Detection of explosive vapors from TNT buried in sand by gas chromatography and tunable electron energy monochromator-mass spectrometry using HS-SPME

DETECTION OF EXPLOSIVE VAPORS FROM TNT BURIED IN SAND BY GAS CHROMATOGRAPHY AND TUNABLE ELECTRON ENERGY MONOCHROMATOR-MASS SPECTROMETRY USING HS-SPME

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ABSTRACT

The finding of buried explosives by detecting vapors emanating from explosives requires using a method that has high sensitivity and selectivity. In this work the results of an alternative methodology for explosive vapor detection based on GC-μECD is reported. A JEOL GCmate II - mass spectrometer coupled to a Tunable Electron Energy Monochromator (GC/TEEM-MS) was used for detected explosives identification. Both used the technique known as solid phase microextraction (SPME) in headspace (HS) mode to collect vapors above the samples. SPME is a simple technique that integrates sampling, extraction, concentration and sample introduction into a single step. Initially the optimum parameters for SPME were determined with the aim of obtain a high-quality extraction. The parameters were: type of SPME fiber, exposure time and desorption time in the port injection of the GC. HS-SPME procedure was carried out in samples with crystals of TNT buried in sand. These samples were analyzed under different environmental conditions such as temperature and water content. Analyses at several times after the TNT-soil mixture preparation were carried out during 1 month. Vapors of TNT and 2,4-DNT were found predominantly in the samples. HS-SPME coupled with GC-μ ECD and GC/TEEM-MS exhibited excellent selectivity and sensitivity.

RESUMEN

El encontrar explosivos enterrados detectando los vapores que emanan de los explosivos requiere usar un método que tenga alta sensitividad y selectividad. En este trabajo se informan los resultados de una metodología alterna para la detección de vapores de explosivos basada en GC-μECD. Un espectrómetro de masa modelo GCmate II acoplado a un monocromador de electrones de energía ajustable (GC/TEEM-MS) marca JEOL se utilizó para la identificación de los explosivos detectados. Ambos usaron la técnica conocida como micro extracción en fase sólida (SPME) en el modo de espacio de cabeza (HS) para colectar los vapores sobre las muestras. SPME es una técnica simple que integra muestreo, extracción, concentración e introducción de la muestra en un solo paso. Inicialmente los parámetros óptimos para SPME se determinaron con el objetivo de obtener una extracción de alta calidad. Los parámetros fueron: tipo de fibra para SPME, tiempo de exposición y tiempo de desorpción en el puerto de inyección del GC. El procedimiento de HS-SPME se llevó a cabo en muestras con cristales de TNT enterrados en arena. Estas muestras se analizaron bajo diferentes condiciones ambientales tales como: temperatura y contenido de agua. Se llevaron a cabo análisis a varios tiempos después de haber preparado la mezcla (TNT-suelo) se llevaron a cabo durante 1 mes. Vapores de TNT y 2,4-DNT fueron encontraron predominantemente en las muestras. HS-SPME acoplado con GC-μECD y GC/TEEM-MS exhibió excelente selectividad y sensitividad.

To God, to my parents, my sister and my brother.

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CHAPTER I

INTRODUCTION

A critical environmental problem found in many regions of the world is the presence of explosives in water and soils. Particularly the soils are contaminated with explosives during wars and conflicts between nations and between political sectors within a territory. The majority of explosives from warfare are buried in soils as landmines. Buried anti-personal (AP) and antitank (AT) landmines represent a severe problem in humanitarian, economic and environmental terms in many countries. The detection of landmines is an acute and urgent worldwide problem that needs specific, rapid, and cost effective solutions. Therefore, many detection techniques have been developed to find explosives with high level of sensitivity, and low false alarm rates. Currently, the detection of trace amounts of explosives by sensing the explosive vapors evolving from buried landmines has been a new chemical detection concept. This technique requires high specificity, selectivity and it focuses on decreasing the limits of detection (LOD) and increasing the discrimination among the various types of explosives and other interfering compounds (Jenkins, 2000).

On the other hand, the type of explosives present in landmines is very significant in the detection process. Almost 80% of all the types of mines manufactured worldwide contain 2,4,6-trinitrotoluene (TNT) or mixtures of explosives containing TNT. The mass of TNT contained in these mines ranges from as little as 50 grams up to 11 kilograms. This mass of TNT is enough to produce vapors of explosive signature compounds that can be released into the soil for decades, (Fisher, 2000).

TNT can exist as six diverse isomers. The isomer that is used in the explosive industry is the symmetrical isomer 2,4,6-trinitrotoluene. The well known nitroaromatic explosive has a number of advantages which have made it widely used in military explosives, such as: it has low manufacturing costs, it can be manufactured from cheap raw materials, it is reasonably safe to store and handle, and it has a low impact and friction sensitivity. Besides TNT has good chemical and thermal stability, good compatibility with others explosives and low volatility (Akhavan, 1998).

However, the process of TNT manufacture generates nitroaromatic compounds, some of which many remain as part of the bulk explosive as contaminants at a level of up to several percent by mass. Some of these compounds are significant contributors to the chemical fingerprint of landmines. Many of these compounds found in TNT, are most prevalent in the vapor phase chemical signature of landmines for example: 2,4-dinitrotolune (2,4-DNT) and 2,6-dinitrotolune(2,6-DNT). Also, when TNT is degraded other several compounds appear in the vapor phase. Some of these are 2-amino-4,6-dinitrotoluene (2-A-DNT), 4-amino-2,6-dinitrotoluene (4-A-DNT), 2,4-diamino-6-dinitrotoluene (2,4-DANT) and 2,6-diamino-4-nitrotoluene (2,4-DA). All TNT degradation products and the explosives related with TNT must be considered in landmines vapor detection. (Jenkins, 1999 and 2000)

In addition, when TNT is buried as landmines, vapors of signature compounds escaping from the mine are quickly adsorbed onto nearby soil particles or dissolve in soil water. These molecules are adsorbed by most surfaces. The explosives into the liquid and gas phases are governed by environmental parameters such as soil moisture, temperature and type of soil (Fisher, 2000).

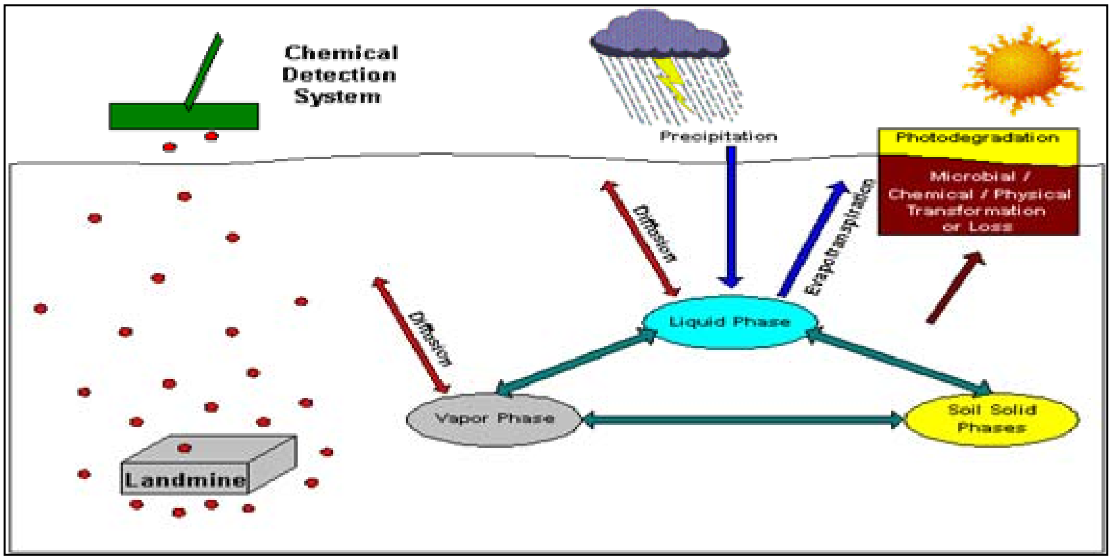


Figure1. Environmental effects affecting the detection of vapor phase explosives (Nomadics, 2000).

In this work, a methodology designed to identify and analyze explosives in the vapor phase has been developed. Solid phase microextraction (SPME) operating in headspace (HS) mode provides a powerful technique for explosive extraction in vapor phase. SPME can integrate sampling, extraction, concentration and sample introduction into a single step, resulting in high sample throughput. It is a fast, simple, precise, sensitive and selective technique that does no require use of organic solvents.

A Gas Chromatograph–Mass Spectrometer (GC/MS) coupled to a Tunable Energy Electron Monochromator (TEEM) and a GC-Micro Electron Capture Detector (μECD) were used to develop the methods of analysis and identification of explosives. The experiments were done with these two methodologies: GC–μECD SPME-HS for detection of vapor explosives from soil and HS-SPME GC/TEEM-MS for compound identification. Also several environmental effects were analyzed with mixtures of TNT-soil. The effects of temperature, moisture and contact time were evaluated with the GC–μECD SPME-HS methodology. SPME parameters such as: type of fiber, desorption time and extraction time were evaluated and optimized in order to obtain a high-quality extraction. The results obtained using the GC/TEEM-MS were used for identification of explosives.

CHAPTER II

PREVIOUS WORKS

Thomas Jenkins has contributed to the field of explosives detection for over 30 years. In 1999 he published a special report for the U.S. Army Corpse of Engineers, Cold Regions Research and Engineering Laboratory (CREEL) in which he documents on experiments that were conducted to investigate the qualitative and quantitative effects of soils barriers at various temperatures on the vapor signature from buried military grade TNT, (Jenkins, 1999). The explosive samples were buried beneath 2.5 cm of either a sand, silt or clay soil in small amber glass vials. The vials were held at temperatures of -4, 12 and 23 °C for contact times ranging between 63 and 173 days before the soil was removed and analyzed for explosive signatures. In this report the headspace vapor was sampled in the vials periodically using polyacrylate, solid phase microextraction (SPME) fibers. Six sampled were quantified using GC-μEC. No equilibrium calibration procedure was incorporated to the analysis. Qualitatively, the isomers of dinitrotoluene (DNT), dinitrobenzene (DNB) and Trinitrotoluene (TNT) accounted for all of vapors detected in headspace above the soils. Vapor concentrations were generally larger above sandy soils than above silt soils, and longer above silts than clay. Soil moisture level was also an important variable in controlling headspace vapor concentrations. For air-dried soils, vapor concentrations were lower than for either of the higher moisture content for all three soils at all temperatures. Soil–air partition coefficients were computed for samples that had detectable signature in both headspace and the surface soil. These coefficients were higher for 2,4,6-TNT than for 2,4-DNT or 1,3-DNB. They were found highest for clay and lowest for sand. Thus, it was possible to use the natural pre-concentration of signature vapors that takes place on surface soil to increase their detectabilty.

A special report from Sandia National Laboratories presented a study by Phelan in 2001 (Phelan, 2001). This work describes the ability to collect, concentrate and detects explosives in water and soil at concentrations representative of buried explosive. Phelan developed experiments in order to find the soil-air partitioning of TNT and DNT at several soil water content. These experiments were carried out using 2 gallon paint cans. Analytical grade of 2,4-DNT and TNT were added to each paint can respectively, ten samples of soil were collected from top surface. The samples were placed into 40 mL amber vials; deionized water was then added to each vial (5, 10 or 20 µL) and SPME fibers were used to sample the headspace vapor. The polyacrylate SPME fibers used were desorbed into a HP 6890 Gas Chromatograph equipped with a micro electron capture detector. The results demonstrated, in general, that vapor concentration in the headspace increased with the water content for 2,4-DNT up to 0.070 g/g soil moisture content. At this point the headspace concentration was constant. In the case of TNT the vapor concentration increased until 0.060 g/g water soil content, following constant. Also, Phelan and collaborators performed the SPME fibers calibration. They measured the amount of analyte sampled by the SPME fiber per unit time and estimated the effective sampling rate from the assumed vapor density for both TNT and 2,4-DNT. This effective sampling rate increased with the temperature for both TNT and 2,4-DNT. Finally, after SPME fibers calibration, the vapor phase concentration in the headspace was quantified for all samples.

In 2001, Jenkins and collaborators measured the headspace equilibrium above several real landmines, such as: PMA-1A and PMA2 (Plastic case Yugoslavian antipersonnel land mine), TMA5 (Plastic case Yugoslavian antitank landmine) and TMM1 (Metal case Yugoslavian antitank landmine) these mines are Yugoslavian type landmine (Jenkins, 2001). The experiments were carried out using solid phase microextraction fibers for sampling. The analytes were determined using gas chromatography with an electron capture detector. The major vapors detected were the various isomers of DNT, dinitrobenzene (DNB) and TNT with 2,4-DNT and 1,3-DNB often predominating. Although TNT made up from 50 to 99% of solid explosive, it was only a minor component of equilibrium vapor. The flux of chemical signature from intact mines was determined by placing several of these mines in Tedlar bags and measuring the mass accumulation on the walls of the bags after equilibrating the mine at one of five temperatures. TNT was the major component of the surface contamination on these mines, yet it accounted for less than 10% of the flux for the three plastic-cased mines, and above 33% from the metal antitank mine. Either 2,4-DNT or 1,3-DNB produced the largest vapor flux from these four types of landmines. The environmental stability of the most important landmine signature chemicals was determined as function of temperature by fortifying soils with low aqueous concentration of suite of these compounds and analyzing the reaming concentration, indicating that half-life is concentration dependent. At 23°C, the half-life of 2,4,6 TNT was found to be only about 1 day. Under identical condition, the half-life of 2,4-DNT was about 25 days . A minefield for research was established and a number of these same four mines types were buried. Soil samples were collected around these mines at several times after burial and the concentration of the signature chemicals was determined by acetonitrile extraction and GC-ECD analysis. Relatively high concentrations 2,4-DNT and 2,4,6-TNT were found to have accumulated beneath a TMA5 antitank mine, with lower concentrations in the soil layers between the mine and the surface. Signatures were distributed very heterogeneously in surface soils and concentrations were very low.

In 2003, Calderara and co-workers studied the capabilities of the SPME coupled with GC/ECD to detect and identify explosive traces directly from water extract. They used four different SPME fibers (PDMS/DVB, CAR/PDMS, PDMS, and Polyacrylate). These SPME fibers were tested to analyze the most common explosives including nitroaromatics, nitramines and nitroesters. The nitroesters family showed the best affinity for PDMS/DVB. The Polyacrylate fiber was more efficient in trapping explosives than Carboxen/PDMS. The results show that PDMS/DVB was the best fiber to trap the majority of organic explosives from aqueous residues and can be used for rapid screening to detect their presence. Another SPME parameter, the agitation was optimized. A special device was designed to improve the agitation. All explosives enhanced the extraction with stirring, except RDX. Direct desorption effect of SPME fiber on the column compared with to normal split-splitless injection was shown. In this way, the degradation of the most sensitive explosive was decreased. The sensitivity was improved associated with an on-column injection mode, (Caldera, 2003).

CHAPTER III

THEORY OVERVIEW

This chapter presents some important concepts related with the experiments performed during this investigation. The explosives studied and techniques used for their analysis are presented. Besides, the instruments involved in this study are described in this chapter.

3.1. Explosives

An explosive is a material, either a single substance or a mixture of substances, which is capable of producing an explosion by it's the energy released on detonation. The explosives can be classified in three categories: propellants, primary or low explosives and secondary or high explosives.

The propellants are combustible materials and do not detonate as their principal reaction, but rather deflagrate. Primary explosives or initiators can be easily detonated when they are heated or subjected to shock or spark. Finally, high or secondary explosives detonate under the influence of the shock wave of explosion of a suitable primary explosive. (Davis, 1998). All explosives studied in this investigation: TNT and DNT are secondary explosives.

3.1.2. Trinitrotoluene (TNT)

The main explosive used during this study was TNT. This explosive is a nitroaromatic compound. It has a pale yellow color when in crystalline form. Both orthorhombic and monoclinic TNT have been observed. Its structural formula is presented in the Figure 2. TNT is made by toluene nitration in one, two o three stages with a mixture of nitric and sulfuric acids. The predominant impurity of this process is 2,4-DNT. (Gibbs, 1980)

Figure 2. Chemical structure of 2,4,6-trinitrotoluene

It is sparingly soluble in water (0.0130 g TNT dissolved in 100 g of water) but highly soluble in acetonitrile and acetone. Its density is 1.65 g/mL, the melting point 80.65 ºC and the bolding point is 210 ºC, (Akhavan, 1998). The vapor pressure is 6.71×10^{-6} torr at 23°C (Pella, 1977). TNT is relatively insensitive to impact, friction, shock and electrostatic energy. Besides it can be detonated by moderate force when confined between metal surfaces such as on threads of bolts. On the other hand TNT is toxic and its absorption can cause anemia, cyanosis, gastritis and dermatitis (Yinon, 1993).

TNT contains a number of impurities, including 2,4-DNT, other isomers of dinitrotoluene, l,3-dinitrobenzene (DNB) and other isomers of trinitrotoluene, especially 2,4,5- and 2,3,4-TNT.

Table 1. Summary of major impurities and environmental transformation products associated with military grade TNT.

COMPOUND	SOURCE*
2,4-dinitrotoluene	I
2,6-dinitrotoluene	I
1,3-dinitrobenzene	I
2,4,5-trinitrotolene	I
2,3,4-trinitrotoluene	I
2-amino-4,6-dinitrotoluene	M
4-amino-2,6-dinitrotoluene	M
Tetranitroazoxytoluene	M
2,4-diamino-6-nitrotolune	M
2,6-diamino-4-nitrotoluene	M
2-hydroxylamino-4,6-dinitrotoluene	M
4-hydroxylamino-2,6-dinitrotoluene	M
1,3,5-trinitrobenzene	I, P
1,3,5-trinitrobenzaldehyde	I, P
1,3,5-trinitrobenzoic acid	I, P
3,5-dinitroaniline	P
2-amino-4,6-dinitrobenzoic acid	P
3,5-dinitrophenol	P
3,5-dinitrocatechol	P
3,5-dinitrohydroquinone	P
4,6-dinitroanthranil	P
2,4,6-trinitrobenzonitrile	P

I = impurity in production grade TNT ; M = Microbial transformation product of TNT
P = photodegradation product of TNT.

In addition, it is subject to photo and microbial degradation from which a variety of transformation products have been identified in laboratory studies (Jenkins, 1995, and 1992) TNT manufacturing processes vary around the world, which produce a variety of impurities at various levels, for example, Table 1 presents some nitro compounds associated to military grade TNT.

Some compounds are present by TNT degradation or TNT impurity from production. Usually when TNT is buried in soil, others compounds appear at the surface. The analytes most commonly detected in soil samples collected near to landmines are 2,4-DNT, 1,3-DNB and amino DNT isomers (Jenkins, 2000). Specially 2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene are produced by biodegradation of TNT. Aerobic and anaerobic microorganisms attack TNT and reduce it to the corresponding amino derivatives via the formation of nitroso and hydroxylamine intermediates (Esteve-Núñez, 2001).

The soils, where TNT containing landmines is buried, are a complex medium that contains air, water and soil particles. The landmine chemicals can exist in the air as vapors, in the water as a solute and on soil particles as a residue (Phelan, 2001). Currently, the techniques for detecting explosives in soils are based in finding explosive vapors that evolve to the soil surface. However, vapor phase TNT and its degradation products in air over minefield soils is often five to six orders of magnitude less than the concentration in the soil. As the distance from the mine increases, these concentrations decrease (Nomadics, 2002).

Explosive vapors concentrations at these levels can be detected using two kinds of methods: biological sensing or chemical sensing. Biological detection methods involve the use of mammals, insects or microorganisms to detect explosives. For example dogs, bees, bacteria and rats are often used. Chemical detection includes remote sensing methods such as infrared or laser methods. Also other methods like florescence measures changes in polymer fluorescence quenching in the presence of explosive vapors. Other methods consist of electrochemical and piezoelectric measurements. Moreover, only a few laboratory instruments, such as a gas chromatograph (GC) utilizing an electron capture detector (ECD) and mass spectrometers are able to detect low explosive concentrations.

In this investigation a GC-μECD was used for analysis of samples and GC/ TEEM-MS was used for identification of explosives. These analytical techniques and some theory concepts are described in the next section.

3.2. Gas Chromatography

Gas chromatography is one of the most important separation processes in chemical analysis for isolation and quantification of individual substances in complex mixtures. All forms of chromatography involve the distribution of compound between two different phases: a mobile phase and the other stationary. In GC the mobile phase is an inert carrier gas and the stationary phase is the column packing material. Capillary columns, which have replaced packed columns, allow the separation. The choice of the correct column is made on the criteria: “like dissolves like”. The polarity of the stationary phase should correspond to the polarity of the substances being separated. The key parts of a gas chromatograph include: a source of gas as the mobile phase, an inlet system used to deliver sample to a column, the column where separations occur, an oven as a thermostat for the column, a detector to register the presence of a chemical in the column effluent and a data system to record and display the chromatogram. (See Figure 3)

The improvements in injection techniques and the incorporation of new detectors with high sensitivity and selectivity have contributed to extensive use of GC in explosive analysis (Hübschamann, 2001 and Yinon, 1996).

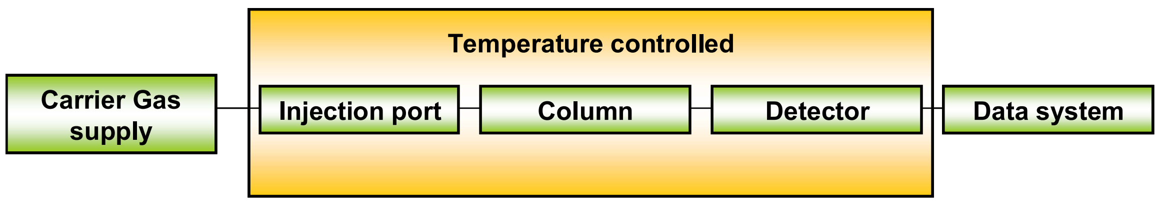


Figure 3. Block diagram of gas chromatograph.

3.2.1 Electron Capture Detector (μ-ECD):

The electron capture detector (ECD) is a very sensitive detector for molecules that contain electronegative atoms such as halogen or nitrogen. Therefore this detector is selective and it presents high response for detection of explosive samples. This detector consists of an ionization chamber, which contains a nickel plate, on the surface of which a thin layer of radioactive isotope ^{63}Ni has been applied. The carrier gas (N_2 or Ar/10% methane) is first ionized by β radiation (electrons emitted from the radioactive nucleus). The free electrons migrate towards the collector electrode and provide the background current of the detector. Substances with electronegative groups reduce the background current by capturing electrons and forming negative molecular ions. Figure 4 shows the GC-μECD used during this investigation.

3.3 Mass Spectrometry

Mass spectrometry has become a frequent technique for explosive analysis. In this technique the sample is ionized in a vacuum, a characteristic group of ions of different mass are formed. When these ions are separated, the plot of their relative abundance versus mass constitutes a mass spectrum. Mass spectrometry can be divided into separate processes: ionization, mass separation and recording of the ions formed. The ionization modes most used are: electron impact and chemical ionization. The ionization process can be produce negative or positive ions under certain conditions. Both positive ion chemical ionization and negative ion chemical ionization are methods used in the detection and identification of explosives (Karasec, 1988 and Yinon, 1996).

Figure 4. Gas chromatograph with micro electron capture detector used in this investigation.

Electron capture negative ion mass spectrometry (ECNI-MS) is a sensitive and selective method of analysis of nitrogen containing compounds. However, the requirement for a buffer gas in the ion source to moderate the electron energy introduces additional variables that affect the analysis. Various ions and neutral molecules in the source can react to give unpredictable false ions making it difficult to interpret the spectra. However, a recently developed MS uses an electron monochromator reduce the impact energy of the electron beam eliminating the need of a buffer gas (Laramée, 1992). The commercial version of this concept is the JEOL Tunable-Energy Electron Monochromator MS (TEEM-MS) coupled to a GC system.

3.3.1 GC/TEEM-MS

This new breed of GC/MS has an electron monochromator to generate negative ions by direct impact with a beam of electrons at very low energies that omit the buffer gas. The operating principle is that electrons emitted by tungsten filament outside the monochromator are collimated and focused by four electrodes into a magnetic field (See Figure 5). A small electric field of about 0.4 V/cm is established between a pair of vertical deflecting plates, oriented perpendicular to the electron beam.

The applied potentials are referenced to the filament center, generating a transverse electric field. This field, together with a magnetic field parallel to the initial beam direction, results in trochoidal motion of the electron. The electrons then move trochoidallly until they reach the exit aperture, which is a funnel-shaped to reduce scattering of electrons at the aperture walls. This assembly produces intense electron beams with energies ranging from 0 to 25 eV (Laramée, 1992 and 2000; Cody, 2000 and 2001).

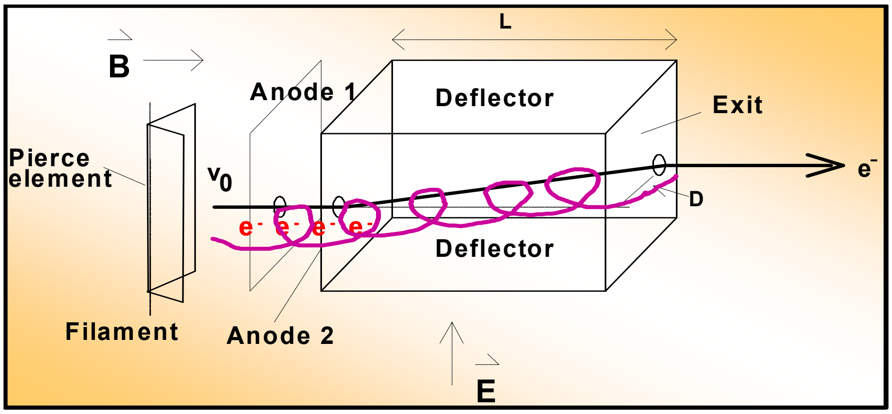


Figure 5. Operating principle of Tuneable Electron Monochromater (TEEM).

Control of the electron energy allows the emitted electron's energy to be tuned to the electron capture energy of a particular compound of interest. Selection of electron energy increases the specificity of the analysis. The electron monochromator also eliminates the need for a moderating gas that can cause reproducibility problems common to ECNIMS. The GC/MS with Tunable Electron Monochromater (TEEM) used in this research is presented in the Figure 6. The power supply controls and the monochromator are shown too.

The maximum energy value is 25 eV and the maximum filament current is 2.4 amps. This instrument presents many advantages over conventional mass spectrometry such as: high resolution, positive and negative ionization, reproducibility, sensitivity and selectivity. In addition, the TEEM-MS promotes selective ionization of the analyte and not the matrix, isomer discrimination and the avoidance of instrumental artifacts.

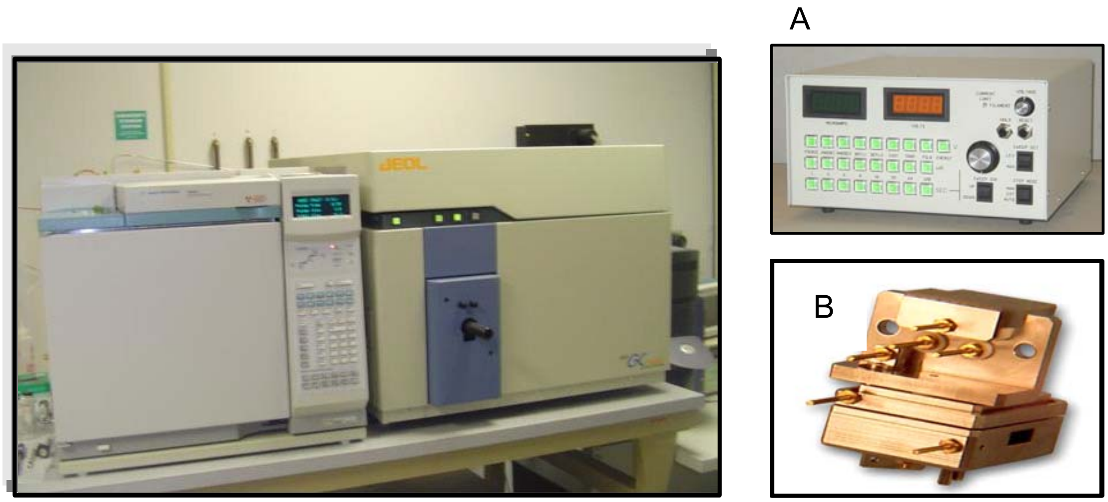


Figure 6. GC/MS with TEEM used in this investigation. A: Power supply control B: Monochromator

3.4 Extraction of explosive vapors from samples

In order to transfer the vapor sample to the GC injector port some techniques currently used have been improved and others have been developed. Because vapor pressures are very low for most explosive materials, vapors are usually pre-concentrated in some manner to improve ultimate volume detection limits. Explosives have been found to adhere to a variety of materials such as Teflon, glass, quartz, nickel, stainless steel, gold, platinum, copper, fused silica, aluminum and plastics (Hübschamann, 2001; More, 2004).

One of most powerful possibilities for instrumental sample preparation is the use of the headspace technique. Particularly when the sample matrix is soil headspace is very useful. There are several types of headspace analysis such as static headspace and dynamic headspace and purge and trap. However a new technique called solid phase microextraction (SPME) developed by Pawliszyn presents more advantages over previous headspace techniques (Pawliszyn, 1997).

3.4.1 Solid Phase microextraction (SPME):

SPME is a very sensitive, rapid, simple to use and solvent-free extraction technique. SPME uses a miniature cylindrical coated fused-silica fiber that can be exposed to liquid o gaseous samples. The fiber coating is an immobilized polymer. Once the analytes are trapped on the fiber, desorption can be made directly on the injection port from GC. This process is governed by temperature and time (Pawliszyn, 1997). There are three basic types of extractions that can be performed using SPME: direct extraction, headspace and membrane protection approach (see Figure 7).

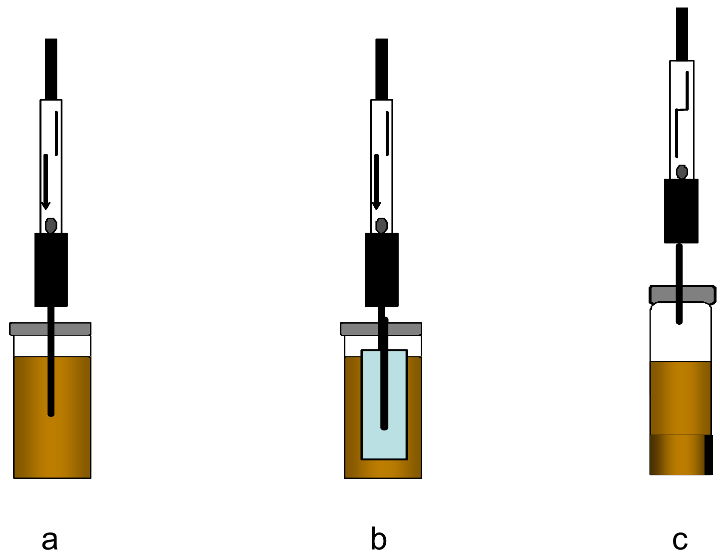


Figure 7. Modes of SPME operation: a = direct extraction, b = membrane protected SPME, c = headspace

When the fiber coating is in the headspace, the analytes are removed from the headspace first, followed by indirect extraction from the matrix. Therefore, volatile analytes are extracted faster than semivolatiles since they are at a higher concentration in the headspace which contributes to faster mass transport rates through the headspace (Pawliszyn, 1997).

3.4.1.1 Parameters that affect the extraction efficiency

Due to the relative simplicity of the technique many parameters can evaluated very fast. Among these parameters are type of fiber, adsorption time, desorption time, and temperature salting effect and stirring effect. The fiber coating selection is a very important parameter. Choice of fiber type is crucial and has to be made very carefully, mainly depending on the polarity and the water solubility of the explosive to trap. Many polymers are now commercially available and the differences are based on the type and thickness of the polymer coated on the fiber. Table 2 presents the most important coating and their properties. The extraction of analytes from samples can be performed by adsorption. This phenomenon also depends of fiber type.

Table 2. Fiber coatings commercially available for SPME use, (Penalver A. 2002).

Fiber coating	Film (µm)	Polarity	Temp* (ºC)	Time (h)	Extraction process	Applications
Polydimethylsiloxane (PDMS)	100[c]	Non-polar	250	0.5	absorption	Volatiles
	30[c]	Non-polar	250	0.5		Non-polar semivolatiles,
	7[a]	Non-polar	320	1		Medium to non polar semivolatiles
Polyacrilate (PA)	85[b]	Polar	300	2	absorption	Polar semivolatiles (phenols)
Polydimethylsiloxane-Divinylbenzene (PDMS/DVB)	65[b]	Bipolar	250	0.5	adsorption	Aromatic hydrocarbons, amines, nitroaromatic
	60[b]	Bipolar	250			
Carboxen/ Polydimethylsiloxane (CAR/PDMS)	75[b]	Bipolar	300	1-2	adsorption	Gases and volatiles
	85[b]	Bipolar	300			
Carbowax/Divinylbenzene (CW/DVB)	65[b]	Polar	220	0.5	adsorption	Polar analytes (alcohol)
	70[b]	Polar	220			
Divinylbenzene/Carboxen/Polydimethyl-siloxane (PDMS/DVB/Carboxen)	50/ 30[b]	Bipolar	270	1	adsorption	Trace level, odors and flavours.
Carbowax/ Template resin (CW/TRP)	50[b]	Polar	240	1	adsorption	Surfactants

* Conditioning temperature; a: Bonded phase; b: Partially cross-linked phase; c: Non-bonded phase

Another parameter that has to be optimized is the exposure time. This time is defined as the time after which the amount of extracted analyte remains constant. Stirring the sample decreases the time needed to reach equilibrium because it enhances the diffusion of analytes towards the fiber. Also an increase in temperature during extraction enhances the diffusion of analytes towards the fiber. Moreover, in the HS-SPME sampling mode, the temperature helps transfer analytes to the headspace.

The final parameter that requires optimization is desorption time. The analytes are thermally desorbed by GC, when the temperature increases, the affinity of analytes towards the fiber decreases and they are liberated. Besides, the flow of carrier gas within a gas chromatograph injector also helps to remove the analytes from the fiber and transfer them into the gas chromatograph column. The temperature of the injection port and the carrier gas flow rate plays important role in desorption time optimization.

CHAPTER IV

MATERIALS AND METHODS

4.1 Reagents and Chemicals

In this investigation high quality, standard solutions of explosives were used. TNT, 2,4-DNT,and 2,6-DNT, were obtained from the Restek Corp., Bellefonte, PA. TNT and 2,4-DNT crystals with a purity of 99%, were purchased from Chem Service Inc., West Chester, PA.

A standard mixture of explosives was also used. “Mix A” contained: cyclotetramethylenetetranitrate or octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), cyclotrimethylenetrinitramine or hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 2,6-dinitrotoluene (2,6-DNT), 2,4-dinitrotoluene (2,4-DNT) 1,3,5-trinitrobenzene (1,3,5-TNB), 1,3- dinitrobenzene (1,3-DNB), 2,4,6-trinitrophenylmethylnitramine (tetryl), 2,4,6-trinitrotoluene (2,4,6-TNT) , 4-amino-2,6-dinitrotoluene (4-A-DNT), 2-amino-4,6-dinitrotoluene (2-A-DNT), in 1000 ppm concentration for all explosives. This mixture was obtained from Restek Corp., Bellefonte, PA.

The mass spectrometer was calibrated for negative ions using primary standard grade nitrobenzene and hexafluorobenzene and perfluorokerosene (PFK) solutions. These were obtained from Aldrich Chemical Company, St. Louis, MO.

The soil-explosive mixtures were prepared using Standard Ottawa Sand (20-30 mesh, EM Science, Darmstadt, Germany). This material was obtained from Fisher Scientific, International, Chicago, IL.

4.1.2 SPME materials:

The headspace vapor was sampled by SPME using several kinds of SPME fibers: 50/30 μm Divinylbenzene/Carboxen on Polydimethylsiloxane (PDMS/DVB/CAR), 85 μm Polyacrylate (PA), 65 μm poly (dimethyl Siloxane)/divinyl benzene (PDMS/DVB), and 100 μm Poly(dimethyl Siloxane) (PDMS).

The analyses were performed using two fiber holders where the fibers were protected. The holders (Cat. No. 57330U) were manual with adjustable depth guide positions. The SPME products were acquired from Sigma-Aldrich-Supelco, Bellefonte, PA.

4.2 Instrumentation

The instruments conditions used for this study are illustrated in this section. All parameters were selected according to preliminary analysis and previous work described in Chapter II and following the work of Jenkins, (Jenkins, 1999).

4.2.1 Gas Chromatography with micro-ECD

The analyses were carried out using an Agilent Technologies, Inc. (Palo Alto, CA), GC Network system model 6890N, equipped with a micro cell, ^{63}Ni Electron Capture Detector (μ-ECD). The temperature of the detector was 325 ^{o}C and the makeup gas was nitrogen (30 mL/min). The temperature at the injection port was 250 ^{o}C. Sample introduction was made using a standard split/splitless type injector in the splitless mode. Two inlet liners types were used, one of them for direct injection analysis with a length of 78.5 mm, an outer diameter (O.D.) of 6.3 mm and a liner diameter (I.D.) of 1.5 mm obtained from Sigma-Aldrich-Supelco, Bellefonte, PA (Cat. No.2051701). The other inlet liner was used for SPME analysis with 0.75 mm I.D (Cat.No. 2637501 Sigma-Aldrich-Supelco, Bellefonte, PA). A capillary column was used for the separations: an RTX-5 (cross bonded 5% diphenil-95% dimethyl polysiloxane) 15 m x 0.25 mm ID x 0.25 μm df, Restek Corp, Bellefonte, PA was used. The oven conditions were: initial column temperature of 100°C (hold 2 minutes), ramp to 200°C at 10°C/min, then ramp to 250°C at 20°C/min and hold for 5 minutes. The carrier gas was nitrogen with a constant flow rate of 1.9 mL/min.

4.2.2 Mass Spectrometer (GC/TEEM-MS)

The second instrument used was the Mass Spectrometer model GCMate II magnetic sector, double focusing and high resolution (JEOL, Peabody, MA) equipped with a Tunable Energy Electron Monochromator. The mass spectrometer is coupled with the GC (6890N, Network GC System) described previously. The GC conditions were initial column temperature of 100 ^{o}C (hold 2 min), ramp to 200 ^{o}C at 10 ^{o}C/min, then 20 ^{o}C /min to 250 ^{o}C and hold for 5 minutes. The temperature for the injection port was 180 ^{o}C, in splitless mode. The liners were the same used for GC-μECD. Soil-explosives samples were analyzed using the GC/TEEM-MS, in negative ion mode at ionizing electron energy of 0.32 eV in full-SCAN (full range mass scan) and SIM (Single Ion Monitoring) modes.

4.3 Experimental Methods

The methodology used includes, instruments calibration, the optimization of the techniques used for the extraction of explosives (SPME) and the analysis of soil-explosives mixtures at several conditions with both instruments GC-μECD and GC/TEEM-MS.

4.3.1 Calibration curves for GC- μECD and GC/TEEM-MS

Two types of calibration curves were run by GC-μECD. These calibrations curves were prepared with 1000 ppm standard solutions of TNT and 2,4-DNT obtained from Restek Corp. Stock solutions of concentrations: 2.5, 1, 0.5, 0.1, 0.05, 0.025, and 0.01 ppm diluted in HPLC grade acetonitrile (Sigma-Aldrich Chemical Co., Milwaukee) were prepared. All solutions were injected directly using microliter glass syringes (Hamilton Series 7000) into the injection port. The analyses were run triplicates for each concentration. The calibration curves for GC/TEEM-MS were obtained with solutions of TNT. These solutions were injected in the GC/TEEM-MS by direct injection with triplicates of each concentration. Additionally, some samples of 2,4-DNT, 2,6-DNT, and “Mix A” obtained from Restek, Corp. of 1000 ppm were injected in the GC/TEEM-MS in order to establish the fragmentation patterns, sensitivity and calibration runs of these explosives with the MS instrument.

4.3.2 SPME-Headspace analysis

Several SPME parameters were evaluated with the aim of finding the best extraction conditions. The experiments designed for the optimization of SPME parameters were run by the GC-μECD. These analyses were carried for solutions of neat explosives.

- **Fiber type:** This was the first SPME parameter to be evaluated. The four SPME fibers were selected in this study because of the enhanced pre-concentration of explosives and vapor phase samples. Before the analysis all SPME fibers were conditioned in the injection port at the specified temperatures and times according to Supelco Company (see Table 2). After the conditioning process, fiber blanks were run to confirm that there was no unrelated peaks which might have been due to contaminants introduced during the manufacturing process of the fiber. The selection of best SPME fiber was carried out using four fibers: 50/30 μm Divinylbenzene/Carboxen on Polydimethylsiloxane on a 2 cm Stable Flex™ (PDMS/DVB/CAR), 85 μm Polyacrylate (PA), 65 μm poly (dimethyl Siloxane)/divinyl benzene (PDMS/DVB), and 100 μm poly(dimethyl Siloxane) (PDMS). Each fiber was introduced into a 15 mL transparent vial, from Supelco with open-top screw caps, septa removed, containing 0.05 g of TNT crystals during 30 minutes at room temperature (20 °C) and then analyzed using the GC-μECD. The extraction efficiency of the fiber was based on the average peak area counts of TNT for the three replicate analyses.

- **Desorption time:** This experiment was done using the best fiber obtained from previous experiment. The desorption time was evaluated by placing 0.05 g of TNT in 15 ml vials and allowing it to equilibrate for 1 hour at room temperature (20 ºC). SPME fibers were exposed to the headspace of the vials during 20 minutes. Then SPME fibers were inserted into the injection port where they were thermally desorbed during 4 minutes. This procedure was repeated at 5, and 6 minutes of desorption time. Once the analysis was finished, the fiber was returned to the injection port and a blank was run to make sure that the sample was unloaded completely. All samples were analyzed as triplicates with corresponding blanks.
- **Exposure time:** The last SPME parameter evaluated was the exposure time. Samples were prepared as before. Headspace over the explosive was allowed to equilibrate for one hour at room temperature (20 ºC). Then each vial was sampled using SPME fiber during exposure times of: 5, 10, 15, 20, 30, 50 and 60 minutes. The same procedure was used for 2,4-DNT crystals.

4.3.3 Methodology for extraction of TNT from vapor phase

The experiments with soils (sand) and explosive (TNT) were performed using the previous optimized SPME parameters for a high-quality extraction. Some soil conditions were evaluated. These analyses were run with both GC-μECD and GC/TEEM-MS. Figure 8 shows a representative scheme for this methodology.

4.3.3.1 Preparation of soil-explosive mixtures

The mixtures used for headspace sampling were prepared by weighting 20 g of Ottawa Sand Standard and transferring to a 40 mL amber vial (Fisher scientific). Samples of 0.10 g of crystalline TNT were placed above the sand, centered in the vial. Care was taken to be sure no TNT touched the vial walls. An additional 20g of sand was carefully placed into the vial, covering the TNT. This preparation was made at room temperature (20°C).

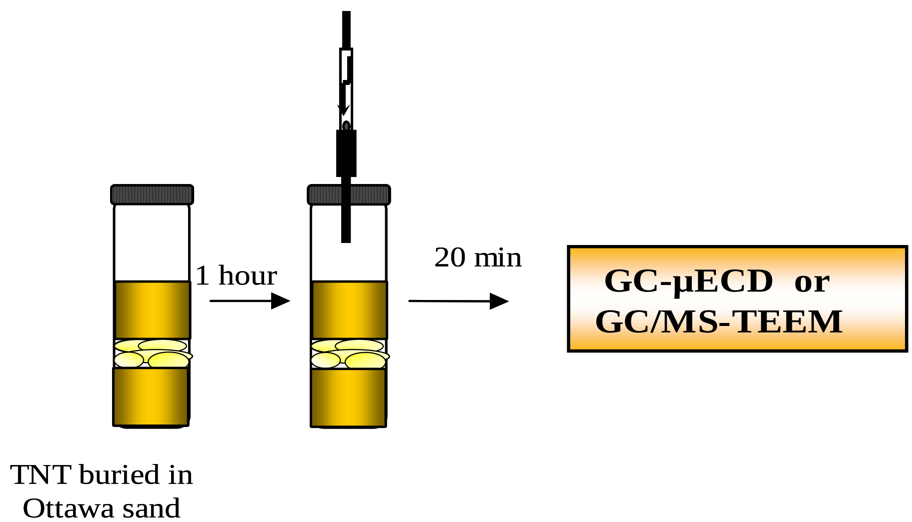


Figure 8. Scheme of the methodology for analysis of TNT buried in sand

4.3.3.2. Effect of Reaction (Contact) Time

In order to observe the evolution of vapors from the buried explosive samples, HS-SPME procedure was carried out at different hours after preparing the mixtures. The fiber was introduced in the vial at 1 cm above the sand. The extraction time used was 20 minutes. After sampling, the fiber was inserted into the injection port of GC-μECD during 5 min. The samples were analyzed during 1 month at 1, 6, 12, 24, 48, 72, 96, 120, 144, 168, 360, 480 and 720 hours after mixture preparation. Different vials were used for each sampling. Triplicates runs were done for each sample. After each extraction the fiber was desorbed to assure that it was clean.

4.3.3.3 Effect of Temperature

Four temperatures were investigated: 20, 30, 40 and 50^{o}C. Triplicates were run for each temperature. Samples were placed in a water bath at the desired temperature and left for 1 hour to equilibrate. After this period, the samples were analyzed with the same fiber used for the previous analyses. The sampling time was 20 minutes.

4.3.3.4 Effect of Water Content

Samples with different moisture levels were ran at room temperature (20 ^{o}C). This experiment was done by placing 0.1 g of TNT above 20 g of Ottawa sand in a 40 mL amber vial, after was covered with other 20 g of Ottawa sand. Three different amounts of water 10, 20 and 30 μL were added into the vials. Deionized water was added through the septum with a 1mL capacity syringe into three different vials. The deionized water was deposited on the sand. Subsequently, the samples were stored for 1 hour and sampled with SPME fiber for 20 min. The fiber was desorbed into the injection port of GC-μECD. Additionally others water amount were added. The samples were analyzed the same way. All analyses were performed with three replicates.

4.4 Experiments using GC/TEEM-MS

Typically the TEEM-MS is used in the negative ion mode since electron capture resonances occur at very low incident electron energies. However, this instrument can be operated in both negative ion and positive ion modes. The analyses performed in this investigation were run in negative ion mode only since they were carried out with the aim of identifying all components from the samples.

The TEEM-MS system includes a monochromator which replaces the standard source filament, described previously (Chapter III). The conditions of monochromator were tuned before the analysis. First a calibration file was generated with the optimum values for the electric potential of the anode, deflectors, electron trap and the exit slit. This file was loaded before each analysis.

Other parameters such as the filament current and electron energy maximum were adjusted manually during the calibration runs. The filament was operated in constant current mode in order to prevent the filament overheating and to maximize the filament lifetime. The current used during all analysis was 2.44 μAmps. The electron energy was adjusted to find a tuning condition for both the monochromator and mass spectrometer that produces an observable signal for negative ions. This tuning was performed gradually reducing the electron energy while monitoring the M^-

(*m/z* 123) and $[M\text{-}H]^-$ (*m/z* 122) ion from nitrobenzene. The value of electron energy was selected near to zero eV and this value produced predominantly the molecular anion at m/*z* 123. The electron energy used in SPME-HS analysis was 3.1 eV.

The monochromator was calibrated using a mixture of hexaflurobenzene (0.5 μL), nitrobenzene (0.5 μL), and PFK (1 μL). The mixture was put into a tube of dimensions 3 cm X 0.5 cm. This tube is let into the MS and under monochromator. The mixture was changed each 15 days.

The instrument was calibrated in SCAN and SIM modes. Scan mode calibration was carried out in mass range of 2- 1000 and using accelerating potential of 2500 V. The INTERSCAN was set at 0.2 seconds and a scan speed of 1 seconds/scan. The file with this calibration was generated used subsequently. In order to ensure the most accurate, a calibration SIM was performed for TNT and a group of (2,4-DNT, 2,6-DNT and 4-amino-2,6-DNT). This SIM calibration was used in all headspace experiments.

4.4.1 SPME-Headspace experiments with TEEM-MS

- **Vapor extraction from TNT**

Vials with TNT were prepared weighing 0.5 g of crystalline TNT into 40 mL amber vials. PDMS/DVB fiber was introduced into the vial and it was withdrawn 20 min after. The fiber was desorbed into the port injection of GC/TEEM-MS. This experiment was carried out in SCAN mode only. Triplicates were run for each sample.

- **Vapor extraction from Mixtures TNT-Sand**

Vials were arranged the same way than the section 3.3.1. All samples were extracted with PDMS/DVB fiber. The fiber was desorbed into the injection port from GC/TEEM-MS. The SIM mode was used in these sample runs.

CHAPTER V

RESULTS AND DISCUSSION

In this section the results of all experiments described in the Chapter IV are presented. The methodology applied for detection of vapors of explosives buried in soils was implemented and the results demonstrated the importance of SPME-HS as powerful detector of vapors over TNT buried in soil.

5.1 Experiments carried out with GC-μECD:

The first experiments performed in this instrument were the calibration curves for TNT and 2,4-DNT by direct injection. These explosives were selected because they are the most important vapor signals over landmines. The calibration curve obtained for TNT in acetonitrile is shown in Figure 9. The volume injected was 1 μL.

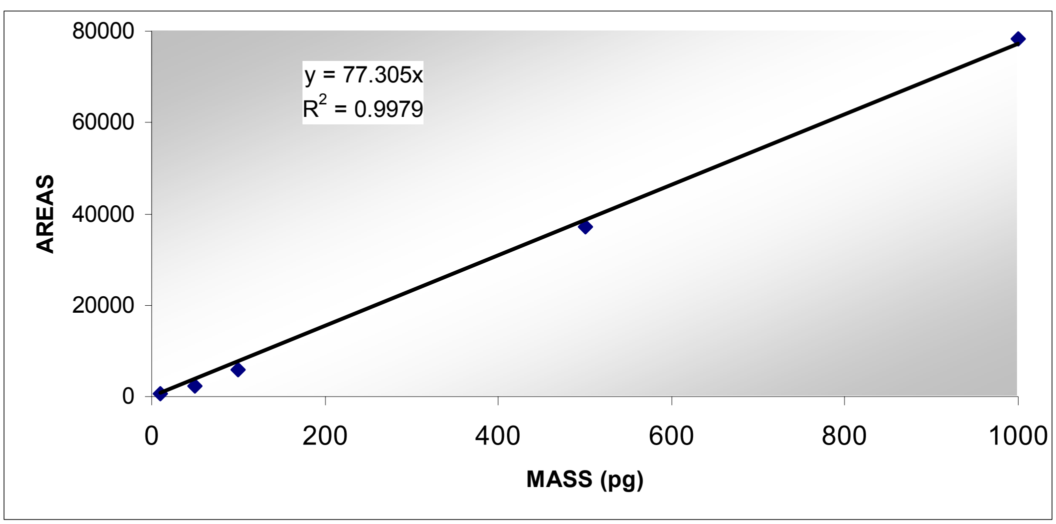


Figure 9. Linear regression for TNT in acetonitrile runs by GC-μECD by direct injection.

A regression coefficient (R^2) of 0.9979 was obtained. The minimum level of detection for this methodology was 10 pg, according to the criterion of signal to noise (S/N) ratio of 3. The peak corresponding to TNT had a retention time of 9.58 min. The standard deviation (σ) and the percent relative standard deviation (% RSD) for this curve is presented in Table 3.

Table 3. Calibration data obtained for TNT by direct injection using GC-μECD.

Mass(pg)	Area (counts)	Average	σ	RSD (%)
10	553	539	5.26E+01	9.7
	585			
	482			
50	1997	2286	3.56E+02	15.6
	2684			
	2177			
100	7495	5970	1.37E+03	23.0
	5572			
	4841			
500	37382	37067	1.30E+03	3.5
	38181			
	35637			
1000	91264	78355	1.83E+04	23.3
	65445			
	78353			

The calibration curve for 2,4-DNT in acetonitrile is presented in Figure 10 . Seven concentrations (0.025, 0.05, 0.1, 0.25, 1, and 2.5 ppm) were analyzed in triplicate and 1μL of each sample was injected into the GC-μECD.

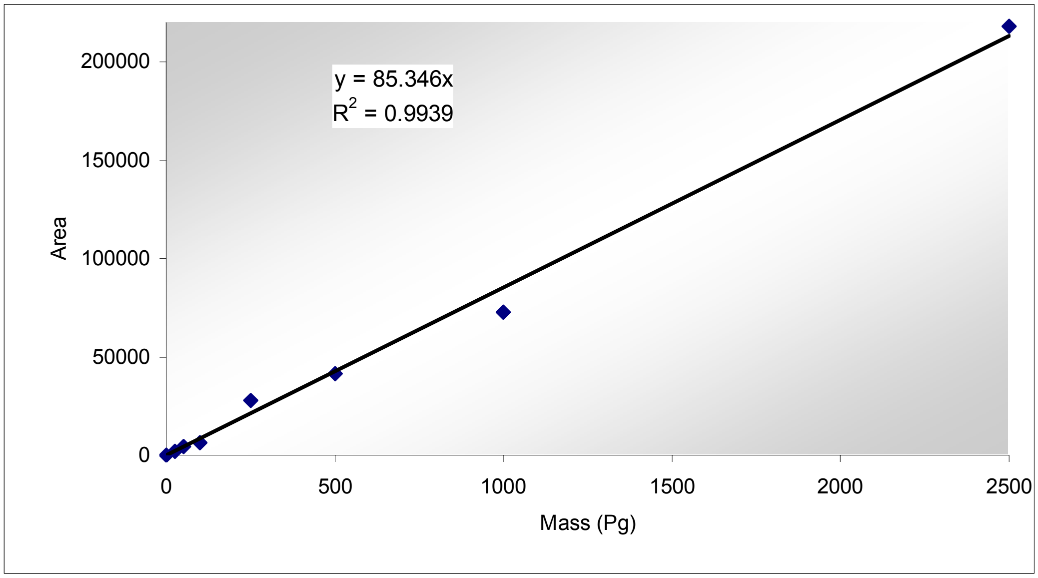


Figure 10. Linear regression for 2,4-DNT in acetonitrile determined using GC-μECD by direct injection.

Table 4 presents the standard deviation (σ) and the percent relative standard deviations (%RSD). These date confirm the linear model for the calibration curve.

Table 4. Calibration data for 2,4-DNT in acetonitrile by direct injection using GC-μECD.

Mass(pg)	Area (counts)	Average	σ	RSD (%)
25	2082 1971 2005	2019	56.8	2.81
50	4360 4297 3962	4206	213.9	5.08
100	6166 8274 3961	6133	1490.5	24.3
250	27014 32585 23158	27585	4739.4	17.18
500	47917 34756	41336	9306.2	22.51
1000	49131 95966 85727	72548	7240	9.97
2500	179190 258260 217236	218228	29008.3	13.29

5.1.2 Optimization of SPME Parameters

The second experiment carried out with the GC-μECD was the optimization of SPME parameters. Optimum values for the type of fiber, exposure time and desorption time were determined.

5.1.2.1 Selection of type of fiber:

The first parameter evaluated was the optimum fiber coating. Several fibers were tested with the aim of finding the best possible extraction conditions for explosive vapors emerging from solid TNT. These experiments were performed only with TNT crystals. The initial fiber tested was 65 μm poly (dimethyl Siloxane)/divinyl benzene (PDMS/DVB). The chromatogram obtained is presented in Figure 11.

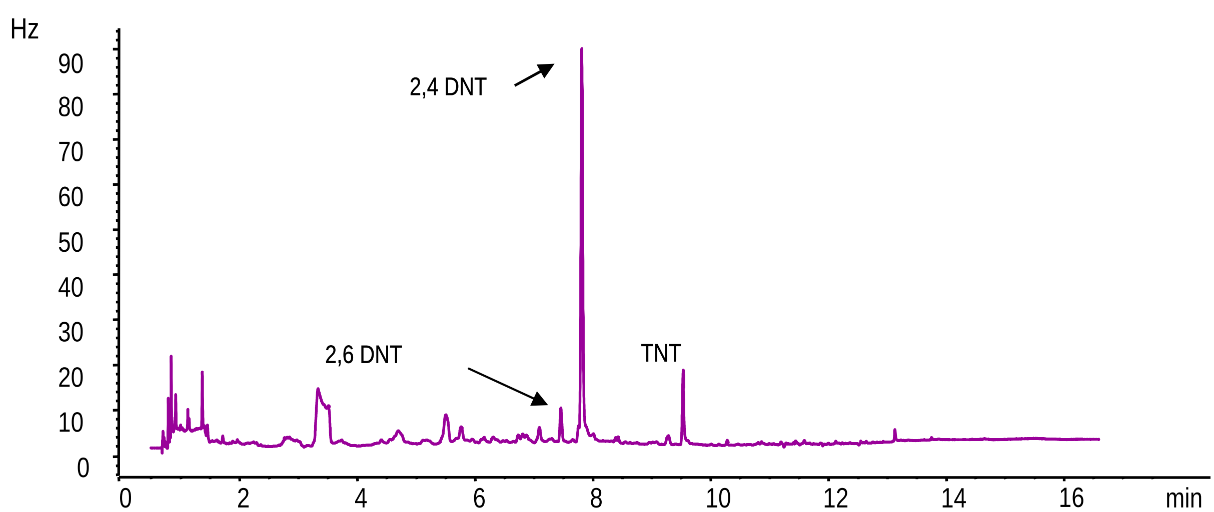
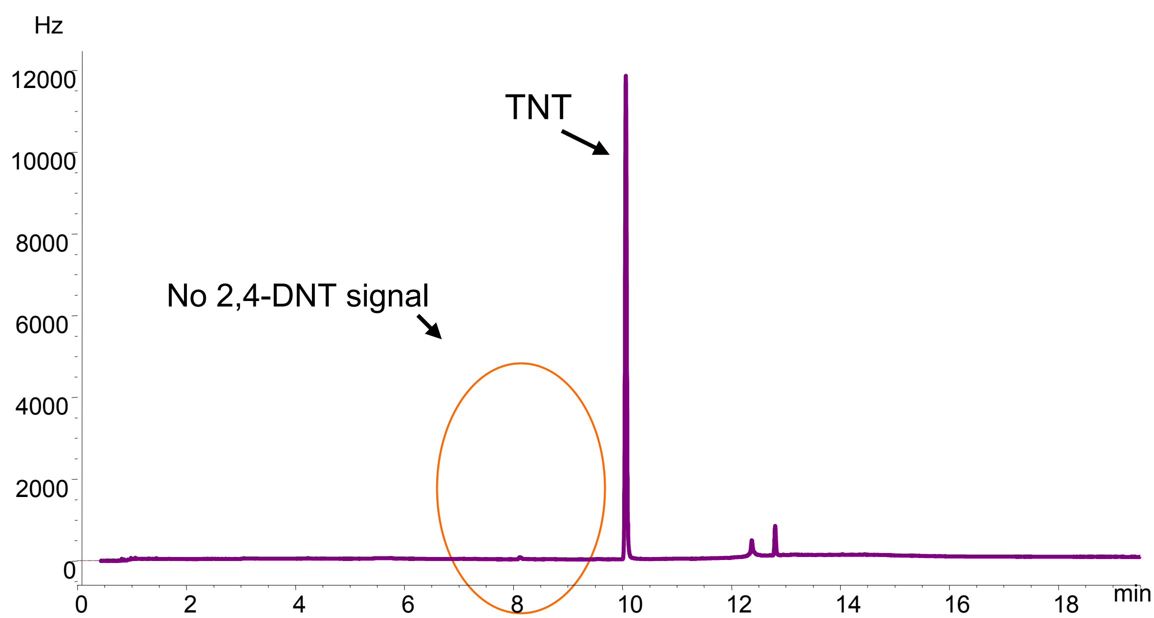


Figure 11. Chromatogram obtained using HS-SPME with PDMS/DVB fiber over TNT.

This chromatogram reveals the efficiency of the SPME fiber capturing vapors emerging from TNT. When this SPME fiber was used for extraction of vapors from TNT crystals, the results demonstrated that two prominent signals be found in the headspace. The most intense signal corresponds to 2,4-DNT and the second highest one is the TNT signal. This result was considered carefully because the TNT used in the experiment had a purity of 99.99%, therefore the 2,4-DNT vapor from TNT crystals could not be impurity from manufacturing process. For this reason some experiments were carried out with TNT standards solutions and solid sources.

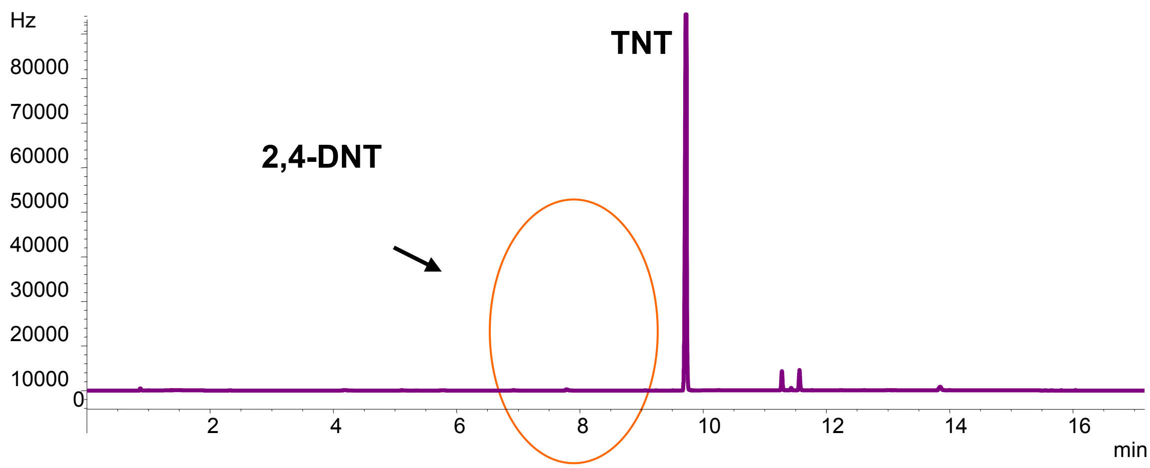
A 1 mL sample of TNT standard solution in acetonitrile was left to evaporate during several hours until crystals formed. These crystals (0.0001g) were put into a 4 mL amber vial. After 1 hour the SPME fiber (PDMS/DVB) was introduced in the vial for 30 min. at room temperature (20°C). The result obtained is shown in Figure 12.



Figue 12. Chromatogram of crystals of TNT from a TNT standard solution in acetonitrile sampled with SPME fiber PDMS/DVB.

The chromatogram shows that the TNT signal is the most prominent peak and the signal corresponding to 2,4-DNT is not present. This confirm that the most TNT crystals purity doesn't contain 2,4-DNT in the headspace.

A second experiment was performed but this time TNT crystals from ChemService used in the previous analysis was diluted in acetonitrile making a 10 ppm TNT solution. This solution was injected into the GC-μECD and the result is illustrated in Figure 13.



Figue 13. Chromatogram of 10ppm TNT solution in acetonitrile by direct injection using GC- μECD.

This chromatogram presents the absence of 2,4-DNT signal. The TNT signal is very strong as well as the previous experiment. This experiment evidences that the TNT crystals have not detectable impurity using the GC- μECD. Using these results it was decided that the SPME fiber were evaluated considering the two most intense signals into the headspace. The criterion used for choose the best fiber was the ability to collect both TNT and 2,4-DNT vapors from TNT crystals.

The results obtained when HS-SPME procedure was carried out with TNT crystals, using several SPME fibers, are shown in Figure 14. The PDMS/DVB SPME fiber was the most efficient for collecting TNT vapors from TNT crystals in the sample headspace. Besides this, SPME fiber requires just 30 min of conditioning time. Polyacrylate based fiber exhibited low efficiency for collecting TNT vapors emanating from the samples. However, Polyacrylate fiber was the most recommender fiber for polar compounds detection. The PDMS was the second best fiber, this SPME fiber is the most used in every kind analysis and it was the first used for coating fibers for SPME.

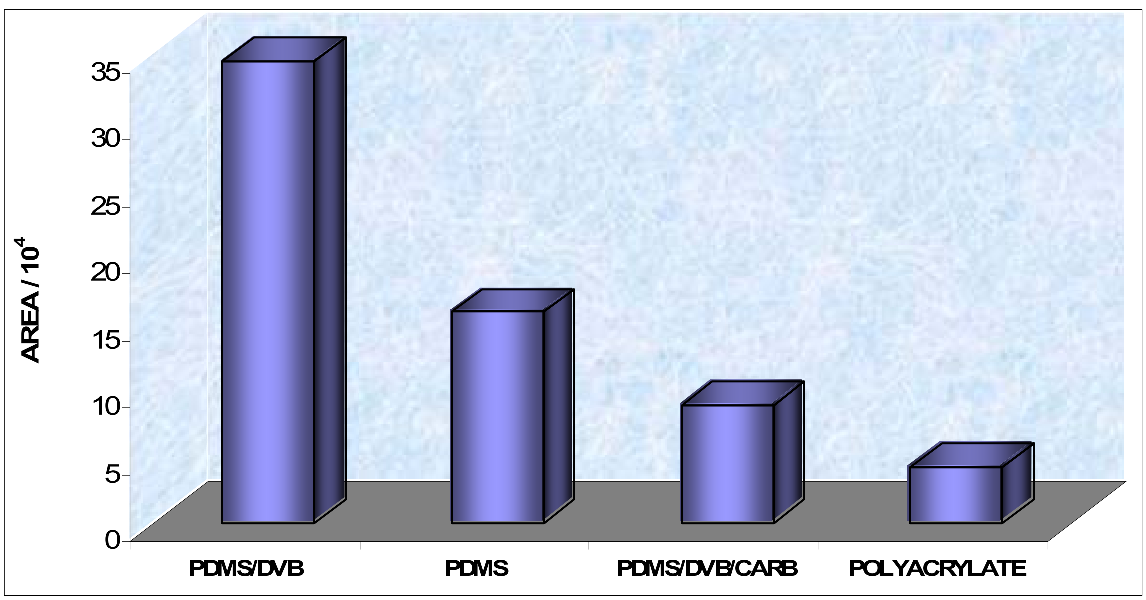


Figure 14. Vapors of TNT from TNT crystals detected by different types of SPME fibers.

The vapors of 2,4-DNT detected by the SPME fiber are presented in Figure 15. The experiments demonstrated that Polyacrylate was highly efficient for extracting 2,4-DNT from the headspace. In contrast this fiber was the least efficient for extraction of TNT vapors. The Polyacrylate is a polar fiber and it extracts more polar compounds. However the second best fiber was PDMS/DVB. Based on these results it is possible to conclude that there are two types of fibers appropriate to measure the vapors emanating from TNT: PDMS/DVB and Polyacrylate. PDMS/DVB was preferred because is sensitive to both vapors TNT and 2,4-DNT.

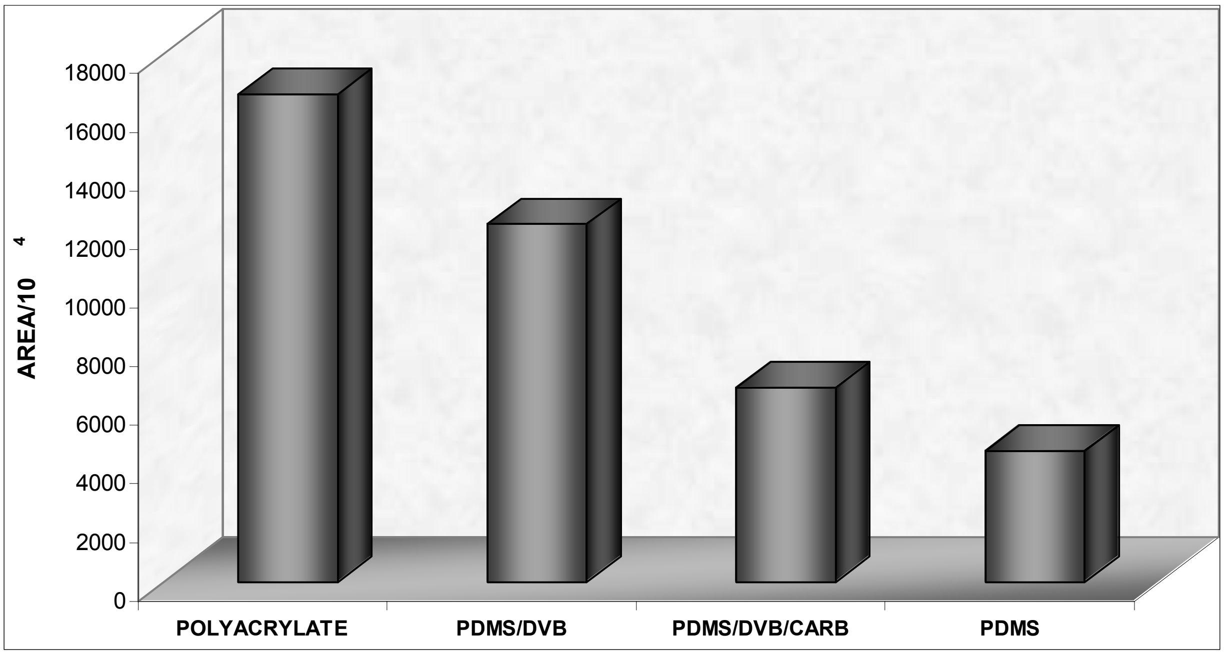


Figure 15. Vapors of 2,4-DNT from TNT crystals detected by several type of SPME fibers

5.1.2.2 Selection of desorption time

The explosives retained in the PDMS/DVB fiber were desorbed by thermal desorption using the GC injection port. Two parameters were considered: desorption time of the fiber at the injection port and GC injection port temperature. The first parameter was analyzed using three several times to leaving the fiber into the GC port. The PDMS/DVB fiber was desorbed during 4, 5 and 6 minutes. The results were based on comparison of the average areas obtained for TNT and 2,4-DNT sample desorption. The first time evaluated was 5 minutes. This time was sufficient to desorbed the fiber completely, therefore 4 minutes was tested. A desorption time of 6 minutes was evaluated to assure that the fiber was completely desorbed. The results are shown in Table 5. Five minutes was the best time for to leave the fiber into the injection port after the sampling. At this time the areas obtained for TNT and 2,4-DNT were high. Also the areas after desorption demonstrated that five minutes was the best time for to leave the fiber into the injection port after sampling (see Figure 16). No significant analyte mass is desorbed after the first 5 minutes of exposing the fiber to the injection port of the GC. Desorption time is usually achieved in less than two minutes for most compounds. However high desorption times can help to avoid the carry over effects.

Table 5. Desorption time of PDMS/DVB fiber for extraction of TNT in the headspace.

Time desorption	TNT Retention Time(min)	TNT Areas	2,4-DNT Retention Time (min)	2,4-DNT Areas	TNT Areas after desorption	2,4-DNT Areas after desorption
4 min	9.585 9.586 9.588	23045 11953 10995	7.652 7.650 7.653	780000 504000 602900	0	1938 255 329
5min	9.595 9.588 9.593	18179 10652 21234	7.668 7.644 7.645	855263 449445 657890	0	0
6 min	9.582 9.583 9.585	10787 14010 17967	7.634 7.631 7.640	500000 457496 796543	0	0

The second parameter was tested using two temperatures: 270°C (maximum temperature for PDMS/DVB) and 250°C (conditioning temperature). The time in the injection port was 5 minutes for both temperatures. The results are shown in the table 6. The areas obtained at 270°C were not significantly high with respect to 250°C. Therefore 250°C was the temperature chosen for injection port. Besides, some researchers recommend that the injector port temperature be set at the maximum temperature recommended by the manufacturer of the fiber coating. In the case of PDMS/DVB fiber coating the maximum recommended temperature is 250°C. In summary, 5 minutes was selected as the optimum desorption time at the GC injection port at a temperature of 250°C.

Table 6. Injection port temperatures using PDMS/DVB fiber at 5 min of desorption time

Temperature Injection Port	TNT Areas	2,4-DNT Areas	TNT Areas after desorption	2,4-DNT Areas after desorption
270°C	11240 15876	789548 457890	0	0
250°C	18179 10652	500000 457496	0	0

5.1.2.3. Selection of exposure time:

The exposure time is the time that the SPME fiber samples the headspace. First the selection of exposure time was carried out using five several times: 5, 10, 15, 20 and 30 minutes. The PDMS/DVB fiber was used for to extract the vapors over TNT crystals. The results during first 60 minutes are presented in Figure 17.

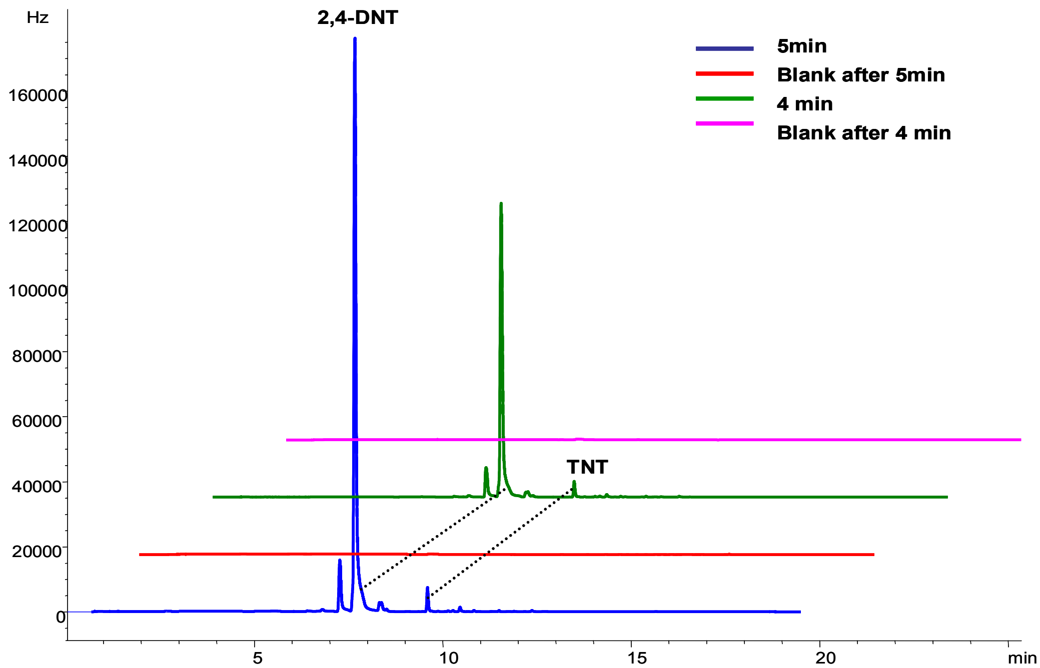


Figure 16. Time desorption chromatograms of 5 minutes and 4 minutes with their blanks obtained using PDMS/DVB fiber

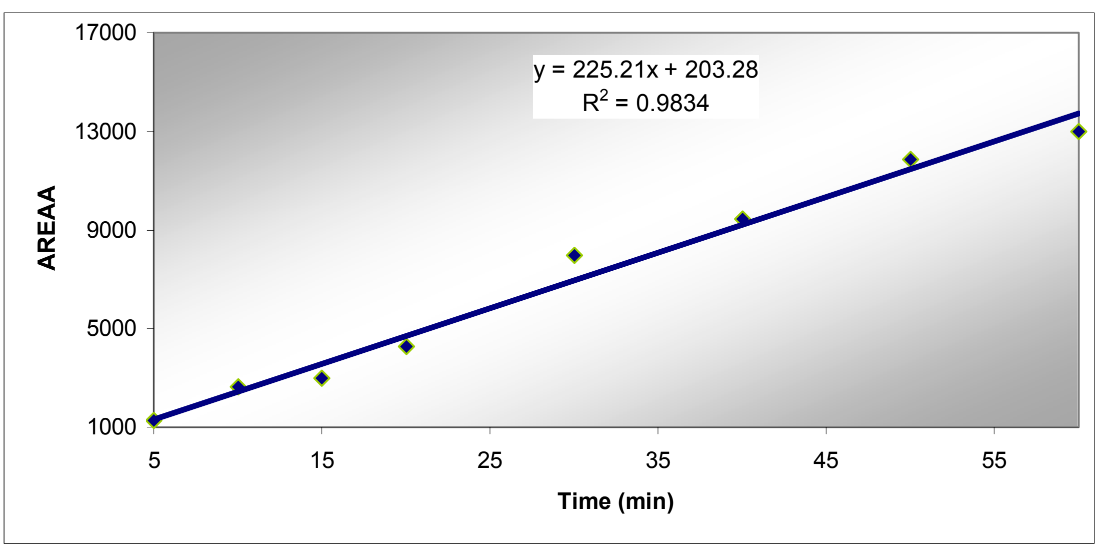


Figure 17. Vapors of TNT from sampling of TNT vapor by PDMS/DVB fiber at different times.

The results for the experiments the exposure time illustrate that the increase of vapor explosives adsorbed by the fiber increases fast for the first 20 minutes and the levels off with the increase of exposure time. The plots indicate that the TNT vapors from TNT buried can be described by a linear model. However to confirm the linearity other times were evaluated (40, 50 and 60 minutes). As expected, the data obtained indicated that at 60 minutes the vapors of TNT from TNT crystals increased with the time (see Figure 18).

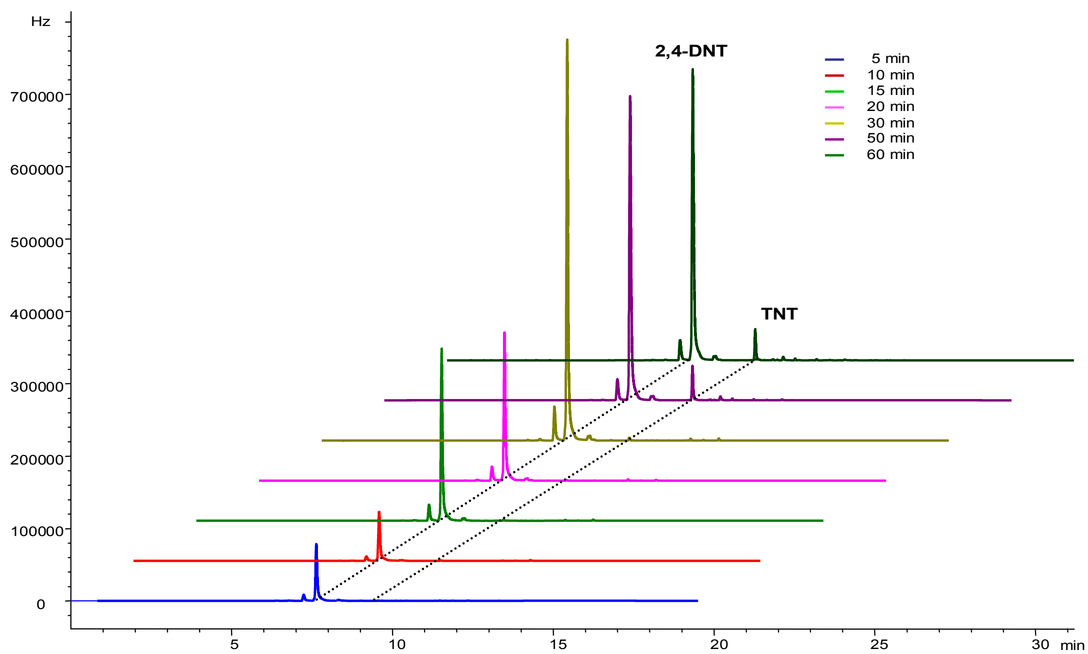


Figure 18. Chromatogram of vapors extracted by PDMS/DVB fiber at several exposure times

The chromatogram shows the increase of the TNT and 2,4-DNT signal with the increased of the exposure time. Particularly TNT vapor signal was augmented after 30 minutes of time exposure. This experiment to confirm that PDMS/DVB fiber did not come to equilibrium with vapors of TNT even after an hour. Besides at 50 and 60 minutes of exposure times were tested with the objective to observe other prominent peaks detected by PDMS/DVB fiber. Nevertheless both explosives signals (TNT and 2,4-DNT) were the most persistent peaks in the chromatogram. For a fast and efficient analysis 20 minutes was selected as the time in order that the fiber is exposed in the headspace during the experiments.

On the other hand, the exposure time for 2,4-DNT was evaluated with the aim to confirm the same behavior than for TNT. An experiment with 2,4-DNT crystals was performed using the same SPME fiber. PDMS/DVB fiber was introduced into the vial with 0.05g of 2,4-DNT at several times. The results are observed in Figure 19.

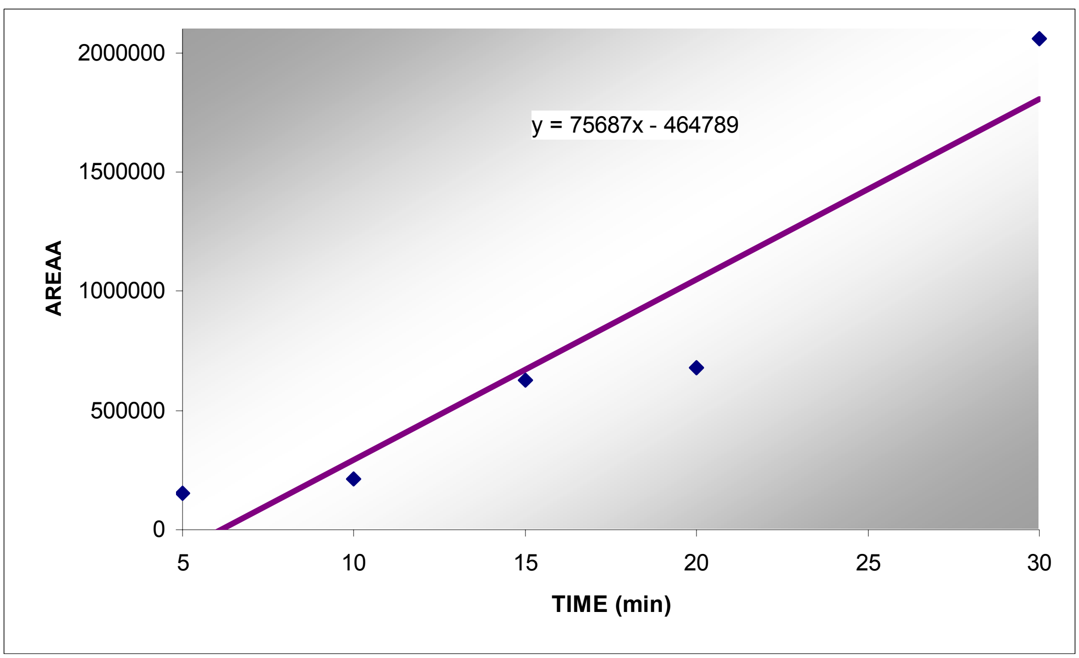


Figure 19. Vapors of 2,4-DNT from sampling of 2,4-DNT crystals by PDMS/DVB fiber at different times.

The 2,4-DNT areas detected by the SPME fiber were increased with the increased of exposure time. The headspace sampling over 2,4-DNT crystals detected vapors of 2,4-DNT, 2,6-DNT and 2,5-DNT. The highest signal detected corresponded to 2,4-DNT. Only, 2,4-DNT was evaluated at several times. This experiment corroborated the selection of 20 minutes as a convenient time to leave the fiber into the headspace.

In summary the SPME parameters selected were:

Fiber type: PDMS/DVB, desorption Time: 5min, and Exposure Time: 20min

5.1.3 Detection of vapors from TNT buried in sand

5.1.3.1 Effect of contact time in the vapors from TNT buried in sand

After choosing the best parameters (fiber, desorption time, extraction time) for a high-quality extraction, the experiments with soils (Ottawa-sand) were began applying the alternative methodology to detect explosive vapors in soils: HS-SPME. In the next experiments previous SPME optimized parameters were used. In order to observe the tendency that the vapors from TNT buried in sand present, the HS-SPME procedure was carried out at several hours after adding the TNT to the sand. Samples were collected and analyzed during 1 month. The results are showed in the figure 20. This graph presents the vapor concentration in the headspace (pg/mL) of TNT and 2,4-DNT in function of the time .

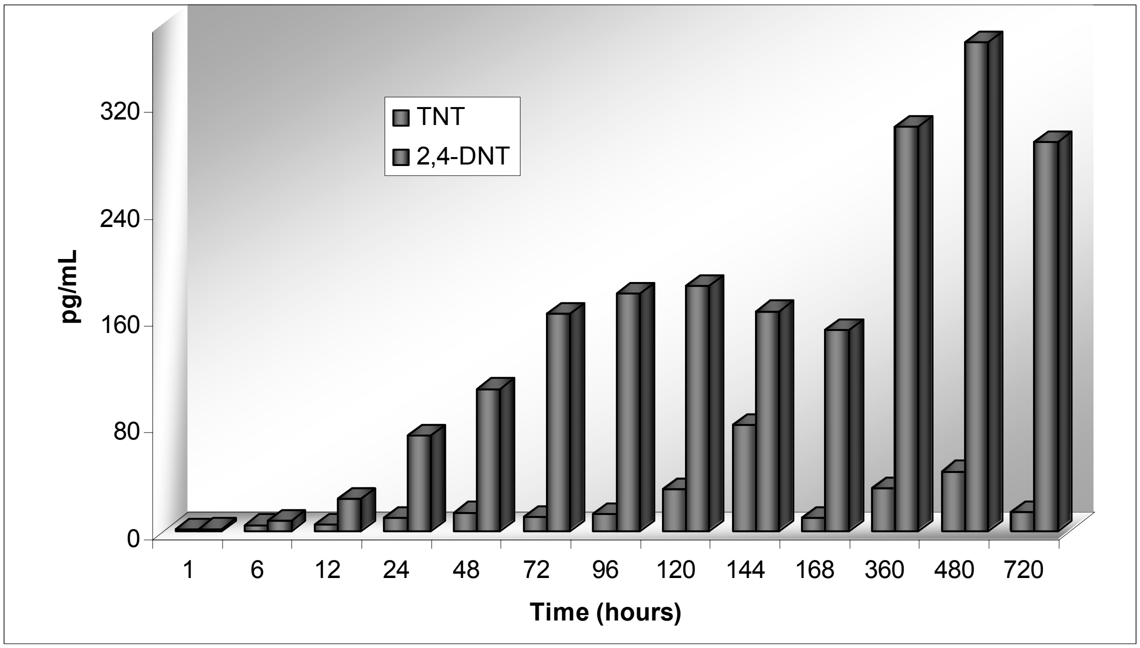


Figure 20. Detection of TNT and 2,4-DNT vapors from TNT buried in sand during 1 month.

When TNT crystals were buried in sand the TNT and 2,4-DNT vapors detected by the PDMS/DVB fiber were extracted at an hour after the mixture (TNT-sand) was prepared. Detectable levels of TNT vapors in the headspace over sand were measured at one hour after sample preparation and after one month after the mix preparation. This experiment evidences that TNT vapors can be detected over sand-TNT mixtures long before equilibrium in the vapor pressure is achieved. After six hours the signature chemicals observed in the headspace samples over sand were: 1,3-dinitrobenzene (DNB), 2,6-dinitrotoluene (2,6-DNT), 2,4-dinitrotoluene (2,4-DNT), 2,4,6,-trinitrotoluene (TNT), 4-Amino-2,6-dinitrotolene and 2-Amino-4,6-dinitrotoluene. An example GC-μECD chromatogram obtained at six hours after mix preparation is presented in the figure 21.

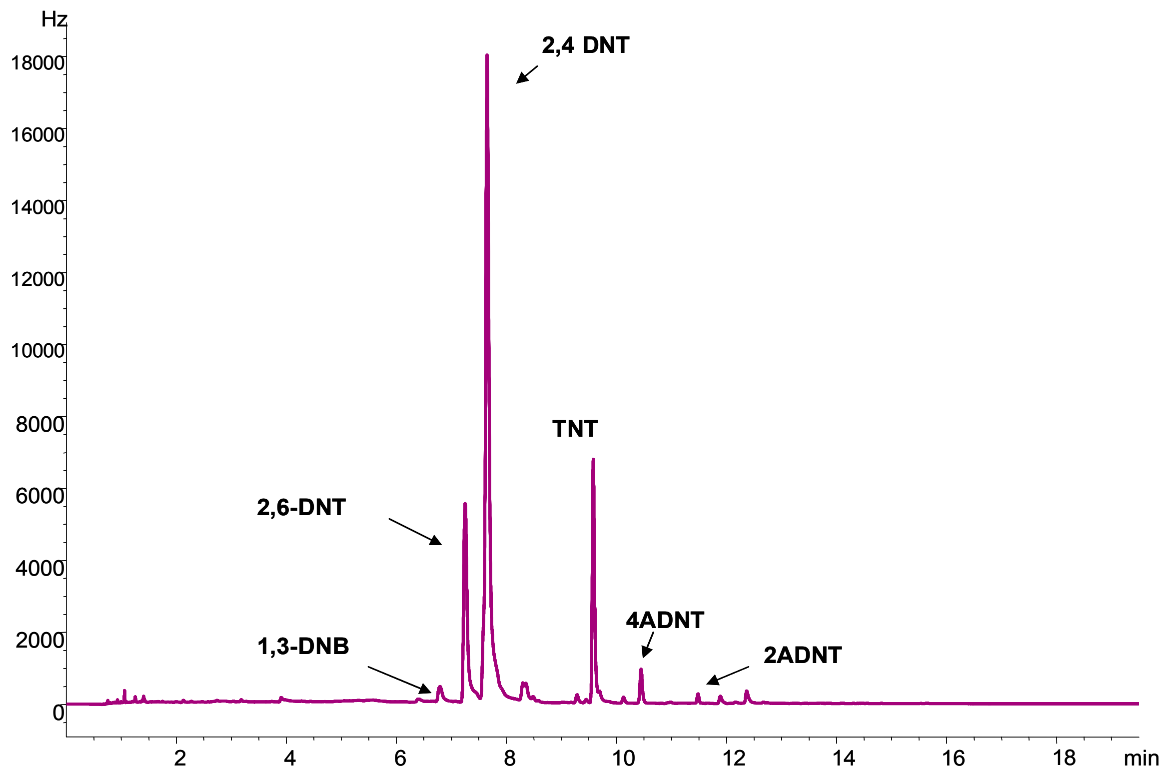


Figure 21. Chromatogram of vapors explosives detected after 6 hours of mix preparation.

After twelve hours another explosive vapor was detected into the headspace. This explosive corresponded to 3,4-DNT, the retention time was of 8.30 min. After four days increased up to 2 weeks and it was stable until 4 week after the mix was prepared. Other explosive vapor identified in the headspace was the 2,6-DNT, with retention time of 7.20 min. 2,4-DNT vapors were increased with the time, throughout the first three days following they decreased up to 3 weeks after the mix was prepared (see Figure 22). The amino DNT isomers were present after the six hours. The signal of 4-amino-2,6-DNT was more high than 2-amino-4,6-DNT during the first four days, after 1 week the signal of 2-amino-4,6-DNT increased four times with respect to 4-amino-2,6-DNT.

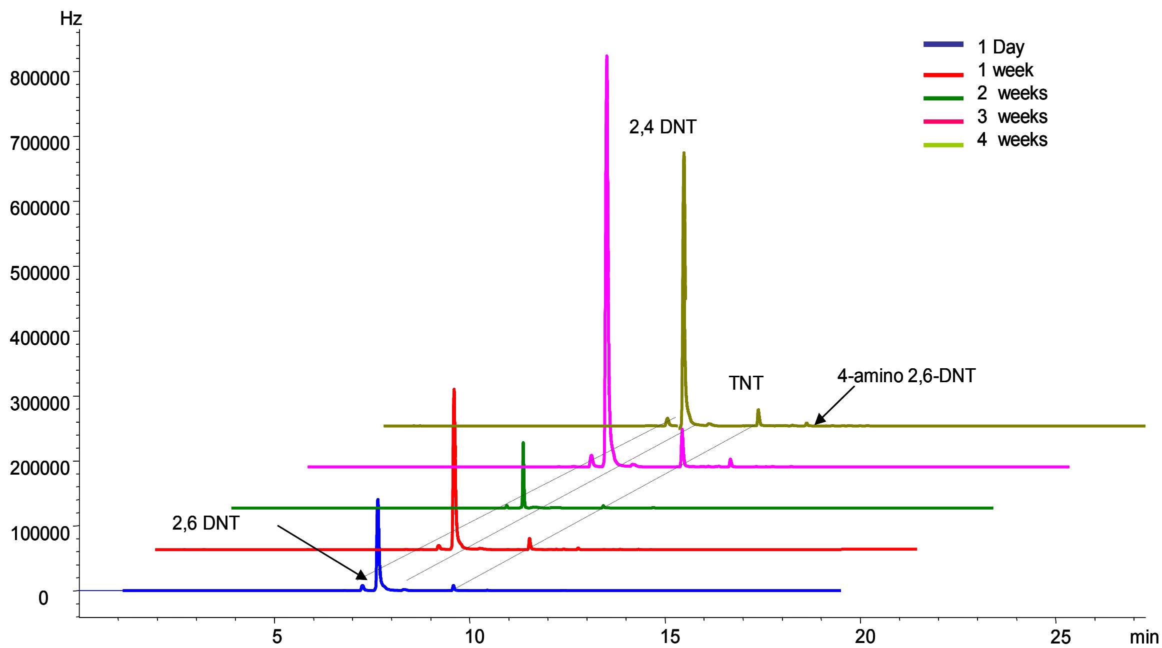


Figure 22. Time evolution chromatograms for explosives vapors from TNT buried in sand.

The mass of TNT vapors was transformed to vapor concentration (pg/mL) using Effective Sampling Rate (EVSR), method developed by Jenkins (Jenkins, 1999). This method measures the amount of analyte sampled by the SPME fiber per unit time and estimates the Effective Sampling Rate.

$$EVSR_{SPME} = \frac{MSR_{SPME}}{VD_T} \tag{1}$$

Where, the $EVSR_{SPME}$ is the effective volumetric sampling rate (mL/min) for SPME, the MSR_{SPME} is the measured sampling rate (pg/min) .Finally; VD_T is the assumed vapor density (pg/mL) at the measured temperature. In the quantification carried out in this experiments, the effective sampling rate measured by Jenkins were used for vapor concentration determination.

$$C_G = \frac{M_{SPME} / T}{EVSR_{SPME}} \qquad (2)$$

Where, M_{SPME} is the mass measured on the SPME fiber and T is the sampling time. An example of the calculus obtained for this quantification is:

The area obtained for TNT at 6 hours was 16190 counts; the effective sampling rate developed by Jenkins was 2.30 mL/min for TNT at 20°C, so the equation from calibration curve from figure 9 (section 5.1) was used to determine the mass of TNT extracted by the fiber.

$$Y = 77.305 X$$

$$16190/77 = 209 \text{ pg}$$

$$C_G = \frac{M_{SPME} / T}{EVSR_{SPME}} = \frac{209\text{pg}/20 \text{ min}}{2.30 \text{ ml/min}} = 4.5 \text{ pg/mL}$$ Headspace vapor concentration

5.1.3.2 Effect of temperature in the vapors from TNT buries in sand

The effect of temperature on TNT-sand mixtures was studied from 20 to 50˚C. After 1 hour of equilibrium at the selected temperature the headspace was sampled using the PDMS/DVB fiber. The results are presented in Figure 23.

The two representative signals for TNT and 2,4-DNT were detected into the headspace at several temperatures. An increment of mass in the headspace with increasing temperature was observed for TNT. The results of the experiments are illustrated in Figure 24. The behavior of 2,4-DNT was significantly different. At 20 and 30 ˚C the vapors of 2,4-DNT were larger that for TNT. However, vapors of 2,4-DNT diminished at 40 and 50 ˚C. Increasing the temperature of the mixtures the total mass of TNT extracted by the fiber increased significantly.

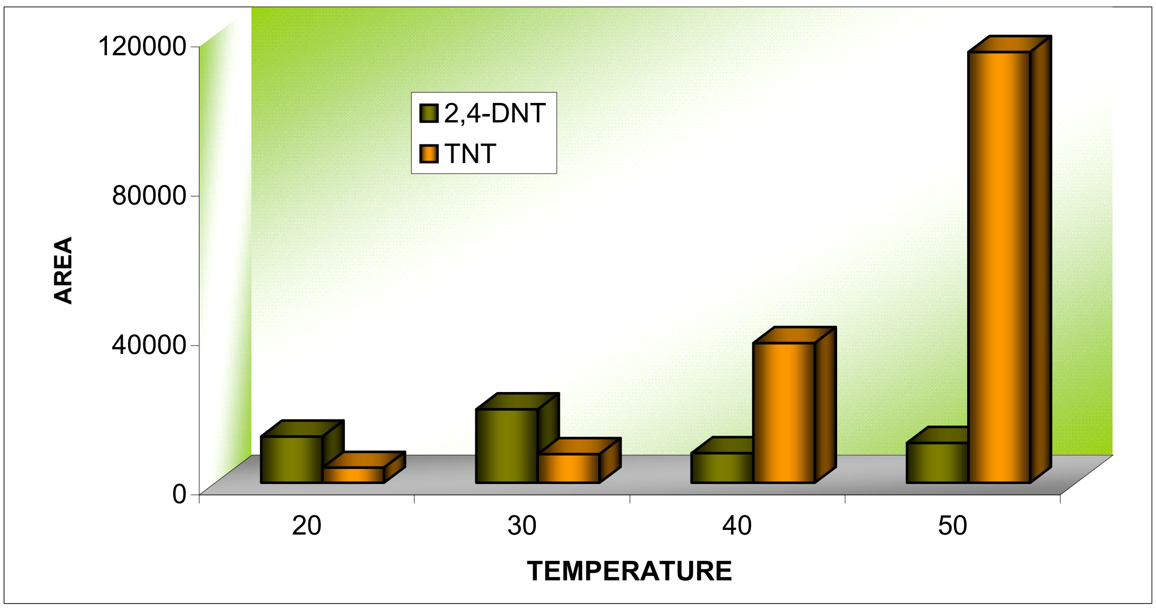


Figure 23. Vapors from TNT buried in sand detected after 1 hour at several temperatures.

The chromatograms, illustrated in the Figure 24, show the presence of amino DNT isomers like 4-amino-2,6-DNT and 2-amino-4,6-DNT when the temperature reach 50°C.

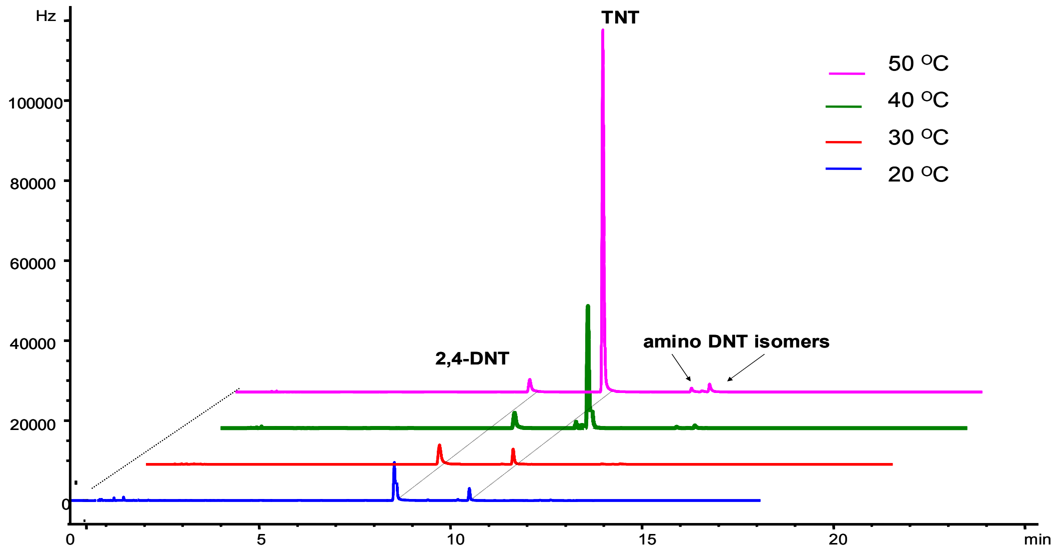


Figure 24. Chromatograms for TNT buried in sand at several temperatures.

The results obtained with these experiments confirm that TNT vapor reach the surface faster when the temperature increased. At high enough temperature, the less volatile amino derivatives begin to reach the soil surface.

5.1.3.3 Effect of water control in the vapors from TNT buried in sand

The mix TNT-Sand was submitted to changes in water content, with the aim of identify the explosive vapors detected into the headspace. Figure 25 illustrates that 2,4-DNT vapors detected increased with water added. TNT vapors increased upon addition of 20 µL and diminished after adding 30 µL of distilled water. The vapor concentration of TNT at 10 µL was 0.36 pg/mL. When the water content was 20 µL the headspace concentration for TNT raised to 3.21 pg/mL, while at 30 µL 2.07 pg/mL. These values were compared with dry vials at 1 hour (1.15 pg/ml).

When water content increased to 20 μL the vapor concentration in the headspace was three times higher (3.21 pg/mL) with respect to dry vial at equal temperature.

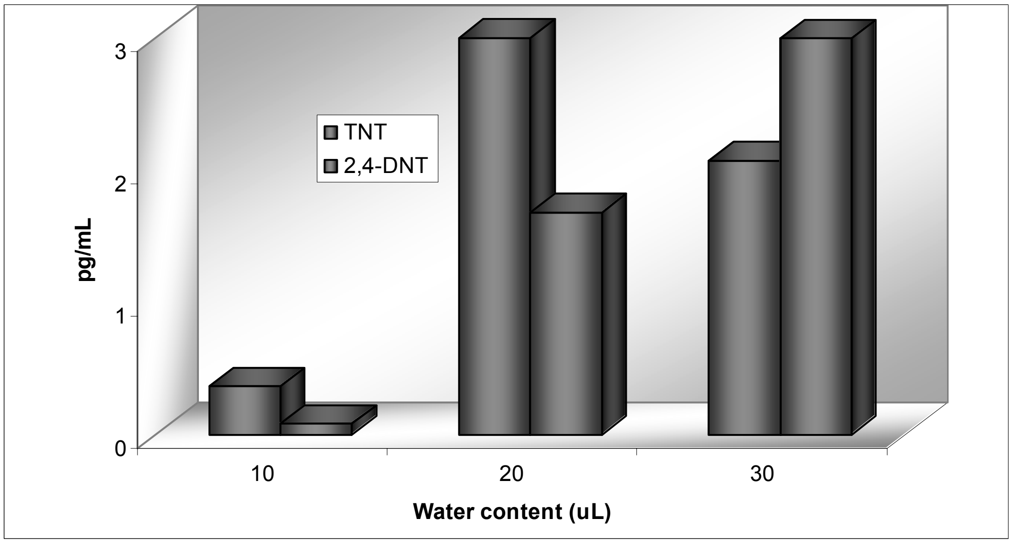


Figure 25. Vapor concentration of TNT and 2,4-DNT detected at several water content

Samples with high water content showed only the major signals of vapors emanated by TNT buried in Ottawa sand: TNT and 2,4-DNT vapors (Figure 26). A possible explanation of this finding is that the vapors of the other degradation products correspond to highly polar compounds. These compounds would be tightly bound to water containing sand. However the chromatograms to 20μL and 30μL present peaks corresponding to amino DNT isomers. These signals are smaller but this suggests that with the increase of water content the production of amino DNT isomer augmented.

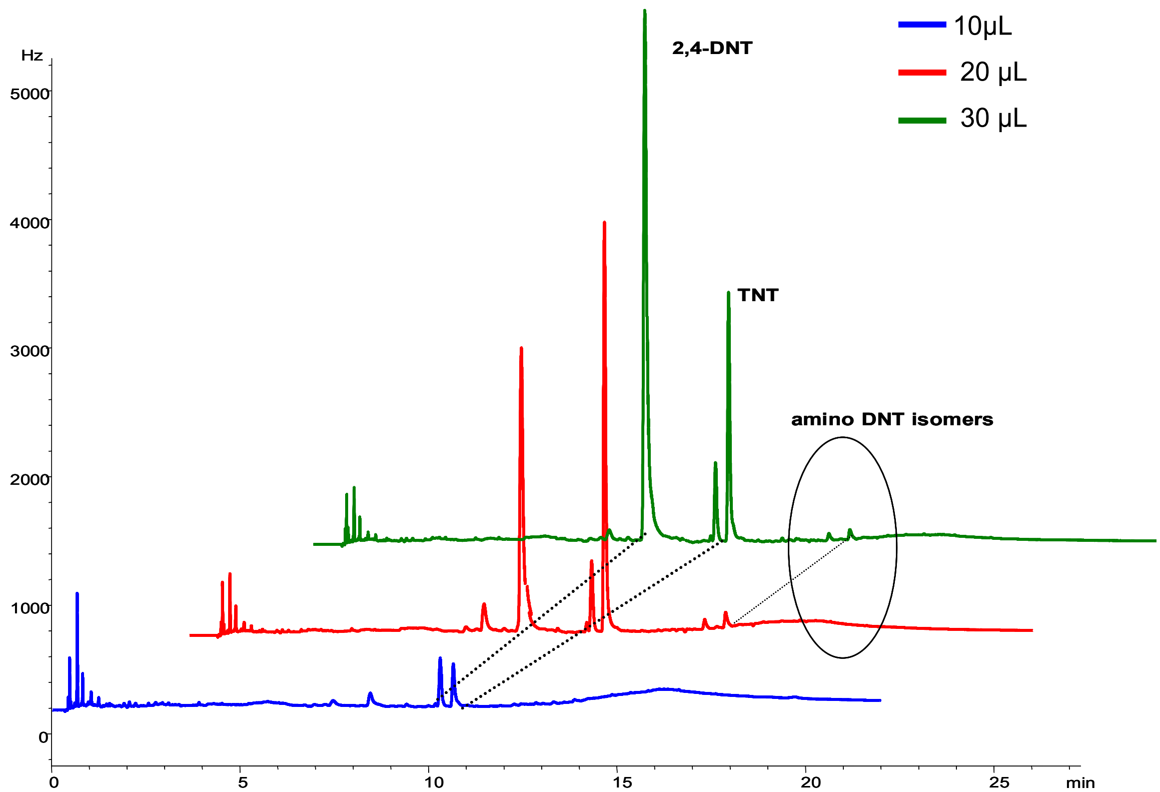


Figure 26. Chromatograms at several water content in TNT buried in Ottawa sand during 1hour.

5.1 Analysis performed using GC/ TEEM-MS

The experiments done with GC/TEEM-MS were used for identification of all vapor explosives in the headspace. The samples were analyzed in negative ion mode and the monochromator was tuned with a filament output current of 2.44µA in and 3.2 V of electron energy.

5.1.1 Analysis of TNT with GC/ TEEM-MS

The instrument was calibrated in SCAN mode to locate the retention times of TNT, 2,4-DNT, and 2,6-DNT. A calibration curve for TNT was made in SIM mode using a TNT standard of 1000 ppm. Figure 27 show the calibration curve for TNT.

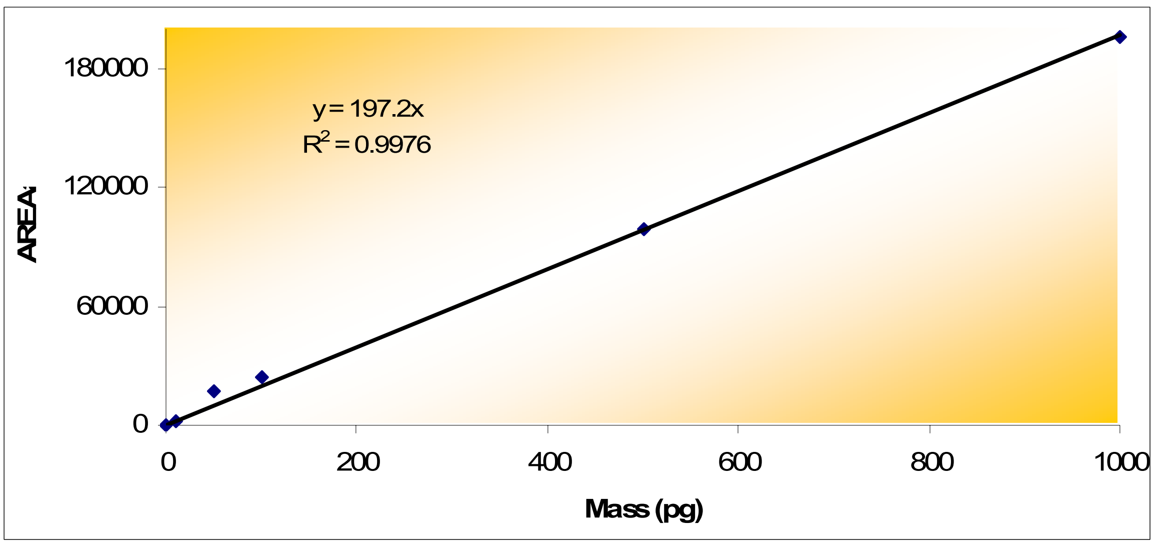


Figure 27. Linear regression for TNT in acetonitrile runs using GC/TEEM-MS in SIM mode by direct injection .

Then, SIM calibration was performed for TNT. Five concentrations (0.01, 0.05, 0.1, 0.5 and 1ppm) were run by GC/ TEEM-MS using direct injection and 1μL of each solution was injected. The calibration data was plotted describing a linear model. The coefficient of correlation (R2) was 0.9976. The detection limit obtained was 500 fg based in signal to noise 3:1 for TNT. A typical TIC (Total Ion Chromatogram) for TNT is presented in the figure 28.

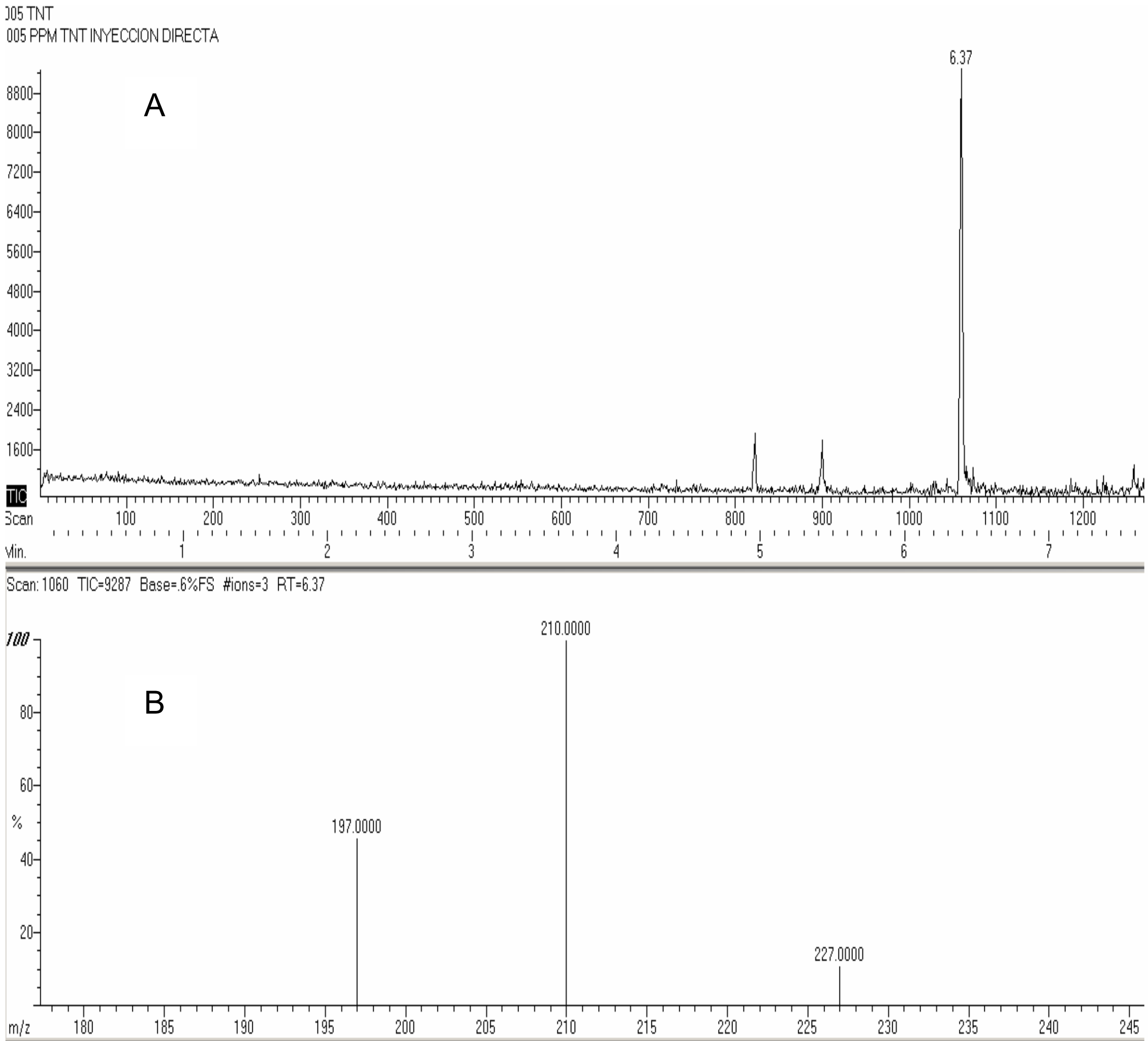


Figure 28. Total ion chromatogram (A) and fragmentation patter (B) obtained for 0.05 ppm of TNT in acetonitrile by direct injection using GC/ TEEM-MS

The retention time of TNT corresponds to 6.37 min. Also, the TNT fragmentation patter is showed in the figure. The molecular ion (m/z = 227) was found in the low energy electron impact mass spectrum. Additionally ions at m/z = 210, at m/z = 181 and at m/z = 197 were found. The maximum ion intensity was m/z = 210 this ion is produced when the molecular ion m/z = 227 loss a OH group; thus the ion m/z = 210 is the $[M\text{-}OH]^-$ ion. Also the molecular ion loses an NO group, forming the $[M\text{-}NO]^-$

ion, m/z = 181. Finally the ion with m/z = 197 was originated from $[M-OH]^-$ ion, when it loses CH group. The possible fragmentation pathway is presented in Figure 29.

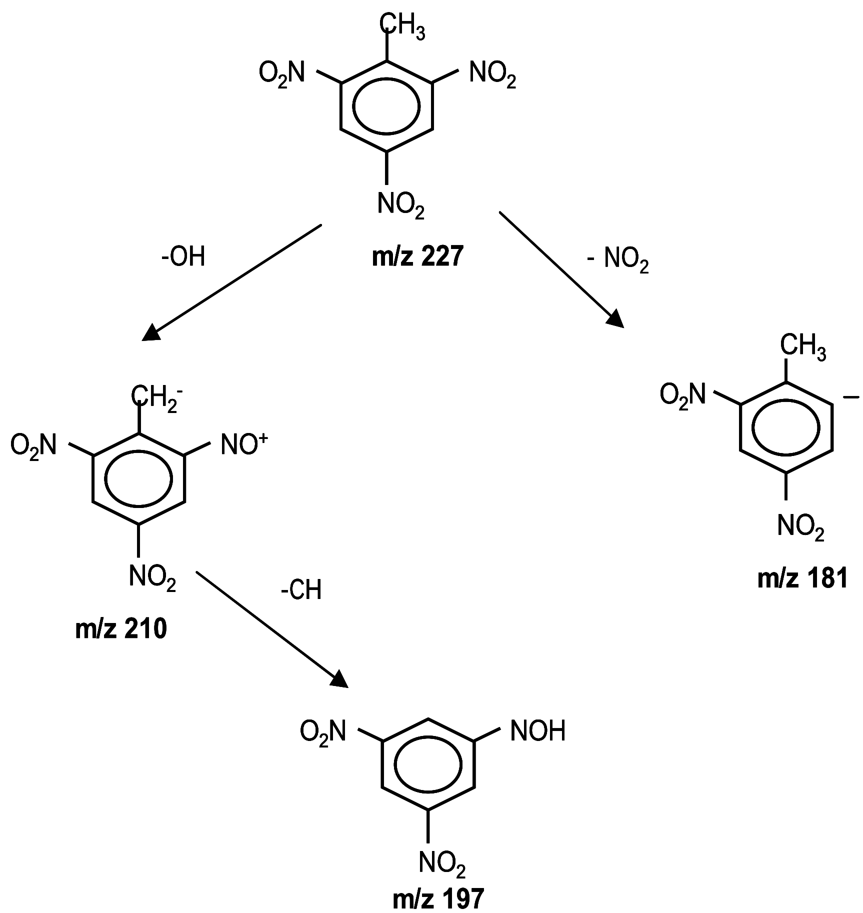


Figure 29. Fragmentation pathway of TNT by negative ion

The fragmentation pattern obtained for TNT was compared data base made by JEOL for explosives measured on the same mass spectrometer by JEOL Company. All samples analyzed in GC/TEEM-MS were compared with explosives library generated by JEOL for explosives in negative ion mode. For this experiment a selected ion monitoring (SIM) scan was conducted for the ions m/z = 227, m/z = 210 and m/z = 197 from TNT. The ions selected were monitored at same ionization energy of 3.0 eV. Figure 30, illustrates the electron energy scan for these ions.

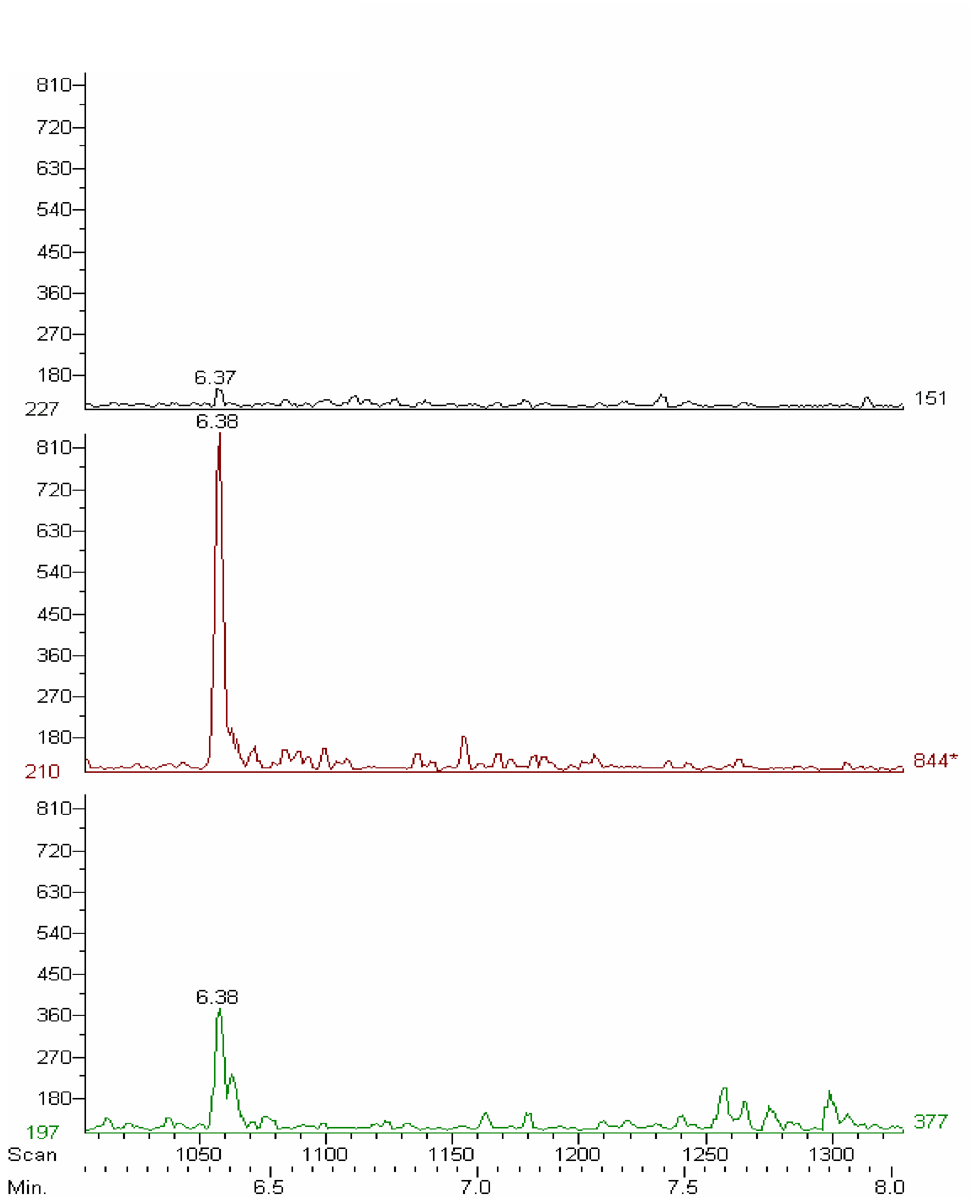


Figure 30. Electron energy scans of TNT for the ions m/z 227, 210 and 197 at 3.0 eV.

5.1.2 Analysis of Mix A with GC/TEEM-MS using HS-SPME.

As already mentioned, GC/TEEM-MS analysis was used for identify the all explosives in the samples. Therefore a standard solution of Mix A containing 10 explosives was analyzed by direct injection. A 1µL aliquot of a dilution of the cocktail solution was injected. GC/TEEM-MS was calibrated in scan mode. A typical TIC obtained for Mix A is presented in Figure 31.

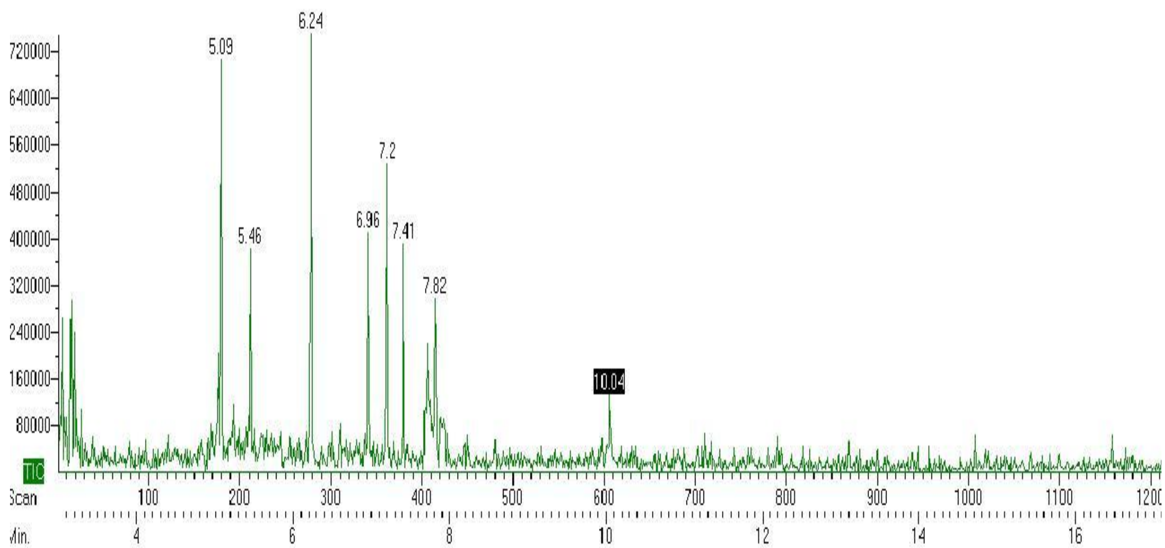


Figure 31. Total ion chromatogram obtained for 1 ppm of Mix A analyzed by direct injection using GC/ TEEM-MS.

The retention times sown in the Figure 31, correspond to seven explosives identified with this instrument. 2,6-DNT (Rt=5.09 min), 2,4-DNT (Rt= 5.46 min), 2,4,6-TNT (Rt= 6.24 min), RDX (Rt= 6.96 min), 4-A-DNT (Rt=7.20 min), 2-A-DNT (Rt=7.41 min), tetryl (Rt= 7.82 min). The fragmentation patter for each explosive confirms this assignment, see appendix A.

5.1.3 Analysis of TNT buried in sand using GC/ TEEM-MS

Replicates of experiments where TNT was buried in Ottawa sand during several extended periods were run using GC/TEEM-MS. The purpose of these experiments was to identify other explosives in the headspace of the samples. The conditions were similar to the one described in Section 3.3.1 in Chapter IV. An example of total ion chromatogram and electron energy scan for main ions is showed in Figure 32.

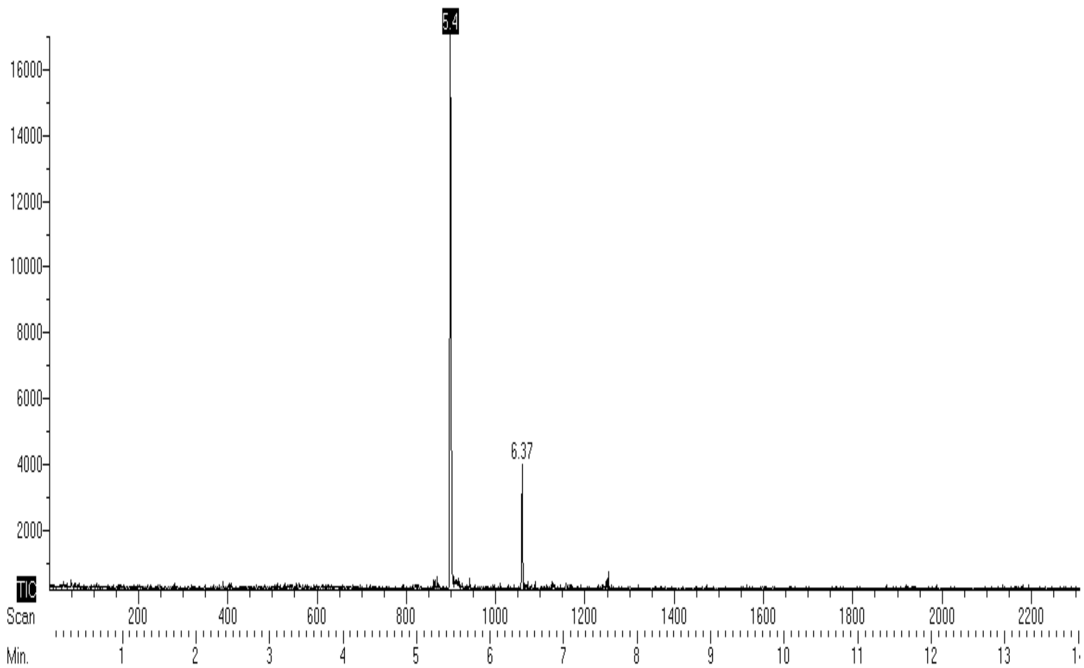


Figure 32. Total ion chromatogram for vapors from TNT buried in sand during an hour sampled with PDMS/DVB fiber.

The TIC presents the highest signals of explosive vapors into the headspace. TNT eluted at a retention time of 6.37 min and 2,4-DNT at 5.4 min. The TIC confirmed that the highest signal in the headspace was 2,4-DNT for TNT buried in Ottawa sand during 1 hour. The fragmentation pattern shown in Figures 33 and 34 verify that TNT and 2,4-DNT were the highest signal in the headspace of this sample.

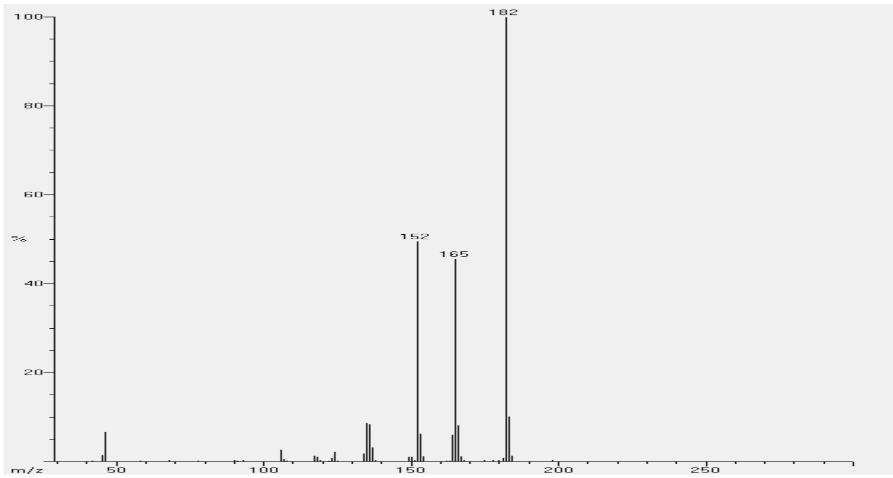


Figure 33. Electron monochromator mass spectra of 2,4-DNT obtained sampling headspace of TNT buried in sand during 1 hour using GC/TEEM-MS and HS-SPME.

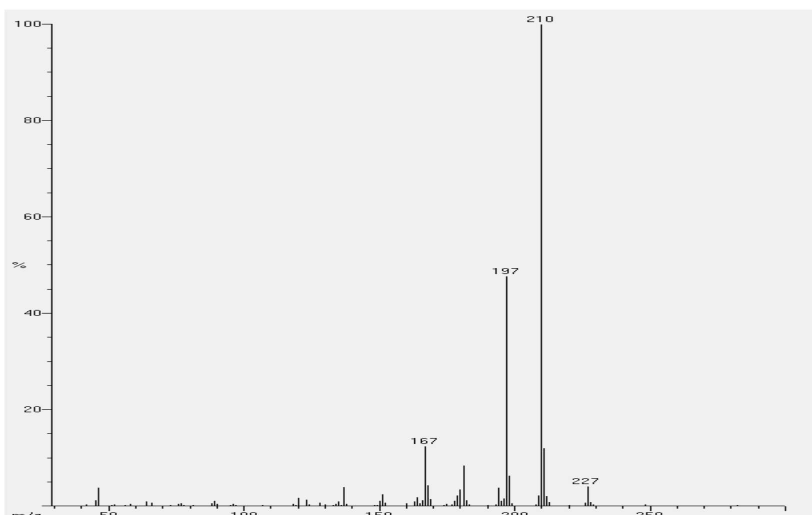


Figure 34. Electron monochromator mass spectra of 2,4-DNT obtained sampling headspace of TNT buried in sand during 1 hour using GC/TEEM-MS and HS-SPME.

The molecular ion m/z = 182 from 2,4-DNT and the molecular ion m/z = 210 from TNT were present in the fragmentation patter.

CHAPTER VI

CONCLUSIONS

The SPME analysis in headspace mode was optimized for experiments in which TNT was buried in sand. The PDMS/DVB was found to be the best fiber type to concentrate the vapors of TNT and their degradation products from TNT-sand mixtures. The optimum desorption time was 5 minutes to leave the fiber into the injection port from GC. TNT vapors from crystals detected by the fiber increased with the exposure time. The same behavior was observed when 2,4-DNT crystals were used, 2,4-DNT vapors increased with the exposure time.

The results obtained in with GC-μECD established that the transport of TNT to the vapor phase depends on the environmental conditions present: soil temperature, soil water content and contact time of TNT with sand (aging effects). The factors studied had a significant impact on the mass transport of the explosive in soil-air interphase. Degradation products from TNT buried in sand in vapor phase were detected as early as one hour after of sample preparation.

Vapor concentration of TNT was measured using the Effective Sampling Rate (EVSR) that correlated the mass colleted by the fiber with the vapor concentration of the explosive in the headspace. High concentrations of TNT were detected above sand when the temperature increased and when the time reaction of TNT-sand reached 144 hours after mix preparation. During whole month of sampling, 2,4-DNT vapor concentration was the most prominent signature in the headspace. A possible reason is that 2,4-DNT has vapor pressure significantly higher than TNT. The concentration of 2,4-DNT in the vapor phase signature may be orders of magnitude larger than that of TNT even though there is much more TNT in the soil. The amino DNT isomers and 2,6-DNT were present after the six hours into the headspace over TNT buried in sand.

In general using SPME methodology, TNT in the headspace can be adsorbed and detected from sand-explosive mixtures very efficiently. Therefore an alternative methodology was optimized and tested confirming that explosive vapors can be detected and distinguished using SPME in headspace mode coupled with gas chromatography and mass spectrometry.

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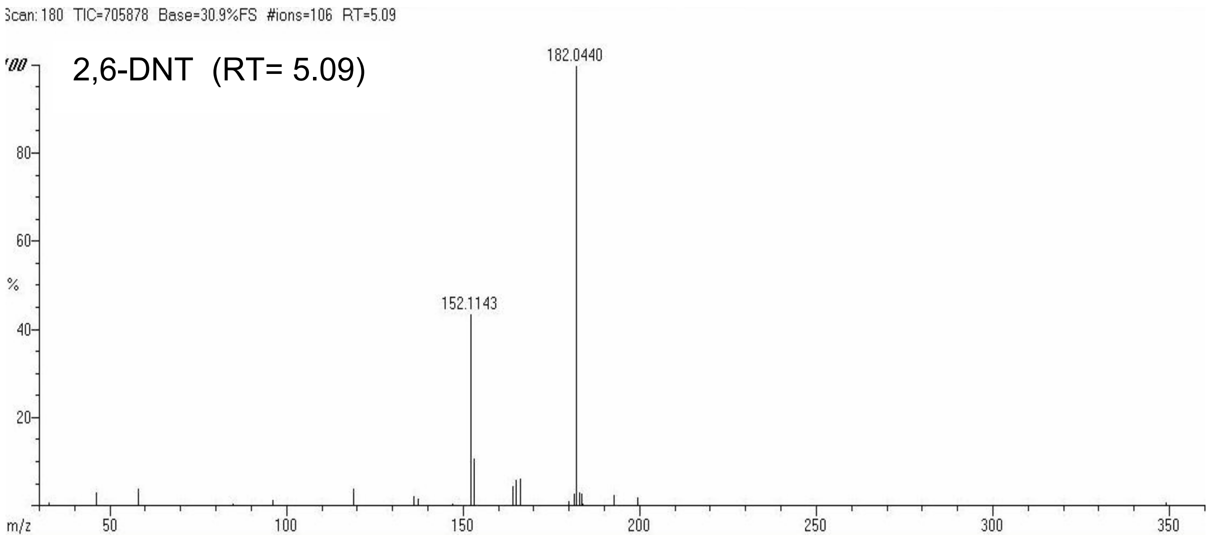
APPENDIX

APPENDIX A

FRAGMENTATION PATTERS FROM MIX A



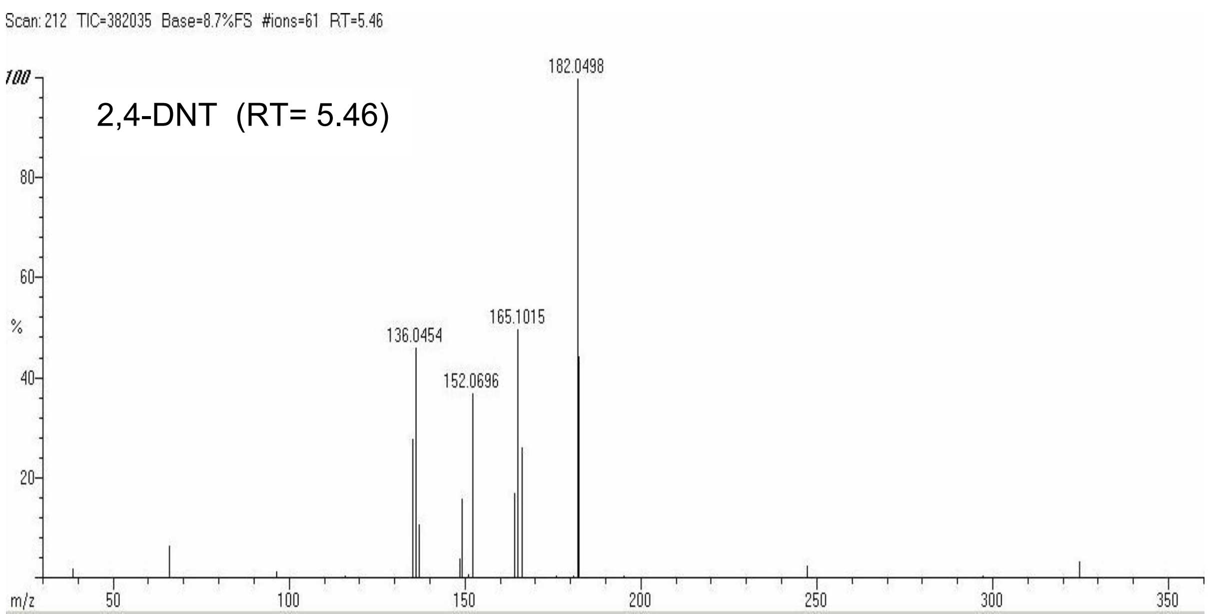


Figure 1A. Fragmentation pattern in negative ion for 2,6-DNT, and 2,4-DNT obtained of Mix A explosives using a GC/ TEEM-MS.

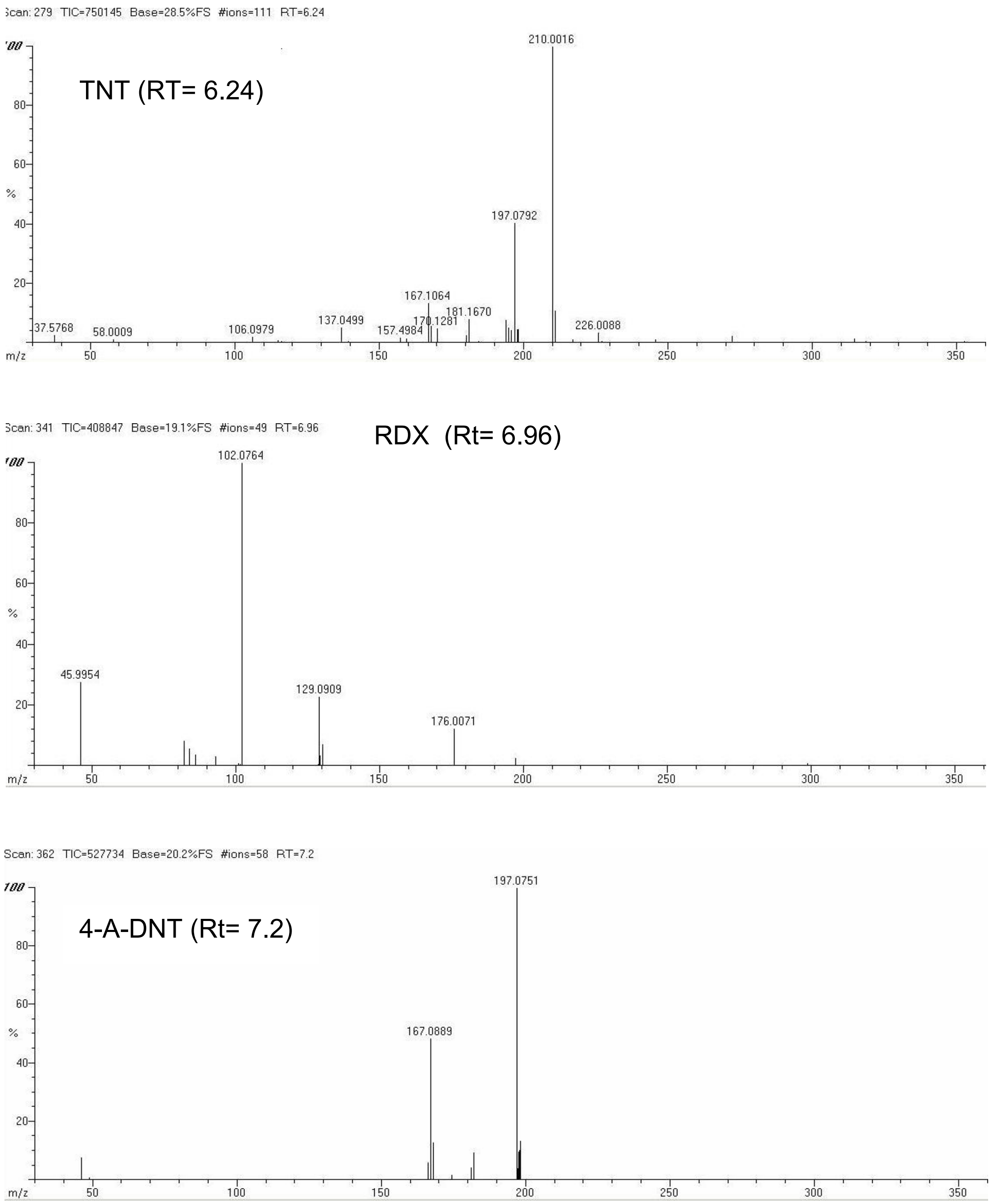
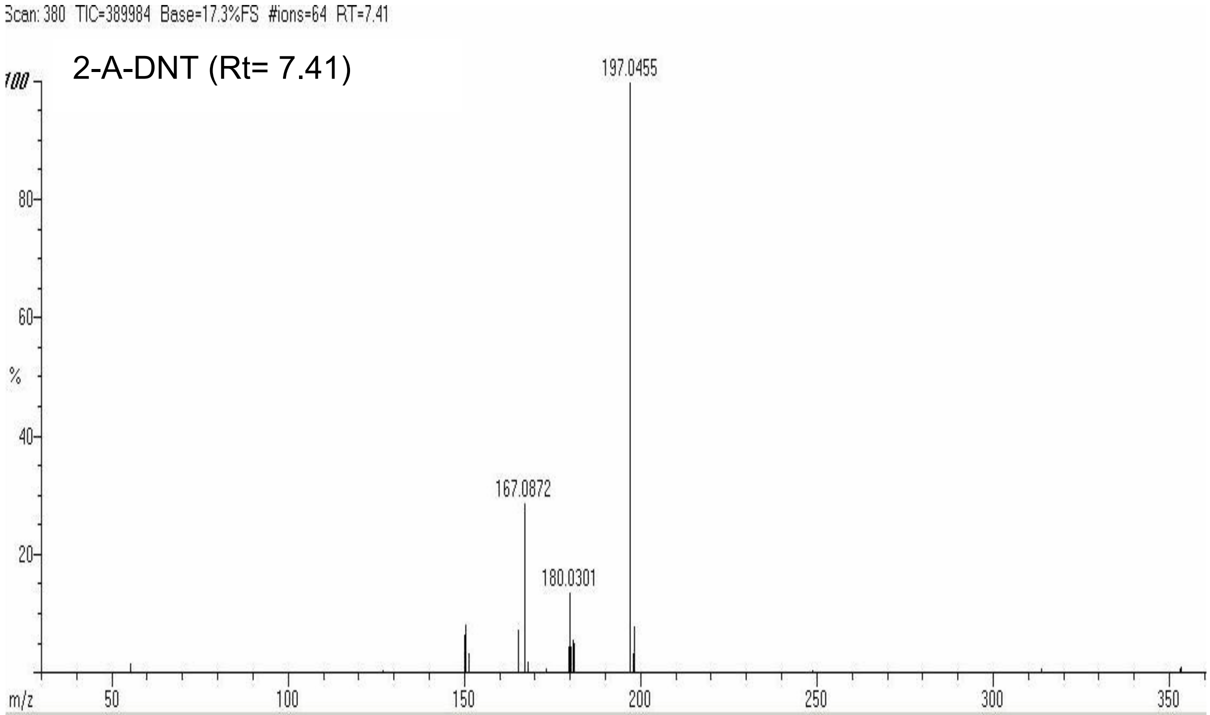


Figure 2A. Fragmentation pattern in negative ion for 2,4,6-TNT, RDX, and 4-A-DNT obtained of Mix A explosives using a GC/ TEEM-MS.



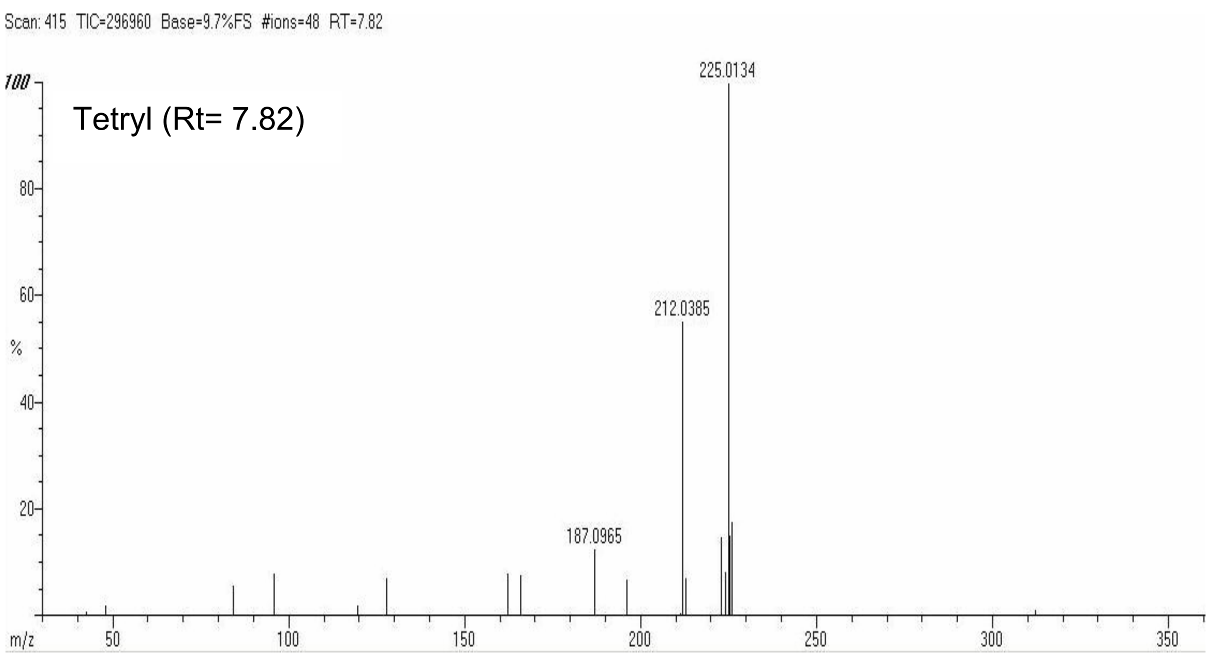


Figure 3A. Fragmentation pattern in negative ion for 2-A-DNT, and Tetryl obtained of Mix A explosives using a GC/ TEEM-MS.