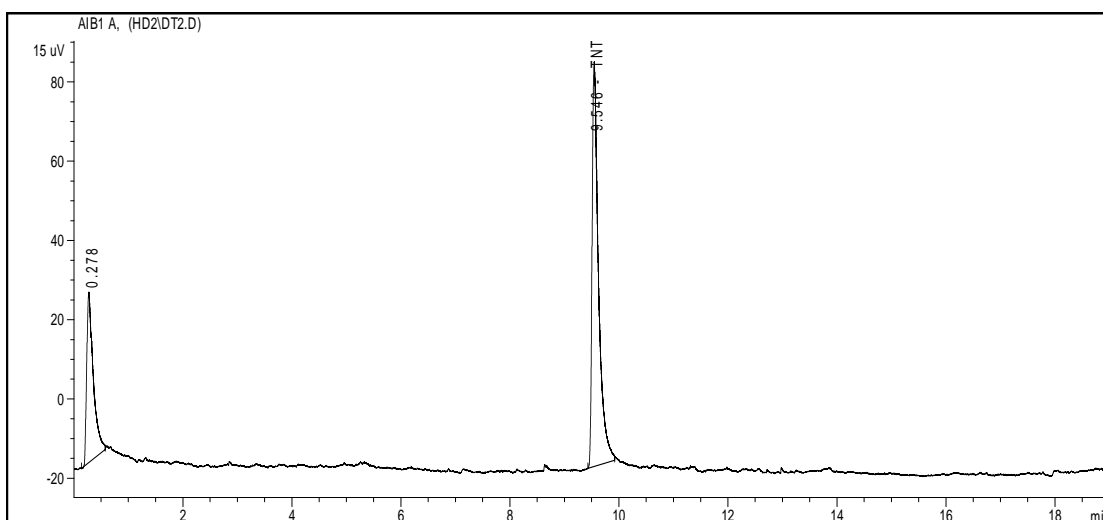


Figure 3.21 GC-TEA analysis result of postexplosion TNT sample after 1 day.

The chromatograms observed after the analysis of postexplosion soil samples were very simple due to the sensitivity of the instrument against nitro groups and the identification of the peaks were performed by the computer automatically by comparing the retention time of the observed peak with the retention times of the standard explosives which exist in the memory of the instrument. The peak height was dropped to the half of it after 1 week time passed from the explosion.

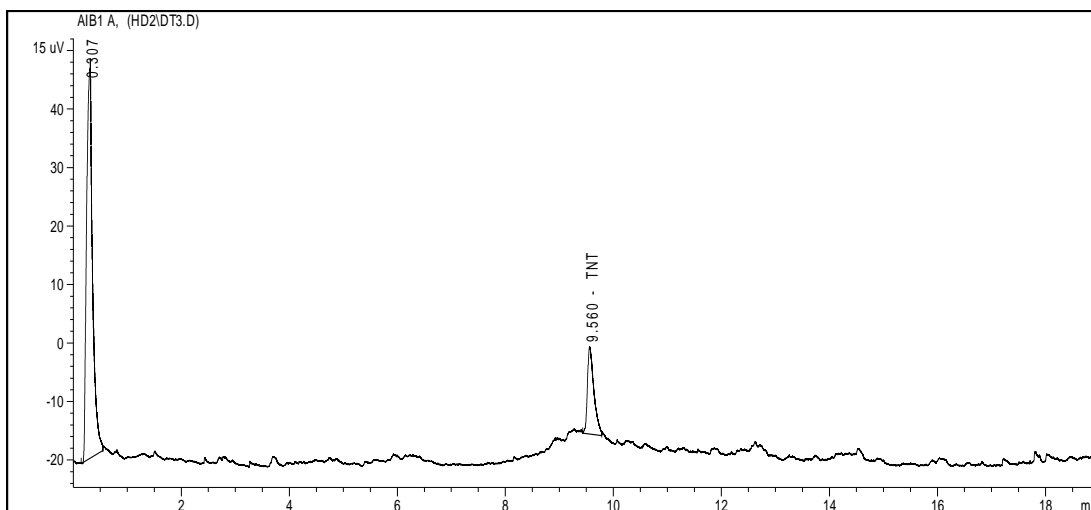


Figure 3.22 GC-TEA analysis result of postexplosion TNT sample after 1 week.

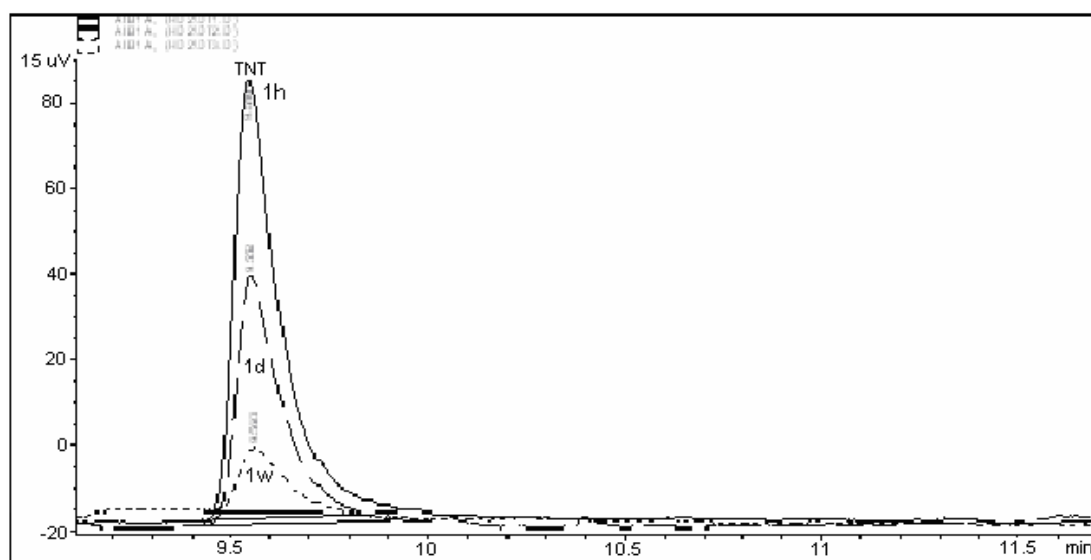


Figure 3.23 GC-TEA chromatograms of postexplosion TNT samples.

Due to its sensitivity against nitro groups, only TNT peaks were observed after the analysis of postexplosion soil samples with GC-TEA. The peak height again dropped to the half after 1 day time as in GC-MS. But with contrast to GC-MS other organics than TNT in soil sample did not effect the result and it was still easy to detect the peak of TNT after 1 week time.

3.3.2 Analysis of Postexplosion C-4 Samples

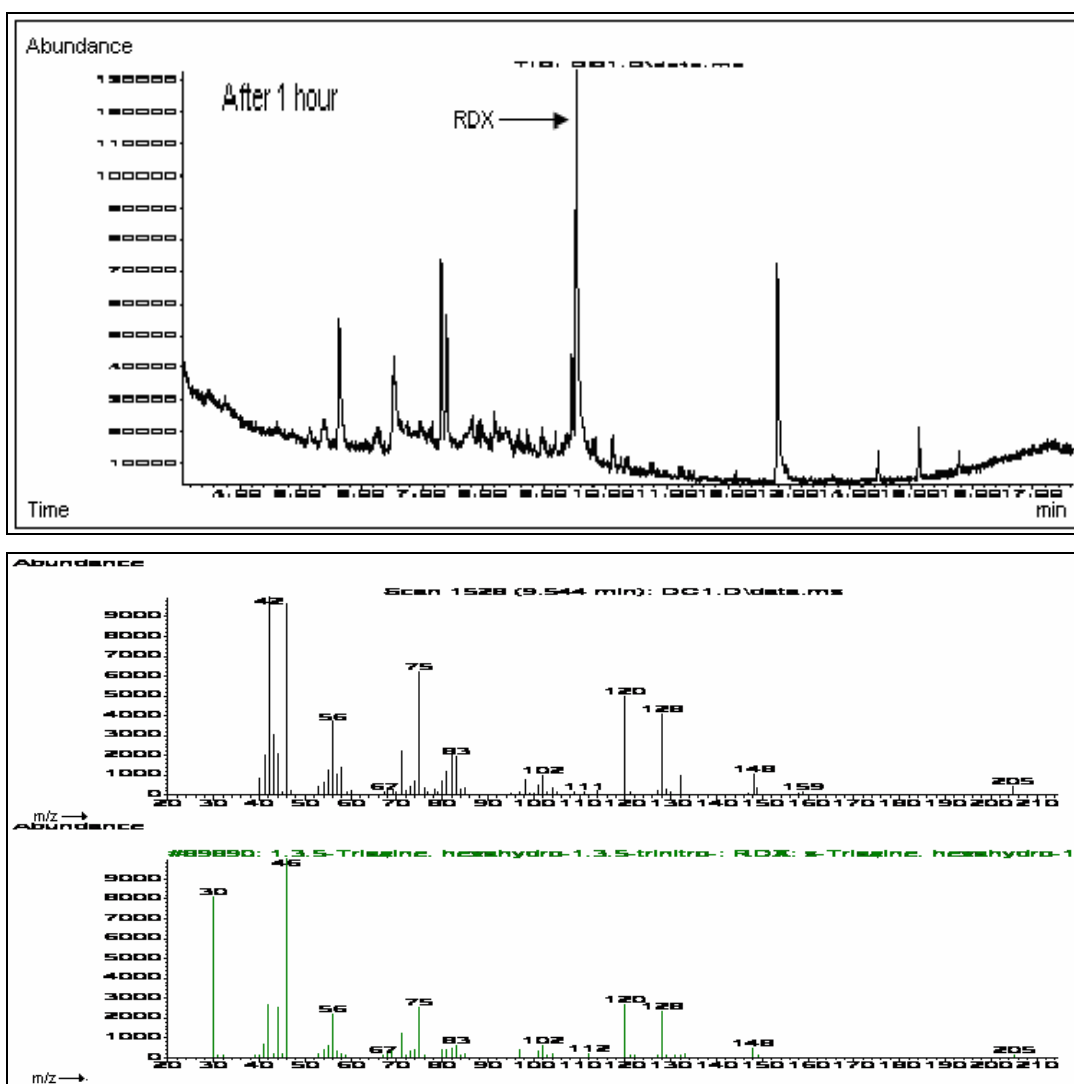


Figure 3.24 GC-MS total ion chromatogram and mass spectrum of postexplosion C-4 sample after 1 h. Retention time of RDX peak is 9.544.

Retention time of the RDX peak was determined by analysing a Standard C-4 solution in method validation studies. Abundance of the peak of RDX was quite high and identification of RDX was done by determining the mass spectrum of that peak.

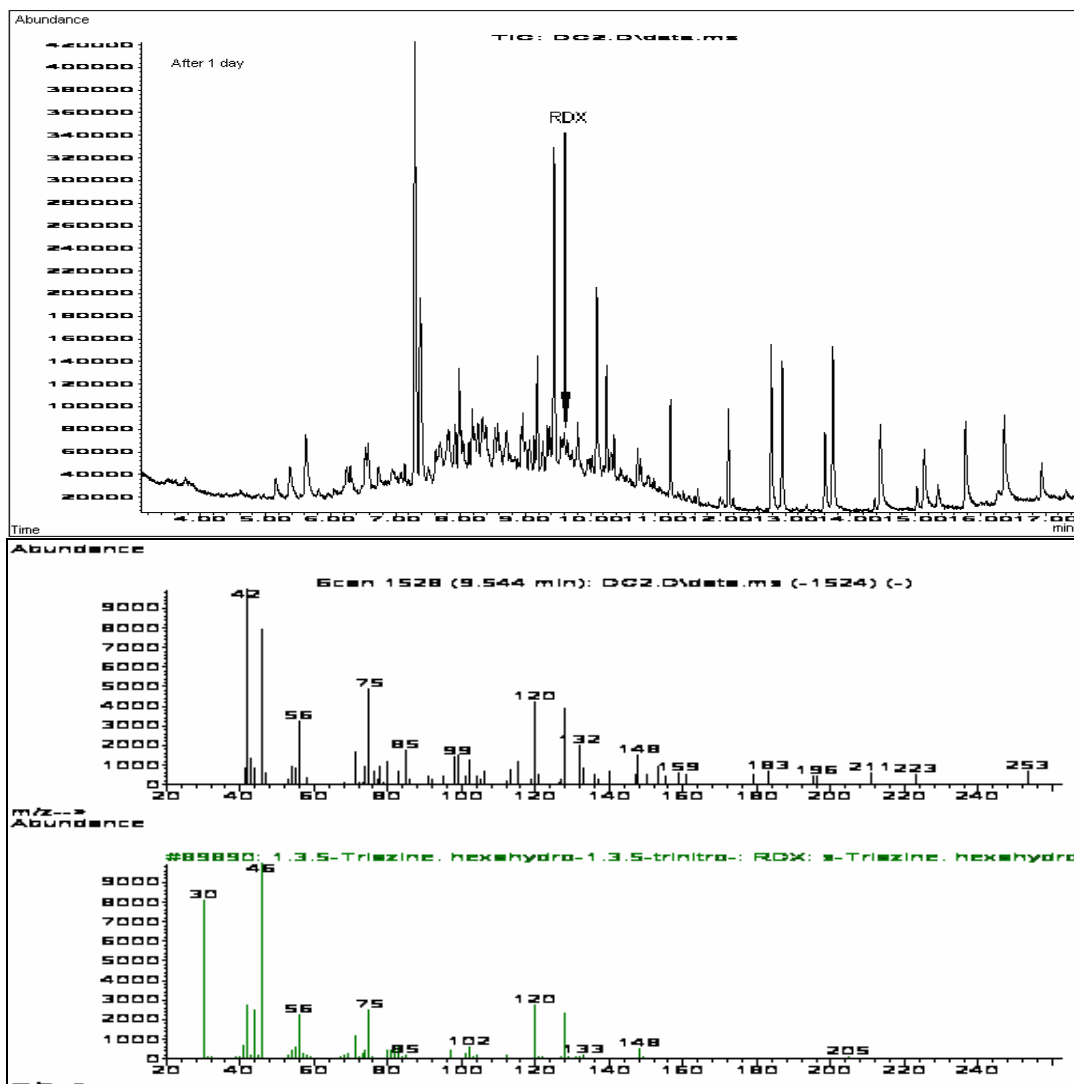


Figure 3.25 GC-MS total ion chromatogram and mass spectrum of postexplosion C-4 sample after 1 day.

Instrument adjusts the scale of the total ion chromatogram with respect to the highest peak that it was difficult to determine the peak of RDX after 1 day from the explosion. Again software operations were applied to isolate the peak of RDX and identification was done by determining the mass spectrum of it.

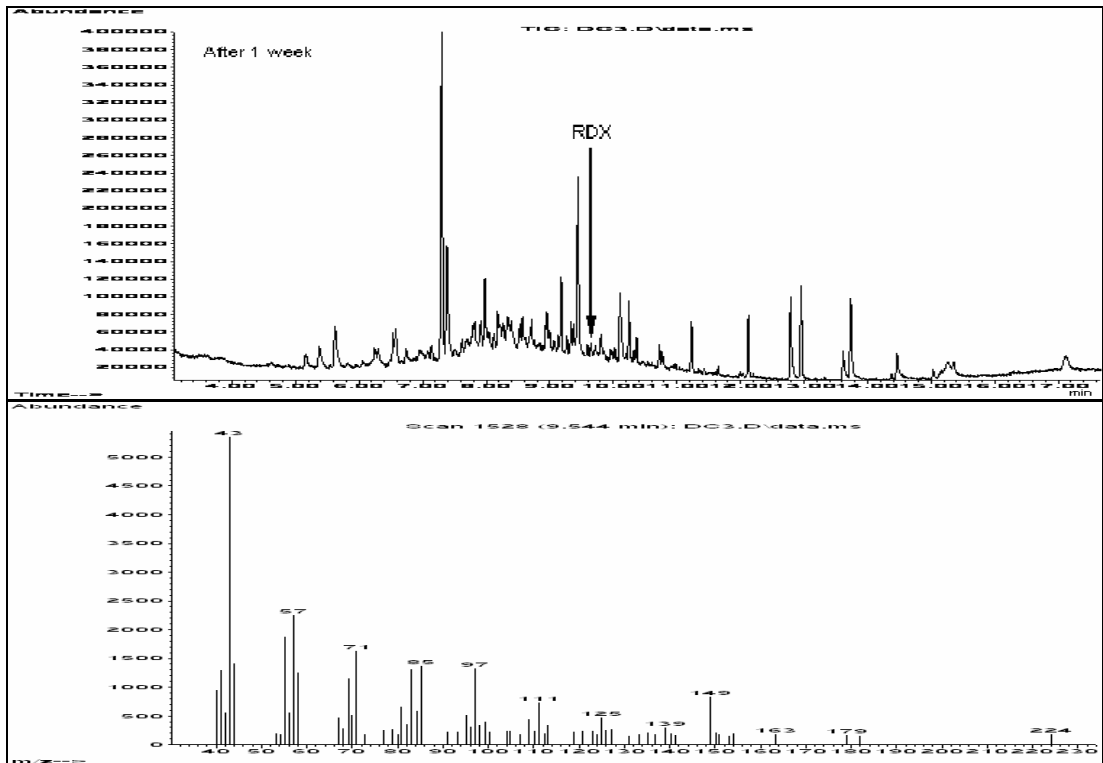


Figure 3.26 GC-MS total ion chromatogram and mass spectrum of postexplosion C-4 sample after 1 week.

After 1 week time from the explosion it was impossible to detect the peak of RDX and the mass spectrum at the retention time did not match with the spectrum of standard RDX.

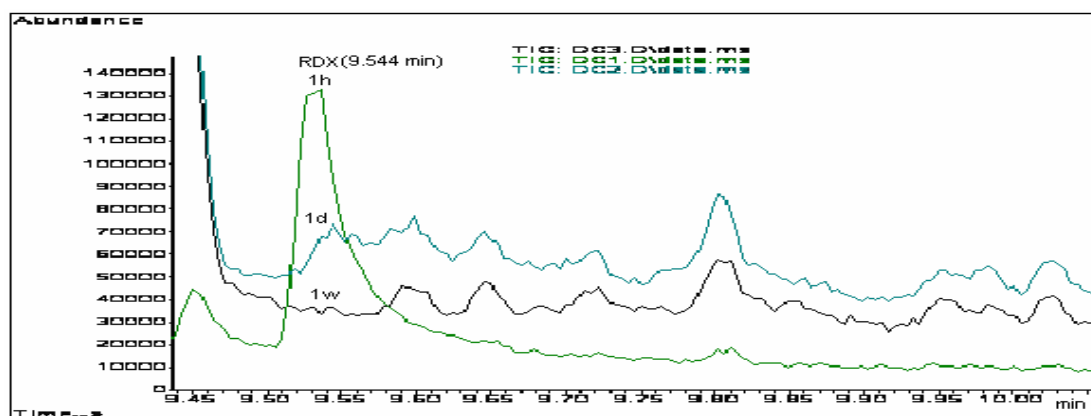


Figure 3.27 GC-MS total ion chromatograms of postexplosion C-4 samples. (Three chromatograms were overlaid and maximized.)

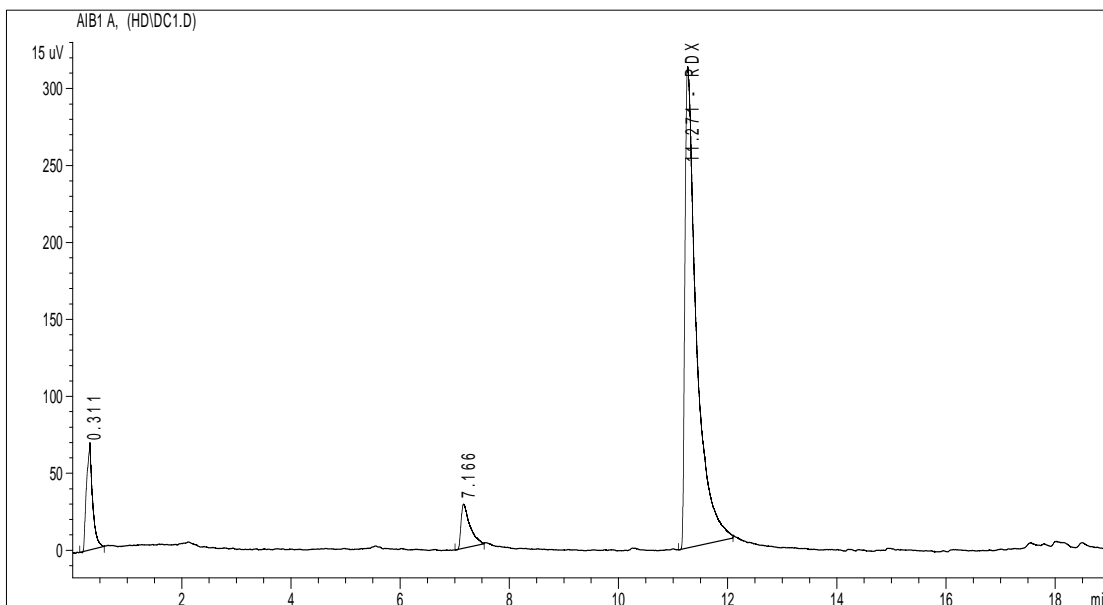


Figure 3.28 GC-TEA analysis result of postexplosion C-4 sample after 1 h.

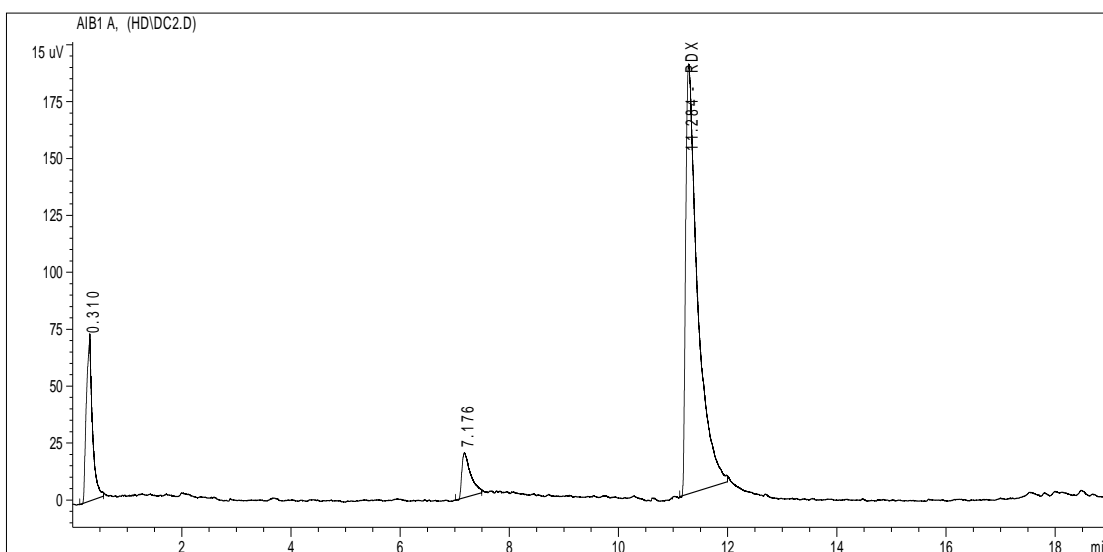


Figure 3.29 GC-TEA analysis result of postexplosion C-4 sample after 1 day.

The chromatograms observed after the analysis of postexplosion soil samples were very simple hence the identification of the RDX was easily performed. An additional peak was observed at 7.116 min which is characteristic to RDX. The peak height of RDX was dropped nearly to the half after 1 day time passed from the explosion.

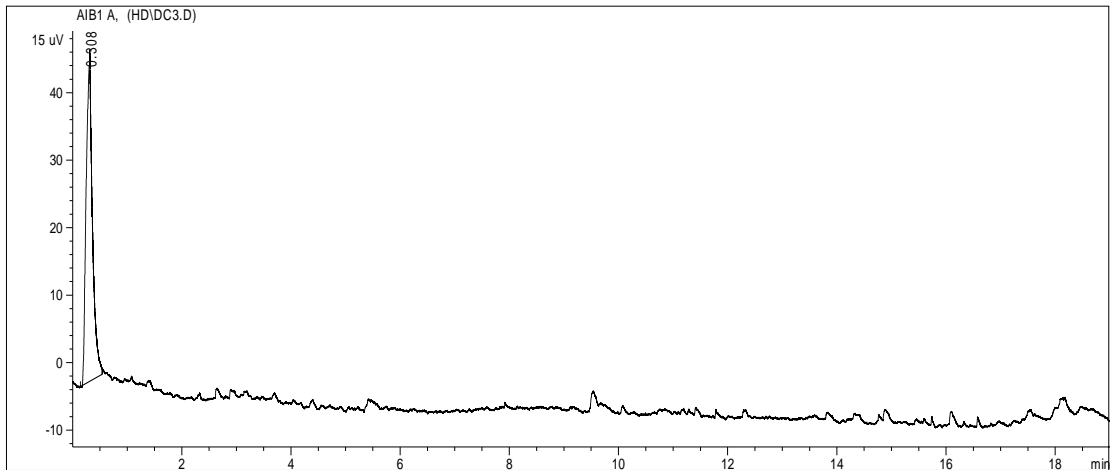


Figure 3.30 GC-TEA analysis result of postexplosion C-4 sample after 1 week.

No RDX peak was observed by the analysis of postexplosion soil sample after 1 week time passed from the explosion.

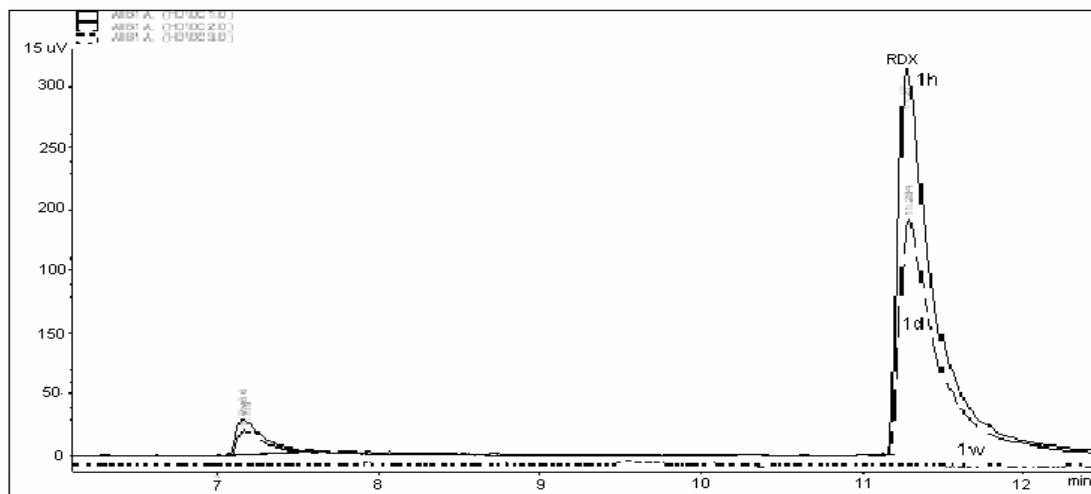


Figure 3.31 GC-TEA chromatograms of postexplosion C-4 samples.

During the analysis of the postexplosion soil samples, complex total ion chromatograms were observed with GC-MS while the GC-TEA chromatograms were very simple. There was a gradual decrease in the peak heights for the explosives and separation and identification of these peaks at GC-MS became more difficult as the time of sample collection increases. The concentrations were nearly dropped to the

halves in one day after the explosion. Background and spectrum subtraction operations by using the computer software was needed to isolate the analyte peak at such low concentrations. This type of operations was used to obtain the spectrum in Figure 3.29. However, it was still possible to see the peak of the TNT after 1 week period from the explosion with GC-TEA. On the other hand, C-4 could not determined neither with GC-MS nor with GC-TEA when 1 week time passed after the explosion. After two weeks time passed, no result could be obtained with both systems. Observed TNT and C-4 concentrations in postexplosion soil samples are shown in Table 3.7. The values were calculated by taking the averages of three injections of each sample.

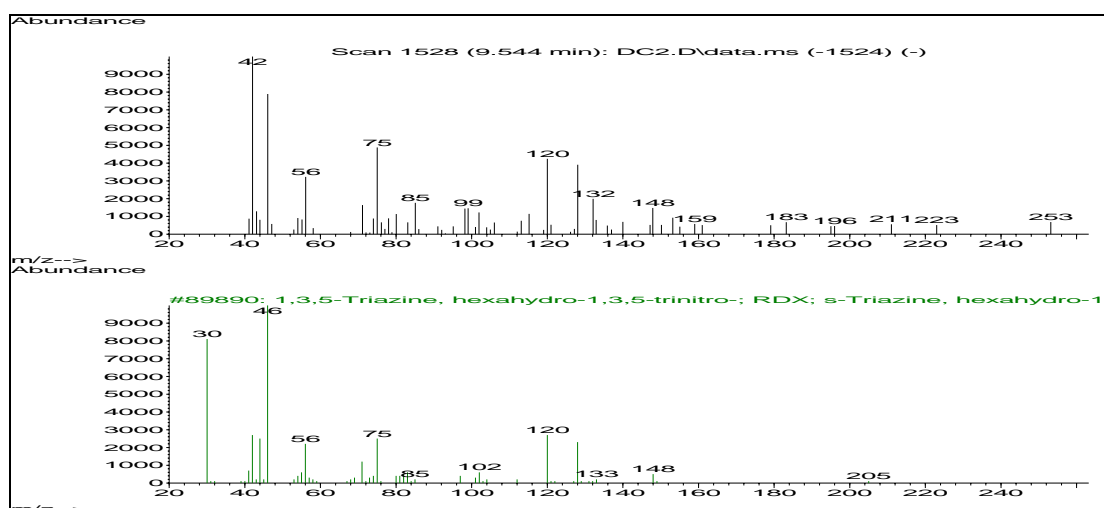


Figure 3.32 GC-MS mass spectrum of postexplosion C-4 sample after 1 day.

Table 3.7 Results of the analysis of the postexplosion soil samples. (* result was obtained by using the software operations.)

Sampling Time	GC-MS		GC-TEA	
	TNT ($\mu\text{g/g}$)	C-4 ($\mu\text{g/g}$)	TNT ($\mu\text{g/g}$)	C-4 ($\mu\text{g/g}$)
1 hour	1.26 ± 0.03	5.85 ± 0.24	1.35 ± 0.01	6.97 ± 0.04
1 day	0.71 ± 0.03	3.13 ± 0.03	0.77 ± 0.01	2.16 ± 0.13
1 week	$0.21 \pm 0.05^*$	-	0.08 ± 0.005	-
2 weeks	-	-	-	-

CHAPTER 4

CONCLUSIONS

Determination of the explosive materials in postexplosion samples is an important subject for forensic laboratories, in order to help the investigations. The expertise reports prepared after these analysis are used by the police and the courts, thus the results have to be correct and exact. Because of this fact the applied analytical methods and procedures have to be valid and short enough to reach the correct results as soon as possible. Also this is the situation for an applicable analytical method which should be short, low cost, valid, possible to confirm and easy to apply, also environmentally friendly.

In this study two analytical methods which are regarded as the most reliable and sensitive methods in analysis of organics, were used for the analysis of the postexplosion soil samples after optimization of both methods and the procedure. The previously used GC-MS and GC-TEA methods were optimized by changing the parameters (injection temperature, column temperature program) by evaluating the parameters in the literature.

Sample preparation is the crucial step that the trace amounts of explosives that survived the explosion have to be extracted and determined with instruments. Thus a sample preparation procedure must provide the maximum recovery of the sample. As being a postexplosion residue the samples were really full of organic and inorganic contaminants and interferences. The procedure and the methods must be capable of eliminating the effects of these contaminants to the results.

There is always a risk of sample loss with time as some of the explosives materials are volatile. To overcome this risk, sampling should be done as soon as possible after

an explosion and these samples should be kept in cool (i.e. in a refrigerator) if immediate analysis is not possible. There were different extraction procedures in the literature, some of them require 18 hours, some of them require shaking on a cooled sonic bath, in some of them manual shaking is applied. In this study in order to shorten the analysis time of postexplosion samples; the soil samples were extracted with acetone and filtered after shaking manually, then concentrated in a preheated oven which serves the maximum recovery of the analyte and short time period.

The results showed that GC-TEA is the method of choice for the postexplosion analysis which has high sensitivity and high selectivity, due to this it provides simple chromatograms. Sometimes using such an instrument which is only selective to a certain group of organics will be a disadvantage if additional components which can help to determine the explosives also exists, as in composition type explosives. To overcome this disadvantage and to determine the unidentified peaks at GC-TEA a reliable and sensitive confirmation method is needed.

GC-MS which is the widely used method in forensic laboratories can be used for this confirmation analysis. It is better to use a GC-MS for only explosives analysis if financial ability of the laboratory allows, to avoid contamination of the column with other materials. As can be seen from the total ion chromatograms of the samples, organic constituents in the sample will co-elute with the analyte and suppress the peak of the analyte or worsen the resolution. The analyst should be aware of this fact to isolate and determine the peak of the analyte by using the advantages of modern instruments' softwares.

As the experts working in Police Criminal Laboratory the results of this study made us feel comfort to see the efficiency of analytical methods and procedures in analysis of the postexplosion samples. As future aspects of the study the application of different methods and different sampling methods like SPME to the analysis of peroxide explosives which hardly survive after an explosion and really difficult to determine by solid-liquid extraction methods, should be studied.

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