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Entitled Evaluation of the Odor Compounds Sensed by Explosive-Detecting Canines

For the degree of Master of Science

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EVALUATION OF THE ODOR COMPOUNDS SENSED
BY EXPLOSIVE-DETECTING CANINES

A Thesis
Submitted to the Faculty
of
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by
Erica H. Lotspeich

In Partial Fulfillment of the
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of
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First and foremost I would like to dedicate this to God for His guidance and blessings. I would like to dedicate this to my husband, Chris, for his support and tolerance through my long educational journey. I would also like to thank my daughter, Bobbi, for always giving me hugs and kisses. Lastly, I would like to dedicate this to my parents for always believing in and praying for me.

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ABSTRACT

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Trained canines are commonly used as biological detectors for explosives; however, there are some areas of uncertainty that have led to difficulties in canine training and testing. Even though a standardized container for determining the accuracy of explosives-detecting canines has already been developed, the factors that govern the amount of explosive vapor that is present in the system are often uncertain. This has led to difficulties in comparing the sensitivity of canines to one another as well as to analytical instrumentation, despite the fact that this container has a defined headspace and degree of confinement of the explosive.

For example, it is a common misconception that the amount of explosive itself is the chief contributor to the amount of odor available to a canine. In fact, odor availability depends not only on the amount of explosive material, but also the explosive vapor pressure, the rate with which the explosive vapor is transported from its source and the degree to which the explosive is confined. In order to better understand odor availability, headspace GC/MS and mass loss experiments were conducted and the results were compared to the Ideal Gas Law and Fick's Laws of Diffusion. Overall, these findings

provide increased awareness about availability of explosive odors and the factors that affect their generation; thus, improving the training of canines.

Another area of uncertainty deals with the complexity of the odor generated by the explosive, as the headspace may consist of multiple chemical compounds due to the extent of explosive degradation into more (or less) volatile substances, solvents, and plasticizers. Headspace (HS) and solid phase microextraction (SPME) coupled with gas chromatography/mass spectrometry (GC/MS) were used to determine what chemical compounds are contained within the headspace of an explosive as well as NESTT (Non-Hazardous Explosive for Security Training and Testing) products. This analysis concluded that degradation products, plasticizers, and taggants are more common than their parent explosive.

CHAPTER 1. INTRODUCTION

1.1 Canine Detection

Canines have the ability to use their keen sense of detection to hunt for food, to be aware of and prepared for danger, to locate a mate, and to recognize family members [1]. Tracking using canines has taken place for thousands of years. 12,000 years ago canines were first utilized as hunting dogs. After World War II, canines were used by the military for the detection of explosives. Canines were then utilized to search for people and locate narcotics. Today, canines are used for the detection of a wide variety of materials, including guns, pipeline leaks, gold ore, contraband food, melanomas, gypsy moth larvae, and brown tree snakes [2]; due to their ability to detect and differentiate a large amount of volatile chemicals with a vast array of structures [3]. Even though canines are widely used for detection, the process whereby dogs recognize and respond to odors is still not very well understood [4, 5]. In order to improve the reliability of this remarkable detection system additional research must be completed.

The canine's olfactory system functions to facilitate the detection, discrimination, and signaling of chemical compounds. Sniffing commences the collection of chemical compounds for interpretation by the canine's olfactory system. Vapor-phase odor molecules, coming from the explosive vapor are dissolved into the mucosal lining within the nasal cavity [2, 6]. The olfactory sensory neurons (OSNs) are

known as the primary sensing cells. There are approximately 6-10 million OSNs present in the nasal cavity of mammals. Each OSN has a dendrite that extends to the surface of the nasal lining and projecting from each of the dendrites are 20-30 cilia. When an odor molecule is inhaled it comes into contact with the cilia of the nasal mucosal lining and sensory transduction occurs. Sensory transduction is the binding of the odorant molecule to an odorant receptor. The odorant receptors are comprised of three α -helical barrels that form a pocket which is thought to be the binding site for the odor molecule. This starts a cascade of enzymatic activity and a change in membrane potential. Thus, the odorant molecule is changed into a neural signal. This signal is sent to the olfactory bulb where it comes into contact with the mitral cell. Lastly, the neural signal is sent to higher brain functions for interpretation [2, 6]. To cease stimuli from continuing, odor molecules must be purged from the mucosal lining and other areas in the nasal cavity which may possibly result in physiological adaptation in which the canine alters cells to adjust to external stimuli [2]. This alteration may impede future detection and discriminations of odors.

There have been efforts to mimic the canine's olfactory system. Examples include the ion mobility spectrometer which is commonly used for the detection of vapors in the field. It has the ability to detect less than 1 nanogram of chemical substances [7]. There are also examples of "electronic noses" which contains several nonspecific odorant sensors to achieve an accurate identification [1]. Even so, the canine's nose has greater sensitivity and discrimination power [7].

1.2 Odor Availability

The issue of odor availability is concerned with how the chemical properties of an explosive and other factors influence the amount of explosive vapor that can be sampled by a canine. The chemical properties of an explosive that may affect canine recognition include the molecule's vapor pressure, diffusion coefficient and the resultant flux of the molecule from a container. The molecule's total vapor pressure is the partial pressure of the substance when equilibrium is achieved between the liquid and vapor phases. In a mixture, the partial pressure of each gas is independent of the other gases present in the system [8, 9]. Flux is defined as the amount of material that is transferred through a given opening over time [9, 10].

Other factors that may affect the amount of vapor present is the molecule's rate of diffusion as well as the attraction of the molecule to the surface of a container [10, 11]. Ultimately, successful detection of the odor available in the air to the trained canine is based on how well the handler trains and allows for adequate sampling as well as training on multiple sampling volumes [5, 12, 13]. Lastly, there is the canine olfactory system which is able to distinguish and detect a considerable number of volatile chemicals with a vast array of structures, as discussed earlier.

Research into the underlying factors for these stages has shed some light on the issues surrounding vapor detection. This research includes characterization of the vapor pressure [14] and surface adhesion [15] of explosives. In addition, the underlying physical chemistry as well as various instrumental techniques for the detection of explosives have been reviewed [16]. Practical aspects of explosive-detecting canines

have also been studied, such as their detection limit for a volatile explosive like nitromethane [17]. A number of additional measures of canine performance such as sensitivity, accuracy, selectivity, memory, duty cycle and comparisons to instrumental techniques have also been reviewed [2, 18].

To better understand how the explosive's odor is generated and therefore improve current canine testing/training protocols, our objective is to answer questions regarding odor availability and demonstrate how the amount of vapor surrounding an explosive is affected by sample amount, container size, explosive vapor pressure, diffusion coefficient, temperature and confinement. These experiments were completed on pure nitroalkanes (nitromethane, nitroethane, and nitropropane). These compounds are commonly used as fuels in binary high explosives. It would be challenging to complete headspace analysis at room temperature on less volatile explosives such as RDX and PETN because of their a small diffusion coefficients and vapor pressures [4]. Since RDX and PETN are difficult to detect by headspace analysis, liquid chromatography analysis is often used [19]. Therefore, given that nitroalkanes are highly volatile and detectable at room temperature as well as being readily available in pure form, they are ideal for our analyses. These odor availability experiments can be related to those explosives that are concealed which causes a barrier to the free movement and predictability of the odor [2].

1.3 Explosive Odor Compounds

In a post September 11, 2001 world the need to detect explosives has become of great interest to our country. The development of a dependable and effective mode of detection is in great demand by the government. The most effective mode of explosive detection are sniffing dogs because they have the ability to detect explosive as well as explosive residues [20]. Therefore, more canine detection research is needed to gain more knowledge regarding their tractability. For example, explosives detection is desirable in order to locate and deactivate anti-personnel landmines that have been placed around the world [20]. Another related issue is tracking down hidden explosive devices assembled by criminals and terrorist organizations. To date, the detection of explosive devices generally relies upon four main methods: 1) irradiation of a suspect item with electromagnetic radiation or sub-atomic particles, 2) swabbing an item directly for explosive residues, 3) sampling an item with high-velocity air flows for explosive particles, or 4) detecting volatile compounds emitted from the item using vapor detectors and/or explosive-detecting canines [16]. These methods each have their own strengths and weaknesses, and often are used in conjunction as exemplified by the simultaneous presence of x-ray scanners, chemical analyzers, portal detectors as well as explosive-detecting canines at many airports and other secure facilities around the world [21].

The explosive's vapor composition is complex and the explosive itself may not be the main contributor to the vapor. Therefore, the headspace may consist of multiple chemical compounds that could stem from multiple species in the sample, degradation products of a single species, or a combination of the two. In addition, some of the other

compounds that are found in explosives may have higher vapor pressures; therefore, they will be detected more easily than the actual explosive [4]. Some explosives generate explosive related compounds (ERC), which are degradation products that are more volatile than the parent explosive. In other cases, energetic volatile compounds (“taggants”) are deliberately added to plastic bonded explosives to increase the likelihood that they can be detected [18]. In this case, the taggant becomes a major component of the explosive odor in addition to other products that may be present from the explosive itself. For example, smokeless powder additives (including phthalates, diphenylamine, ethyl centralite and methyl centralite, and many other volatile organic compounds) are added to the composition to improve stability, burn properties and shelf-life that aim to optimize safety and product performance. Different manufacturers may choose different additives, leading to the potential discrimination of brands [22]. These compounds have been proposed as a possible cause of canine alerts, particularly in materials where the explosive itself is essentially non-volatile. The objective of this study is to characterize the vapors emanating from nitrated explosives. In this case, methods will use solid phase microextraction (SPME) and headspace (HS) sampling coupled with gas chromatography-mass spectrometry (GC/MS).

CHAPTER 2. CHARACTERIZATION OF THE CONCENTRATION AND DIFFUSION OF EXPLOSIVE VAPORS IN CONTAINERS DESIGNED FOR CANINE ODOR RECOGNITION TESTING

2.1. Introduction

Throughout the past twenty years there has been research on the development of instrumentation that delivers a known mass of explosive in vapor form so that explosive vapor detectors can be evaluated and calibrated [7, 20, 23]. However, these efforts to calibrate sources of explosive vapor have not been adapted for canine testing [23, 24]. In the case of explosive-detecting canines, a standardized container that has a defined headspace and degree of containment has already been developed. This simple apparatus consist of a two ounce sniffer tin with a perforated lid that is used to hold a small sample of explosive. The sniffer tin is then placed inside a quart-sized can to ensure that it is not touched or otherwise disturbed by the canine. Finally, the quart-sized can is placed inside a gallon-sized can which provides a defined headspace in which the explosive odor collects, typically for at least 30 minutes prior to allowing a canine to search the container (see Figure 2.1).



Figure 2.1: Geometry of apparatus used in the National Odor Recognition Test (NORT).

This sample geometry has been utilized to estimate the detection limit of canines for the liquid explosive nitromethane. The samples were presented in solutions in water, which allowed for control over the equilibrium vapor pressure of the explosive [17]. These containers are currently used for the National Odor Recognition Test (NORT) [17], which is administered nationwide as a means to evaluate the ability of canines to correctly alert to explosives. However, the factors that govern the amount of explosive vapor that is present in the system are often confused and there are some uncertainties about canine detection that have led to questions regarding the training and testing of canines. This has led to difficulties in comparing the sensitivity of canines to one another as well as to analytical instrumentation.

Several chemical properties of an explosive as well as other factors influence the amount of explosive vapor. A common misconception is that the amount of explosive itself is the main contributor to the amount of odor available to a canine. Yet, odor availability is decidedly more complex; it not only depends upon the amount of explosive material, but also the explosive vapor pressure, the explosive's rate of evaporation, the extent to which the explosive degrades into more (or less) volatile substances and the degree to which the explosive is confined. This concept has remained controversial

because the quantity of explosive used for training and/or testing is easily measured. However, the degree of confinement and amount of vapor available for detection is not. In addition to confinement and amount, it has also been shown that the vapors released from many nitrated explosives end up absorbed onto surrounding surfaces [11, 25-27] which can further affect odor availability.

Furthermore, specifications as to what constitutes an acceptable amount of explosive vary widely by agency and are often based on the agency mission. For instance, TATP is highly volatile [8], but it is also highly sensitive to heat, shock and friction so only small (mg) quantities of the explosive deposited upon inert materials have been used in canine testing [28, 29]. This has led some to question whether the same canines will be at a disadvantage when detecting larger quantities of TATP. The same issue has been raised with other inert training materials that use relatively small amounts of actual explosive adsorbed onto an inert material (i.e., Non-Hazardous Explosives for Security Training and Testing, referred to as NESTT). However, the vapor generated by these training aids is claimed by the manufacturer to be equivalent to a similar mass of explosive [28-30]. On the other hand, NORT administers much larger amounts of each explosive (100 grams) for the testing of canines.

The objective of this chapter is to answer questions regarding odor availability in a container designed for canine testing and to characterize explosive vapors by demonstrating how the amount of vapor surrounding an explosive is affected by sample amount, container size, explosive vapor pressure, diffusion coefficient, temperature and confinement. Experiments were completed on pure nitroalkanes (nitromethane, nitroethane, and nitropropane). These compounds are commonly used as fuels in binary

high explosives. They are highly volatile as well as being available in pure form, which makes them ideal for our analyses. Published studies have shown that they have little or no interaction with surrounding metal surfaces (Pt-Sn alloys) [31].

2.1.1. Theory

All experiments were based upon well accepted theories and equations such as the Ideal Gas Law and Fick's Law of Diffusion. In this case, a simple model system consisting of a closed vessel that contains two phases – a liquid nitroalkane occupying a volume (V_ℓ) and vapor phase occupying a known volume (V_g).

This model exhibits two types of behavior upon equilibration of the liquid and vapor phases. Type 1 behavior occurs if all of the liquid vaporizes, which is a situation that is deliberately used in analytical techniques such as total vaporization headspace analysis. In this case, the moles of gas in the vapor phase (n_g) are equivalent to the number of moles of liquid (n_ℓ) that were initially present. Furthermore, the volume of the vapor phase (V_g) is equivalent to the volume of the container ($V_{\text{container}}$). Therefore, the concentration of the substance in the headspace is directly proportional to the volume that was initially present (V_ℓ) and the literature value of density (ρ_ℓ), and inversely proportional to the volume of the container ($V_{\text{container}}$) and the molecular weight (M) of the compound, see Equation 2.1.

$$\frac{n_g}{V_g} = \frac{n_\ell}{V_{\text{container}}} = \frac{V_\ell \rho_\ell}{V_{\text{container}} M} \text{ (Equation 2.1)}$$

Type 2 behavior occurs when the vapor phase becomes saturated and only a portion of the liquid vaporizes (V_x). Two phases then remain in the container, creating a headspace above the liquid. In this case, the moles of gas in the vapor phase (n_g) are equivalent to the moles of liquid that vaporizes (n_x). The volume of the headspace (V_h) is the volume of the container ($V_{container}$) less the volume of the liquid that remains after equilibration ($V_\ell - V_x$). However, unlike Type I, the partial pressure of the substance above the liquid reaches its vapor pressure at that temperature (P°) [8]. Therefore, by way of the Ideal Gas Law, the number of moles of vapor (n_g) in the headspace (V_h) is equivalent to P°/RT , where R is the molar gas constant and T is the temperature (see Figure 2.2 and Equation 2.2).

$$\frac{n_g}{V_h} = \frac{n_x}{V_{container} - (V_\ell - V_x)} = \frac{P^\circ}{RT} \text{ (Equation 2.2)}$$

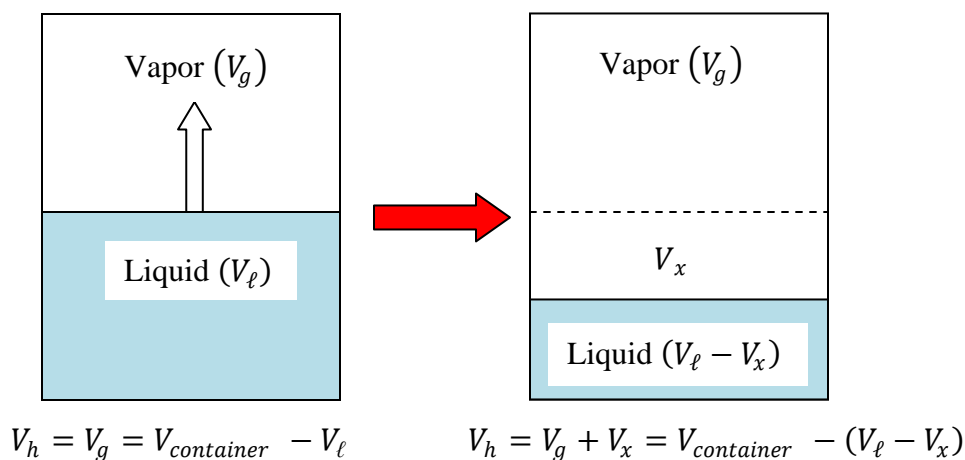


Figure 2.2: Schematic of Type 2 behavior.

Hence, any subsequent increase in the amount of pure explosive (V_ℓ) will not increase the concentration of vapor present in the container. If Equation 2.2 is solved for

the condition where (V_ℓ) is equivalent to (V_x), the minimum number of moles (and hence the minimum volume) of liquid that is required to saturate a given container can be calculated. The results of these calculations can be viewed in Table 2.1 for the three nitroalkanes in various container volumes.

Table 2.1 Calculated minimum values of nitroalkanes.

Nitroalkane	Headspace Vial (20 mL)	2 ounce sniffer tin can (590 mL)	Quart-sized can (946 mL)	Gallon-sized can (3785 mL)
Nitromethane	2.3 μL	6.7 μL	98 μL	392 μL
Nitroethane	1.6 μL	4.8 μL	76 μL	306 μL
Nitropropane	0.98 μL	2.9 μL	46 μL	186 μL

It is understood that the vapor pressure of a liquid rapidly increases with increasing temperature [8]. To calculate the vapor pressure at different temperatures the Clausius-Clapyeron equation, seen in Equation 2.3, was utilized. The equation includes the literature value of the explosive vapor pressure (P_1°), the literature value for the enthalpy of vaporization of the explosive ($\Delta_v H^\circ$) [32], the molar gas constant (R), the temperature at which vapor pressure was measured (T_1) and lastly the elevated temperature at which analysis is completed (T_2). P_2° is then used to recalculate the new volume by use of the Ideal Gas Law, see Equation 2.2 [8, 9].

$$\ln \frac{P_2}{P_1} = -\frac{\Delta_v H^*}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \text{ (Equation 2.3)}$$

The effect of confinement on odor availability was also explored. The diameter of the perforations was increased to demonstrate the subsequent effect on the rate of evaporation of the pure sample. These experiments are based upon Fick's First Law of Diffusion, Equation 2.4a and rearranged in 2.4b, which states that the amount of material that diffuses perpendicular to a perforation at a certain flow rate is known as the flux (J) [33].

$$J = \frac{1}{A} \left(\frac{dn}{dt} \right) = -D \left(\frac{dc}{dx} \right) \text{ (Equation 2.4a)}$$

$$\frac{dn}{dt} = A(-D) \left(\frac{dc}{dx} \right) \text{ (Equation 2.4b)}$$

Therefore, flux is proportional to the area (A) and the flow rate $\left(\frac{dn}{dt} \right)$ or the diffusion coefficient (D) and the concentration difference per unit length $\left(\frac{dc}{dx} \right)$.

Finally, an integrated form of Fick's Law was used to describe unimolar diffusion, see Equation 2.5. This equation is used for uni-dimensional, steady state problems in which the concentration and diffusivity are assumed to be constant [9]. It is comprised of a diffusion coefficient (D), an equilibrium concentration (c), length of the orifice (Δz) (which in this case is the thickness of the sniffer tin lid), and a natural log term that describes the mole fractions of the vapor on either side of the orifice (x_{out} and x_{in}), see Figure 2.3.

$$J = \frac{D_{AB}}{\Delta z} c \ln \frac{1-x_{out}}{1-x_{in}} \text{ (Equation 2.5)}$$

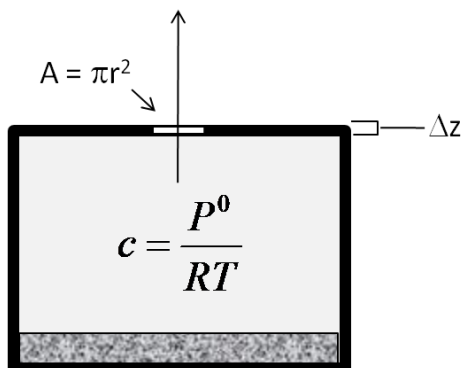


Figure 2.3: Schematic of the integrated version of Fick's Law.

2.2. Material and Methods

Three liquid nitroalkanes were used in this study: nitromethane (Sigma Aldrich, St. Louis, MO), nitroethane (Sigma Aldrich, St. Louis, MO), and 1-nitropropane (Sigma Aldrich, St. Louis, MO).

Headspace analysis was completed in 20mL headspace vials, quart and gallon-sized cans with the three nitroalkanes, in triplicate. The literature values for the boiling point and vapor pressure of the nitroalkanes can be viewed in Table 2.2. The diffusion coefficients of the three nitroalkanes were calculated using the Environmental Protection Agency (EPA) diffusion coefficient calculator available from their website [34], see Table 2.2. This diffusion coefficient calculator uses the Fuller, Schettler, Giddings (FSG) method which was developed in 1966 to predict binary gas-phase diffusion [35].

Table 2.2: Chemical properties of nitroalkanes.

Nitroalkane	Molecular Weight (g/mol) ^[32]	Boiling Point (°C) ^[32]	Vapor Pressure (atm @ 25°C)	Diffusion Coefficient (cm ² /sec)	$\frac{P^{\circ}M}{\rho}$
Nitromethane	61.04	101	0.0473	0.0158	2.59
Nitroethane	75.07	114	0.0275	0.0185	1.98
Nitropropane	89.09	131.1	0.0134	0.0230	1.20

The amount of the nitroalkane sample was varied from 1 μ L to 1000 μ L (in 10-fold increments). The concentration of explosive vapor in the headspace was determined as a function of time, container volume, sample amount, temperature, and extent of containment. The 20 mL headspace vials were purchased from VWR International (Batavia, IL). The Qorpak gallon and quart-sized cans were purchased from W.W. Grainger Inc. of Indianapolis, Indiana.

The samples were analyzed using an Agilent 6890 GC. The capillary column was an HP-5MS 5% Phenyl Methyl Siloxane 30 m x 250 μ m with a 0.25 μ m film thickness. The carrier gas used was Helium with a flow rate of 1.0 mL/min. The MSD transfer line temperature was set at 250°C. The mass spectrometer was a single quadrupole which scanned from 50 m/z to 550 m/z. The Gerstel MPS 2 headspace injection syringe was held at 40°C. The syringe injection volume was 250 μ L. The oven temperature was set at 40°C. The front inlet injector port was set at 200°C in split mode with a split ratio set at

100:1. All data points were normalized to their respective 1000 μL peak areas because this amount exceeded the minimum saturation point. These normalized points were then multiplied by $\left(P^\circ/RT\right)$ to determine their concentrations.

For the temperature effect experiments, headspace analysis was completed on nitromethane in 20 mL headspace vials at room temperature and at an incubation temperature of 40°C. The amount of the nitroalkane sample was varied from 1 μL to 1000 μL (in 10-fold increments). These data points were normalized to the 1000 μL peak area for each temperature. The vapor pressure at 40°C ($P_{40^\circ\text{C}}^\circ$) was calculated with use of the Clausius-Clapyeron equation, Equation 2.3. Then the normalized data points were multiplied by $\left(P_{40^\circ\text{C}}^\circ/RT\right)$ to determine the concentration.

The mass loss of the nitroalkanes was monitored as a function of time, sample amount, temperature and extent of containment. The sample containers were based upon those employed in the National Odor Recognition Test (NORT) for canine testing [17]. These containers consisted of a 2 ounce sniffer tin with a perforated lid. The 2 ounce sniffer tins were purchased from Specialty Bottle of Seattle, Washington. The asterisk pattern on the sniffer tin lid was made with a press purchased from Missile Engineering of Des Moines, Iowa.

The mass loss was measured with an accuSeries accu-124 (Denver Instruments, Denver, CO) digital analytical balance. The accu-124 balance was connected through a USB connection to a Dell computer running Pinnacle USB software. The mass loss of the sniffer tin was measured every two seconds over a 15 minute interval. This data was logged into Microsoft Excel 2007 using a template.

Mass loss measurements of multiple sniffer tins with a perforation of varying nominal diameters were completed to demonstrate the relationship to predicted values calculated from Fick's First Law of Diffusion. Mass loss measurements of sniffer tins with varying number perforations (1-5) were also made for comparison to unimolar diffusion (Equation 2.5). Each perforation was measured with calipers and then averaged to obtain the actual diameter and area.

The raw data gathered during the study was used to calculate the rate of evaporation $\left(\frac{dn}{dt}\right)$. Equation 2.4b was used to determine the flux which is the flow rate with respect to area and time [8, 9, 36, 37].

The mass loss measurements were converted from grams to moles of the liquid nitroalkane being lost. From this, a plot of moles versus time was created. The slope of this line was the rate of evaporation $\left(\frac{dn}{dt}\right)$.

The rate of evaporation, the calculated diffusion coefficient for the three nitroalkanes, as listed in Table 2.1, the equilibrium concentration which was based upon the vapor pressure of the nitroalkanes at room temperature and the thickness of the sniffer tin lid which was 0.5 mm were used to predict the unimolar diffusion. The calculated mole fractions of nitroalkanes on the interior and exterior of the sniffer tin were approximately 0.60 and 0.40, respectively.

2.3. Results and Discussion

2.3.1. Headspace Measurements

As discussed above, a common misconception in canine testing is that increasing the amount of explosive will produce more detectable vapor. However, in a closed container the equilibrium concentration in the headspace of a pure substance is determined by the vapor pressure of the compound (P°) and the temperature (T) of the system. As a result, the minimum volumes of liquid nitroalkanes required to saturate various containers at room temperature can be calculated by the Ideal Gas Law, the molecular weight of the sample, and the literature value for the vapor pressure of the explosive sample as shown in Table 2.1. This equation can be applied to other explosives that are essentially in pure form. Examples include detonating cord (PETN and RDX), peroxide explosives (TATP and HMTD), and military explosives (TNT).

The validity of the Ideal Gas Law has been confirmed through headspace studies of nitroalkanes by placing varying volumes of nitroalkanes in 20 mL headspace vials, quart-sized cans, and gallon-sized cans. For example, a constant headspace concentration was achieved after the minimum calculated volume was exceeded in a 20 mL headspace vial, (see Figure 2.4). The calculated volume for nitromethane is 2.3 μL which was comparable to that seen in Figure 2.4.

Agreement between theory and experiment was also seen with nitroethane which has a calculated value at 1.6 μL and nitropropane at 1 μL with an excellent precision at less than 5%. Figure 2.4 also demonstrated that the minimum volume required for saturation is lower for those compounds with lower vapor pressures, like nitropropane.

Overall, these results indicated that amount of sample did not produce more vapor concentration in the headspace.

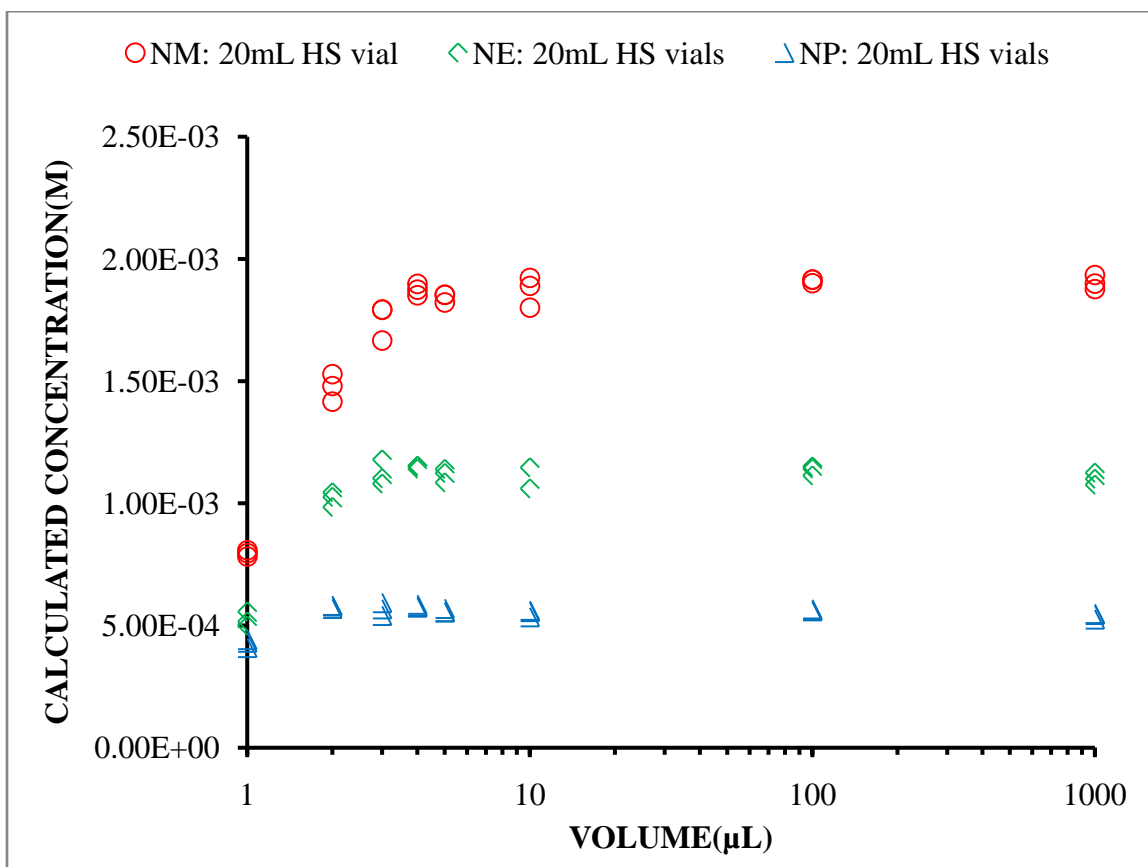


Figure 2.4: This graph shows that once the headspace of the container is saturated an increase in sample amount does not produce more vapors in the headspace. It also shows that vapor pressure effects the amount needed to saturate a container.

Headspace analysis in the gallon-sized and quart-sized cans further demonstrated the validity of the Ideal Gas Law for this system. The calculated value of nitroethane in a 20mL headspace vial was $\sim 1.6 \mu\text{L}$, $76 \mu\text{L}$ in a quart-sized can and $300 \mu\text{L}$ in a gallon-sized can. These calculated values were comparable to our data with an excellent precision at less than 10%, see Figure 2.5.

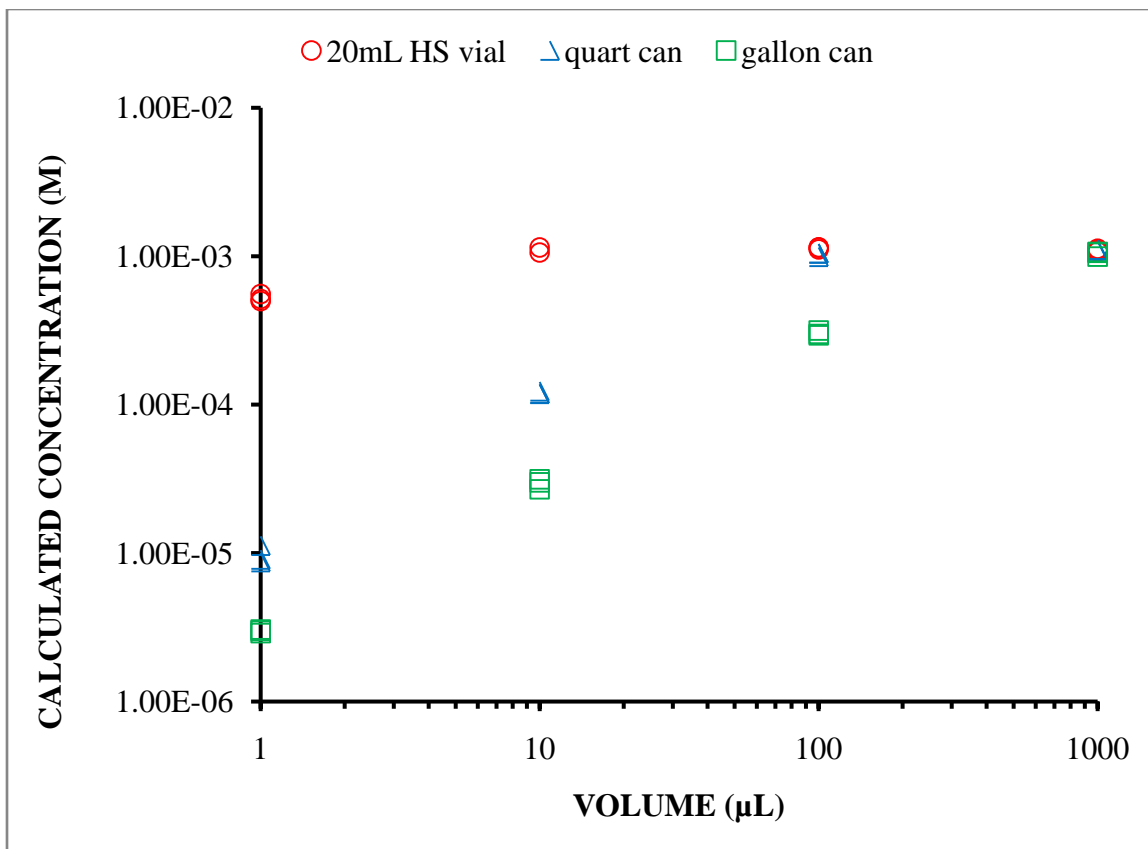


Figure 2.5: This graph demonstrates the effect of volume and container size on the vapor released from nitromethane. It shows that once the vapor reaches equilibrium any further increases of the volume do not affect the vapor.

This indicated that an increase in container size will increase the amount needed to saturate as compared to smaller containers. Furthermore, once the nitroethane vapor in the headspace of the different sized containers was saturated any subsequent increases in the sample amount did not add to the headspace concentration. This trend was seen with analysis of the other nitroalkanes as well.

The effect of temperature on an explosive's vapor pressure was also studied. The determination of vapor pressure at different temperatures is calculated by the Clausius-Clapyeron equation. The temperature of the system increases the vapor pressure of the compound and should therefore increase the minimum volume required for saturation.

This was seen through headspace analysis of nitromethane in 20 mL headspace vials, see Figure 2.6. This figure also demonstrated that once the minimum calculated saturation point was achieved any further increase did not affect the headspace concentration.

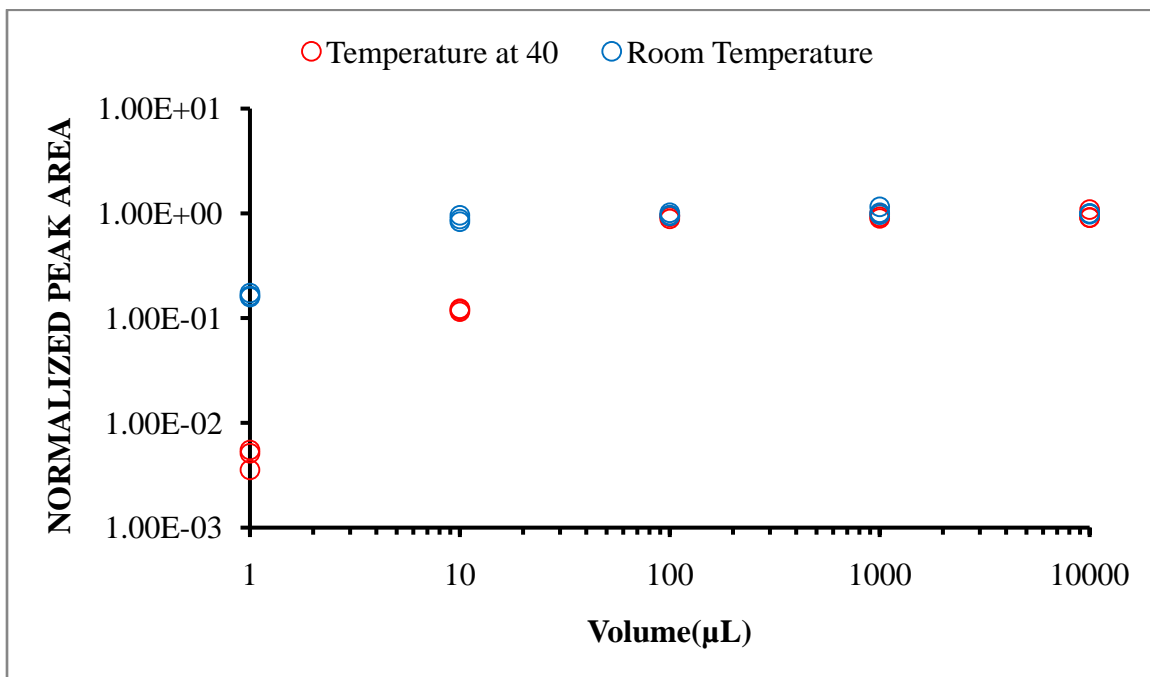


Figure 2.6: This graph displays the effect of temperature on the amount of vapor that is released from nitromethane in a 20 mL headspace vial. It shows that an increase in temperature increases the amount of sample needed to saturate a container.

2.3.2. Mass Loss Experiments

Mass loss experiments showed that an increase of area results in an increase in the rate of evaporation, see Figure 2.7. This finding demonstrated that confinement (area of the hole) does affect the rate of evaporation. In Figure 2.7, it was observed that the flow of material from the sniffer tin was linearly related to area for small holes (e.g., less than 0.2 in²). However, the flow of material began to level off as the area increased and Fick's First Law of Diffusion could no longer be applied. This occurred because $\left(\frac{dc}{dx}\right)$ was no

longer constant, see Equation 2.4b. It was also discovered that the rate of evaporation of an unconfined (i.e. no lid) sniffer tin was much greater (1.6×10^{-1} moles/sec) (~factor of 1,000,000) as compared to the rate of evaporation at an area less than 0.2 in^2 (2.0×10^{-7} moles/sec); indicating that the sniffer tin was saturated and produced a steady flux through the opening.

One last observation seen in Figure 2.7 was the relationship between the flow rate and the diffusion coefficient (as reflected in molecular weight) of the species; a higher flux as was seen with the nitromethane sample as compared to the other higher molecular weight nitroalkanes.

The effect of sample amount on the flux of the material was also analyzed. The flux was not affected by a moderate increase in the sample amount (1 mL, 2 mL, and 3 mL) which further verified that if enough sample amount was present to produce a steady rate of evaporation then the flux of material was not affected. However, with tenfold increments of nitromethane (1 μL -10,000 μL) the flux changed from $5.35 \times 10^{-8} \text{ cm/sec}^2$ at a volume of 1 μL to $8.77 \times 10^{-8} \text{ cm/sec}^2$ at a volume of 100 μL , see Figure 2.8. From 100 μL to 10,000 μL the flux did not change indicating that 1 μL and 10 μL was not enough to sustain a steady rate of evaporation.

This analysis further demonstrated the affect of molecular weights of the nitroalkanes on diffusion through varying perforation sizes in the lid of the 2 ounce sniffer tins. An increase in molecular weight decreased the diffusion/evaporation rate, see Figure 2.9. The flux of the asterisk patterned sniffer tin employed in canine training was comparable to a diameter of $\frac{1}{4}$ inch. It was seen that once the area of the hole became too large Fick's First Law of Diffusion was no longer applicable. However, the

asterisk patterned sniffer tin showed linearity indicating that each hole was operating independently.

Overall, the findings illustrated that flux into the surroundings was linearly dependent on the diffusion coefficient of the substance, which is dependent upon the molecular weight of the substance.

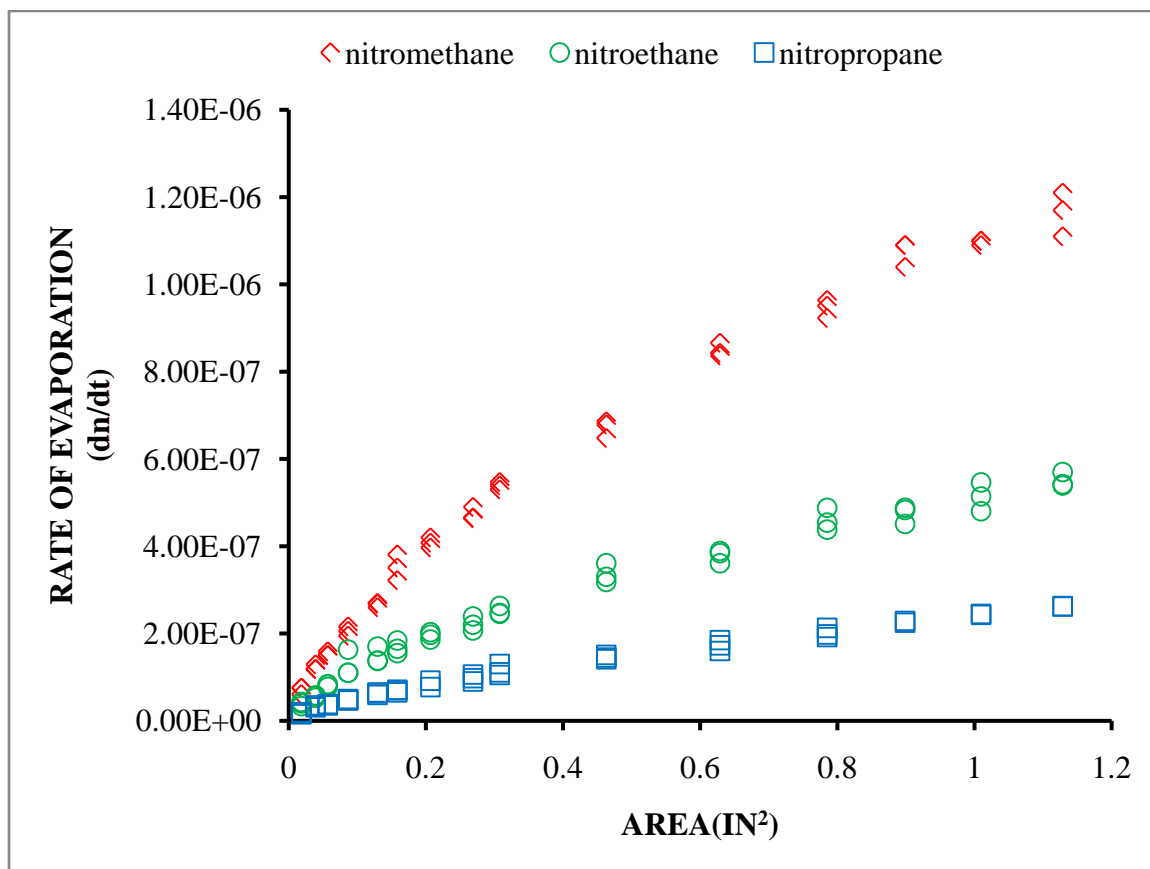


Figure 2.7: This figure illustrated the effect of confinement on the rate of evaporation for the three nitroalkanes. Nitromethane has a faster rate of evaporation as compared to nitroethane and nitropropane due to its smaller molecular weight

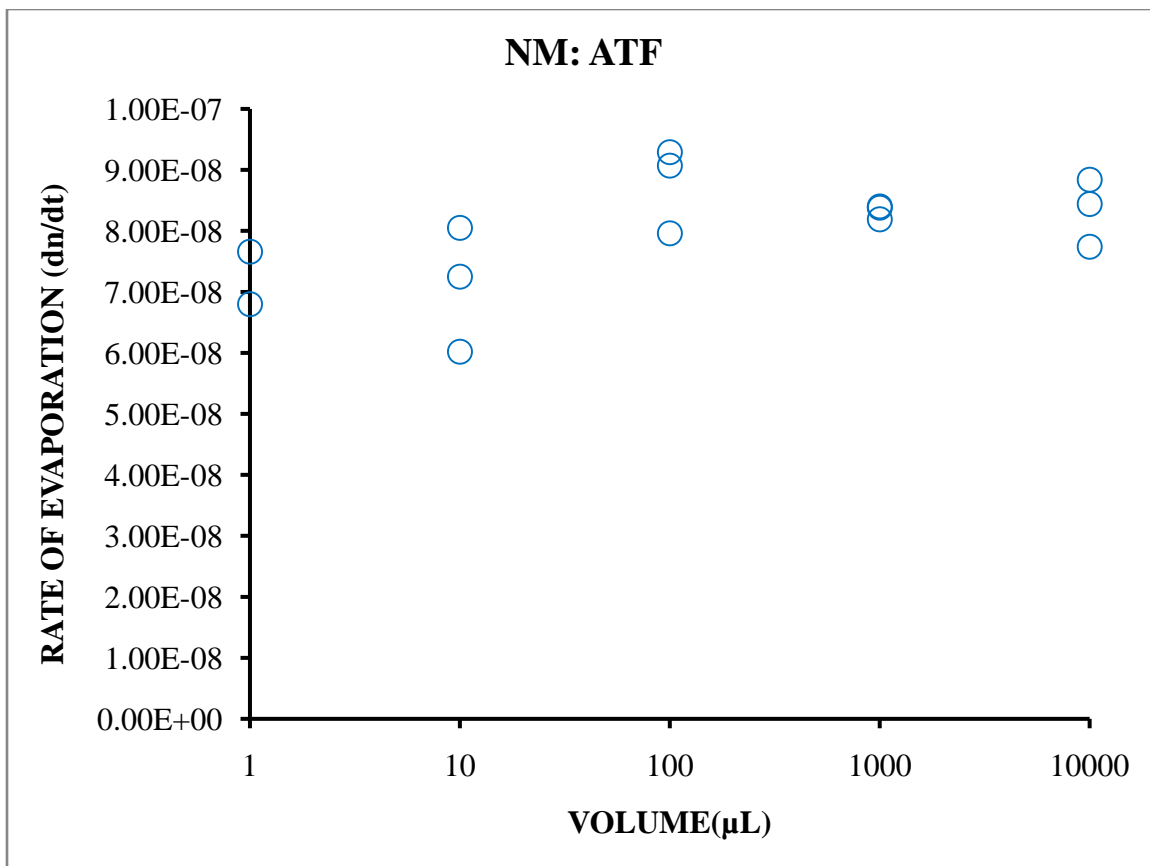


Figure 2.8: This figure demonstrates that the nitromethane sample amount does affect the rate of evaporation of the material through an opening.

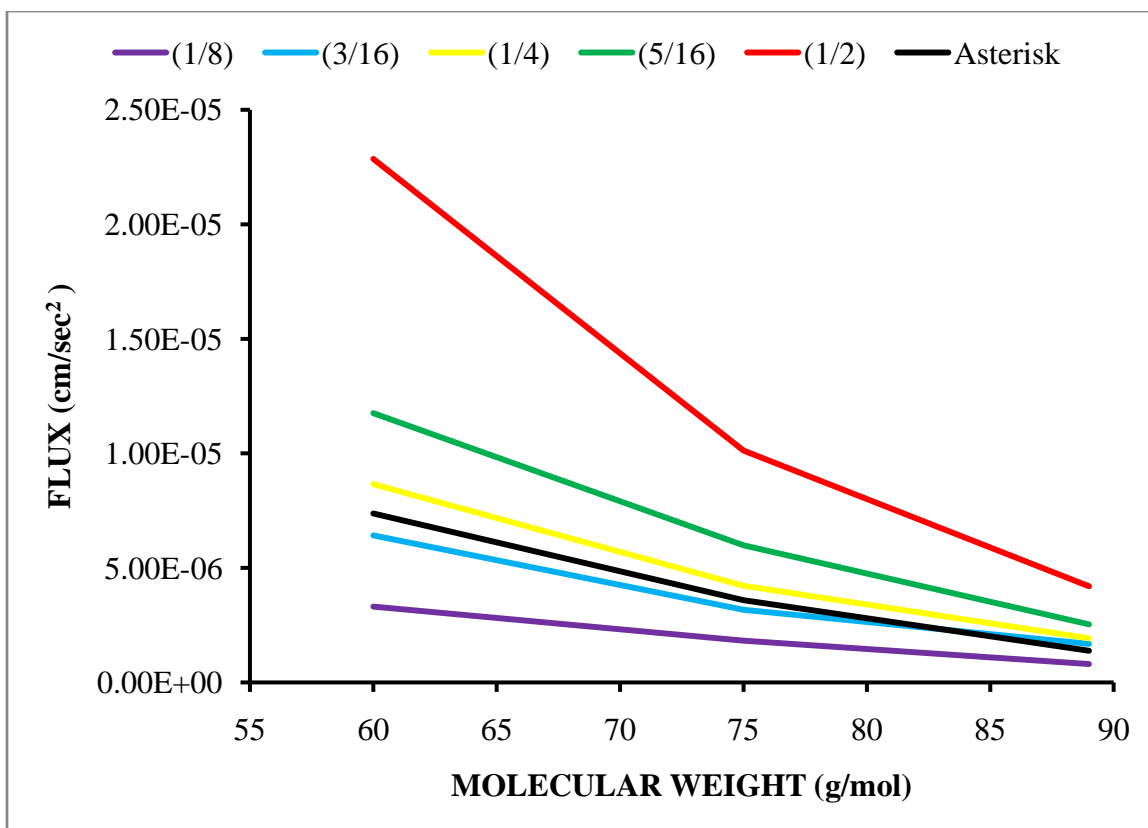


Figure 2.9: This figure demonstrates that lighter materials (nitromethane) will diffuse more rapidly than heavier materials (nitropropane) which is related to their diffusion coefficient.

As revealed above, Fick's Law should govern flow rates for multiple small diameter holes, provided they operate independently. This was seen through comparison of the flow rate of the nitroalkanes from sniffer tins to either one perforation of varying diameter or many perforations of the same small diameter.

From the generation of flux measurements as a function of overall area, the data for multiple holes was successfully fit to an integrated version of Fick's First Law. Figure 2.10 validated this equation in which $D = 0.1 \text{ cm}^2/\text{sec}$ was used, the equilibrium concentration was based upon the vapor pressure of nitromethane at room temperature and the thickness of the sniffer tin lid was 0.5 mm. The calculated mole fractions of

nitromethane on the interior and exterior of the sniffer tin were 0.65 and 0.35, respectively.

Furthermore, the affect of molecular weight on the rate of evaporation (diffusion) of the explosive as well the effect of area on the rate of evaporation was confirmed.

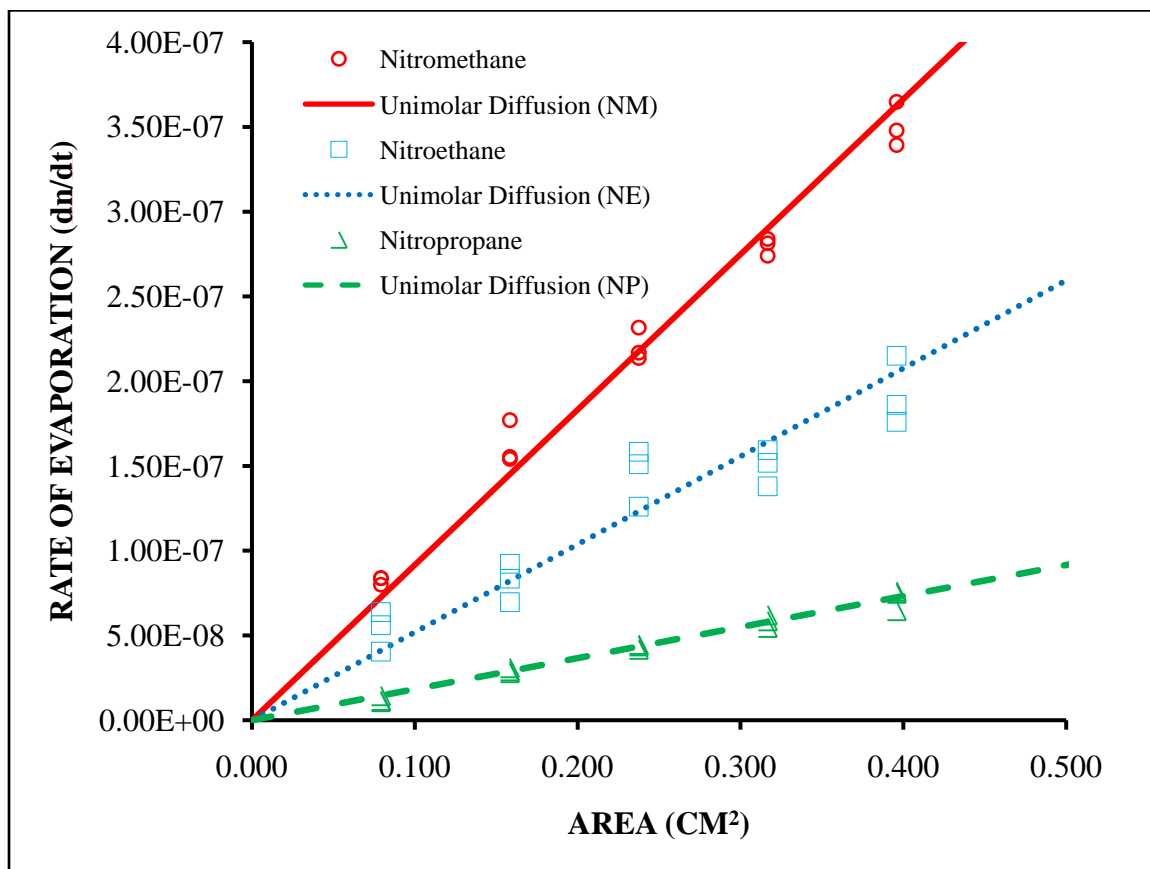


Figure 2.10: This graph displays that the integrated Fick's Law equation is comparable to the multiple hole data of nitromethane which indicates that each opening is acting independently.

2.4. Conclusion

The development of detector sensors, electronic noses, and vapor generators are all reported for the use in the field as explosive detectors [7, 20, 38]. However, the explosive vapor available in canine training has not been well researched. The goal was to create a semi-empirical model for vapor generation and transport of explosives that can be used for laboratory and canine testing. Ultimately, this model will be validated and extrapolated to threat-level quantities of explosives that are sealed within improvised explosive devices (IED).

Experiments were conducted on the mass loss of various explosives as a function of time, sample amount, temperature and extent of containment. Experiments were also performed to determine the concentration of explosive vapor in the headspace as a function of time, container volume, sample amount, temperature, and extent of containment. Through preliminary research, these variables were shown to lead to decreased difficulties in comparison of the sensitivity of canines to one another as well as to analytical instrumentation.

The use of well accepted models and scientific theories were confirmed through the experimental analysis of the nitroalkanes. The affect of multiple factors on the availability of an explosive's vapor was thoroughly investigated. For instance, the effect of vapor pressure resulted in smaller amounts of nitropropane used to saturate a container as compared to the other nitroalkanes. This was verified through calculations by use of the Ideal Gas Law.

Based on the experimental findings, Fick's First Law of Diffusion can only be applied to smaller diameter holes (less than 0.2 in²). Once the diameter became too large

diffusion was no longer uni-dimensional. The utilization of Fick's Laws of Diffusion to demonstrate the diffusion of the explosive was studied and supported the use of the multiple hole pattern in the 2 ounce sniffer tin lid employed in the NORT for canine testing.

It is important to note that the theories and equations modeled and demonstrated in our analysis can be applied to packages, luggage and other containers; provided that the explosive is in pure form and its chemical properties are available. These theories and equations provide more knowledge about the explosive's odor available for canine training and testing; thus, improving their detection and retrieval.

CHAPTER 3. DIFFUSION OF EXPLOSIVE VAPOR IN A CONTAINER USED FOR CANINE TRAINING

3.1. Introduction

Deliberate concealment of explosives to prevent the escape of vapor is the focus of some terrorists. Understanding how an explosive vapor diffuses from its source to the canine for sampling is essential to better understand the odor available for canine detection. The vapor's movement is composed of the molecules rate of diffusion as well as the attraction of the molecule to the surface of a container [8]. Davidson discussed the attenuation of vapors by stating that "only the most volatile species can be detected under 'real-world' conditions" due to the fact that the packaging materials and adsorption of the vapor onto the container effect the vapor's attenuation [11]. Explosive concealment by wrapping can cause a decrease in vapor concentration by a factor of 1000 [39]. This information can be related to other containers like packages, luggage, etc.

Since explosive vapor availability in canine training has not been thoroughly researched and other modes of detection have [7, 20, 23, 24], our objective was to gain more knowledge about the diffusion of the explosive's vapor from its source. Therefore, analysis was completed on containers that were based upon those employed in the National Odor Recognition Test (NORT) for canine training [17]. These containers consisted of a 2 ounce sniffer tin with perforated lid that was housed in an open quart-

sized can. These quart-sized cans were then placed in a gallon-size can, as seen in Figure 2.1.

Experiments were completed over time to observe the equilibration of nitromethane, nitroethane, and nitropropane in a quart-sized and gallon-sized can. Diffusion is based on the movement of a vapor from higher concentration to lower concentration over time. In a closed system (diffusion limited), saturation of the explosive vapor in the headspace of the container remains over time. In an open system, equilibrium is not achieved, but over time if enough vapor is continually released from the explosive sample then a steady state can be achieved.

The initial experiment was related to Fick's Second Law of Diffusion (Equation 3.1) [9, 40] which is based on a one dimensional model that demonstrates the effect of diffusion on the concentration in a container as well as the rate at which the amount changes in the container [40]. This equation was used because it has been employed in explosive diffusion research on nitromethane and unexploded ordnance (UXO) [41, 42]. Fick's Second Law of Diffusion illustrated that the concentration of a species at any position and time ($c(x,t)$) was related to the saturated concentration inside the sniffer tin (c_0) and the diffusion coefficient (D):

$$[c(x, t) = c_0 \operatorname{erfc}(x / \sqrt{4Dt})] \text{ (Equation 3.1)}$$

3.2. Material and Methods

Pure nitromethane, nitroethane, and nitropropane were used for these experiments which were purchased from Fisher Scientific. The Qorpak gallon and quart-sized cans were purchased from W.W. Grainger Inc. of Indianapolis, Indiana. The 2 ounce sniffer tins were purchased from Specialty Bottle of Seattle, Washington. The holes in the gallon cans were punched with a metal punch purchased from W.W. Grainger Inc. The holes were then enlarged with a Greenlee ½ inch radio chassis punch purchased from Greenlee Tools of Rockford, Illinois. The asterisk pattern in the 2 ounce sniffer tin lid was made with a press purchased from Missile Engineering of Des Moines, Iowa. The rubber septa were purchased from Fisher Scientific. The gallon-sized cans containers were either used “as is” or modified with six (½ inch) diameter holes to allow automated sampling while unsealed. For the data points obtained from the open container experiments, the peak areas were normalized to their respective 1000 µL container. This was due to the fact that equilibrium is not achieved because of the open container.

The samples were analyzed via Gas Chromatography/Mass Spectrometer (Agilent 6890). The capillary column was an HP-5MS 5% Phenyl Methyl Siloxane 30 m x 250 µm with a 0.25 µm film thickness. The carrier gas used was Helium with a flow rate of 1.0 mL/min. The MSD transfer line temperature was set at 250°C. The mass spectrometer was a single quadrupole which scanned mode from 45 m/z to 100 m/z. The Gerstel MPS 2 headspace injection syringe was held at 40°C. The syringe injection volume was 250 µL. The oven temperature was set at 40°C. The front inlet injector port was set at 200°C in split mode with a split ratio set at 1:100.

3.2.1. Data Analysis

3.2.1.1. Diffusion-Limited and Steady-State Systems

For these experiments, headspace analysis was completed using a 2 ounce sniffer tin with varying lid perforations (1/8th inch hole, asterisk pattern and without a lid (unconfined)) in a quart-sized can and then placed within a gallon-sized can. The 1000 μL unconfined data was used to normalize the other more confined data points because based upon the Ideal Gas Law this volume will saturate a gallon-sized can. This normalized data was then multiplied by $\left(P^\circ/RT\right)$ to determine the concentration.

Equation 3.1 was used to calculate the concentration of nitromethane through a container over time which included the calculated value of the diffusion coefficient (D) for nitromethane sample, using the EPA website [34] approximately $0.01 \text{ cm}^2/\text{sec}$, the depth of the container (x) measured at 16.85 cm which was based on the depth of the container minus the penetration depth of the syringe, and the initial concentration (c_0) of the sample calculated at 0.00193 (moles/L) in a gallon-sized can.

3.2.1.2. Preliminary Canine Test

A preliminary canine test was conducted, using nitromethane, to determine the effect of confinement and sample amount. These tests were conducted using controlled single-blind studies to assess the response of canines at different levels of odor delivery. A single blind test consists of the handler being informed about the search parameters;

however, the handler is not advised about the outcome. The handler shall also not be advised of the placement or number of target “hot” samples. Only the test administrator shall know the outcome of the search. Once the canine alerts to a possible hit the test administrator informs the handler whether the canine was correct or not. The handler then rewards a positive hit. This type of study is completed so that the canine is not falsely rewarded. Lastly, the search must contain a blank which is used as a control to determine the efficacy of the search [12]. The data obtained was based upon four canines with two trials per canines. Each canine was allowed two searches per trial. This equates to 16 searches of any container. The number of correct responses (positive alerts) to a container was then divided by 16 and converted to a percentage.

3.3. Results and Discussion

3.3.1. Fick’s Second Law of Diffusion

Experiments were completed over time to observe the equilibration of nitroalkanes as a function of container volume. Fick’s Second Law of Diffusion is based upon a one dimensional model that demonstrates the change in concentration gradient over time. However, it was limited in its ability to model the behavior of a three-dimensional system. Even so, the experimental data from certain sample geometries was consistent with the predicted values, see Figure 3.1. The unconfined and asterisk patterned sniffer tin containing nitromethane equilibrated much faster than would be predicted by Fick’s Law. The highly confined ($1/8^{\text{th}}$ inch perforation) nitromethane was consistent with one-dimensional diffusion. This trend was observed with nitroethane and

nitropropane in a quart-sized container. The calculated diffusion for the nitroalkanes was completed in gallon sized-cans as well. The calculated diffusion for nitromethane was consistent with the asterisk patterned sniffer tin. However, the calculated diffusion for nitroethane and nitropropane could not be compared because the unconfined nitroethane and nitropropane did not equilibrate.

Before the commencement of the canine test, the explosive sample in the asterisk patterned tin is allowed to equilibrate in the container for 30 minutes. These results revealed that the asterisk patterned nitroalkanes in quart-sized cans diffused more rapidly than the predicted values. The analysis of nitromethane asterisk patterned sniffer tin in gallon-sized can was consistent with the predicted values. However, the nitroethane and nitropropane explosive samples did not achieve equilibration after 50 minutes with use of the asterisk pattern as well as the unconfined and highly confined sample.

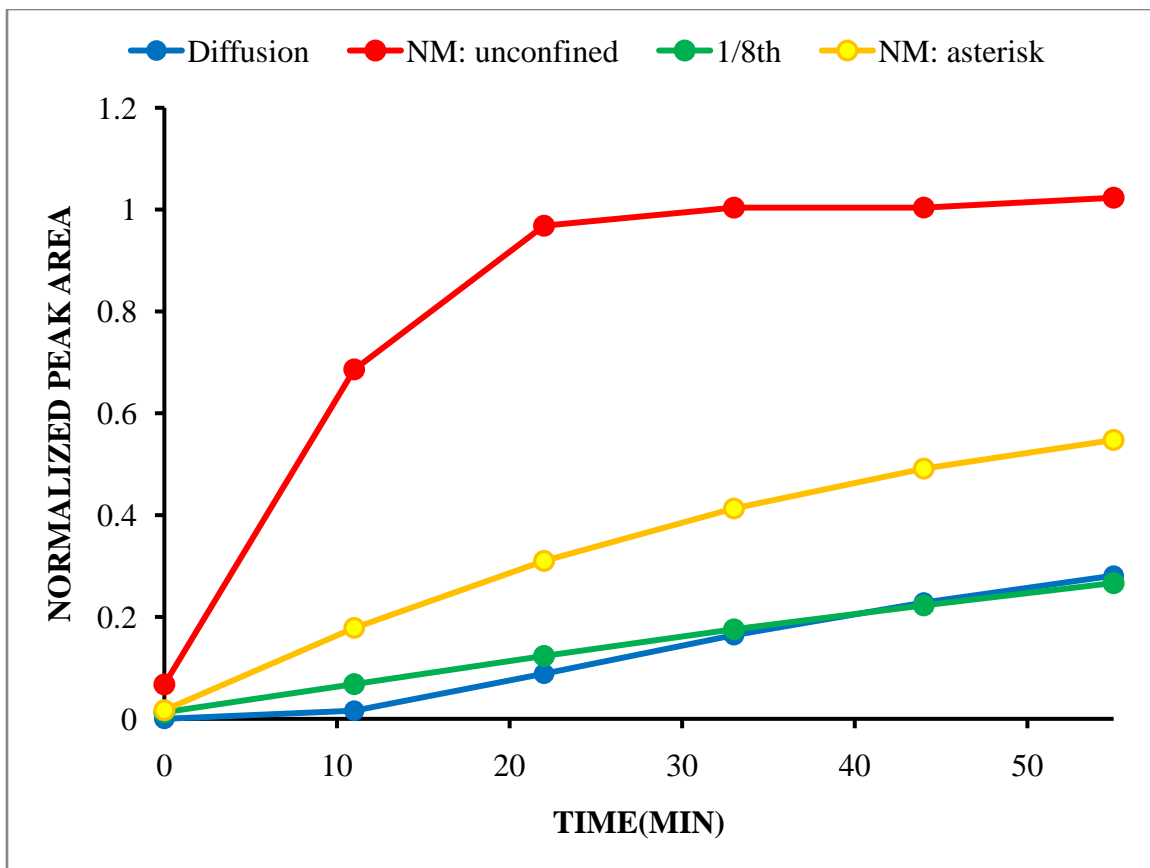


Figure 3.1: Response from use of nitromethane in a 2 ounce sniffer tin with variation to confinement in a quart-sized can.

3.3.2. The Equilibration of Diffusion-Limited and Steady-State Systems

In these experiments headspace analysis was completed on the three nitroalkanes in quart- sized and gallon-sized cans over time to observe steady-state and diffuse-limited equilibration. The quart-sized and gallon-sized can lids were perforated with holes to represent an open system which was consistent with canine testing and training. These experiments included 2 ounce sniffer tins with varied lid patterns as discussed above. Before canine training commences, the cans are allowed to equilibrate for 30 minutes. From the open quart-sized can data, steady evaporation rates were achieved after 10 minutes with all three confinements, see Figure 3.2. Therefore, 30 minutes was enough time to reach a steady evaporation rate. A quart-sized can required 98 μL of nitromethane to saturate a quart-sized can so 1000 μL was sufficient to produce a continued steady evaporation rate. A steady state was also achieved with the highly confined 1/8th lid pattern as well as the commonly used asterisk pattern.

Nitromethane was analyzed at (100 μL and 10,000 μL) to observe their equilibration rate. It was observed that 100 μL was not quite enough to produce a steady evaporation rate. The evaporation rate declined after 25 minutes. This trend was seen with the analysis of nitroethane and nitropropane in quart-sized cans and with the same amounts. Even though nitroethane and nitropropane require only 76 μL and 46 μL to saturate a quart-sized can, these minimum amounts were not enough to reach a continual steady-state; the evaporation rates declined after 25 minutes.

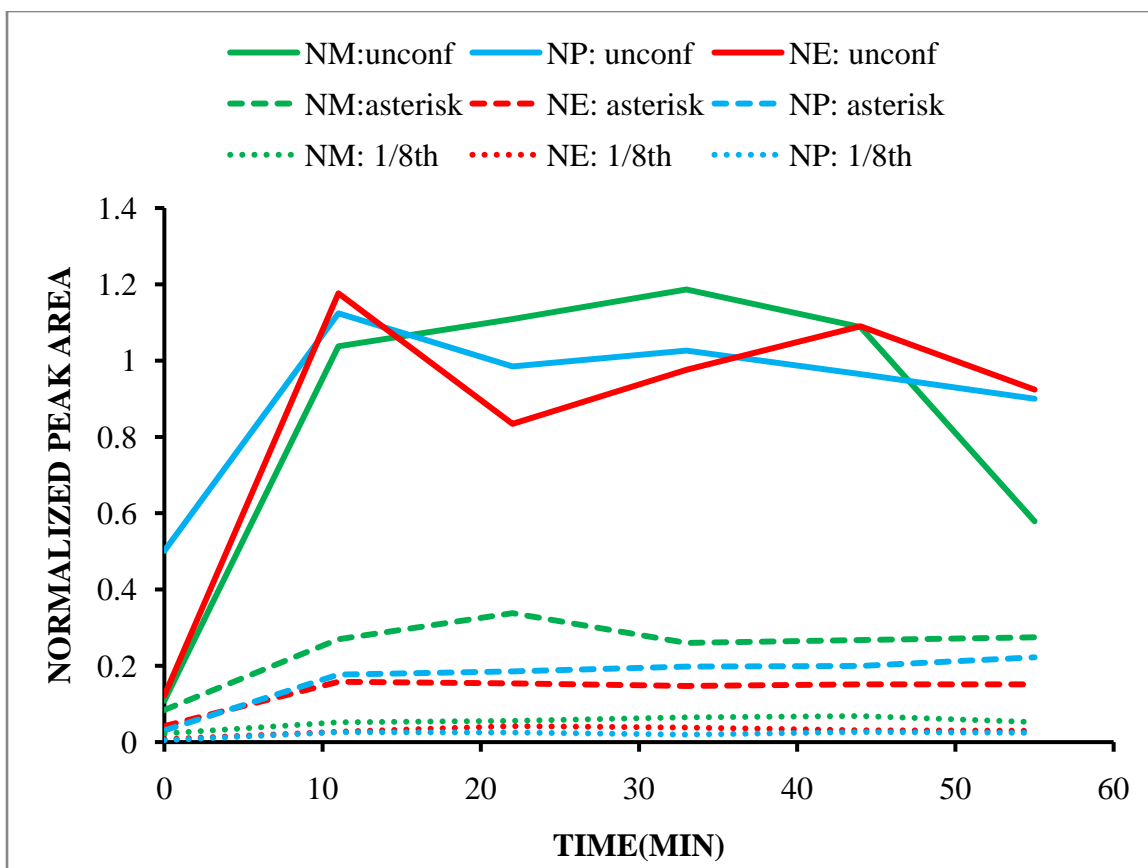


Figure 3.2: Higher equilibration rates were achieved for the unconfined nitroalkanes(1mL) in an open quart-sized can.

The diffusion limited system (closed quart-sized container) demonstrated longer equilibration times especially for those that were confined ($1/8^{\text{th}}$ and asterisk), see Figure 3.3. The headspace concentration of a nitroalkane diffusing through the quart-sized can in both systems was less for the highly confined $1/8^{\text{th}}$ perforation as compared to the asterisk pattern and the unconfined samples.

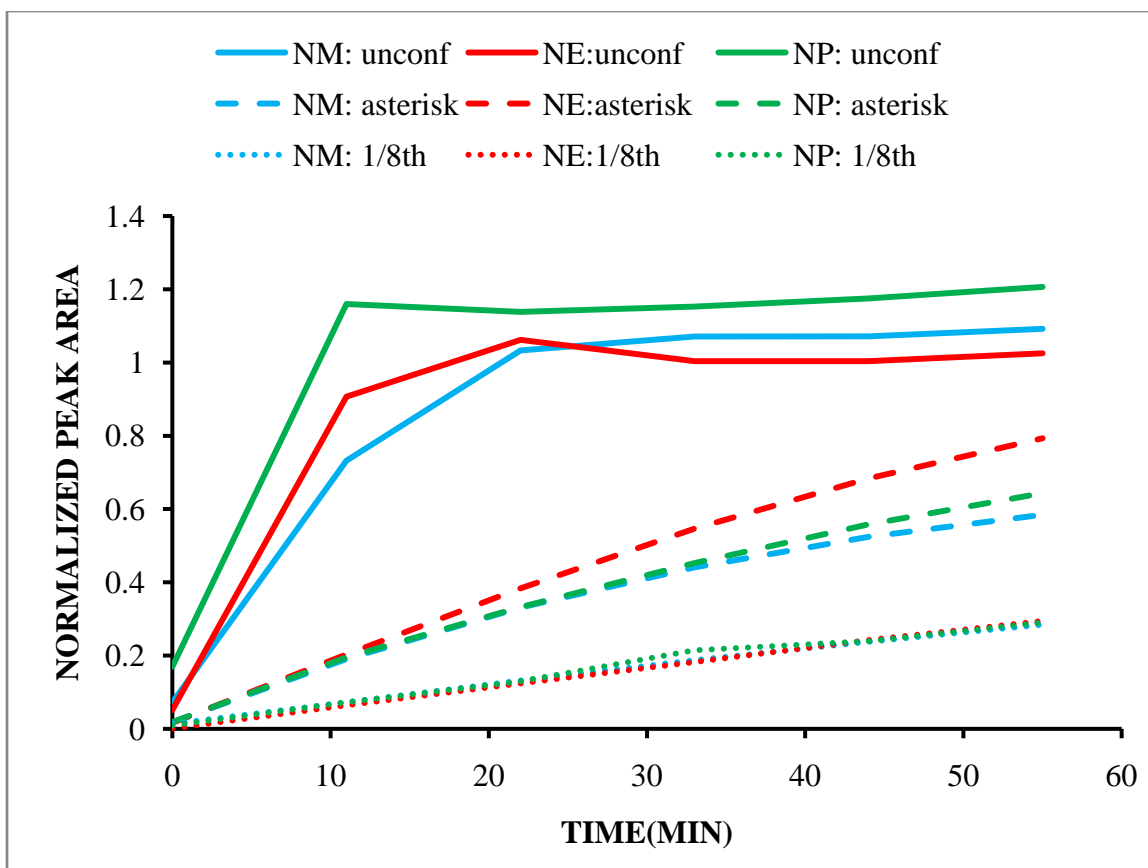


Figure 3.3: 1 mL of nitroalkanes in a closed quart-sized can equilibrated at 10 minutes.

The equilibration time of the nitroalkanes at different volumes (100 μL , 1,000 μL , and 10,000 μL) in a closed quart and gallon-sized container was analyzed. 1000 μL and 10,000 μL of nitromethane in an unconfined quart-sized can had a longer equilibration time as compared to nitroethane and nitropropane as well as higher vapor concentration in the headspace of the containers, see Figure 3.4. The amount of the three nitroalkanes (1 mL and 10 mL) did not affect the equilibration time or the concentration of vapor in the headspace, see Figure 3.4.

1,000 μL and 10,000 μL of nitromethane unconfined in a closed gallon-sized can did not achieve equilibrium after 55 minutes; however 100 μL of unconfined

nitromethane did begin to equilibrate around 50 minutes. Even so, based on calculated values, the minimum amount of nitromethane needed to saturate a gallon-sized can is 392 μL ; thus, it is uncertain if this equilibration will continue after 55 minutes. Smaller containers such as the quart-sized can did generate stability after 25 minutes. Indicating that amount does affect saturation in larger containers. The more confined samples in quart and gallon-sized cans did not achieve equilibrium after 55 minutes. These trends were also seen in the analysis of nitroethane and nitropropane in quart and gallon-sized cans.

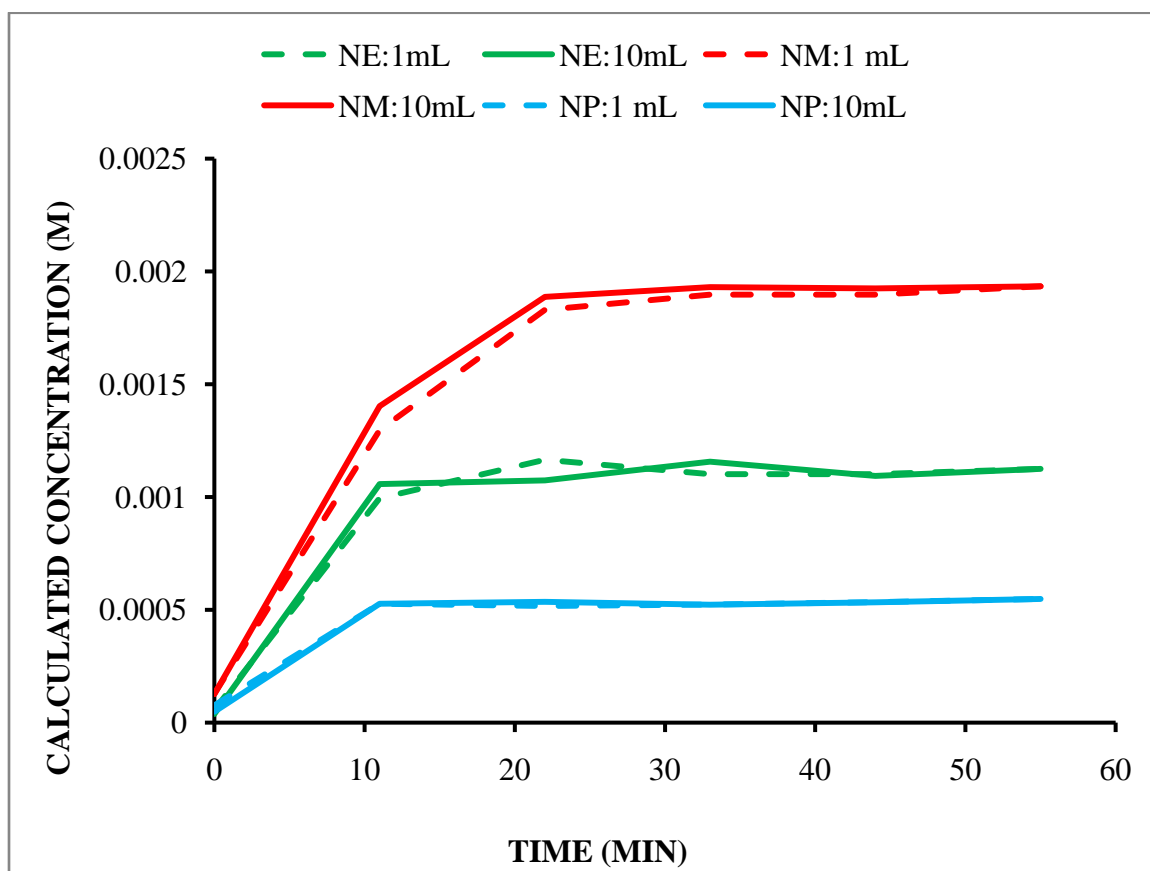


Figure 3.4: Amount of the nitroalkane sample did not affect the headspace concentration in a quart-sized can after 10 minutes

3.3.3. Preliminary Canine Test

Canine testing was completed with use of 2 ounce sniffer with an asterisk punched lid that was placed inside of a quart-sized can and then the two cans were placed inside of a gallon-sized can. Once the explosive sample was placed inside of the gallon sized-cans, it was allowed to equilibrate for 30 minutes. The explosive vapor diffused in the container throughout the test which was approximately 45 minutes. Table 3.1 showed that the amount did have an effect on the canine detection. This study is an inconsistent observation given that the studies discussed above demonstrated that the degree of confinement of the explosive within the sniffer tin was the most crucial (provided that there is sufficient sample present to saturate the headspace and deliver a steady flow rate).

Table 3.1: Percent correct responses to containers varying in sample amount and confinement. Odor availability increased with increase of sample amount and confinement.

Volume	Lid Pattern	
	1/8th	Asterisk punched
0.1mL	50%	63%
1mL	88%	94%

The validity of the canine tests was confirmed by headspace analysis. Our analysis involved the same geometry, as stated above, in order to demonstrate the available odor to the canine. After 50 minutes the evaporation rate of 100 μL of nitromethane drastically declined while 1 mL of nitromethane had a steady rate of evaporation, see Figures 3.5-3.6. As seen in Table 2.2, 392 μL of nitromethane is needed to saturate a gallon-sized can. This indicated that if there was not sufficient sample

present to saturate the headspace of a container then it proved problematic for some canines, as seen by our canine test results. Routinely, no one tracks the accuracy of the canine's alert outside of a training climate.

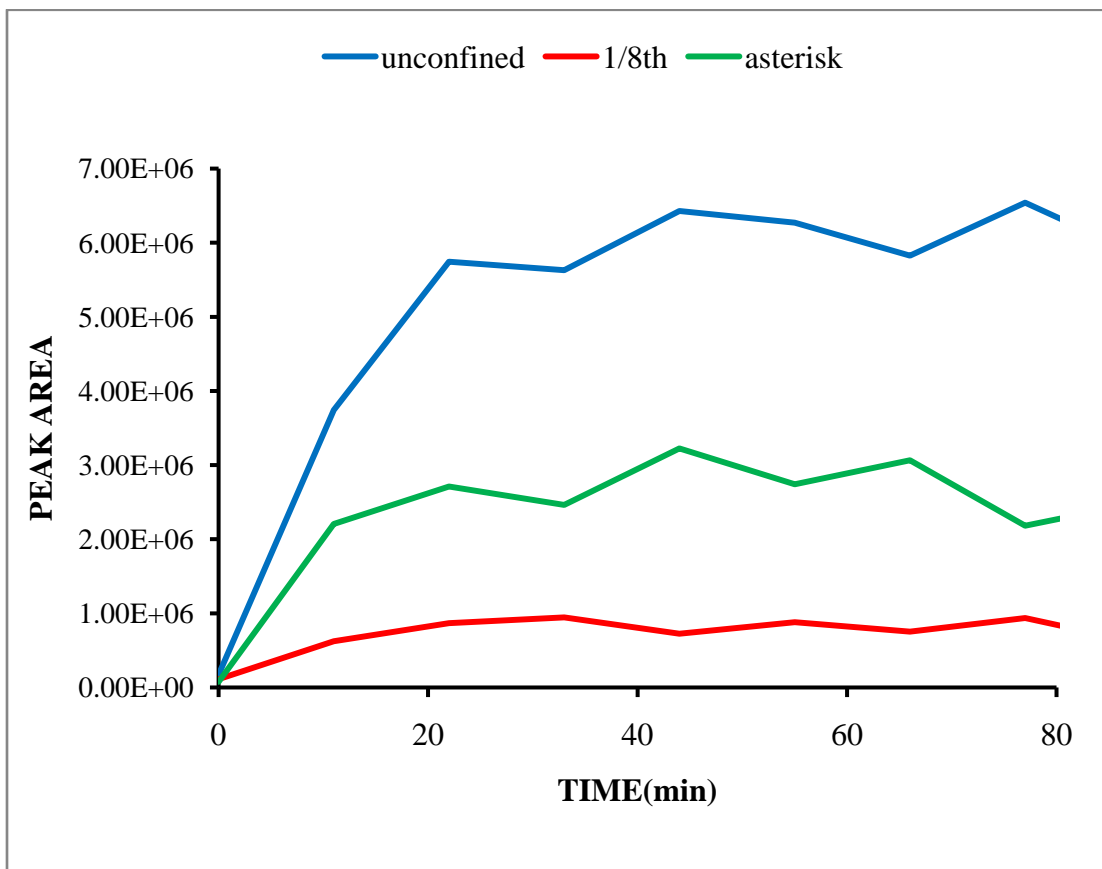


Figure 3.5: Steady state achieved with 1 mL of nitromethane in an open gallon-sized can.

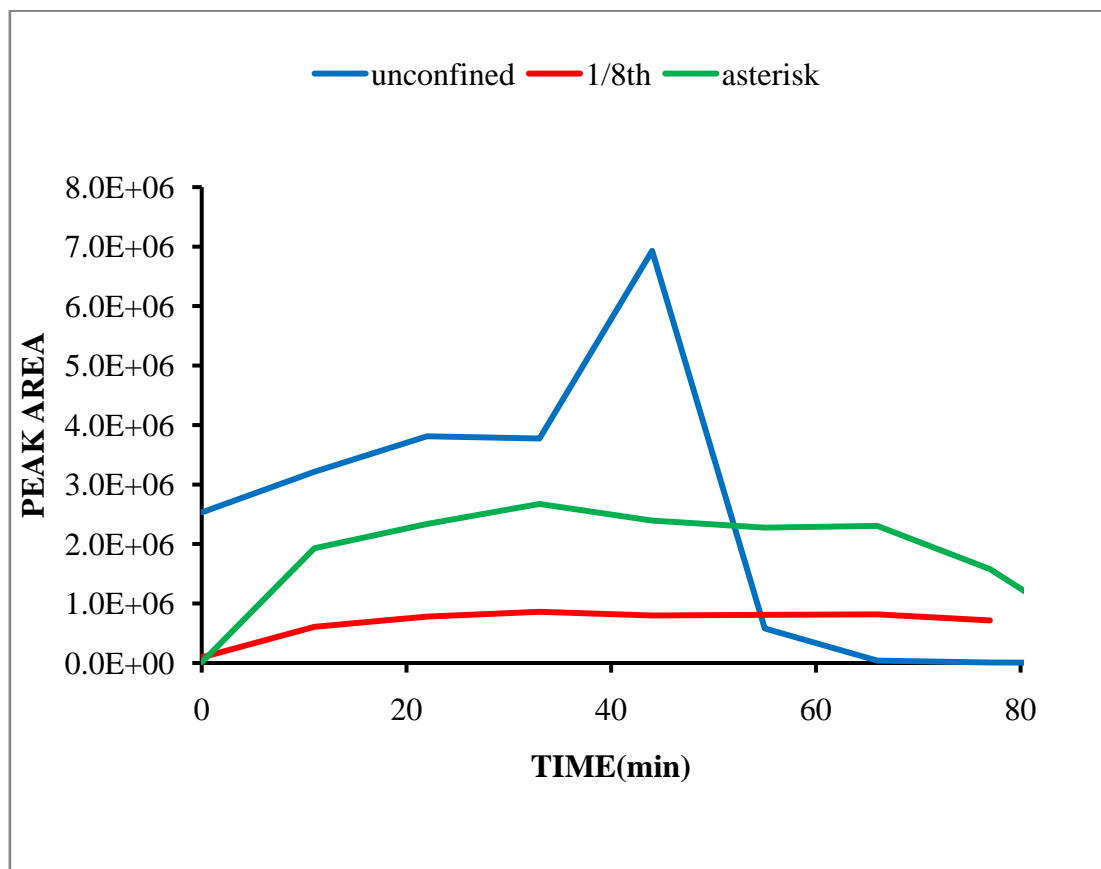


Figure 3.6: A steady-state was not achieved with 0.1 mL of nitromethane in an open gallon-sized can.

3.4. Conclusion

The applicability of Fick's Second Law of Diffusion to containers used in canine training was confirmed through the experimental analysis of the nitroalkanes. Samples in a closed container had a longer equilibration times than those in open containers. The nitroalkane samples in closed and open quart-sized containers produced lesser headspace concentrations for more confined samples as related to the unconfined samples. Initially, based on previous analysis of nitroalkanes, it was assumed that amount did not affect

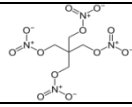
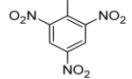
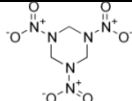
canine detection. However, our preliminary canine test indicated otherwise. Through further analysis, it was determined that the amount used must be enough to saturate a container. These analyses can be related to explosives concealed in luggage and packages which will improve current canine training and testing procedures; thus, improving canine detection and prevention of explosions.

CHAPTER 4. EXPLOSIVE ODOR COMPOUNDS

4.1. Introduction

To date optimal training protocols and the reliability of canine detection have been subjective; which has led to disputes over the acceptability of evidence obtained. Increasingly strict requirements are being applied to the admissibility of canine alerts. There are presently several theories about what is responsible for the canine's high selectivity and specificity to explosives. For instance, there is the possibility that canines are alerting to the parent explosives regardless of their volatility, or that canines are alerting to more volatile, non-explosive chemicals that are present in explosives and lastly, that the canine is detecting the parent as well as other characteristic volatiles [22]. Most organic explosives have a very low vapor pressure at room temperature, see Table 4.1. Their availability in the headspace of a container is low so the headspace will consist of more volatile materials like solvents, impurities, or degradation products [1]. Degradation products occur because explosives are highly reactive compounds and when heated they have the propensity to breakdown; therefore, these decomposed products may be the main contributors to the odor generated for canine detection [38].

Table 4.1: Characteristics of high explosives at 25°C [7, 43].

Explosive	Structure	Vapor Pressure (ppb)	Concentration (ng/L)
PETN		0.0018	0.09
TNT		9.4	70
RDX		0.006	0.04

The intention of this study is to identify the key odors emanating from nitrated explosives and NESTT materials. NESTT products (i.e., Non-Hazardous Explosives for Security Training and Testing) are used in the training of canines and are made with small amounts of the actual explosive which is adsorbed onto an inert material [28-30].

Methods will use solid phase microextraction and headspace sampling coupled with gas chromatography-mass spectrometry. This analysis will include the evaluation of explosives and other odor compounds found in the headspace of a container such as plasticizers like dioctyladipate (DOA) that can be found in Composition C-4 and citraflex (found in PETN-based sheet explosive). All explosives samples utilized in this study were screened via these techniques for comparison purposes.

These samples were analyzed by PDMS and PDMS/DVB SPME fibers due to their common use in the analysis of explosive samples [13, 22, 44-47]. Solid phase microextraction begins with the introduction of a fused silica fiber with a thin layer of a selected liquid organic polymer into a close container with a headspace. The fiber's liquid coating starts to absorb the organic analyte from the headspace. The analyte undergoes a series of transport processes, from solid or liquid phases to gas phase (or

headspace) and eventually to the coating, until the system finally reaches equilibrium [48], see Figures 4.1 and 4.2.

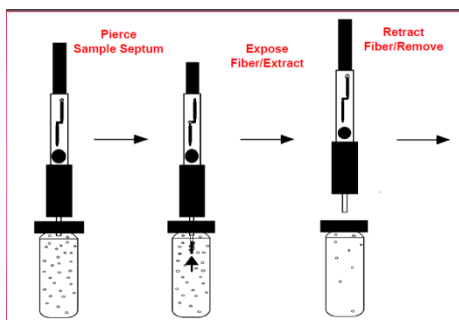


Figure 4.1: Extraction procedure for SPME^[49]

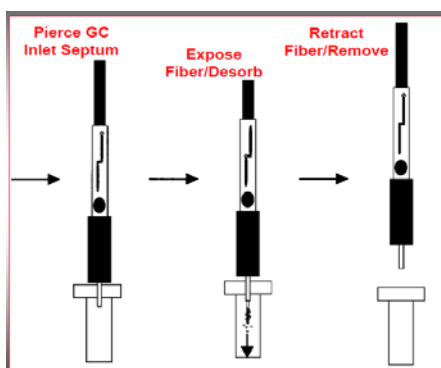


Figure 4.2: Desorption procedure for SPME^[49]

SPME is effective and widely used in the extraction of a wide variety of trace organic compounds that includes water contaminants in food and water, accelerants in fire scene debris, and drugs in blood and urine [43, 46]. Successful recovery of explosives from headspace using other techniques has also been described [21, 43]. The ease of analysis of volatile explosive analytes by solid-phase microextraction makes this the best choice for this study.

4.2. Material and Methods

4.2.1. SPME and Headspace GC/MS

Standards were purchased from Sigma Aldrich and included 1-butanol, butyl acetate, cyclohexanone, DMNB, 2-ethyl-1-hexanol, 2,4 DNT. The explosive materials used were 2,4,6 Trinitrotoluene, Pentaerythritol tetranitrate (PETN), Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), C-4 of military and commercial origin, Shape Charge, and Detasheet. A sample of each was placed into a 20mL headspace vial. The 20 mL headspace vials were purchased from VWR International (Batavia, IL). Plasticizers were also evaluated for identification in the explosives. Plasticizers used included Bis(2-ethylhexyl)adipate (DOA) and Citraflex which were purchased from Fisher Scientific Company (Hanover Park, IL). SPME was used with gas-chromatography-mass spectrometry. The SPME-GC-MS methods used a 100 μ m Supelco Polydimethylsiloxane/Divinylbenzene (PDMS/DVB) (Bellefonte, PA) and a 100 μ m Supelco Polydimethylsiloxane (PDMS) (Bellefonte, PA) fiber which were conditioned before use according to the suppliers instructions. The fibers sampled from the headspace of a 20 mL headspace vial at room temperature with injections into the Thermo SPME inlet liner at 200°C. The SPME exposure time was 5 minutes.

The GC/MS used was the Thermo Trace GC Ultra 200 in conjunction with the Thermo DSQ. The column used was the Thermo TR-5ms 30 m X 250 μ m with a 0.25 μ m film. The injection port was held at 200°C with a 3 minute desorption. The oven temperature was a temperature ramp initially set at 40°C for 1.5 minutes then increased by 20°C until reached a maximum temperature of 320°C. The front inlet injector port

was operated in split mode with a split ratio set at 1:10. 1-butanol, butyl acetate, cyclohexanone, 2-ethyl-1-hexanol were analyzed with a split ratio of 1:100, an exposure and desorption time of 1 second due their high concentration. The mass spectrometer was a single quadrupole which scanned from 50 m/z to 550 m/z. This method was completed for each fiber. All samples were also analyzed by headspace GC/MS using the same parameters, as discussed above. The data analysis was completed with use of Excalibur software. Each sample was searched in the NIST Library (version 2.0) for peak identification. All samples were normalized to the largest peak area.

4.3. Results and Discussion

4.3.1. SPME and Headspace GC/MS

Analysis began with the comparison of the two sampling techniques, SPME and Headspace (HS). For SPME analysis a Polydimethylsiloxane (PDMS) fiber which is commonly used for volatile groups with molecular weights ranging between 60-275 g/mol [49] and a PDMS/DVB fiber which is commonly used for volatile groups with molecular weights between 50-300 g/mol, amines, and nitroaromatics [49]. The ultimate goal was to run experiments for comparison between the different methods of sampling (PDMS, DVB/PDMS, and HS). The SPME fiber produced a higher abundance of an explosive's odor compound as compared to simple headspace analysis. Also, headspace analysis resulted in several ghost peaks. The source of which was not determined. Furthermore, odor compounds detected through headspace sampling were comparable to

those detected through SPME analysis. Upon further analysis of the other explosives it was observed that simple headspace analysis was not as sensitive as the SPME fibers.

Analysis continued with the comparison of the two SPME fiber coatings (PDMS and PDMS/DVB) in order to ensure that the SPME results are in agreement with previous literature. In general, it made no difference in the semi-volatile compounds that were detected, see Figures 4.3, A.1-A.5.

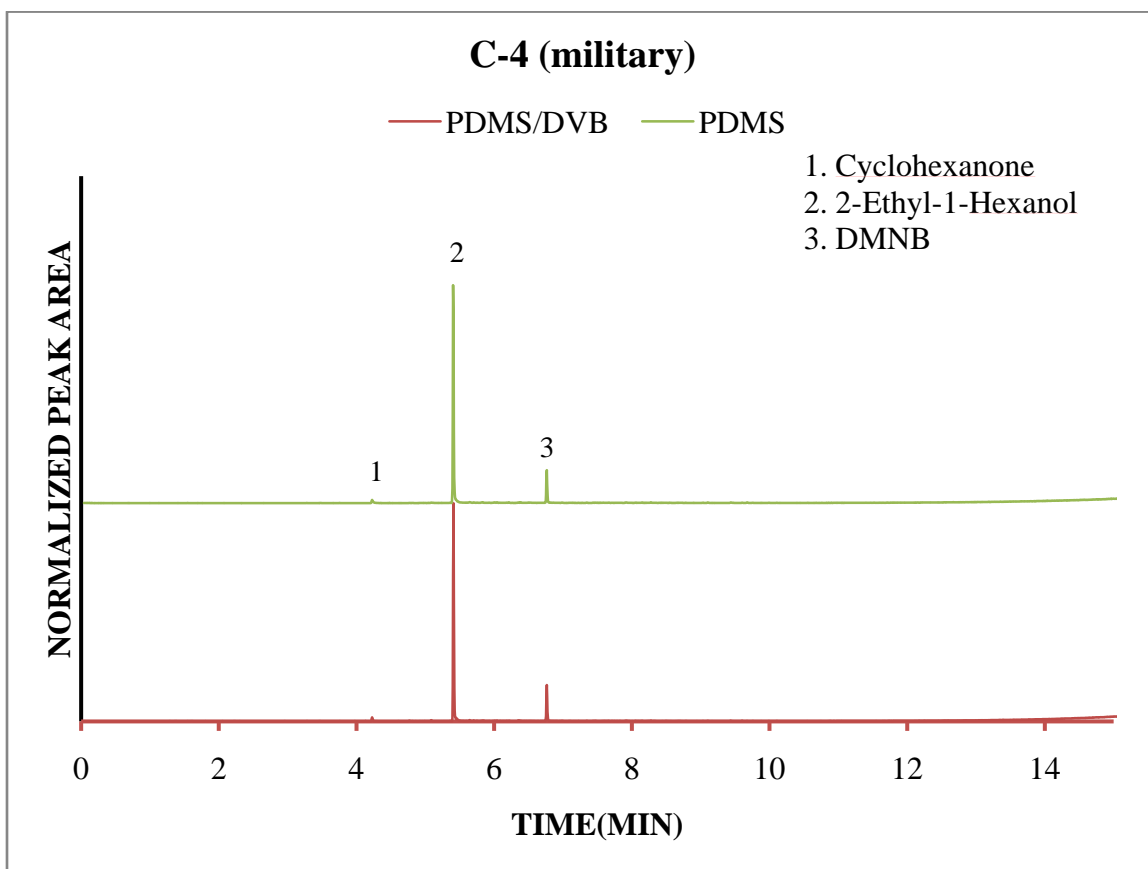


Figure 4.3: Fiber coatings produced comparable results with the analysis of C-4 of military origin

Since the PDMS and PDMS/DVB fiber coatings were comparable, analysis was completed using the PDMS/DVB fiber. Next, plastic explosives such as C-4 of military and commercial origin, Detasheet, Shape charge and their parent explosives RDX

(Trinitro-triazacyclohexane) and PETN (Pentaerythritol tetranitrate) were analyzed.

Analysis on TNT was also completed. C-4 explosives, Detasheet, and Shape Charge contained 2-ethyl-1-hexanol and DMNB (an added taggant), Figures 4.4 and A.6-A.8.

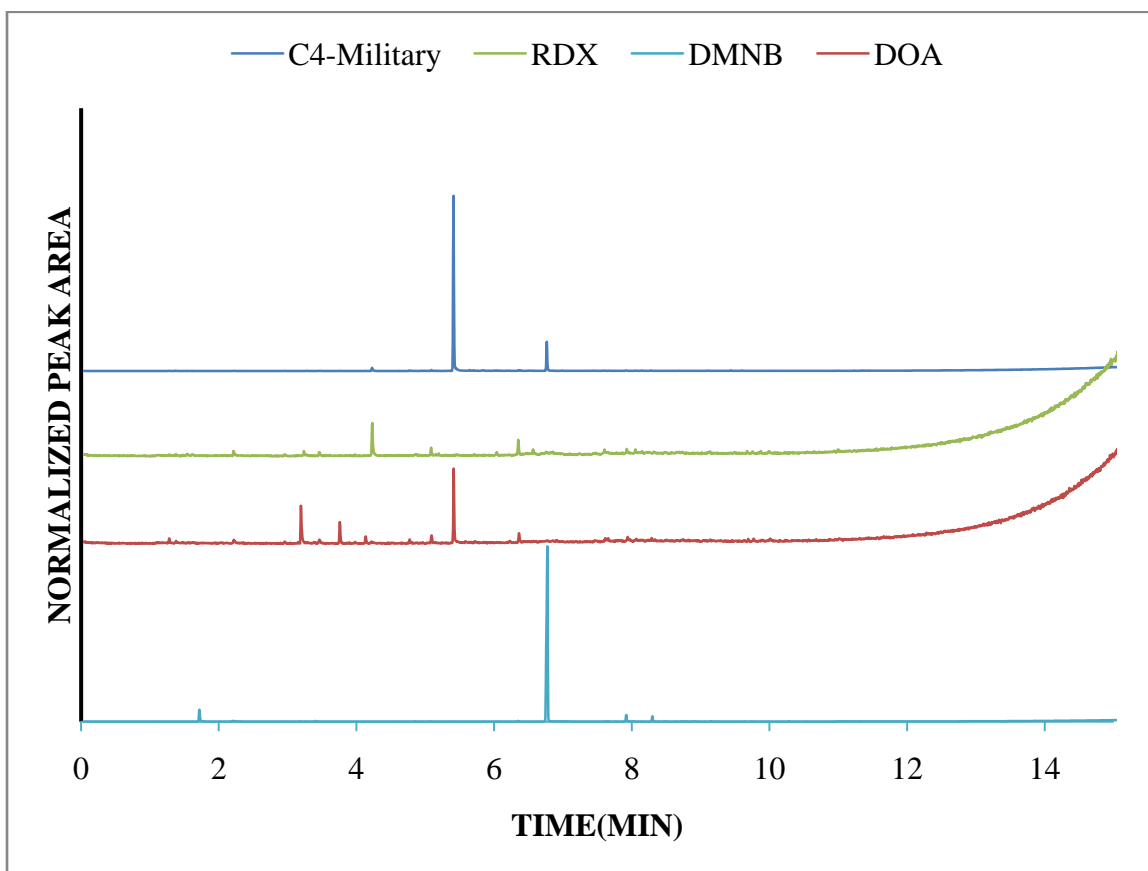


Figure 4.4: Confirmation of odor compounds in the headspace of C-4 (military origin).

The commonality of 2-ethyl-1-hexanol and DMNB in Detasheet was reported by Harper [22] as well as their presence in the C-4 explosives. As stated in the materials and methods section, the standards for the odor compounds were run at a different split ratio which caused a slight shift in the retention time (less than 5%). Cyclohexanone was observed in the headspace of RDX. Cyclohexanone is commonly used as a solvent for the recrystallization of RDX [1, 7]. Cyclohexanone was also seen in the headspace of the

C-4 explosives. No volatile compounds were observed in the headspace of PETN. The headspace of TNT contained itself and 2,4 DNT, 2,6 DNT, and 3,4 DNT, see Figure 4.5; 2,4 DNT was the most dominant. The odor compounds detected in the headspace of the explosives were confirmed with their standards.

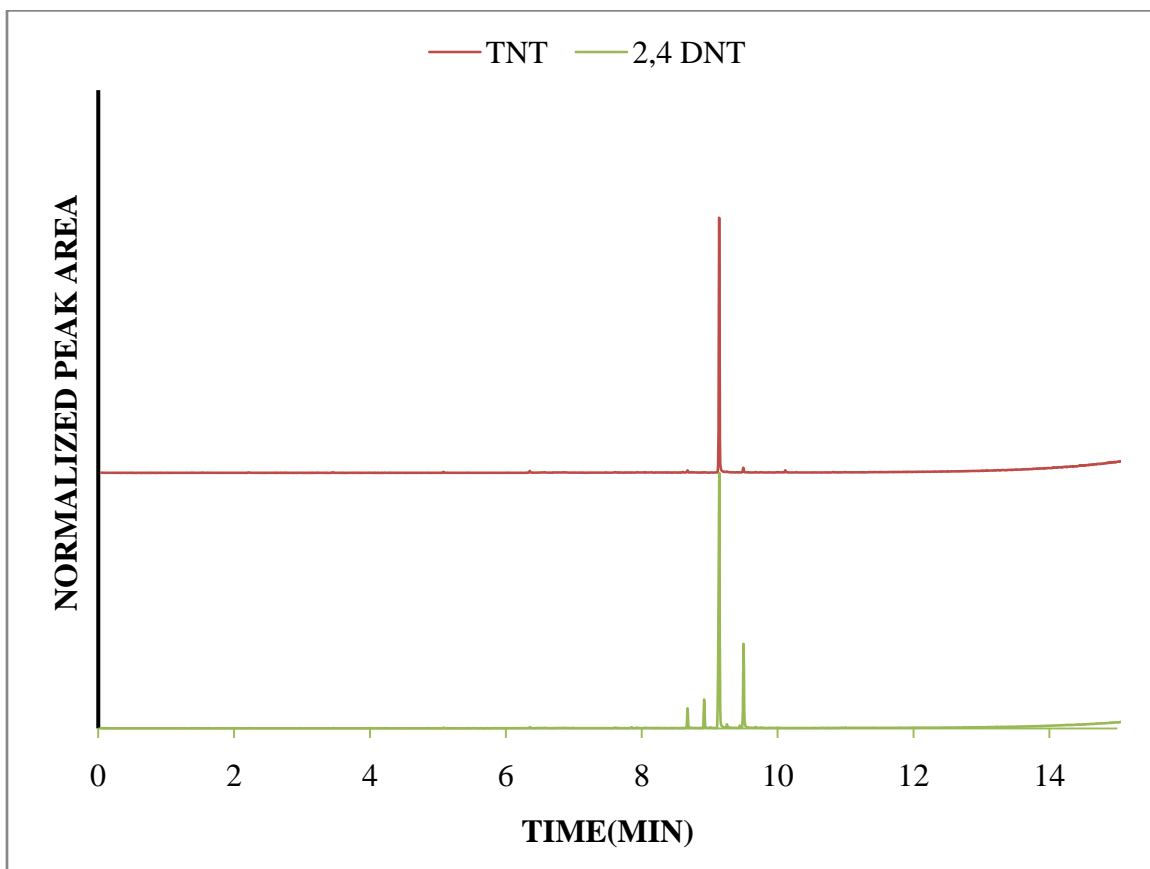


Figure 4.5: Confirmation of odor compounds detected in headspace of TNT.

To provide further confirmation of the presence of the plasticizers in the headspace of plastic explosives, we completed analysis on the plasticizers. Such plasticizers included Bis(2-ethylhexyl)adipate and acetyl tributylcitrate (Citraflex). 2-ethyl-1-hexanol, was a commonly reported odor compound found in the headspace above Composition C-4 [22, 47, 50]. It was predicted that nitric acid from the explosive may

degrade the plasticizer, thus resulting in the production of 2-ethyl-1-hexanol. The experimental analysis of the plasticizer demonstrated that 2-ethyl-1-hexanol was seen regardless of whether the plasticizer was exposed to dilute nitric acid, see Figure 4.6.

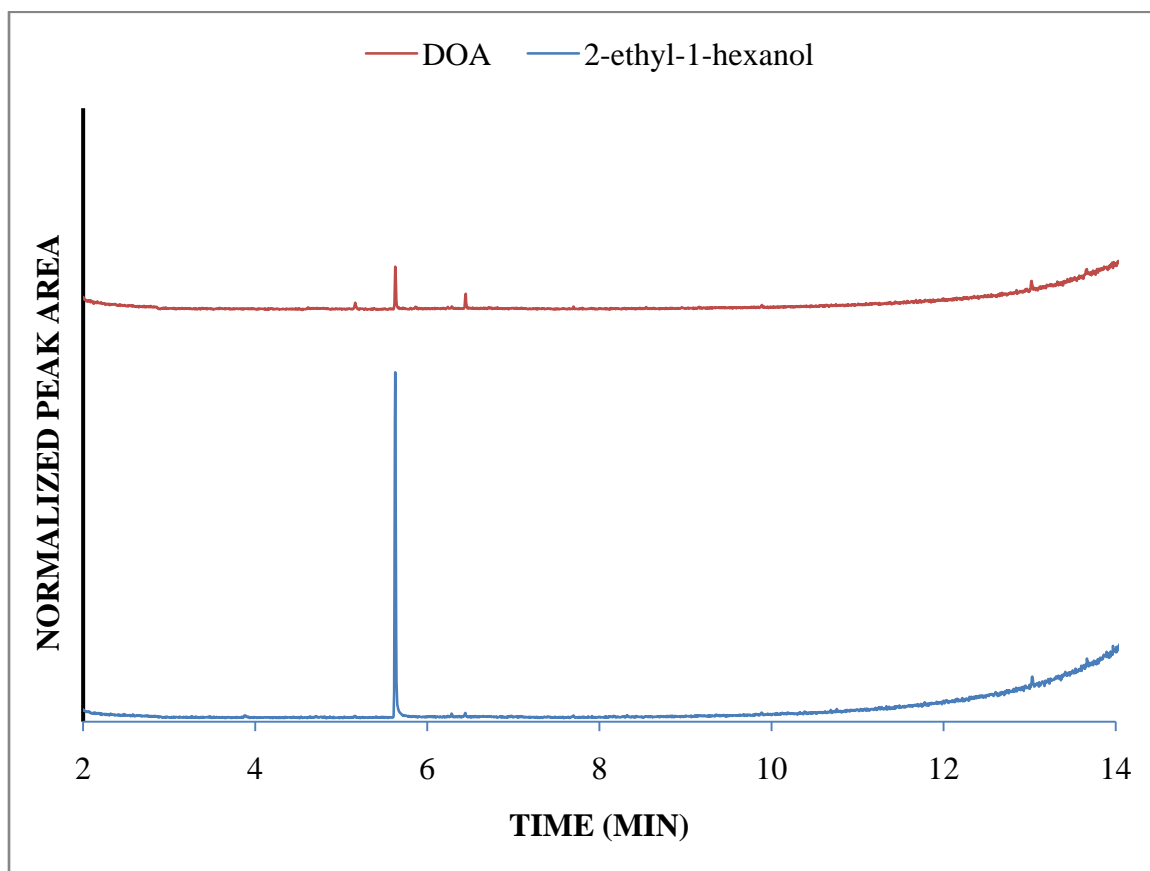


Figure 4.6: Odor compounds detected in the headspace of DOA were confirmed with their standards.

Citraflex was also analyzed which is another commonly used plasticizer in plastic explosives (flexible sheet explosives). The odor compounds 1-butanol and butyl acetate were seen in the headspace above citraflex. The confirmation of the presence of the plasticizer odor compounds in the headspace of the C-4 samples, Detasheet, and Shape Charge was completed through liquid extraction of each explosive, see Figures A.9-A.12.

Experimental analysis on NESTT products which included NESTT TNT, NESTT RDX, and NESTT PETN, were also completed to determine if their parent explosive was detectable. TNT NESTT contained 2,4 DNT and TNT, see Figure 4.7

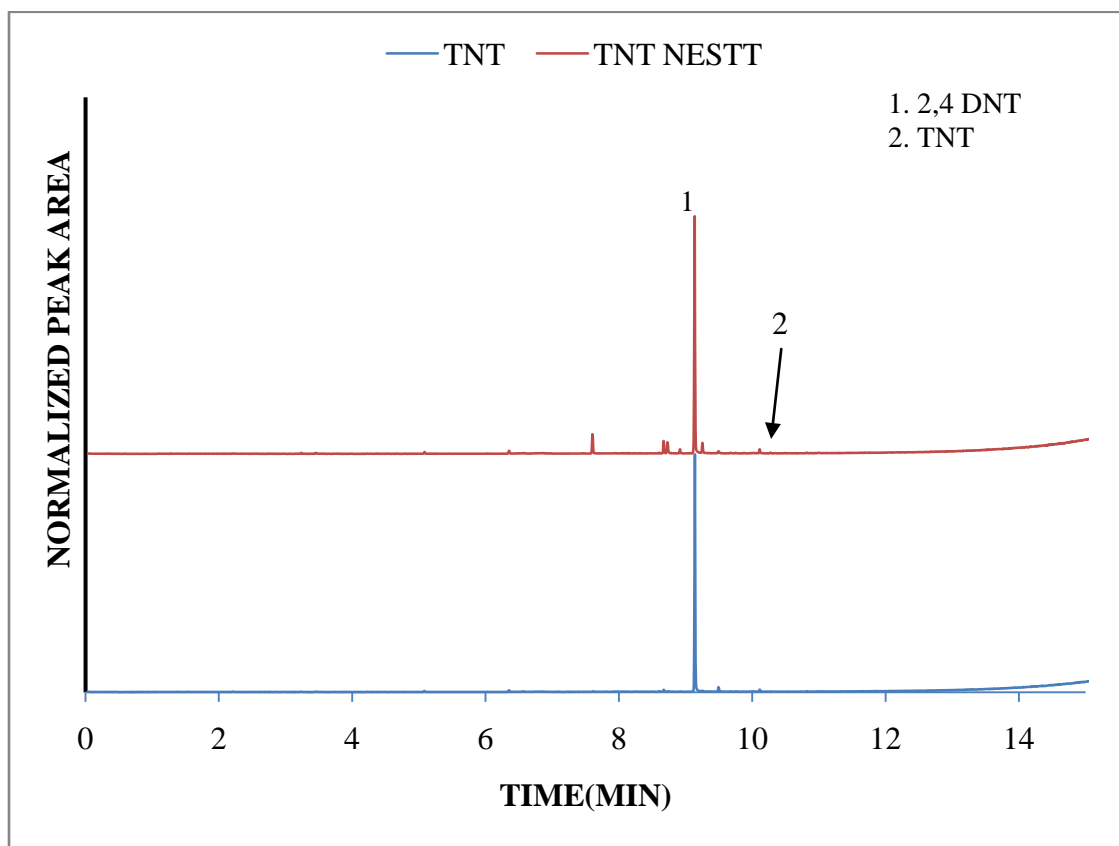


Figure 4.7: Parent explosive and decomposition product were detected in TNT NESTT sample.

RDX NESTT contained cyclohexanone while PETN NESTT did not show the presence of its parent explosive as well as any other odor compounds, see Figures A.13-A.14.

4.4. Conclusion

First, headspace analysis demonstrated that it was not as sensitive as solid phase microextraction. Next, even though plasticizers can be hydrolyzed resulting in the formation of semi-volatile products which can be detected by SPME, our findings indicated that the plasticizer, (DOA), formed 2-ethyl-1-hexanol without the addition of a diluted nitric acid solution. The presence of 2-ethyl-1-hexanol and 1-butanol were observed as common odors found in the headspace of listed plastic explosives. By liquid extraction, the presence of DOA in the C-4 explosives was confirmed as well as its presence in Detasheet and Shape Charge. Through the analysis of NESTT samples, TNT and 2,4 DNT were detected in TNT NESTT as well as the presence of cyclohexanone in RDX NESTT. However, the identification of the parent explosive, PETN, in PETN NESTT was unsuccessful.

CHAPTER 5. RECOMMENDATIONS

5.1. Modifications

For the headspace experiments (using the quart and gallon-sized cans), a reference sample should have been completed prior to the analysis of the other containers. A reference sample for a gallon-sized can includes the explosive sample unconfined in a 2 ounce sniffer which is placed in a quart-sized can and then housed in a gallon-sized can that is not “modified”. This apparatus is allowed to equilibrate for 24 hours to ensure the headspace is fully saturated. Open can experiments produced a steady evaporation rate; however, they did not fully equilibrate so the headspace concentration of experimental data obtained from these analysis of nitroalkanes could not be calculated. This reference sample would be used to normalize peak areas and then the normalized peak area is multiplied by $\left(\frac{P^\circ}{RT}\right)$ (where P° is the literature value of the vapor pressure of the explosive sample, R is the gas constant, and T is the temperature) to determine the headspace concentration. Another issue was that not all cans were run in the same day. This issue brings with it possible experimental error resulting in inaccurate results. These issues have since been resolved with later experiments.

Fick’s Second Law of Diffusion is based upon a uni-dimensional system. It would be advantageous to research another form of this equation that is based upon a three dimensional system to compare to our data. For the study of the effect of

temperature on the explosive vapor in the gallon and quart-sized can, a heater needs to be researched or developed that can house a quart and gallon-sized container.

Odor availability of 2,4 DNT through headspace sampling in the quart and gallon-sized cans is currently being studied. While the nitroalkanes did not have surface adsorption issues, there are difficulties with reproducibility indicating that nitroaromatics adhere to surfaces; thus, affecting odor availability. Due to the possible surface adhesion issue, more research needs to be conducted to confirm this occurrence and to quantitate the amount that adheres. Initial research indicated that the amount of DNT that adsorbs on the walls of a quart-sized can resulted in an average value of 50 μg . However, it was also predicted that the equilibrium concentration of DNT is 1.7×10^{-8} M based upon its vapor pressure. This equates to only 3.1 μg of DNT per liter of headspace at equilibrium. So the majority of the DNT present in the can was actually adsorbed to the walls. It was discovered that confinement and at times sample amount were affecting the odor available; this had been seen otherwise with the three nitroalkanes that sample amount didn't affect odor availability. This research is ongoing.

Further method development is another suggestion for the analysis of chemical explosives. The Thermo GC/MS has with it the ability to run under chemical ionization which would be beneficial mainly for molecular weight determination and then electron impact ionization could be used for positive identification [19, 51]. The use of CI with explosives (TNT, NG, RDX, and PETN) is well reported by Jehuda Yinon. He was able to successfully detect the molecular weight of these explosives. This identification of PETN using electron impact was unsuccessful. Therefore, it would be beneficial to analyze the explosives under CI conditions; furthermore, researching other columns that

will increase sensitivity of explosives. The detection of the plasticizer in some of the high explosive compositions using liquid extraction produced weak results; therefore more method development is advised.

Methods for identifying NO_x in the headspace of nitrated explosives need to be developed. Explosive molecules are made to yield small gaseous molecules. The decomposition product molecule nitrous oxide (NO) is seen most commonly [4]. Currently, analysis was completed to discover the presence of nitrate ions in RDX, TNT, and PETN as well as Non-explosive Security Testing and Training (NESTT) aids by using the Thermo LC/MS. However, the data was weak and further method modifications need to be completed using an ion exchange column or on-fiber derivitization. On-fiber derivitization involves exposure to the analyte and then to the derivitization agent before desorption [52].

Some more method development should be completed on the SPME method that was used for our explosive's analysis. Suggestions include varying the temperature of the needle and inlet as well as exposure time while keeping in mind that some explosives are thermally unstable. Further analysis on explosives should be completed with different fiber coatings such as SPME CW/DVB fibers which is well documented [47]. To prevent a retention time shift and overloading the column with the pure standard, the standard should have been diluted. Lastly, the liquid extraction of the high explosives to determine what plasticizer was present was successful; yet, the results were poor. Therefore, more research and experimentation should be conducted to optimize this method.

At the American Academy of Forensic Scientists meeting a student presented on the development of PAH-SPME phases for the Forensic Science application of selective absorption of nitroaromatic explosives. This experimental process can be related to the development of a SPME fiber with a canine's biological membrane. This would better evaluate what the canines are detecting and provide more knowledge about how the canine's need to be trained.

Selection of a coating should be based upon the chemical properties of the target analyte which affect the overall extraction performance, including method sensitivity, selectivity and reproducibility. Currently, only a limited number of different fiber coatings are commercially available such as PDMS and PA and dispersions of solid adsorbents like carboxen and divinylbenzene. Once the coating is deposited on the fused silica fiber then its morphology can be viewed using an electron scanning microscope [53].

Lastly, canine tests should be conducted to evaluate the odor compounds detected in the headspace of 20 mL headspace vials, quart-sized, and gallon-sized cans. Ultimately, the objective is to better understand the airborne materials found in explosives which may not come from the explosive, but may be present from aerosols and microscopic particles [11] which will improve the canine training.

5.2. Future Directions

The need for further research into the canine detection of explosives is still greatly desirable. This will aid in the scientific validity of a canine's alert. Exploration into the

explosive's basic physical chemistry involved in vapor transport, particle contamination, and sampling and concentration techniques should be further analyzed. For instance, measurements of diffusion coefficients, molecular sticking coefficients, vapor pressure over non-ideal solutions, as well as, partitioning in solvents, explosive particle adhesion forces, and particle morphologies [4]. For example, a study by Liu was completed regarding the quantification of adhesion forces between particles and substrates through measurements of their detachment velocities. This analysis included the variation of the particle's compositions and surfaces, along with diameter and techniques of deposition [26]. Also, research on how explosive mixtures affect odor availability.

The development of other methods of detection that support canine detection would be optimal. This would enable scientists to better identify the explosive odor compounds thus further calibrating and validating the methodologies used in canine training and testing. One example includes Direct Analysis in Real Time (DART) which is based on the atmospheric pressure interactions of electronic excited atoms or vibrated excited state molecules. DART can be used for positive and negative ion detection of materials on surfaces as well as the detection of gases and liquids [54].

No explosive has yet to be found that DART could not directly detect including RDX and HMX, which have very low vapor pressures. They have been detected and unambiguously identified in or on a wide variety of materials that includes ditch water, luggage, clothing, airline boarding passes, and living tissue (human and plant). Other explosives have been successfully analyzed by DART and include nitroaromatic explosives such as trinitrotoluene and trinitrobenzene and isomers of dinitrotoluene. Peroxide-based explosives (TATP), nitramines (RDX) and nitrate esters (PETN) formed

adducts. It has been reported that corona discharge causes a high production of NO_2^- and NO_3^- anions from atmospheric oxygen and nitrogen. These atmosphere-related anions interfere with the formation of analyte ions and mask the presence of ions characteristic of nitrate based explosives. These interferences are absent in DART because the electrical discharge is separated from the atmosphere [55], which makes DART a great choice for analysis as well as its ability to sample a wide variety of chemicals from a wide variety of materials/surfaces.

An additional area of research is “electronic noses”/sensors. Singh states that there is a need to develop portable, easy to operate and low cost sensors. Based on the origin of obtainable signals, most commonly used sensors for the detection of explosives can be broadly be classified as: (1) electrochemical sensors, (2) mass sensors, (3) optical sensors, and (4) biosensors. The categorization of these sensors is based primarily on the principal physics and operating mechanisms [20]. By combining multiple sensors (either nonselective or with sensitivity to different species or classes of chemicals) with pattern recognition, an artificial olfaction system can be produced [56].

Another area of research which would be to beneficial for the improvement and scientific validation of canine detection, is the study of the plume from the explosive’s vapor as well as residue from an explosion. This will help determine how much vapor the canine is receiving from various locations. It has been stated that canines are only trained on specific concentrations of the explosive; thus, when they are testing they alert where that odor is recognized. This might be 50 ft from the actual explosive which indicates to the handler that they need to train the canine on various amounts; therefore, knowing what the plume concentrations are would be beneficial. Furthermore, research

can be completed on cross contamination. For instance, the bomber deposits explosive materials onto the container in which the bomb was assembled.

To determine how much vapor the canine is receiving at a various locations, basic knowledge about the formation of the plume should be acquired. The emission of a plume is based upon on the rise, fall, or stay from the concealed explosive, which depends on the velocity of the gas, the confinement, the temperature, and the temperature of the air. A Gaussian plume is the spatial distribution of concentration along a transverse axis. This is used when wind speed in constant; the system is steady state; diffusion in the x-direction is ignored and other diffusion coefficients are anisotropic, contaminants is conservative, gas is assumed to be ideal and inert [57].

The progress of the canine research discussed in previous chapters is valuable to the canine training procedures already in place, as well as guiding the development of sensors. Additional research will be advantageous for the continued improvement of canine detection protocols and sensors.

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APPENDIX

APPENDIX

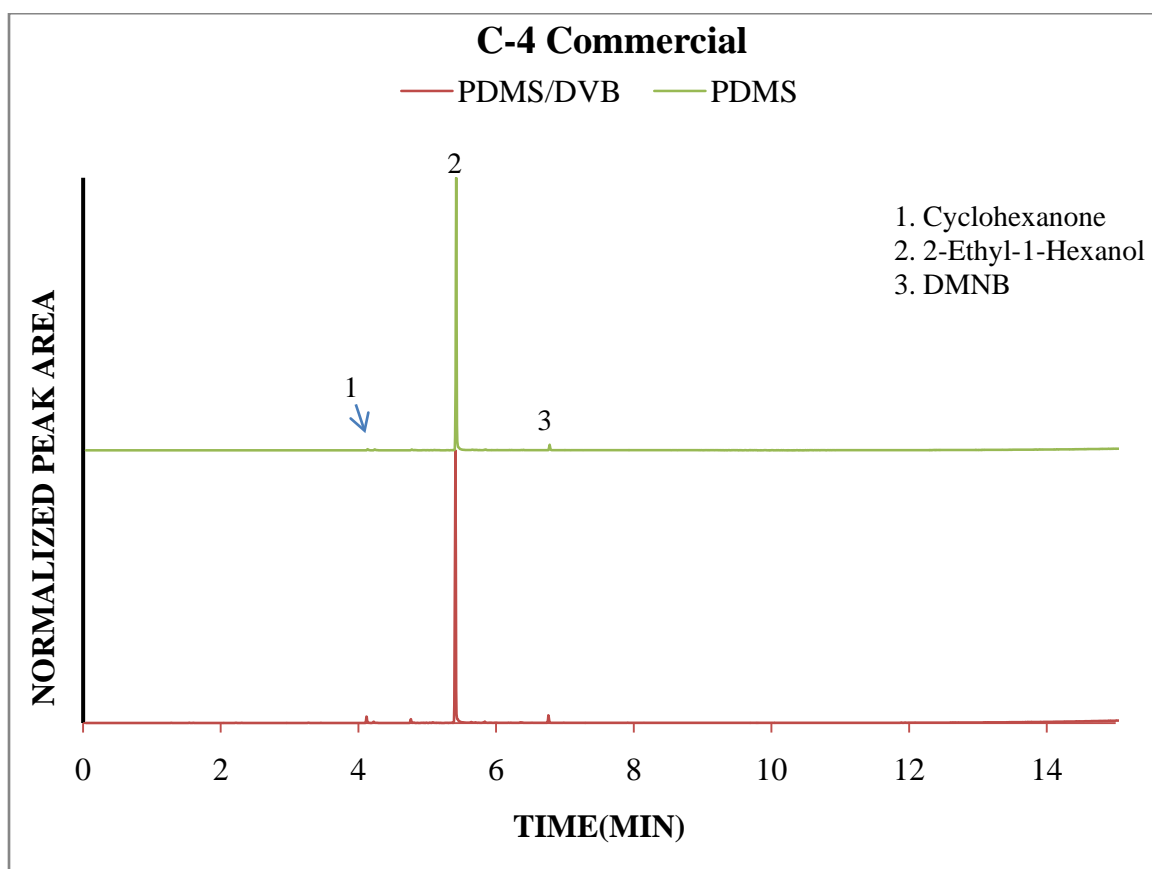


Figure A.1: Demonstrated the comparability of fiber coatings with the analysis of C-4 commercial origin.

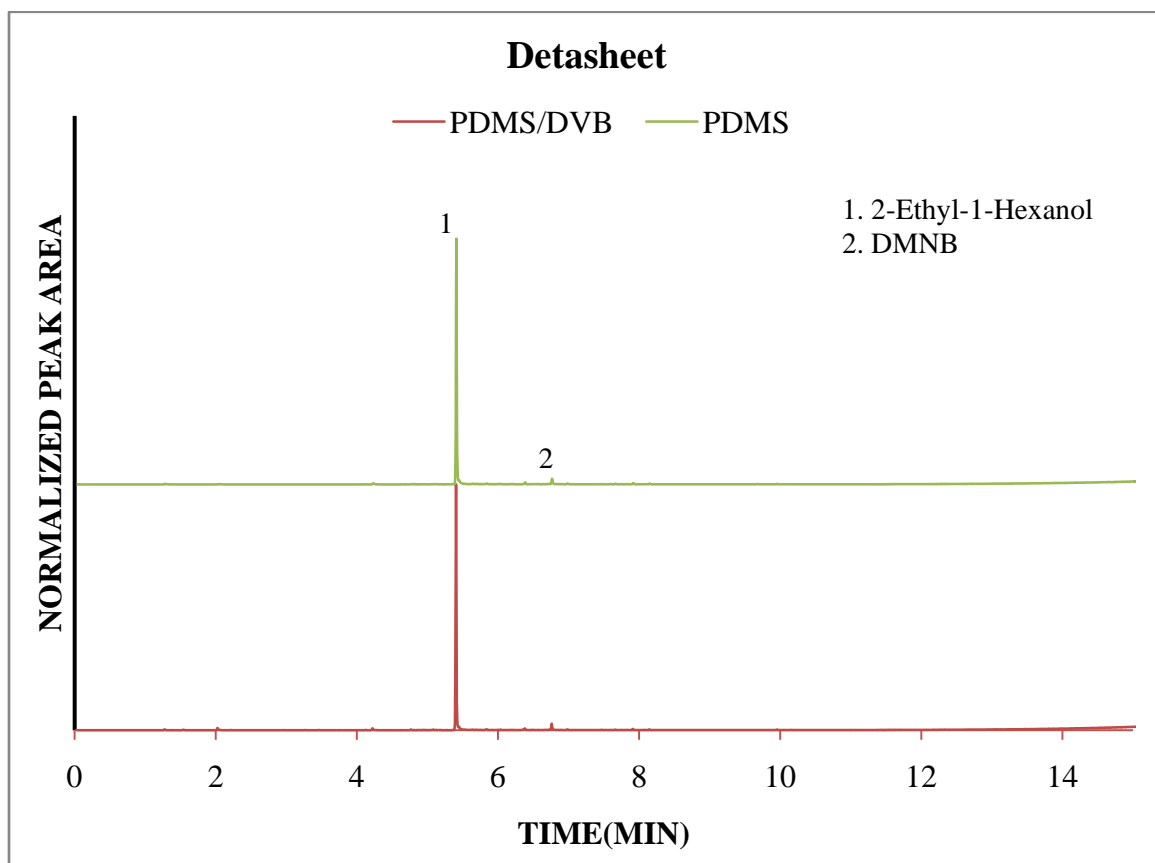


Figure A.2: Demonstrated the comparability of fiber coatings with the analysis of Detasheet.

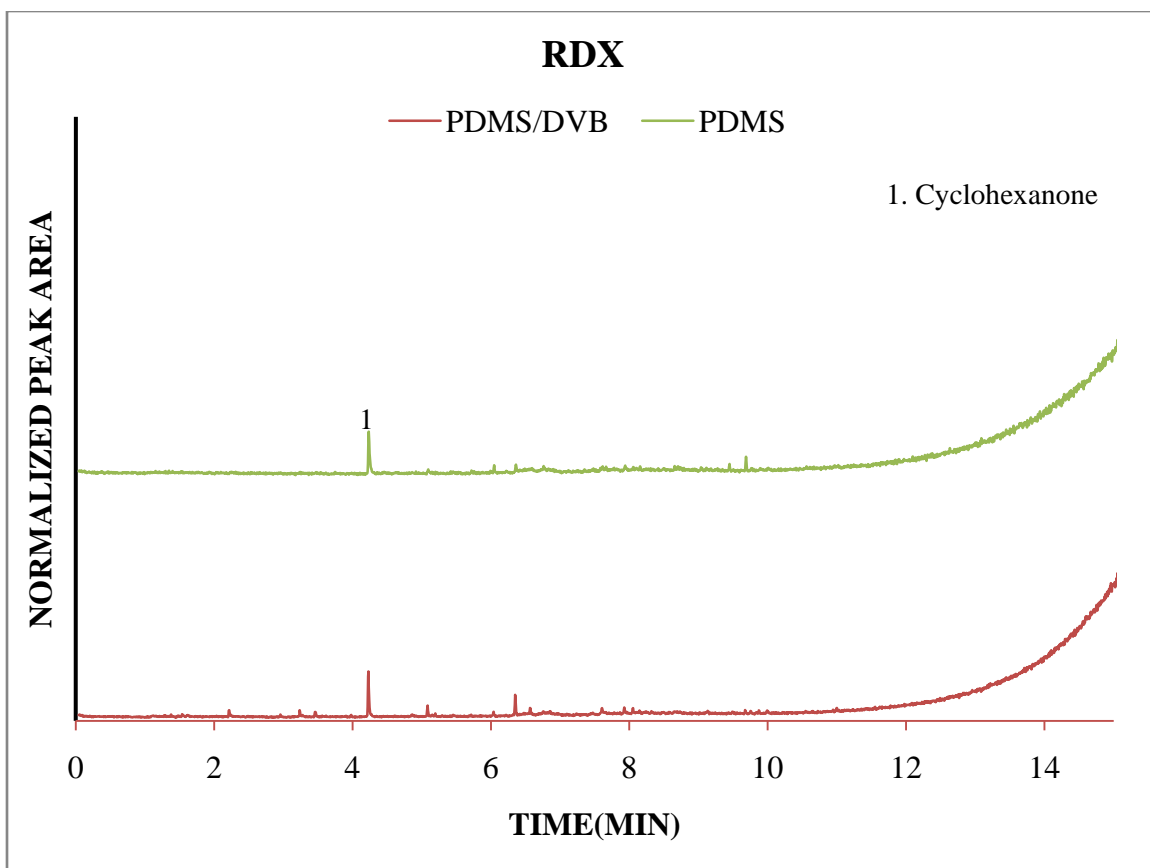


Figure A.3: Demonstrated the comparability of fiber coatings with RDX.

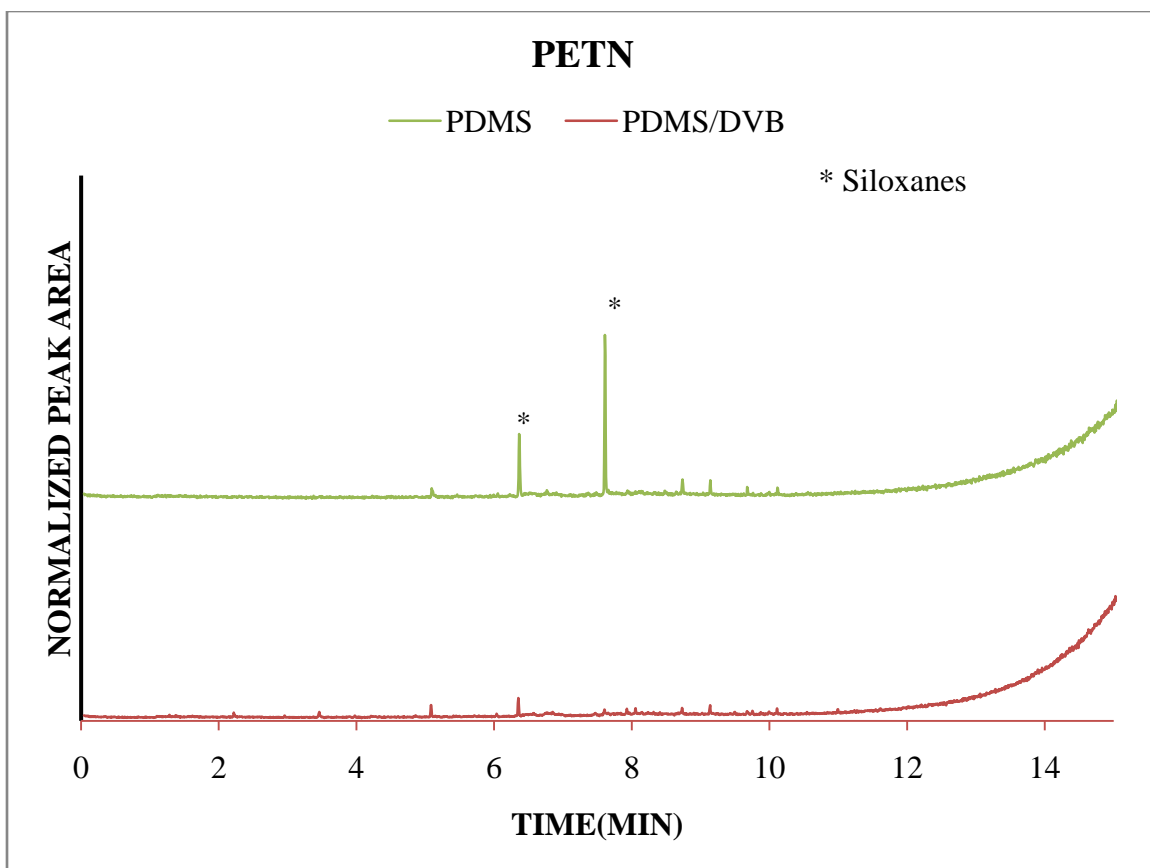


Figure A.4: Demonstrated the comparability of fiber coatings with the analysis of PETN.

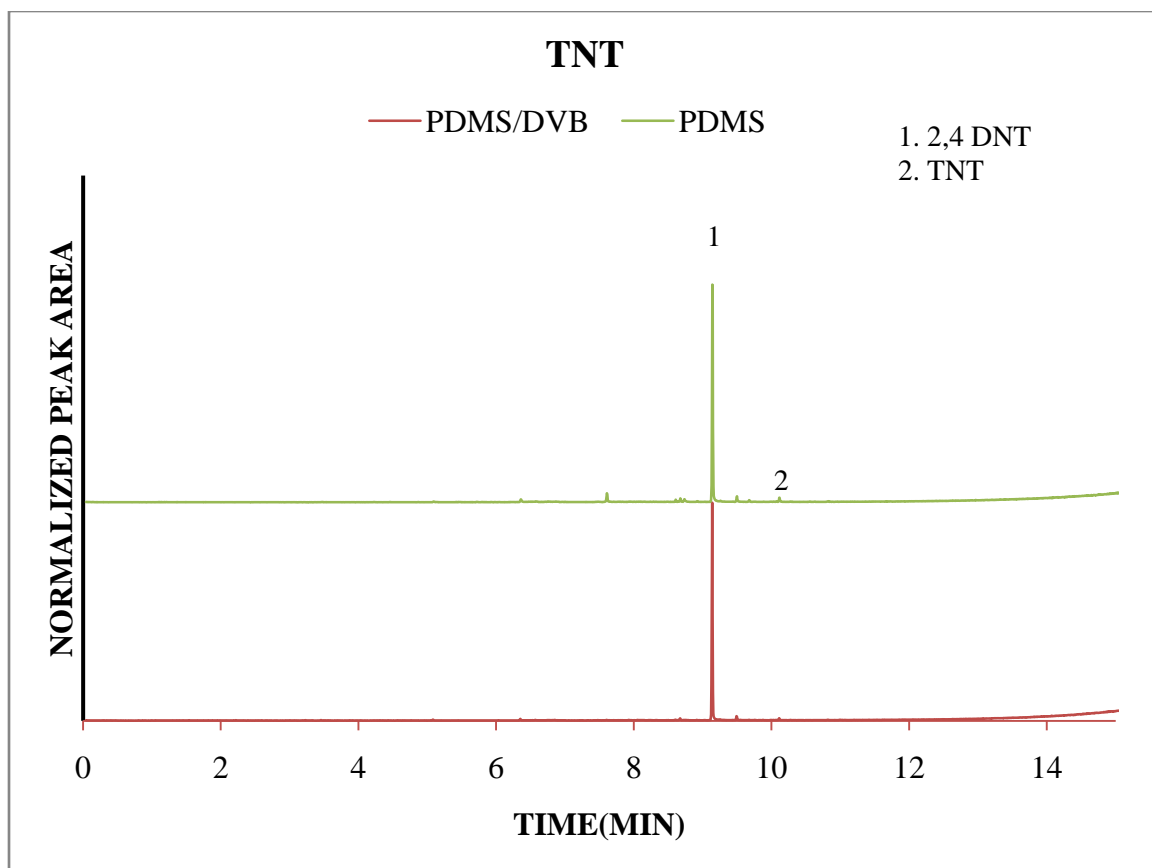


Figure A.5: Demonstrated the comparability of fiber coatings with the analysis of TNT.

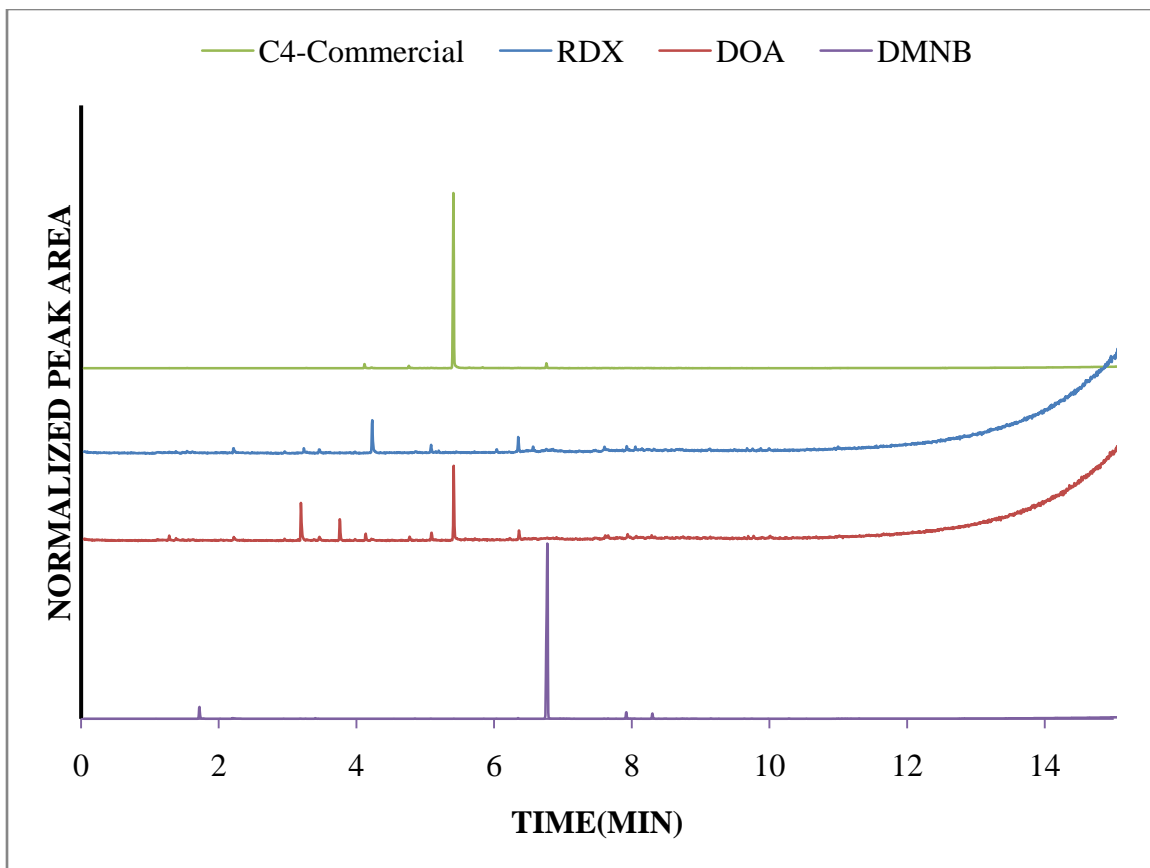


Figure A.6: Confirmation of odor compounds in the headspace of C-4(commercial origin).

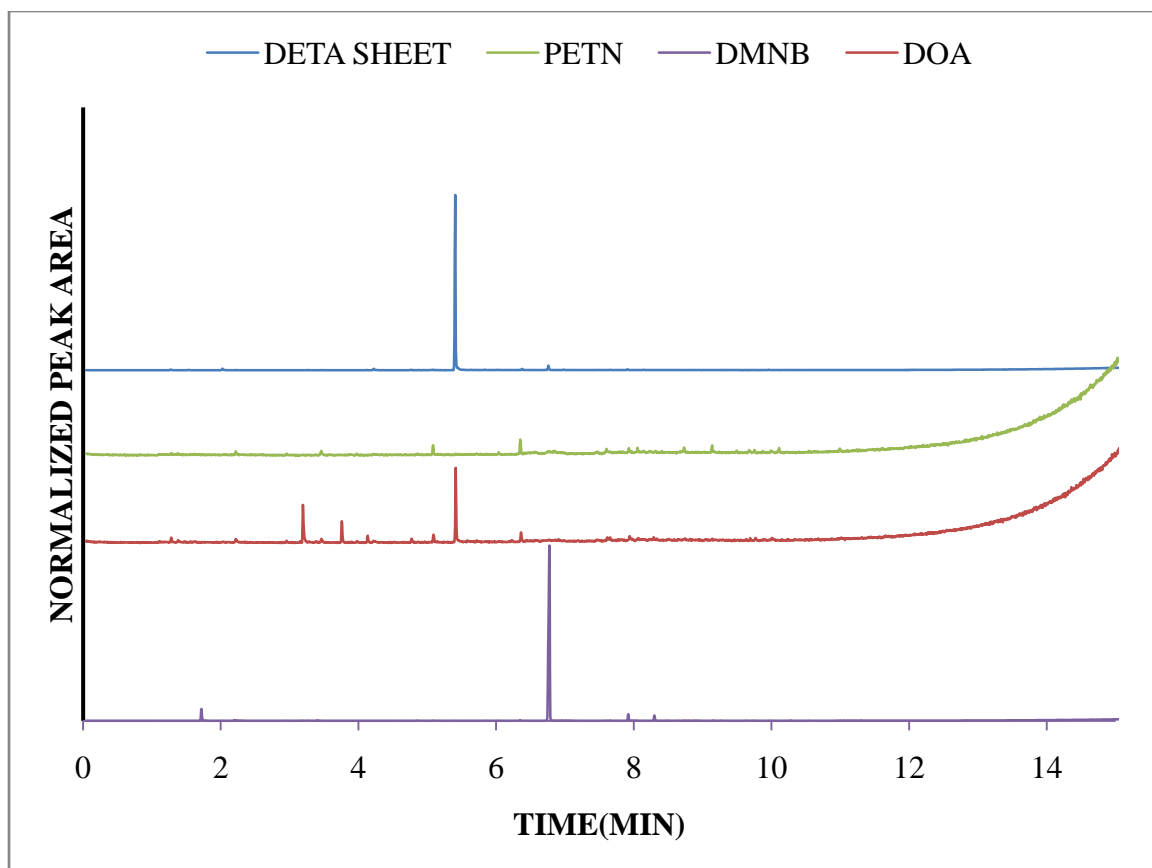


Figure A.7: Confirmation of odor compounds in the headspace of Detasheet.

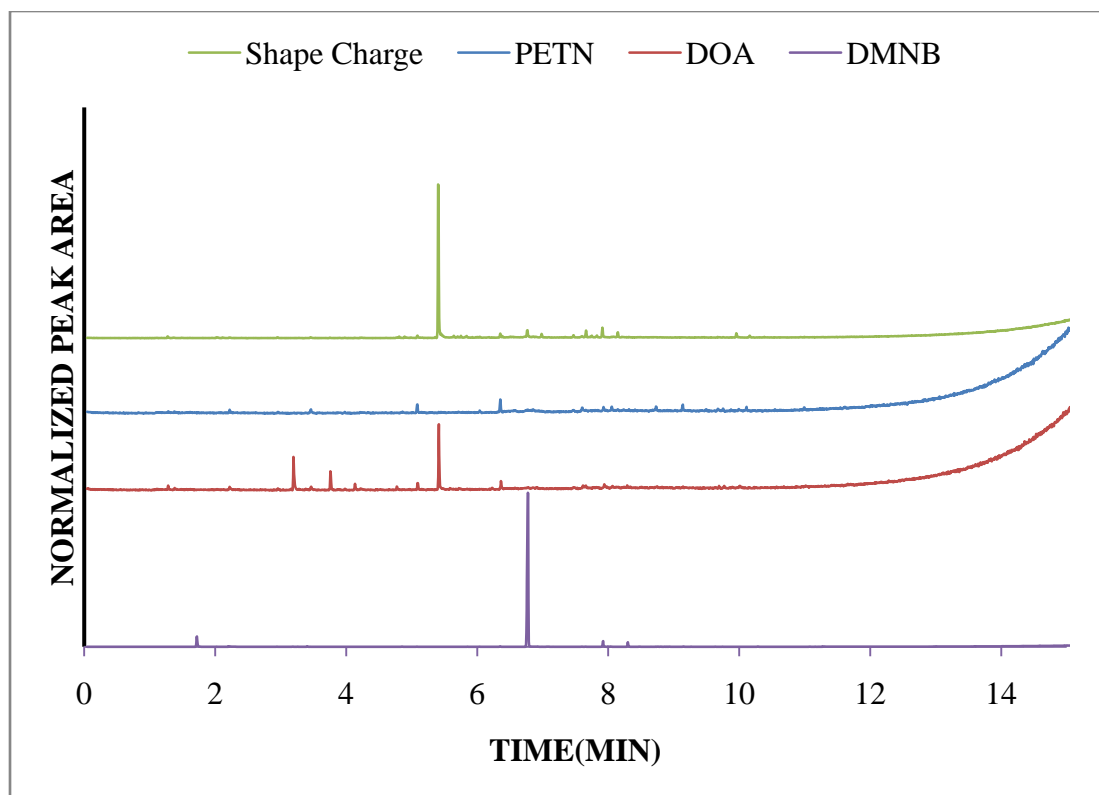


Figure A.8: Confirmation of odor compounds in the headspace of Shape charge.

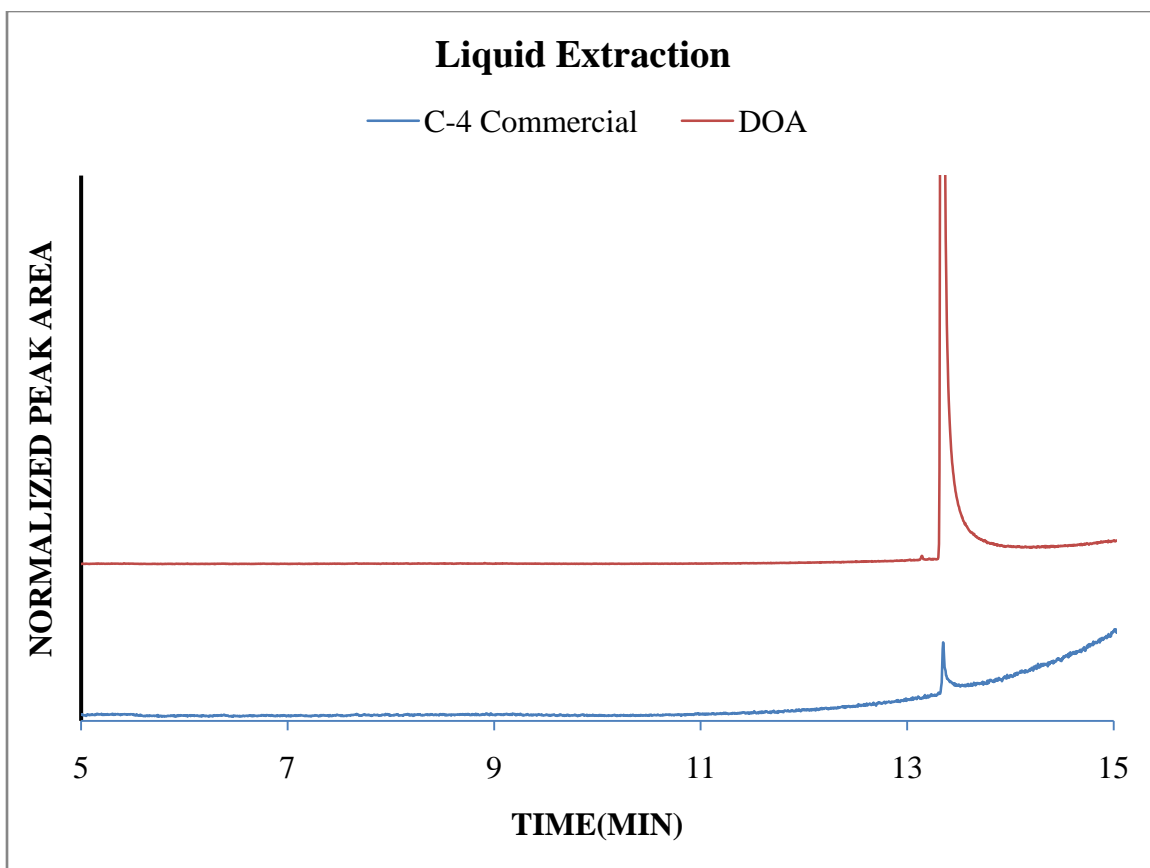


Figure A.9: Confirmation of the plasticizer's presence in C-4 (commercial origin).

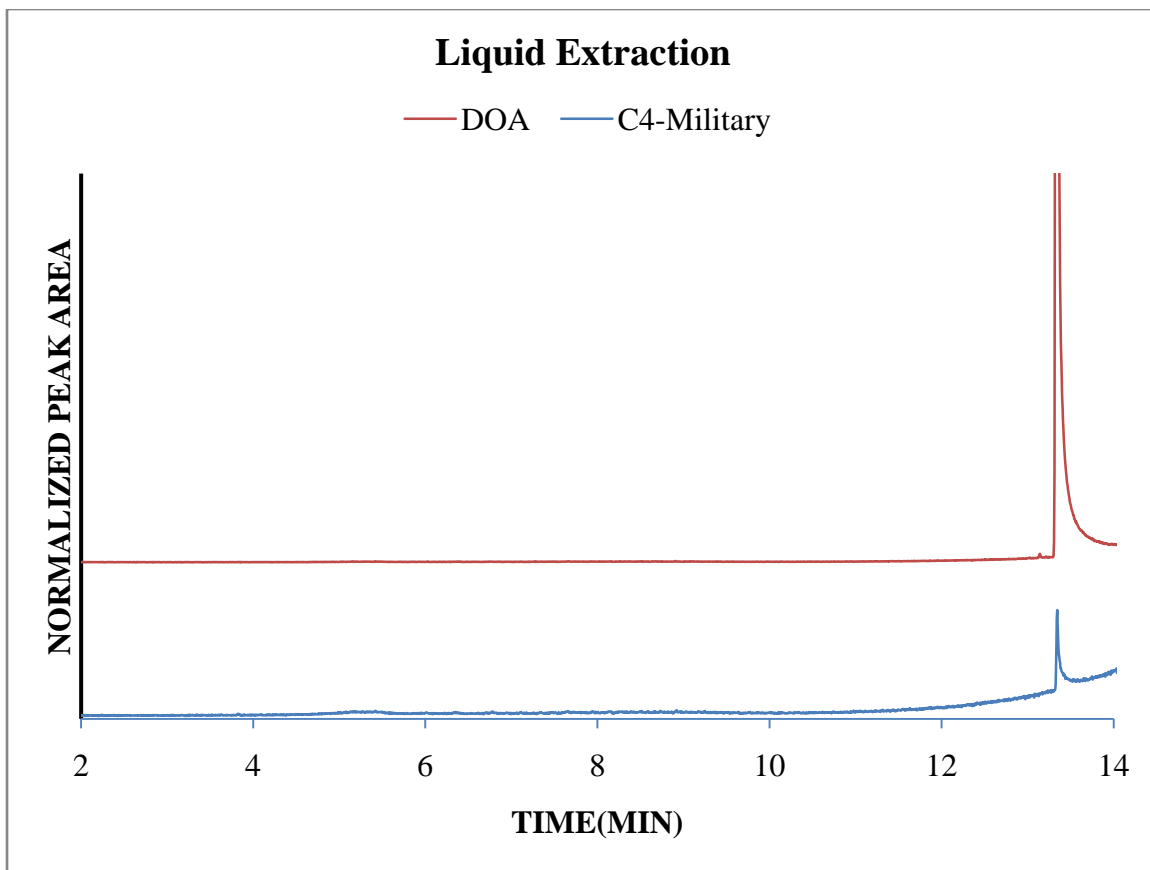


Figure A.10: Confirmation of the plasticizer's presence in C-4 (military origin).

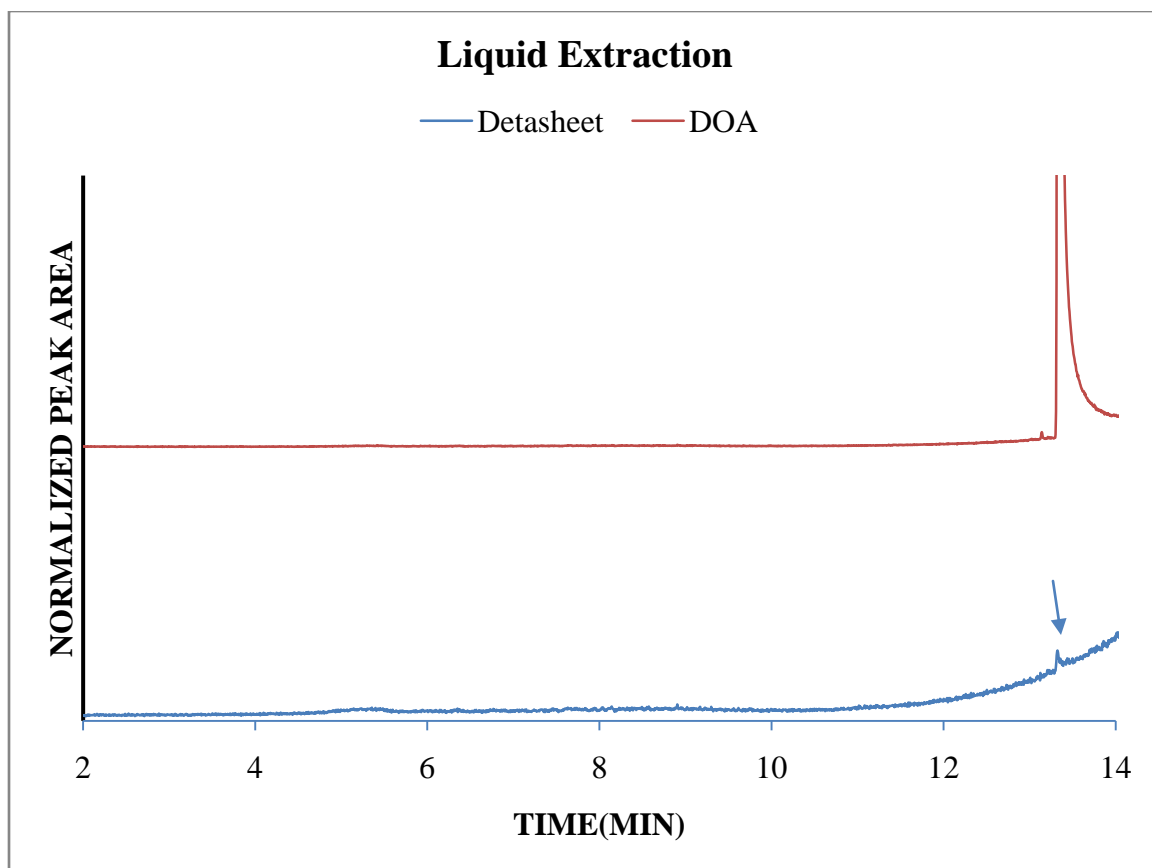


Figure A.11: Confirmation of the plasticizer's presence in Detasheet.

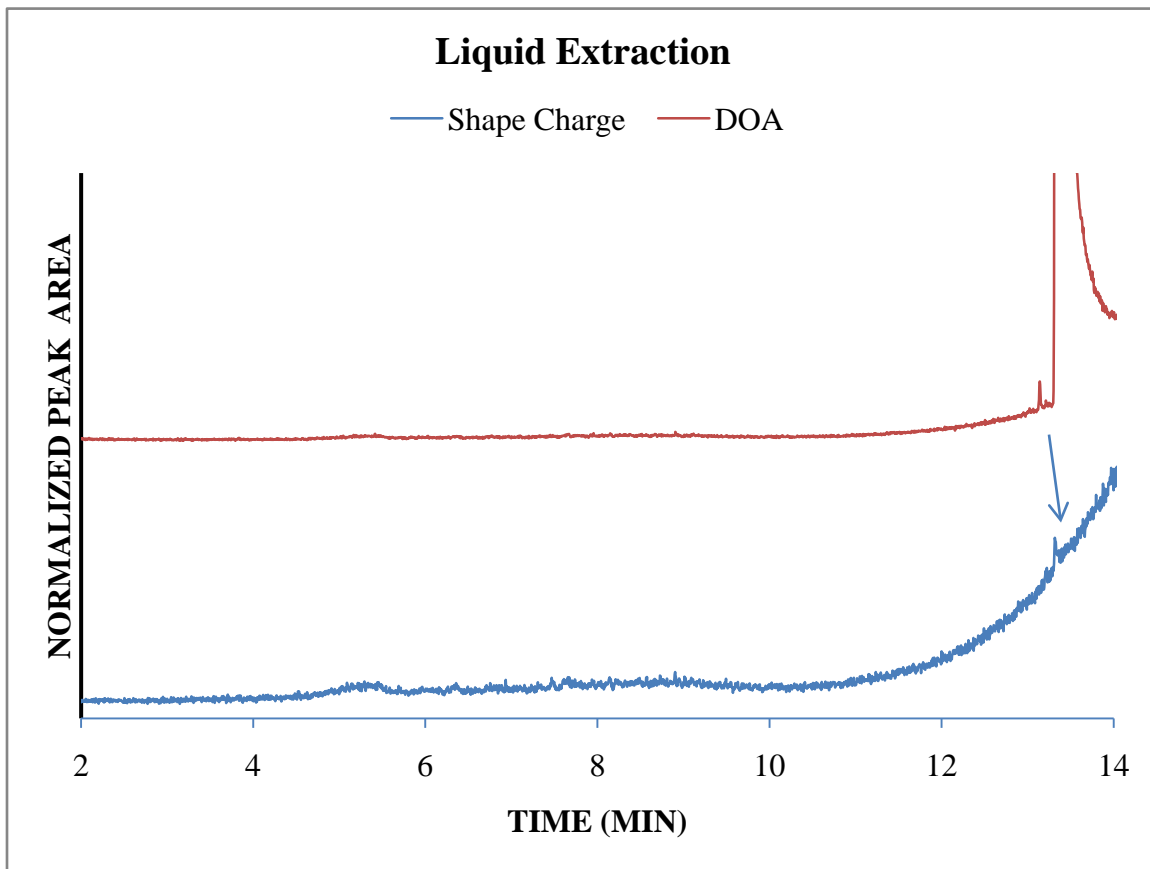


Figure A.12: Confirmation of the plasticizer's presence in Shape Charge.

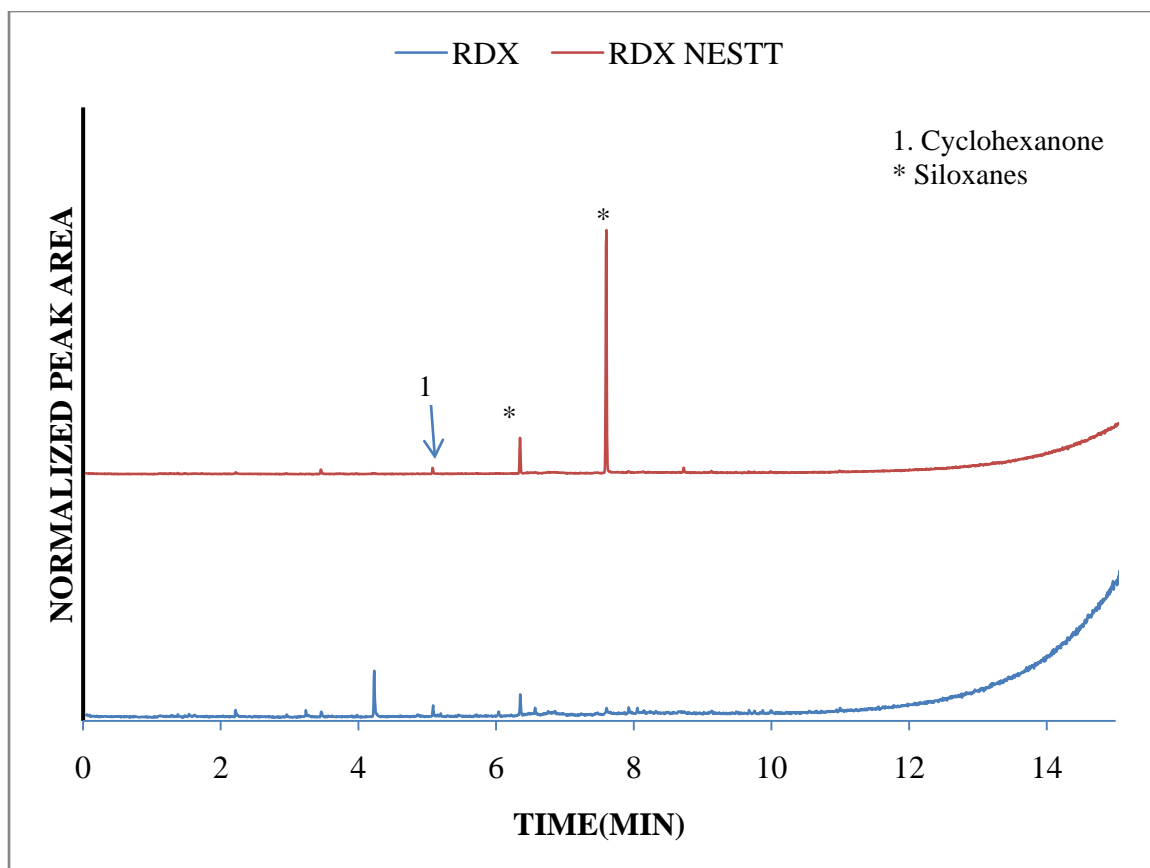


Figure A.13: Identification of pure explosive (RDX) in NESTT sample.

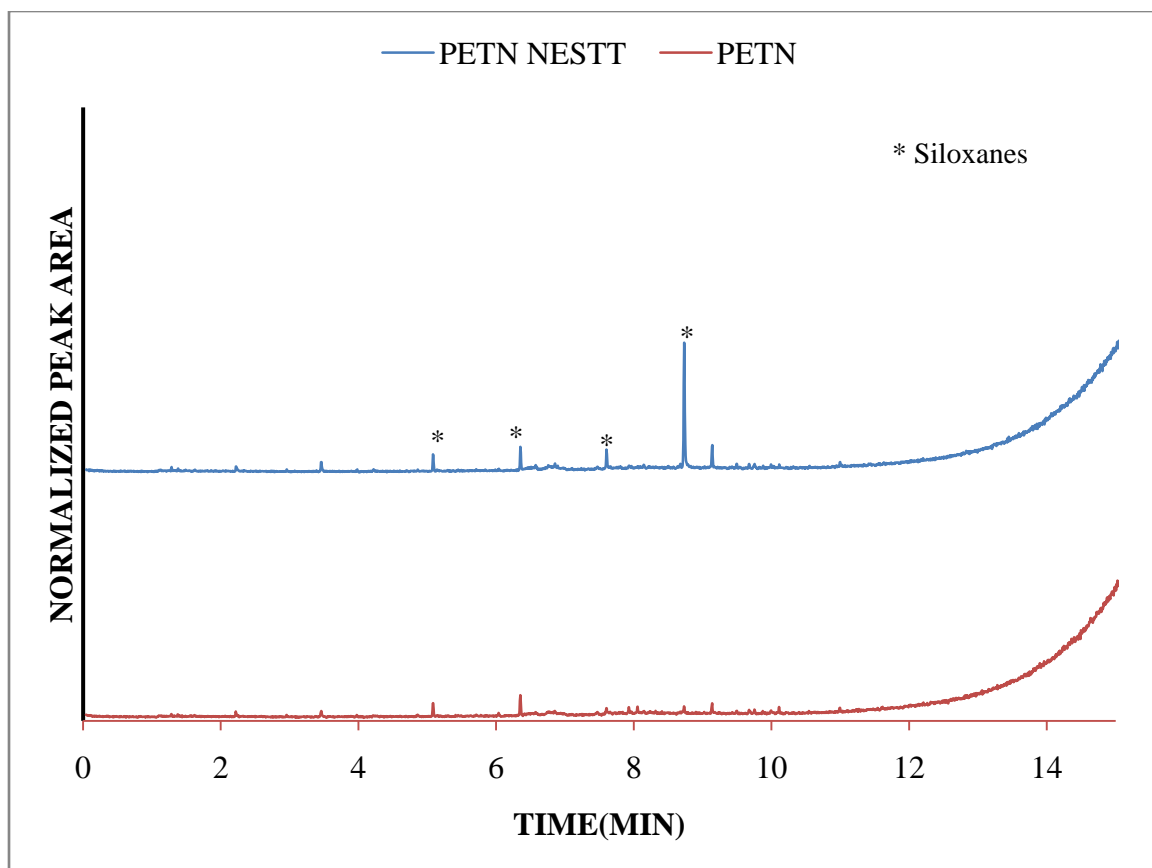


Figure A.14: Identification of pure explosive (PETN) in NESTT sample.