2-13-2013

# The Development of Calibrants through Characterization of Volatile Organic Compounds from Peroxide Based Explosives and a Non-target Chemical Calibration Compound

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# THE DEVELOPMENT OF CALIBRANTS THROUGH CHARACTERIZATION OF VOLATILE ORGANIC COMPOUNDS FROM PEROXIDE BASED EXPLOSIVES AND A NON-TARGET CHEMICAL CALIBRATION COMPOUND

A dissertation submitted in partial fulfillment of

the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

CHEMISTRY

by

Katylynn Beltz

2013

To: Dean Kenneth G. Furton
College of Arts and Sciences

This dissertation, written by Katylynn Beltz, and entitled The Development of Calibrants through Characterization of Volatile Organic Compounds from Peroxide Based Explosives and a Non-target Chemical Calibration Compound, having been approved in respect to style and intellectual content, is referred to you for judgment.

We have read this dissertation and recommend that it be approved.

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Date of Defense: February 13, 2013

The dissertation of Katylynn Beltz is approved.

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# DEDICATION

This dissertation is dedicated to my family: Jim and Laura Beltz for being the best and most supportive parents a girl could have; to Crissy and Danny for calling me a nerd like a good sister and brother should to keep me working hard; and to my nephew and nieces (and their father Gregg) for giving me the laughs I needed.

ACKNOWLEDGMENTS

First I would like to acknowledge Dr. Kenneth G. Furton, my boss and mentor throughout my time at FIU. Without his guidance and aid I would have never been able to complete my research that I love. Thank-you, boss-man, for allowing me to spend my days working with dogs and cops. Sometimes I think those field days were the only reasons I kept my sanity in between analyzing data and running samples. I would also like to thank Lorraine Sweeny, Dr. Furton's right hand woman, for without her I don't think things would go nearly as smoothly. Thank you to the Chemistry department for providing me with the opportunity and funding to attend graduate school and expand my horizons. A big thank you to my other committee members, Dr. Almirall, Dr. Cai, Dr. Landrum, and Dr. Mills; thank you for keeping me on my toes with your questions and being fantastic sounding boards and mentors throughout this research endeavor. Thank you to the Furton lab members for giving me that extra push to finish. Thank you Howard, for being there through the laughs, tears, and breaking points; you are more than just a lab manager, you are my friend and remember that You Rock!

Without my family and friends I do not think that I could have made it through. Thank-you mom and dad for supporting me through all of this, even buying my house and then helping with the remodeling. I know it was hard on you guys with me being so far away for so long. Thank you Clay, Cayla, and Abigail for making me realize that it was time to wrap things up and head back to VA because that is where home will always be. To Crissy, Gregg, and Danny, thank you for being great brothers and sister and for not asking me too many questions about what I do, so that way if the fire department gets called after a back yard experiment I can claim ignorance.

To my friends, thank you for all of the support and becoming my Miami family. Thank you, Kevin for being my shoulder to cry on and roommate during my "transient" period. Thank you, Kelley and Michelle for becoming such great friends and ones that I will always want to tell my stories to. Thank you, Kelly, Jeff, and Kinleigh for your friendship and support. Thank you, Vanessa, Madeline, Melissa, Alex, Josh and Melissa, Erika, Britt, Sarah, Emily, Eladio, Teréza, and Maiko for being great friends and colleagues.

And a final thank you to all of the canine handlers and trainers I worked with during this research. Without their willingness to participate, this research would have never left the ground level. A special thank-you must go to Peter Nunez for his friendship and knowledge that he shared and to Bill "Action" for always being Pete's right hand man and for making me laugh. Thank you Pete for giving me my lovable (and infuriating) puppy, Bella, I'm sure once she calms down we will be inseparable.

The Science and Technology Directorate of the U.S. Department of Homeland Security partially sponsored the production of this material under Interagency Agreement IAA # HSHQDC-10-X-00297 with the National Institute of Standards and Technology (NIST). This project was partially supported by Award No. NFSTC Project Code No. 25-6370-11, awarded by the National Institute of Justice, Office of Justice Programs, U.S. Department of Justice. This project was partially funded through financial support of a Florida International University Graduate School Doctoral Evidence Acquisition Fellowship.

ABSTRACT OF THE DISSERTATION

THE DEVELOPMENT OF CALIBRANTS THROUGH CHARACTERIZATION OF VOLATILE ORGANIC COMPOUNDS FROM PEROXIDE BASED EXPLOSIVES AND A NON-TARGET CHEMICAL CALIBRATION COMPOUND by

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Florida International University, 2012

Miami, Florida

Professor Kenneth G. Furton, Major Professor

Detection canines represent the fastest and most versatile means of illicit material detection. This research endeavor in its most simplistic form is the improvement of detection canines through training, training aids, and calibration. This study focuses on developing a universal calibration compound for which all detection canines, regardless of detection substance, can be tested daily to ensure that they are working with acceptable parameters. Surrogate continuation aids (SCAs) were developed for peroxide based explosives along with the validation of the SCAs already developed within the International Forensic Research Institute (IFRI) prototype surrogate explosives kit. Storage parameters of the SCAs were evaluated to give recommendations to the detection canine community on the best possible training aid storage solution that minimizes the likelihood of contamination. Two commonly used and accepted detection canine imprinting methods were also evaluated for the speed in which the canine is trained and their reliability.

As a result of the completion of this study, SCAs have been developed for explosive detection canine use covering: peroxide based explosives, TNT based

explosives, nitroglycerin based explosives, tagged explosives, plasticized explosives, and smokeless powders. Through the use of these surrogate continuation aids a more uniform and reliable system of training can be implemented in the field than is currently used today. By examining the storage parameters of the SCAs, an ideal storage system has been developed using three levels of containment for the reduction of possible contamination. The developed calibration compound will ease the growing concerns over the legality and reliability of detection canine use by detailing the daily working parameters of the canine, allowing for Daubert rules of evidence admissibility to be applied. Through canine field testing, it has been shown that the IFRI SCAs outperform other commercially available training aids on the market. Additionally, of the imprinting methods tested, no difference was found in the speed in which the canines are trained or their reliability to detect illicit materials. Therefore, if the recommendations discovered in this study are followed, the detection canine community will greatly benefit through the use of scientifically validated training techniques and training aids.

TABLE OF CONTENTS

LIST OF TABLES

TABLE PAGE

LIST OF FIGURES

FIGURE PAGE

ACRONYMS AND ABBREVIATION

| | |
|---|---|
| 2,4-Dam-NT | 2,4-diaminonitrotoluene |
| 2,4-DNP | 2,4-dinitrophenylhydrazine |
| 2,4-DNT | 2,4-dinitrotoluene |
| 2,6-Dam-NT | 2,6-diaminonitrotoluene |
| 2-Am-4,6-DNT | 2-amino-4,6-dinitrotoluene |
| 2-HADNT | 2-hydroxylamino-4,6-dinitrotoluene |
| 2-MNN | 2-nitronaphthalene |
| 2-MNT | 2-nitrotoluene |
| 2-nDPA | 2-nitrodiphenylamine |
| 4-Am-2,6-DNT | 4-amino-2,6-dinitrotoluene |
| 4-HADNT | 4-hydroxylamino-2,6-dinitrotoluene |
| 4-MNT | 4-nitrotoluene |
| AFP | Amplifying fluorescent polymers |
| AN | Ammonium nitrate |
| ANFO | Ammonium nitrate fuel oil |
| AOTF | Acousto-optic tunable fiber |
| AP | Ammonium perchlorate |
| ATF | Bureau of Alcohol, Tobacco, Firearms and Explosives |
| C-4 | Composition of 91% RDX plus waxes and oils |
| CARS | Coherent anti-Stokes Raman scattering |
| CCD | Charge coupled device |

| | |
|---|---|
| CE | Capillary electrophoresis |
| CEC | Capillary electrochromatography |
| CL-20 | Hexanitroisowurzlitane |
| CMOS | Complementary metal oxide semiconductor |
| CNT | Carbon nanotube |
| CRDS | Cavity ring down spectroscopy |
| DADP | Diacetone diperoxide |
| DAPCI | Desorption atmospheric pressure chemical ionization |
| DATB | Diamino trinitro benzene |
| DBP | Dibutyl phthalate |
| DEGDN | Diethylene glycol dinitrate |
| DESI | Desorption electrospray ionization |
| Detesheet | Composition of PETN and NC with plasticizers |
| DIAL | Differential absorption LIDAR |
| DMNB | 2,3-dimethyl-2,3-dinitrobutane |
| DNB | Dinitrobutane |
| DNN | Dinitronaphthalene |
| DNT | Dinitrotoluene |
| DNTO | Dinitrogen tetroxide |
| DPA | Diphenylamine |
| EC | Ethyl centralite (N,N'-diethyl-N,N'-diphenylurea) |
| ECD | Electron capture detector |

| | |
|---|---|
| EGDN | Ethylene glycol dinitrate |
| ELISA | Enzyme linked immunosorbent assay |
| FAP | Fluorescence amplifying polymers |
| FET | Field effect transistor |
| FSWC | Fused-silica wall-coated |
| FTIR | Fourier transform infrared |
| GC | Gas chromatography |
| GCE | Glassy carbon electrode |
| $H_2O_2$ | Hydrogen peroxide |
| HMTD | Hexamethylene triperoxide diamine |
| HMX | Cyclotetramethylene-tetranitramine or Octogen |
| HNS | Hexanitrostilbene |
| HPLC | High performance liquid chromatography |
| HTPB | Hydroxyl terminated polybutadiene |
| ICCD | Intensified CCD |
| IDLIF | Indirect laser-induced-fluorescence |
| IED | Improvised explosive device |
| IFRI | International Forensic Research Institute |
| IM | Insensitive munitions |
| IMS | Ion mobility spectrometry |
| IR | Infrared |
| LC | Liquid chromatography |

| | |
|---|---|
| LCQ | Ion trap mass spectrometer |
| LIBS | Laser induced breakdown spectroscopy |
| LIDAR | Light detection and ranging |
| LiDS | Lithium dodecyl sulfate |
| LIF | Laser-induced-fluorescence |
| LOD | Limit of detection |
| LTQ | Linear ion trap mass spectrometer |
| LU | Lowest unoccupied (molecular orbital) |
| MAN | Monomethylamine nitrate |
| MCC | Multicapillary column |
| MEKC | Micellar electrokinetic chromatography |
| MEMS | Micromechanical systems |
| MIMS | Membrane introduction mass spectrometry |
| MMA | Methyl methacrylate |
| MS | Mass spectrometry |
| NATO | North Atlantic Treaty Organization |
| NB | Nitrobutane |
| NC | Nitrocellulose |
| Nd:YAG | Neodynium doped yttrium aluminum garnet |
| NG | Nitroglycerin |
| NGU | Nitroguanidine |
| NM | Nitromethane |

| | |
|---|---|
| NMR | Nuclear magnetic resonance |
| N-nDPA | N-nitrosodiphenylamine |
| NQ | Nitroguanidine |
| NQR | Nuclear quadrupole resonance |
| NT | Nitrotoluene |
| NTO | Nitro-1,2,4-triazole-3-one |
| ODS | Octyldecyl silica |
| PA | Picric acid |
| PAED | Photo-assisted electrochemical detection |
| PBX | Plastic bonded explosive |
| PBX-9501 | Plastic bonded explosive with HMX |
| PBX-9502 | Plastic bonded explosive with TATB |
| PBXs | Polymer bonded explosives |
| PDMS | Polydimethyl siloxane |
| PE-4 | British Comp C: RDX with waxes and/or heavy oils |
| PEG | Polyethylene glycol |
| PETN | Pentaerythritol tetranitrate |
| PL | Photoluminescence |
| PN | Potassium nitrate |
| ppb | Parts per billion |
| ppm | Parts per million |
| ppt | Parts per trillion |

| | |
|---|---|
| PTFE | Polytetrafluoroethylene |
| QCM | Quartz crystal microbalance |
| Qtrap | Hybrid triple-quadrupole-linear ion trap |
| RDX | Cyclotrimethylenetrinitramine |
| READ | Reversal electron attachment detection |
| REMPI | Resonance enhanced multiphoton ionization |
| ROC | Receiver operating characteristic |
| SAM | Self-assembled monomer |
| SAW | Surface acoustic wave |
| SBSE | Stir-bar sorptive extraction |
| SCA | Surrogate continuation aid |
| SCOT | Support-coated open tubular |
| SDB-RPS | Styrene divenylbenzene reversed-phase sulfonated |
| SDME | Single-drop microextraction |
| SDS | Sodium dodecyl sulfate |
| Semtex-H | Composition of RDX and PETN with heavy oils and rubbers |
| SERRS | Surface enhanced resonance Raman scattering |
| SERS | Surface enhanced Raman scattering |
| SESI | Secondary electrospray ionization |
| SFE | Supercritical fluid extraction |
| SGC | Solvating gas chromatography |
| SIMS | Secondary ion mass spectrometry |

| | |
|---|---|
| SLE | Solid-liquid extraction |
| SPE | Solid phase extraction |
| SPIE | The International Society for Optical Engineering |
| SPME | Solid phase microextraction |
| SPR | Surface plasmon resonance |
| SS-MIMS | Single-sided membrane introduction mass spectrometry |
| STP | Standard temperature and pressure |
| TAT | 2,4,6-triaminotoluene |
| TATB | Triamino trinitro benzene |
| TATP | Triacetone triperoxide |
| TDS | Time domain spectrometry |
| TEEM | Tunable energy electron monochromator |
| Tetryl | Methyl-2,4,6-trinitrophenylnitramine |
| TNB | Trinitrobutane |
| TNM | Tetranitromethane |
| TNT | 2,4,6-trinitrotoluene |
| TOF-MS | Time of flight mass spectrometry |
| TSQ | Triple stage quadrupole |
| UDC | Universal Detector Calibrant |
| UN | Urea nitrate |
| UV | Ultraviolet |
| UXO | Unexploded ordinance |

| | |
|---|---|
| WCOT | Wall-coated open tubular |
| WWI | World War I |
| WWII | World War II |
| μFIA | Microflow-inject analysis |

# 1 INTRODUCTION

This study presents the improvement of detection canines through scientific examination of training, training aids, and calibration. A universal detector calibrant (UDC) was developed for which the reliability of the biological and instrumental detectors can be studied. Similarly to the daily calibration of laboratory instruments, an UDC for which biological detectors can be calibrated would ensure the detector is working within acceptable limits, thus making the biological detector analogous to a laboratory instrument. Twelve mandatory and desirable requirements were chosen for compound selection resulting in the selection of a single safe, non-target, rare compound for use. The UDC can be used before each working day, providing the handler with documentation detailing the daily working parameters of the canine. The UDC has the potential to also be used in selecting future biological detectors by determining the time it takes to train the canine, to alert to the compound, and the sensitivity of detection that the canine can achieve.

This study also presents the design and development of scientifically validated non-hazardous canine training materials. One of the primary goals of this study was the development of a peroxide based explosive surrogate continuation aid (SCA) through the characterization of the volatile organic compounds (VOCs) within the headspace of the explosives. The SCAs were developed by isolating the dominant headspace odor constituents found in various forms of peroxide based explosives, and which of these compounds are used by biological detectors as identifiers was discovered. The compounds were isolated using solid phase microextraction (SPME) in conjunction with gas chromatography-mass spectrometry (GC-MS) or gas chromatography-electron

capture detection (GC-ECD), which has previously been proven as an effective method for extracting and detecting volatiles from the headspace in both explosives and other materials (1-4). Once identified, the compounds were used to develop a system of mimics as substitutes during training. The SCAs were selected so that there was minimal risk to the detector teams and a reduced number of target odors used for training. This allowed for the introduction of a more uniform system to be utilized universally allowing for the direct comparison between biological and instrumental detectors. In addition, the design and isolation packaging of these SCAs permitted them to be stored for long periods of time without affecting their potency or reliability.

Field trials testing the developed SCAs were conducted double blind and were used to determine detection canine interest in the observed odors contained within the SCAs and to evaluate the reliability of the mimicked odor. Field studies were completed to validate the SCAs by training new canines only to the training aids and recording the responses when exposed to actual explosive material. A third and final field trial was conducted to compare the detection rates between various commercially available SCAs in order to determine the best alternative when actual illicit material is unavailable.

The primary goals of this research study were to develop a method for the calibration of detection canines using a non-target compound and the development of safe, long lasting peroxide based explosive SCAs. Additional goals of this study were to validate and improve the prototype surrogate explosives kit previously developed by the International Forensic Research Institute, IFRI, and to determine the optimal storage parameters, training protocol, and type of training aid for detection canines (5). Once

completed this research will aid in the standardization of biological detectors and increase the number of explosives a detection canine can reliably detect.

# 2 LITERATURE REVIEW

## 2.1 Explosives

Explosives can be defined as any chemical compound, mixture, or device that functions by explosion. An explosion is a sudden conversion of potential energy to kinetic energy with the production and release of gases under pressure (6). Explosions can be classified into five main types: atomic, physical, chemical, mechanical, and electrical. Atomic explosions emit infrared (IR) and ultraviolet (UV) radiation along with a high quantity of heat and gas, as a result of either fission or fusion of atoms. Atomic explosions have energies one million to one billion times that of chemical explosions, with longer shockwaves than that of chemical explosions (7). Physical explosions are ones in which potential energy is rapidly converted to kinetic energy when a substance undergoes a rapid physical change while being compressed. An example of a physical explosion is a volcanic eruption. Chemical explosions are rapid exothermic reactions with the generation of high pressure gases because of the initiation of chemical explosives or fuel gases. Most explosives encountered function as chemical explosions, since the initiation begins with the chemical reaction of an explosive composition. Mechanical explosions typically occur from the sudden rupture of a container under high pressure in which the contained gases are released. Electrical explosions are caused by high energy electrical arcs which can generate sufficient heat to cause initiation of the surrounding gases.

Explosive materials behave according to known energy and thermochemistry transformations; however, their behavior can be further described by explosive power,

metastability, oxygen balance, and sensitivity. The explosive power of an energetic material can be arbitrarily determined by comparing the heat evolved (Q) and the volume of gases produced (V) from one explosive to picric acid (7,8). The power index can be calculated, Equation 1, which allows for the comparison of various explosives using one gram of explosive material.

$$\mathrm{PI} = \frac{\mathrm{QV}_{\mathrm{explosive}}}{\mathrm{QV}_{\mathrm{picric\ acid}}} \times 100$$

**Equation 1. Power Index of explosives (Q= heat evolved, V=volume of gaseous products produced)**

The metastability of an energetic material is used to describe the time in which the energetic material remains unreacted under the natural driving forces (entropy) for further reaction (9). Essentially the metastability of an energetic material is the period of time before the energetic material spontaneously initiates. Generally, explosive compositions contain ideal ratios of carbon, hydrogen, and oxygen to form carbon dioxide and water as reaction products; however, the introduction of nitrogen plays a strong role in increasing the metastability of the energetic material. Nitrogen holds the fuel (carbon) and oxidizing components together strongly enough to provide additional metastability, but loosely enough so that the reaction can proceed with suitable initiation. When the oxidizer and fuel are in exact proportions to form carbon dioxide and water, the energetic material is oxygen balanced. Having oxygen balance in an energetic material is ideal because the energy released per unit of weight of material is greatest at stoichiometric balance of oxygen, Table 1. This knowledge resulted in newer explosive formulations to be created at oxygen balance, the addition of other fuel sources to consume the excess oxygen in

older formulations, such as nitroglycerin (NG) and ammonium nitrate (AN), or the addition of oxidants such as nitrates, to oxygen poor energetic materials to reduce the production of toxic gases (7).

**Table 1. Balanced reaction formula for some explosives (7)**

| ***Energetic material*** | ***Balanced reaction formula for complete combustion*** |
|---|---|
| Ammonium nitrate | $NH_4NO_3 \rightarrow 2H_2O + N_2 + 1O$ |
| Nitroglycerin | $C_3H_5N_3O_9 \rightarrow 3CO_2 + 2½H_2O + 1½N_2 + ½O$ |
| TNT | $C_7H_5N_3O_6 \rightarrow 7CO_2 + 2½H_2O + 1½N_2 - 10½O$ |
| RDX | $C_3H_6N_6O_6 \rightarrow 3CO_2 + 3H_2O + 3N_2 - 3O$ |

The sensitivity of an explosive relates to the ease in which the explosive material can be initiated. The sensitivity of an explosive has no direct relation to bulk physical or chemical properties, however, explosives can be classified as sensitive or insensitive. Explosives that are easily initiated via heat, friction, shock, spark, or flame are said to be sensitive explosives. Insensitive explosives typically need a large driving force for initiation such as a shockwave. In some cases insensitive explosives can be burned and used as a fuel source with no fear of detonation (10).

Depending upon the explosive material, decomposition may occur via deflagration or detonation. Explosive materials that deflagrate have combustion zones which move at a velocity slower than the speed of sound. Explosive materials that detonate have combustion zones which move at a velocity greater than the speed of sound. Explosives can be classified by several means; however, the most common classification schemes are described in section 2.3.

## 2.2 History of Explosives

It is believed that black powder was the first explosive and was made accidentally by the Chinese in 220 BC (7). Since this explosive formulation consisted of materials widely available in the ancient world; potassium nitrate (saltpeter), charcoal, and sulfur; black powder was the first explosive used for mining purposes. Black powder's usefulness extended to military applications as the Chinese also used black powder and stones in bamboo tubes to make rockets (9). By the end of the 13$^{th}$ century black powder found a niche in military uses for breeching castles. Black powder was the only known explosive material until the 17$^{th}$ century when Baron Johann Kunkel von Löwenstern developed mercury fulminate. Löwenstern's discovery was widely forgotten until 1799 when Edward Howard rediscovered mercury fulminate and proposed its viability as an initiator for black powder (7,9).

It was not until 19$^{th}$ century that industry began looking for a better explosive and in 1846 Ascanio Sobrero obliged by developing nitroglycerin (NG). While NG was found to have superior explosive power and sensitivity, it was not until the mid-19$^{th}$ century when the Nobel family developed a new cold manufacturing process that reduced the hazards associated with NG making it a viable black powder alternative. The cold manufactured NG was not without fault and after the untimely accidental death of several members of the Nobel family, dynamite was developed. Dynamite consisted of liquid NG absorbed into diatomaceous earth, which made a paste that was far safer to transport and use. This development along with Alfred Nobel's blasting cap allowed dynamite to corner the market of explosives for the next 70 years (9).

Around the same time that NG was developed, nitrocellulose (NC) was also being proposed as an energetic material. Similar to the manufacturing of NG, the manufacturing of NC proposed several hazards as well. Sir Frederick Abel improved the stability of NC through a pulping process; however, his assistant E. A. Brown made a significant discovery that blocks of wet NC were relatively stable and detonated by dry NC with a mercury fulminate detonator (7). Brown's observation led to the principle of explosive trains and boosters. As a result of the comparative safety of wet NC, in 1868 NC became widely used in military and commercial applications. Experimentation with NC led to the discovery of the Munroe effect, in which Charles E. Munroe discovered that partial focusing of the blast energy can be achieved by altering the shape of the explosive material. Schonbein also studied NC in an effort to build a better propellant than black powder. While Schonbein's first formulations burned too quickly for the munitions of his time, his work became the basis for NC use in all propellants, which increased the capability and reliability of firearms (9).

Even with superior energetic materials being produced, improvements upon black powder were concurrently undertaken. First developed in 1654, ammonium nitrate (AN) did not find use as an energetic material until the 19$^{th}$ century when it was evaluated as a replacement for potassium nitrate in black powder. AN was not classified as an energetic material until after World War II (WWII) when several ships, most notably the "Grand Camp" in Texas City, Texas, exploded after the hot fertilizer grade AN self-accelerated its decomposition (7,9). This accident led to the implementation of safe practices and handling of industrial explosives, which in turn led to AN formulations replacing dynamite in commercial applications due to AN's superior safety.

## 2.3 Classification of Explosives

### 2.3.1 Low and High Explosives

Low explosives decompose via deflagration and are easily ignited through heat, spark, friction, or impact. Alternatively, high explosives decompose via detonation, which is initiated through a shockwave. High explosives can further be classified as primary, easily ignitable through heat, friction, shock, or impact; or secondary, insensitive and stable explosives that require a shockwave for initiation. The pressure wave and speed of released gases in high explosives lends more brisance, or shattering power, associated with the blast wave. While high explosives do not need confinement to be effective, typically low explosives need containment to be most effective because they lack brisance in comparison to high explosives. Containment of a low explosive can however turn from deflagration to detonation if the confining tube has sufficient length such that the compression waves accelerate to supersonic speeds (11). This can result from the positive feedback cycle that accelerates the compression waves produced as increased pressure from the compression waves increases the heat of the reaction. As a result, there is an increase in the energy released and speed of the compression wave. As the cycle continues, eventually a compression wave will travel at supersonic speed and the resulting shockwave will detonate. It is in this detonation zone where mechanical pressure initiates combustion. The process can be seen in Figure 1.

Initiation of both low and high explosives can be completed through the use of an explosive train. Explosive trains can be classified as high or low depending on the last explosive in the train and have two or more steps, Figure 2. Low explosive trains

typically have two steps in which a fuse is used to ignite a low explosive. High explosive trains have two or more steps in which an initiator is used to detonate a secondary explosive. The insensitivity of secondary high explosives requires an initiator for detonation.

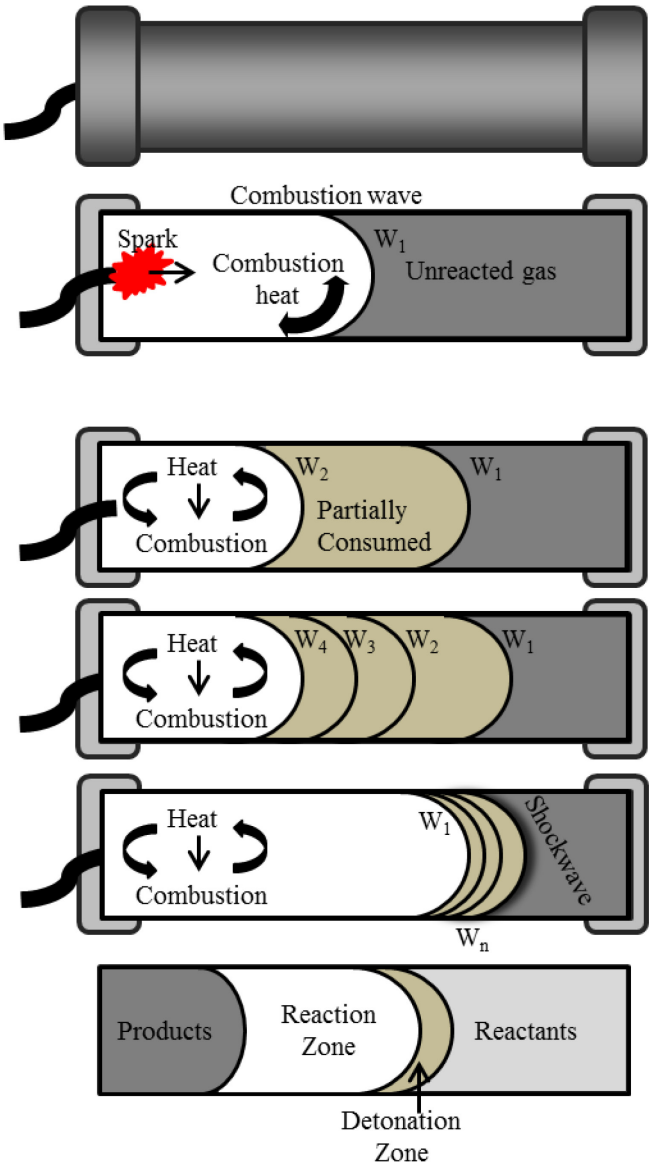
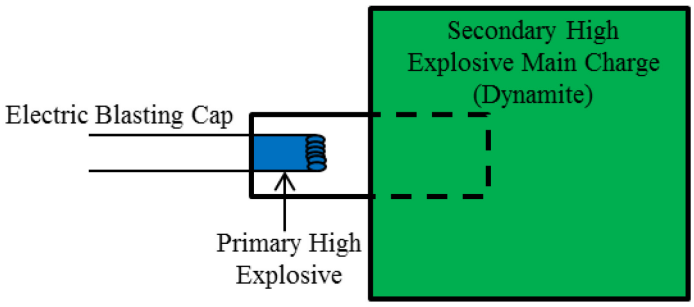
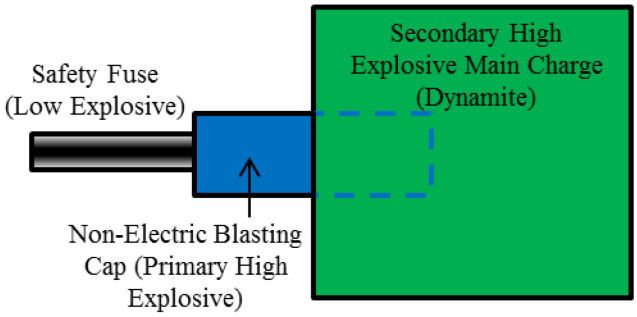



**Figure 1. The process of a confined deflagration progressing into a detonation event (Adapted from Bell S. Explosives. Forensic Chemistry. 1st ed. Upper Saddle River, New Jersey: Pearson Prentice Hall; 2006. p. 384-431.)**

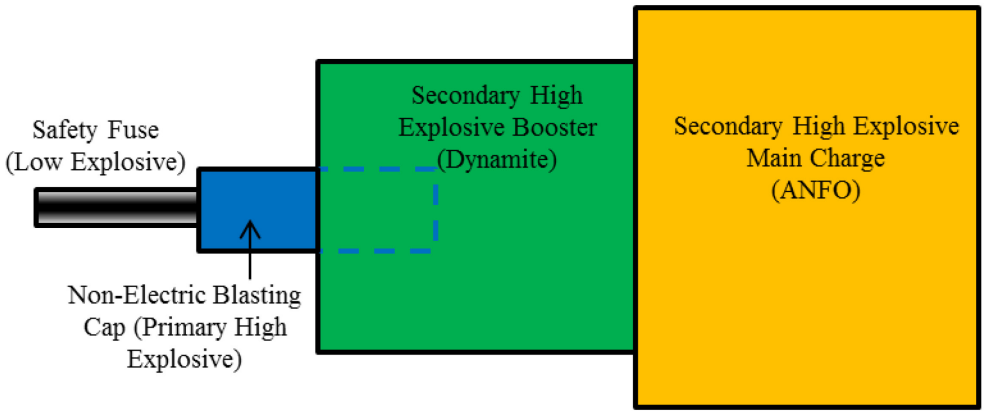
In high explosive trains the initiator/detonator is normally a primary high explosive. In a two-step explosive train the initiator would produce a shockwave to detonate the main charge (secondary high explosive). Adiabatic heating results from the shockwave as the particles within the secondary explosive are compressed. As the heat increases the explosive will surpass the decomposition temperature of the explosive material resulting in acceleration of the shockwave through an exothermic chemical decomposition of the explosive crystals. In three or more step explosives trains, a secondary high explosive having a different composition than the main charge, may be added to increase the overall power of the explosion.




**Two-step Explosive Train**




**Three-step Explosive Train**




**Four-step Explosive Train**

**Figure 2. Examples of explosive trains**

A comparison of the effects of low explosives vs. high explosives can be seen in Table 2.

**Table 2. A comparison the effects of low and high explosives (7)**

| | ***Low Explosives (Deflagrating Materials)*** | ***High Explosives (Detonating Materials)*** |
|---|---|---|
| ***Initiation*** | Flame, sparks, friction, and high temperature | Primary: flame sparks, friction, and high temperature<br>Secondary: shockwave |
| ***Initiation while wet*** | No | Yes |
| ***Oxygen present in the composition*** | Yes | Yes |
| ***Noise associated*** | Long dull noise with hissing and fire | Sharp loud bang sometimes accompanied with fire |
| ***Production of gases*** | Used for propulsion in propellants | Generates shockwave and is a destructive force |
| ***Burn rate*** | Subsonic | Supersonic |
| ***Propagation of decomposition*** | Based on thermal reactions | Based on shockwave |
| ***Effect on increasing ambient pressure on burn rate*** | Increases directly with increasing ambient temperature | No effect on rate |
| ***Effect of strength container on burn rate*** | No effect | Effected |
| ***Effect of mass on burn rate*** | No effect | Dependent on diameter of explosive charge (critical diameter) |
| ***Conversion to deflagration/detonation*** | Can detonate under favorable conditions | No reversion to deflagration |

2.3.2 Use

Explosives are classified into four groups when classified by use: commercial, military, gun and rocket propellants, and improvised. While this leads to a simple classification scheme, in actuality several energetic materials can be cross classified within the four groups depending upon the organization using the material. The Bureau of Alcohol, Tobacco, Firearms and Explosives (ATF) estimates that 85-90% of all

explosives are used annually for mining purposes; with military, propellants, and improvised explosives making up the latter 10-15%.

Black powder dominated the commercial explosives market until 1870, when several accounts of injuries led to efforts to improve the safety of black powder. Attempts to use pure NC and NG were made for blasting applications, however, they were found unsuitable in gaseous mines. Nobel's development of dynamite led to an industrial revolution of mining, but also an increase in gas and dust explosions. Concern led to commissions to set standards for the maximum safe temperature for explosions and the determination of permitted explosives. The results of the commissions' findings determined that AN based explosives were suitable while black powder and dynamite failed to meet safety standards. This also led to the Coal Mines Regulation Act of 1906 which calls for testing of blasting agents prior to implementation in mines (7). By 1913 nearly all commercial mines were using AN based explosives, however, a waterproof AN formulation was needed for use in the wet mines. To fill this need, ammonium nitrate and fuel oil (ANFO) explosives were developed in 1950. By the 1970's explosives manufacturers began adding monomethylamine nitrate (MAN) to AN formulations to produce easily detonable gel explosives. Emulsion and slurry explosives soon followed the development of ANFO as they were safer and easier to manufacture than other dynamite formulations. Most commercial explosives on the market today are based on ANFO and emulsion explosives for blasting use.

Black powder was commonly used with military applications up until 1885 when picric acid was developed. While picric acid was widely accepted, it has several drawbacks including corrosion if shells in the presence of water, super sensitivity leading

to accidental initiation, and prolonged high heat temperatures to melt (7). Tetryl was also developed around the same time as picric acid and used as a base charge in blasting caps. By World War I (WWI) 2,4,6-trinitrotoluene (TNT) had replaced picric acid and became the standard explosive for armies. Since the production of TNT in WWI was limited by the shortage of toluene produced from coal tar, mixtures of TNT and AN became commonplace on the battlefield. By the end of WWI research programs started to develop more powerful explosives resulting in the creation of cyclotrimethylenetrinitramine (RDX) and pentaerythritol tetranitrate (PETN).

In World War II (WWII) RDX was used more than PETN because RDX had greater stability and was insensitive to detonation. PETN and TNT mixtures, known as Pentrolit or Pentolite, were however used for the energetic material in hand and anti-tank grenades and detonators. RDX was first developed in 1899 for medical use, but in 1920 Herz determined its value as an explosive. Through several iterations of synthesis by several groups, Bachmann developed the greatest yield manufacturing process. The Bachmann process was used worldwide and led to the discovery of cyclotetramethylene-tetranitramine (HMX) and several other explosives. Brockman perfected the synthesis of RDX and developed Type A RDX consisting of pure RDX. By the end of WWII more powerful mixtures of TNT/RDX/aluminum (Torpex) and plastic explosives were developed for military use.

As the power of military explosives increased, a means of sensitivity reduction was necessary. This need led to the development of polymer bonded explosives (PBXs) also known as plastic explosives which embedded the explosive crystals in a polymeric matrix. The most common PBXs formulations include RDX, HMX, PETN, or mixtures

of the aforementioned explosives. In order to improve the explosive performance, energetic prepolymers such as hydroxyl terminated polybutadiene (HTPB) were added, however, this addition made PBXs more sensitive to impact. To reduce impact sensitivity plasticizers were added to the formulations which additionally improved the mechanical properties and process ability of the explosive. Like the prepolymers, plasticizers can be in both inert and energetic formulations with 2-ethyl-1-hexanol being a common inert plasticizer and ethylene glycol dinitrate (EGDN) being a common energetic plasticizer (7).

Recent developments in military explosives have led to the development of hexanitrostilbene (HNS), nitro-1,2,4-triazole-3-one (NTO), and the nitrocubanes. NTO has found niches outside of military applications and can be found in vehicle airbags systems and gas generators. The nitrocubanes are thought to be the most powerful explosives since all of the available hydrogens are replaced with nitro groups. Insensitive munitions (IM) are also a recent development to improve the survivability and safety of munitions. Explosives meeting IM rules will not detonate under any condition other than its intended use even in extreme temperatures.

In 1998 the Committee on Marking, Rendering Inert, and Licensing of Explosive Materials was charged by the National Research Council to determine the viability of adding tracer elements to explosives for detection and identification, the feasibility of producing energetic materials from common chemicals, and the feasibility of introducing controls on the precursors of explosive materials in response to the Antiterrorism and Effective Death Penalty Act of 1996 (12,13). The committee found that many explosives contain energetic materials with low vapor pressures (e.g., RDX or PETN), which are

difficult to detect in the vapor form. This spawned the theory of adding volatile chemical markers to explosives, or taggants, for easy detection and identification of explosives. Four taggants were proposed for use: 2,3-dimethyl-2,3-dinitrobutane (DMNB), 2-nitrotoluene (2-MNT), 4-nitrotoluene (4-MNT), and EGDN; however DMNB is the most commonly encountered taggants and the most indicative of an explosive material present. DMNB is additionally favorable because it has a high vapor pressure ($2.1 \times 10^{-3}$ torr at 25°C), high permeability through materials, and no known industrial uses. All military plastic explosives are tagged with a minimum of 0.1% w/w DMNB after the International Civil Aviation Organization (ICAO) convention on the Marking of Plastic explosives for the Purpose of Detection determined that the ability to source military explosives is necessary (12).

Gun and rocket propellants have both commercial and military applications but are classified separately since their intended use is to propel an object which is responsible for the destruction rather than the energetic material itself. Propellants can be further classified as homogenous where the fuel and oxidizer are contained within the same molecule or heterogeneous in which the fuel and oxidizer are contained in separate compounds. Propellants are designed to only deflagrate and contain sufficient oxygen for complete combustion. Examples of propellants include: black powder, smokeless powders, and other energetic materials that lack NG or other aromatic nitro compounds. Black powder was the first propellant, but in 1884 smokeless powder was introduce by the French (14). Smokeless powder revolutionized modern warfare since it suppressed the smoke associated with black powder firearms allowing for armies to see the enemy even after multiple shots.

The compositions of propellants are typically NC based with grain shapes specific to burning requirements, Figure 3. As the size of the gun increases, the grain size of the propellant increases, and the burn time increases. To increase the burn rate, grain shapes with high surface area, such as multi tubular or slotted cylinder, can be selected because as the surface area of the grain increases the burn rate increases. The composition of the propellant also plays an important role which led to sub classifications including single-base, double-base, triple-base, and high energy liquid and composite gun propellants.

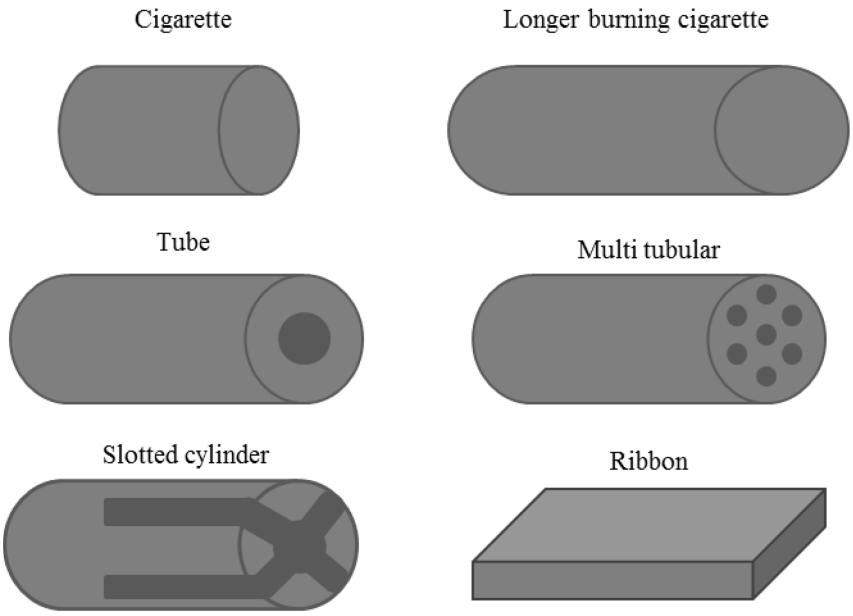



**Figure 3. Examples of gun propellant shapes**

Single-base gun propellants are typically composed of 90% or more NC. Double-base gun propellants are a combination of NC and NG and release a higher amount of energy than single-base propellants. Unfortunately double-base propellants have a higher flame temperature resulting in erosion of the gun barrel and muzzle flash. As the presence of muzzle flash can indicate the location of the shooter, the military introduced nitroguanidine into double-base propellants to form triple-base propellants. The addition

of nitroguanidine reduces the temperature of the flame, consequently reducing the barrel erosion and muzzle flash. Triple-base propellants are known as military propellants because they are typically found in tank guns and large caliber guns used exclusively by the military. In high energy propellants the nitroguanidine is replaced with RDX in order to increase the projectile's velocity. High energy propellants are capable of piercing armor and consequently only used in tank guns. Liquid propellants are relatively new propellants and have similar energy outputs as their solid propellant counterparts; however, liquid propellants are less susceptible to accidental initiation making them safer.

While gun propellants are designed for rapid burning and high pressure outputs, rocket propellants require longer burn times and lower pressures for a sustained impulse. Similar to gun propellants, rocket propellants function according to the size, shape, number, and composition of the grains of explosive materials. Rocket propellants commonly contain fewer and larger grains for short range rockets, or one to two large grains for long range rockets, Figure 4. There are two main types of solid rocket propellants, double-base and composite, along with liquid rocket propellants. Like gun propellants, double-base rocket propellants are composed of NC and NG and extruded into smaller grains or larger casts depending on the size of the rocket. Composite rocket propellants are composed of a finely dispersed powder oxidizer in a polymeric fuel binder mixture. Liquid rocket propellants are either monopropellants or bipropellants. Hydrazine is the most common monopropellant used in small low thrust missiles. Monopropellants are composed of liquids that are capable of burning without oxygen. Alternatively, bipropellants consist of a fuel and oxidizer that are separately contained

until the time of ignition. Once the fuel and oxidizer meet, they instantly ignite in the combustion chamber. Common bipropellant fuels are methanol and kerosene and common oxidizers include nitric acid and dinitrogen tetroxide (DNTO) compounds.

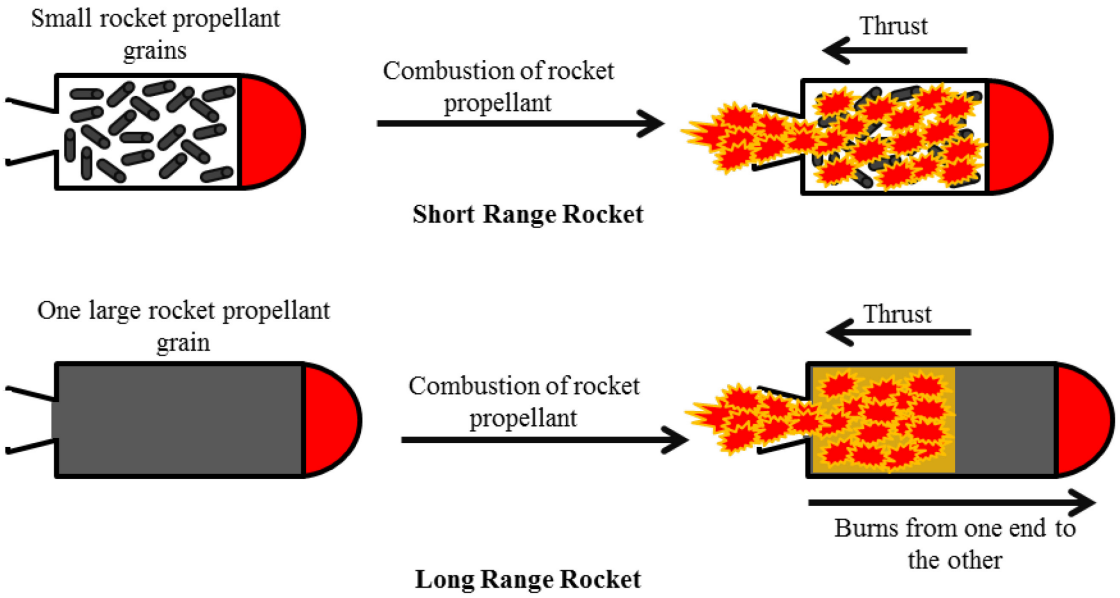



**Figure 4. Examples of rocket propellants for short and long range rockets**

In addition to the main energetic materials contained within gun and rocket propellants, several additives are added to the formula. Since NC is the backbone of most propellants, a stabilizer is needed to increase the shelf life of the propellants as NC spontaneously decomposes into nitrous and nitric acid (14). Commonly encountered stabilizers include: carbamite (ethyl centralite), methyl centralite, chalk and diphenylamine (DPA) (7). Plasticizers are added to propellants because NC is hygroscpoic and will take up moisture, which reduces its effectiveness. The addition of a plasticizer such as dibutyl phthalate, ethyl centralite, or methyl centralite reduces the hygroscopicity of the propellant along with softening the grains for easier extrusion, and reducing the need for solvents by gelling the NC. Detterents or coolants like dibutyl

phthalate, ethyl centralite, methyl centralite, or dinitrotoluene (DNT) are added to reduce the flame temperature and burn rate of the propellant. Graphite may be added as a surface lubricant to improve the flow characterisics. Reduction of muzzel flash is often desirable and achieved through the addition of potassium chloride, potassium sulfate, potassium nitrate, potassium aluminium floride, or sodium cryolite salts which act as antioxidants reducing the flash (7,14). Finally decoppering agents (lead or tin foil) and anti-wear agents (titanium dioxide or talc) are added to aid in maintaing the integrty of the firearm by removing the copper deposits left by the driving band or reducing the erosion of the gun barrel, respectively.

Improvised explosives, more commonly encountered as improvised explosive devices (IEDs), consists of a device placed or fabricated in an improvised manor composed of commercial or military components incorporating destructive, lethal, noxious, pyrotechnic, or incindiary chemicals and designed to destroy, incapacitate, harass, or distract (15). Essentally IEDs consist of a fuel and oxidizer used in conjunction for a purpose other than the manufactures' direction. IED's have gained popularity in recent years because they can be easily manufactured using common household chemicals following directions posted on the internet or in anarchist publications (16-18). IEDs can be created according to the skill level of the maker, ranging from the most simplistic of designs to ones which compete with the skill and intracacies of military explosives, Figure 5. While any energetic material can be used as the main charge in an IED (Figure 5 gasoline or smokeless powder), peroxide based explosives, AN, and urea nitrate (UN) explosives are of notible interest. Common IEDs include the simply constructed molotov cocktails and pipe bombs or more sophisticated multicomponent

devices (15). More sophisticated IEDs may have components including: containers, power sources, switches, initiators, and main charges (Figure 5 C).

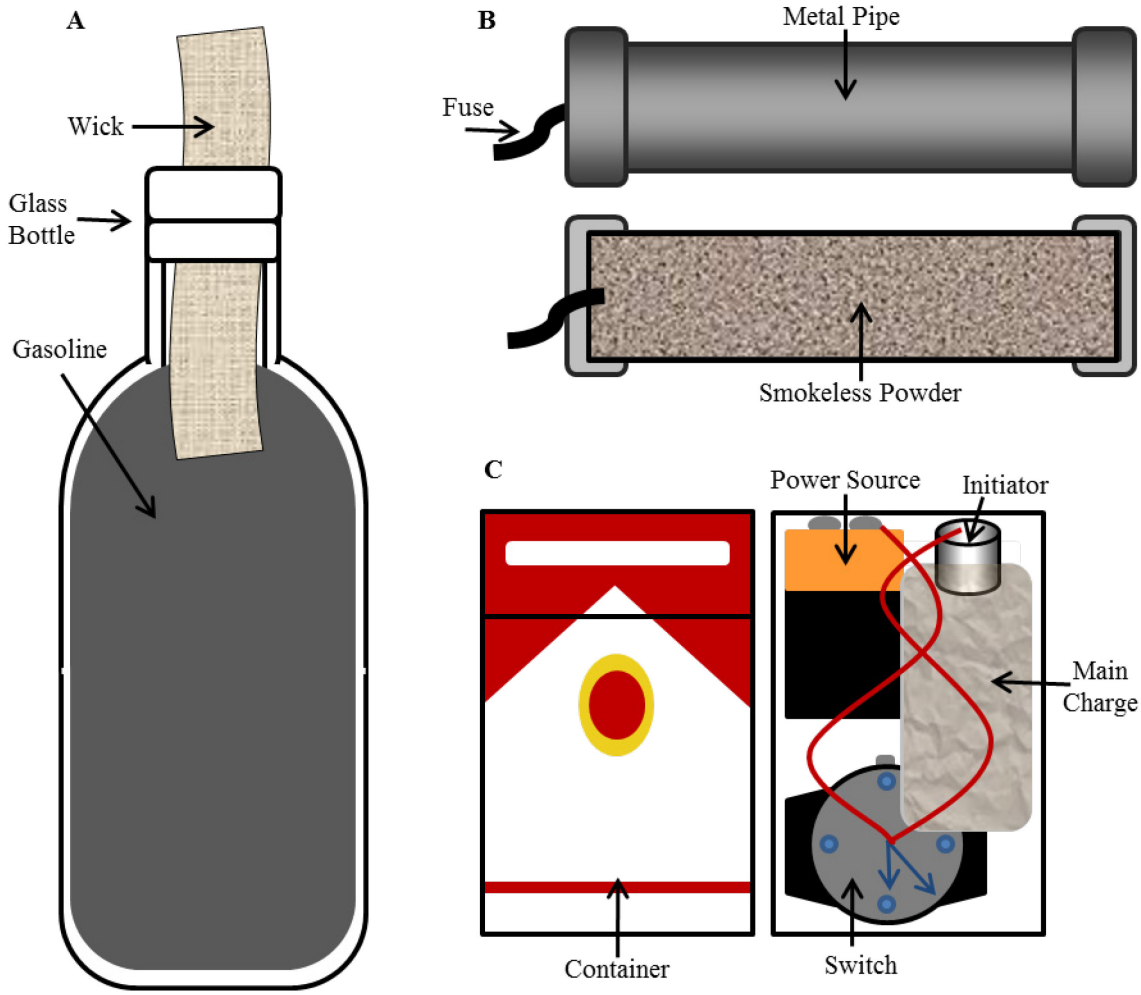



**Figure 5. Examples of IEDs. A) Molotov cocktail, B) Smokeless powder pipe bomb, C) Sophisticated cigarette box bomb**

IEDs have garnered interest by various terrorist organizations, both domestic and international with 85-90% of all acts of terrorism involving bombings (15). Some notable IED attacks include the bombing of the United States Marine Corps Barracks in Beruit, Lebanon on October 23, 1983 in which a large delivery truck containing the equivalent of 12,000 pounds of TNT was driven into the lobby of the barracks (19). The compressed

gas assisted explosive was responsible for killing 220 U.S. marines, 18 U.S. navy, three U.S.army, and 58 French soldiers attacked in a coordinated bombing. This attack was the largest single-day loss of life for the marines since the Battle of Iwa Jima in WWII and recorded as the deadliest single-day death toll for the United States military since the Vietnam War (20).

In 1988 a sophisticated device containing a plastic explosiv known as Semtex was set to detonate once the barometric presssure of the luggage dropped below it's threshold on Pam Am flight 103 (21). The device was hidden in luggage that was mysteriously placed on the aircraft. The bomb detonated over Lockerbie and killed all 259 passengers and crew along with 11 residents on the ground in Lockerbie. Upon searching the 845 square mile wreckage, fragements of the time delay detonator and residues of RDX and PETN were found. Libyan, Adb al-Basset Ali Mohammad al-Megrahi, was tried and convicted in 1999 and given a life sentence while his assitant Al Amin Kalifa Fhimah was found not guilty. In 2003 Libya accepted responsibility for the bombing and paid out $2.7 billion dollars in damages to the familes of the victims.

The World Trade Center in New York City, New York has long been a target of IED attacks with the first occuring in 1993 and then again in 2001 which resulted in the complete distruction of both towers. The attack in 1993 was initiaited by Islamic extrimist groups who drove a van containing aproximately 600kg of urea, NG, sulphuric acid, aluminum azide, magnesium azide, and bottled hydrogen into the subterranean levels of the parking garage of the north tower (22). While initially intending for the explosion to cause the north tower to fall into the other tower and subsiquently release cyanide, the explosion resulted in a 100 foot crater spanning several stories and the

complete combustion of the cyanide. This bombing resulted in six deaths, 1000 people injured, and is credited as the first international act of terrorism on US soil. On September 11, 2001 the militant Islamic group, Al Qaeda, under the direction of Osama bin Laden completed the goals of the first bombing in 1993 by brining down the two main World Trade Center towers, seven towers in total (three towers fell as direct result of the attack and four others required demolition during the clean-up), and attacking the pentagon (23,24). In this coordinated attack, 767 and 757 jetliners filled with fuel were hijacked and then flown into the first tower (8:46 AM, flight 11), the second tower (9:03 AM, flight 175), and the pentagon (9:38 AM, flight 77). (23). The 9/11 attack resulted in the deaths of 202 persons on the flights, 421 firefighters, 2,245 people in or around the towers, and resulted in the US entering the War on Terror which lasted approximately ten years.

While the 1993 attack on the World Trade Center is known as the first international act of terrorism in the US, domestic IED attacks have also occurred. Theodore "Ted" Kaczynski was responsible for the bombings of several universities and airlines from 1978 to 1996 earning him the monicker "Unabomber" (25). His first attack took place at the University of Chicago in which a crude pipe bomb with wooden plugs was placed in a box marked "return to sender". With each bombing, the devices became more sophisticated moving from smokeless powders and gasoline to ammonium nitrate and aluminum powder; and then to potassium sulfate, potassium chloride, ammonium nitrate, and aluminium powder which had enough power to take the lives of many. It was not until the release of his manifesto that Ted was identified as the unabomber by his brother and sentanced to four consecutive life sentances in a maximum security prison.

In 1995, in Oklahoma City, Oklahoma, Timothy McVeigh and his accomplice Terry Nichols were responsible for the truck bomb filled with ammonium nitrate fertilizer and nitromethane that was left to exploside in front of the Alfred P. Murrah Federal building (26). The Oklahoma City Bombing resulted in the deaths of 169 persons, over 680 injured, damage to 324 buildings in a 16 block radius, and $652 million dollars in damage (27).

Between 1996 and 1998 Eric Robert Rudolph was responsible for a series of bombings, most notibly the Olympic Cenntenial Park bombing at the 1996 olympic games (28). Rudolph's bombs were typically contructed as pipe bombs using dynamite surrounded by nails. While Rudoph's intentions were only to stop the Olympic Games, the detonation of the bomb resulted in one death and 111 persons injured. After several more bombings of abortion clinics and subsiquent identification as the purpitrator by law enforcement, Rudolph went on the run until he was captured in 2003 and sentenced to four consecutive life sentances plus 120 years and $2.3 million dollars in damages in a maximum security prision.

Known as the worst terror attack in Europe since the Lockerbie in 1988, the 2004 Madrid, Spain train bombings were responsible for the deaths of 191 people and 1,841 wounded (29). In these coordinated attacks, four trains leaving the Alcala de Henares station were targeted with 13 bombs in total. Ten of the 13 bombs detonated and the remaining three were disabled by bomb squads. The bombs were constructed using stolen mining explosives from a mine in Northern Spain, suspected Goma 2 ECO explosives which are NG based (26).

The peroxide explosive TATP is commonly encountered in IEDs because it is easily prepared using household chemicals. December 22, 2001 Richard Reid earned the monikor of the "shoe bomber" when attempted to light a fuse that would then ignite TATP which would subsequently detonate the PETN explosive hidden in the sole of his shoe (30). The fuse was too wet to inginte giving the flight crew and passengers time to subdue Reid until the plane could safely land in the US. Reid plead guilty in 2002 to his acts of terrorism and is currently serving a life sentence in prison. The attempted bombing, however, led to changes in security measures at airports, since previous methods of passenger screening were unable to detect the shoe bomb. Airports now require passengers to remove their shoes to detect evidence of tampering or hidden contraband.

While Reid's bombing attempt was thwarted, in 2005, Islamic terrorist waged a successful assault on London's transport system in a series of coordinated attacks. On July 7, 2005 three train stations and a bus were attacked using suicide bombers armed with IEDs thought to contain TATP (31). This bombing was responsible for killing 52 travelers, four suicide bombers, and injuring approximately 700 people. On July 21, 2005 four additional suicide bombers attempted a second attack on London's transport system, however, they were less sucessful as only the detonators and not the main charges exploded. It is believed that the first attacks in July were motivated by the bombers' percieved injustices by the West against the Muslims and their desire for martyrdom. However, Al Qaeda claimed responsibility for both attacks though the amount of Al Qaeda influcence on the bombings is unknown.

### 2.3.3 Chemical Structure

Explosives fall into six categories when classified by chemical structure. These categories include: nitro alkanes, nitro aromatics, nitrate esters, nitramines, peroxides, and acid salts. Examples of explosives and their properties for each category can be seen in Appendix B.

#### 2.3.3.1 Nitro Alkane Explosives

Nitro alkane explosives are characterized by carbon (C) bound to nitrogen dioxide ($NO_2$) with an alkane backbone. Examples of nitro alkane explosives are nitromethane (NM) and DMNB. NM is a clear, volatile liquid commonly used in the racing industry because it is a highly oxygenated fuel. IEDs can easily be constructed using NM purchased at hobby shops with other fuels (powdered aluminum) to make powerful binary explosives. DMNB is the most commonly used tagging agents in explosives and has been discussed in section 2.3.2 under military explosives. Examples of commercial nitro alkane explosives include any plastic explosives manufactured after 1997 which are required to contain the taggants DMNB and Kine-Pak or Kine-Stick explosives and are AN and NM based (32).

#### 2.3.3.2 Nitro Aromatic Explosives

Similar to the nitro alkanes, nitro aromatic explosives are characterized by carbon (C) bound to nitrogen dioxide ($NO_2$) situated around an aromatic ring. The most common nitro aromatic explosive encountered is TNT, which is a yellow crystalline solid formed through successive nitrations of toluene. Mononitrotoluenes including 2-nitrotoluene (2-MNT) and 4-nitrotoluene (4-MNT) are taggants and result from a single nitration of

toluene. Dinitrotoluenes such as 2,4-dinitrotoluene (2,4-DNT) are commonly encountered as additives in smokeless powders. Six isomeric forms of TNT exist, however, the 2,4,6 substitution is thermodynamically favored and used as an explosive (7). Tetryl and picric acid (PA) are also categorized as nitro aromatic explosives and were developed around the same time. Tetryl is a light yellow crystalline solid commonly encountered in blasting caps and explosive mixtures in WWII before it was replaced by PETN. Commercial explosives containing nitro aromatics include: TNT "flake," TNT demilled military "flake," nitropel, smokeless powders (DNT and TNT), and cast explosives (PA and tetryl) (32).

#### 2.3.3.3 Nitrate Ester Explosives

Nitrate ester explosives are characterized by carbon bound to oxygen bound to nitrogen dioxide (C-O-$NO_2$). Examples of nitrate esters include PETN, EGDN, NG, NC, and nitroguanidine which have all been previously discussed in section 2.3.2. Commercial explosives containing nitrate ester explosives include: unadulterated PETN, datasheet A (PETN and binder), PETN detonating cord, primasheet 1000 (PETN and plasticizers), semtex A (PETN and plasticizers), dynamite (EDGN and NG), single-base smokeless powders (NC and DNT), double-base smokeless powders (NC and NG), and triple-base smokeless powders (NC, NG, and nitroguanidine) (32). Other nitrate ester explosives include methyl nitrate and diethylene glycol dinitrate. Methyl nitrate is produced by the nitration of methanol by a mixture of sulfuric and nitric acids. Methyl nitrate was once used as a rocket fuel by Germany in WWII, however, it was disregarded as a viable explosive as a result of the transportation and storage challenges it presents.

Diethylene glycol dinitrate has a similar structure to NG, however, it is extremely difficult to initiate and does not propagate a shockwave making it a viable desensitizer and plasticizer.

#### 2.3.3.4 Nitramine Explosives

Nitramines are characterized by nitrogen bound to nitrogen dioxide ($N\text{-}NO_2$). Examples of nitramine explosives include RDX, HMX, MAN, and nitrocubanes which have been discussed in section 2.3.2. The nitramines are widely recognized as stable explosives and have gained widespread military use due to their high explosive power. The nitrocubanes represent the newest explosives with hexanitroisowurzlitane (CL-20) garnering use as a specialty military explosive. Examples of commercially available nitramine explosives include: unadulterated RDX, RDX detonation cord, composition C-4 (RDX and plasticizers), datasheet (RDX and plasticizers), demex 200 (RDX and plasticizers), PE-4 (RDX and plasticizers), primasheet 2000 (RDX and plasticizers), HMX detonating cord, PAX11/PAX29 (CL-20, aluminum, and plasticizers), and DLE-C038 (CL-20 and plasticizers) (32).

#### 2.3.3.5 Peroxide Explosives

Peroxide based explosives capitalize on the small number of detonatable organic peroxides having properties similar to primary explosives. Peroxide based explosives are characterized by -O-O- bonds which are more reactive than nitrate groups, lowering the stability of the material. Examples of peroxide explosives include triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD). Peroxides are powerful oxidizers when mixed with a fuel source and are known to violently self-decompose (33).

Hydrogen peroxide is one of the most commonly encountered peroxides in both home and in the making of explosives. It is sold as an aqueous solution in varying concentrations depending on the intended use, 3% for disinfection and 40% for hair and tooth bleaching. Hydrogen peroxide decomposes violently above 80°C and can be easily detonated in concentrations of 86% or more (33). Detonation velocities of hydrogen peroxide range from 5500 m/s to 6700 m/s depending on the concentration and compounds it is mixed with (34). Hydrogen peroxide can be mixed with several fuels; diesel fuel, ethanol, glycerol, dimethylhydrazine; to form explosives with detonating powers equivalent to TNT (33). These mixtures of fuel and hydrogen peroxide have applications to propellant systems on space shuttles and blasting. While the previously listed mixtures have found applications, most peroxide explosives have no application because of their instability.

The simplest of clandestine peroxide explosives is hydrogen peroxide mixed with a fuel source. The fuel source is commonly a sugar, compound containing carbon, or alcohols. Peroxide explosives require an initiator, blasting cap or heat source to start the detonation. As a result of the variability of components used in these explosives, specific detonation velocities and stabilities are not known. Some studies looking at the explosive nature of hydrogen peroxides and alcohols have been completed, but the full nature of this type of peroxide explosive is still unknown (35).

HMTD, was first synthesized in 1885 by Legler as a primary explosive to replace mercury fulminate (36,37). The structure of HMTD is unique in that four optically isomeric conformers exist, two high energy and two low energy conformers (38). Once synthesized, HMTD found no use as a detonator or primer due to its volatility and

sensitivity (8). HMTD can be synthesized from several different chemicals, however it is generally precipitated from hydrogen peroxide, hexamine, and citric acid. Other formulations may include formaldehyde solution, hydrogen peroxide, and ammonium sulfate (39). During the precipitation process the precipitate, HMTD, is filtered off from the supernatant liquid and allowed to dry. The dried powder is unstable at high temperatures, friction sensitive, degrades quickly, and is corrosive. Wet HMTD is considered to be semi-stable; however the wet powder can detonate if exposed to high heat or friction.

Acetone peroxide explosives are similar to HMTD in that they were also developed as possible primary explosives to be used as initiators and they found no viable military or blasting application because of their sensitivity. Acetone peroxide can be manufactured from hydrogen peroxide, 3%-30%; acetone; and an acid, such as sulfuric or hydrochloric acid which are the commonly used acids (39). The resulting crystals are a mixture of the cyclic dimer, cyclic trimer, and the less commonly seen monomer and tetramer (40). The cyclic trimer is the most abundant product, triacetone triperoxide (TATP), and was first synthesized in 1895 by Wolffenstien, Figure 6 (41). The dimer, diacetone diperoxide (DADP), is produced as a byproduct in the synthesis of TATP and is formed as TATP degrades over time.

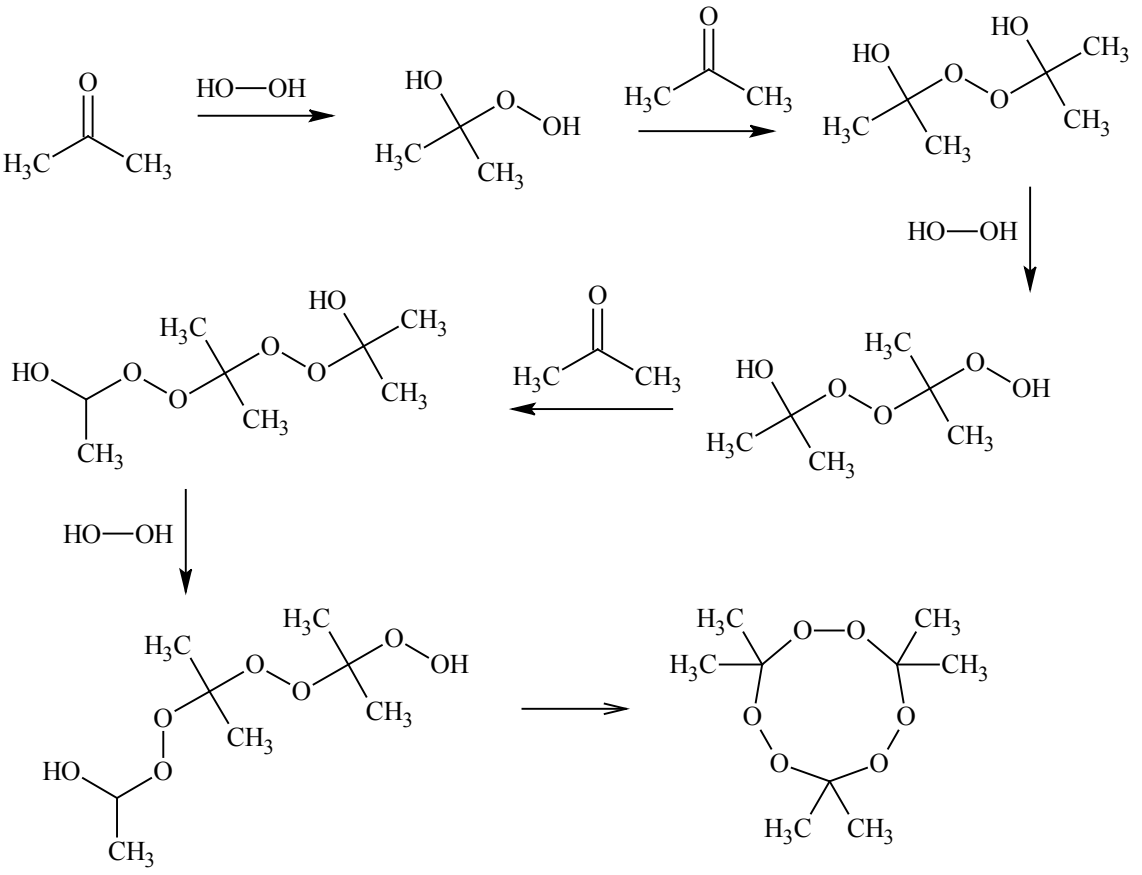


**Figure 6. The believed synthesis of TATP**

Acetone peroxide is most commonly encountered as a crystal, is highly unstable, and shock sensitive. Similar to HMTD, acetone peroxide explosives can detonate while the crystals are wet and can be used underwater (33). Because of these characteristics TATP has earned the street name “Mother of Satan” as a warning for persons choosing to manufacture TATP. It has a distinctive pungent odor and rapidly sublimes (42). Acetone peroxide explosives are unique in that the main isomer, TATP, detonates as an entropic explosion (43). The explosive nature of TATP is not thermochemically favored, however as TATP sublimes, and one ozone to three acetone gas molecules are formed, an entropic burst initiates the detonation producing no heat. The detonation velocity of TATP is equivalent to TNT at 5290 m/s (33).

Peroxide explosives are also inadvertently formed in scientific laboratories. The peroxide explosives are commonly formed in organic chemicals and some metals, and seen as crystals or white powder at the top of a chemical bottle (44). Peroxide explosives formed in chemicals may be formed over time, formed through concentration by evaporation or distillation, or from a peroxide initiated polymerization. Peroxides formed over time have been responsible for fatalities and include the following chemicals: diisopropyl ether, potassium metal, vinylidene chloride, sodium amide, and chemicals with similar structures (44). Air, light, and/or heat initiate peroxide formation and the formation of free radicals. The free radicals continue to generate more free radicals through autooxidation or a catalytic chain reaction. As the number of free radicals increases, the heat from the formation increases. This heat and subsequent decomposition can lead to an explosion. Peroxide explosives formed within chemical bottles share other peroxide explosive characteristics because they are shock, heat, and friction sensitive.

#### 2.3.3.6 Acid Salt Explosives

Acid salt explosives, also known as inroganic salt explosives are commonly found in binary mixtures because they are heavily oxygenated molecules. Nitrates ($NO_3^-$), chlorates ($ClO_3^-$), and perchlorates ($ClO_4^-$) are often mixed with ammonium ($NH_4^+$), sodium, or potassium; which can further be blended with a fuel such as ANFO. Acid salt explosives are commonly found in pyrotechnics whereby a specific combination of fuel, oxidizer, and/or additives are mixed to produce the desired effect. Commercial acid salt explosives can be found in blackpowder (potassium nitrate, charcoal, and sulfur), chemical grade potassium nitrate (PN), kine-pak (AN), kine-stick (AN), agricultural

fertilizers (AN), chemical supply or fireworks stores (ammonium perchlorate, potassium chlorate, or potassium perchlorate), or prepared by a trained chemist (UN) (32).

## 2.4 Detection of Explosives

Several considerations must be made prior to selecting one of the numerous techniques for detecting explosives as the detection parameters will determine the technique selected. If the detection of a mass of explosive concealed within a device devoid of explosive molecules on the surface is required, then a bulk detector is ideal. If the concern is the detection of explosive particles released from the concealed mass of explosives, then a trace chemical sensor is more suitable. If the detection substance is a vapor rather than a particle, such as the odors associated with explosives, then a trace vapor sensor is more appropriate. A brief synopsis of explosive detection techniques will be addressed in the following sections, Figure 7, and a detailed table of detection techniques, detection limits, and associated references can be found in Appendix B.

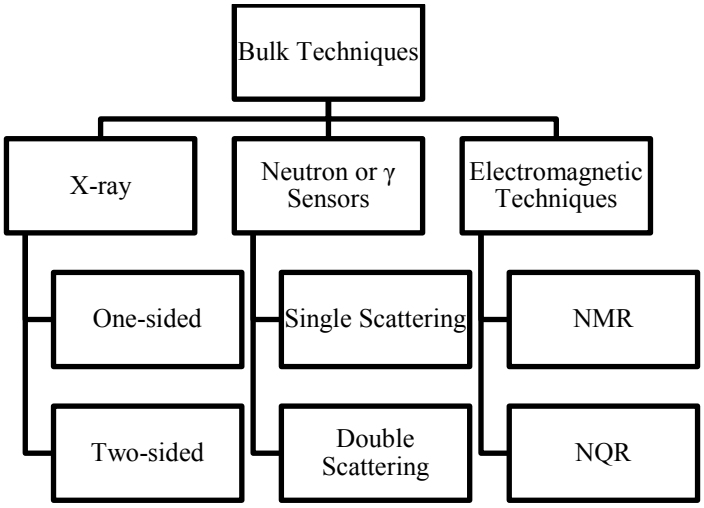



**Figure 7. Explosives detection techniques**

### 2.4.1 Bulk Detectors

Bulk detection of explosives is depends on the following parameters: geometry, material density, elemental composition, and vapor emission. While explosives can come in a variety of shapes, the geometry of the enclosure can be indicative of an illicit material along with the presence of a metallic detonator. A high resolution system is needed however to produce viable imaging of small wires. A known density range can be used to detect suspected explosives as most explosives are more dense than most organic materials, but less dense than most metals. As most explosives contain nitrogen, the presence of a high concentration of nitrogen can be suggestive of a nitrogen based explosive. Finding a high concentration of both nitrogen and oxygen, however, provides a non-ambiguous indicator of the presence of an explosive. Withdrawing a small sample of vapor from the suspected object can be used to easily and sensitively detect the residual explosives. However, vapor testing is high risk as there is a potential to accidentally detonate the device.

Conventional x-ray detection uses photons to detect varying densities within an object determined by how the x-rays are absorbed and scattered. This conventional system uses low-energy photons which can make imaging explosives difficult as photon absorption (photoelectric effect) dominates, making low atomic number compounds difficult to distinguish. To overcome this challenge, Compton scattering can be used to obtain additional density information, which in combination with atomic number information obtained by the photoelectric effect, can be used to identify explosives. Compton scattering is the inelastic scattering of a photon by an electron or other free charged particle. Compton scattering increases linearly with atomic number because it

depends on the number of electrons available as targets scatter. Since electron density is directly proportional to atomic number, and mass density is proportional to electron density, the ratio of atomic number to mass number is approximately one-half for most elements. For explosives detection, dual energy radiographic systems are employed to provide both Compton scattering (high energy) and atomic number (low energy). Rayleigh scattering can also be monitored using photon interaction by detecting the photons which are deflected at a small angle after striking the object without losing energy. Rayleigh scattering is more sensitive to metals as the probability of the reaction is small and proportional to the cube of the atomic number. Conventional x-ray techniques are valuable for the detection of explosives as long as both sides of the object are available as the technique is transmission based. Additionally, x-ray detection is disadvantageous because without computed tomography, the image can become muddled by overlaying objects. Computer tomography overcomes this challenge by deconvoluting the radiation-attenuated measurements into pixel specific slices of the object using a complex scanning and numerical image reconstructing process.

X-ray backscattering techniques take advantage of Compton scattering though the use of a collimated x-ray beam that is scanned across the surface of an object. The single scattered photons are then measured using a collimated detector which allows for discrimination between the explosive and environment because the photoelectric effect is more prevalent. X-ray backscattering is an advantageous technique because it can be used to look for bulk explosives through one and two-sided imaging.

There are a number of occasions where only one side of an object is available for inspection in which traditional radiography using transmitted radiation is not possible,

e.g., landmines or boxes against a wall. One-sided imaging presents several challenges because the radiation tends to diffuse in all directions making it difficult to concentrate the signal, unlike transmission imaging where a defined beam of radiation is monitored in a focused location. Since the radiation diffuses in multiple directions it is challenging to detect the incident radiation as only a small fraction of the incident radiation will find the detector resulting in low image forming efficiencies. One-sided imaging also has inherently lower resolution as the emerging radiation will pass through multiple regions of the object before it reaches the detector, increasing the probability of superimposed artifacts.

Land mine detection can be accomplished using infrared thermography which capitalizes on the difference in thermal capacitance between the soil and mine. Infrared thermography is a passive technique that can detect the changes in heating and cooling rates and subsequent infrared emissions when deployed. This allows for infrared thermography to be an effective technique for large area screening in a short time, however, an ineffective technique for the detection of explosives in small enclosures as the explosive will likely be in thermal equilibrium with the contents of the room.

Pulse-induction metallic detectors and ground penetrating radar have also been used for landmine detection by capitalizing on the eddy-currents generated in metals and microwave radiation which is completely reflected on metal surfaces. Detection techniques based solely on eddy-currents are viable for explosive detection in which the explosive is incased in metal, whereas microwave radiation detectors can give detection signatures anomalous to the surrounding area because of dielectric objects scattering the microwave radiation.

Electromagnetic techniques such as nuclear quadrupole resonance (NQR) and nuclear magnetic resonance (NMR) have also been used for bulk detection of explosives. NQR uses a radiofrequency coil to detect the unique $^{14}N$ absorption frequency (45). NQR relies on the observations of nuclei with a nuclear quadrupole moment in the absence of a static magnetic field. NQR has challenges in the sense that the signals are weak and are easily buried by electronic noise in the detection coil. NMR uses a strong magnet that takes advantage of the coupling seen between the hydrogen and nitrogen nuclei found in many explosives by detecting the dipole moments. The dipole moments and interaction with the magnetic field produces characteristic energy levels, which can be used to detect and image explosives which are not contained in metal.

Neutron or γ sensors are model techniques for elemental mapping because the neutron interaction with a nucleus is unique to the neutron energy and target nuclei resulting in an identifiable signal. This signal is composed of scattering, absorption, and activation interactions which can all be monitored. Scattering interactions typically occur from elastic collisions in which the energy lost and direction of scattering is unique to the mass number of the target nucleus. Inelastic collisions are possible and result from the neutron entering the nucleus and then leaving the nucleus with a different energy associated with gamma emissions. Inelastic collisions can be optimized by selecting specific neutron energies such that the probability of resonance energies is increased, allowing for element identification. Neutron absorption occurs when the neutron is completely absorbed by the target nucleus with a resultant gamma emission and absorption resonances specific to the target nucleus. The gamma emission can be classified as a prompt, simultaneous emission of gamma–rays and neutron activation or

delay in which the target nucleus is transmuted into a radioactive material that decays after the nucleus is activated. Of all the possible interactions, neutron activation is the most powerful elemental identifier as the gamma-rays produced are characteristic of the neutron absorbing element. Improved image reconstruction is possible because the attenuation of fast neutrons is lower than that of thermal neutrons. Depth information and a reduction of background gamma-rays can be achieved through pulsed fast neutron activation, which gives a better image of the explosive device. Neutron sources are found as either radioisotopes or neutron generators. Radioisotopes produce neutrons through spontaneous fission or via radioactive decay. Neutron generators produce fast neutrons by accelerating nuclear particles (deuterons or protons) into a solid (deuterium, tritium, or beryllium).

### 2.4.2 Trace Detectors

As the name states, trace detection is used to find vapors or particles of explosives that are inherently sparse in the environment. Regardless of the detection scheme, the identification of trace explosives requires five steps for detection. First the sample must be selected for introduction into the detection system. The next steps are concentration and separation, which can be performed concurrently or reversed depending upon the detection system. During concentration the explosive is collected from the entirety of the sample into a single space such that a detectable amount is obtained. Separation steps pass the sample through a process that separates the individual components of the sample. Once separated, identification and quantification are necessary to determine how much of a specific explosive is detected. Finally, the culmination of the four previous steps must

be presented in a form that can be interpreted and evaluated by the operator such as a chromatogram or report.

Selection of the sample for introduction into the trace detection scheme must be completed in a fashion such that the best results are probable. Trace explosive detection is most commonly encountered for threat and contamination analysis, looking for the presence of an explosive on the surface or within the matrix of a sample. Identifying all the potential sources of samples that can be encountered for trace explosive detection is endless. Commonly samples may consist of soil, water, air, baggage, vehicles, mail, and people. There is a large variety of techniques used in the field for sample introduction; however, contact methods or non-contact methods are used for the collection of a representative aliquot of the sample for further processing (46). Contact sampling methods may include the use of a swipe to sample the surface (47), chemical reagents sprayed onto the surface for in-place detection, or vaporization in which a technique is used to volatilize the surface material, such as a high power strobe lamp (48). Extraction techniques such as supercritical fluid extraction (SFE), solid phase extraction (SPE), solid-liquid extraction, stir-bar sorptive extraction (SBSE), and solid-phase microextraction (SPME) have all been successfully used to extract explosives from a solid or liquid matrix (49-53). Non-contact sampling methods include near-field, in which the explosive must pass through the instrument for detection, or stand-off, in which the explosive can be detected at a specified distance from the instrument.

Concentration of trace explosives can be completed through a variety of means and is typically necessary in the detection scheme for trace vapor detection as the vapor pressures of explosives are quite low (54,55). Commonly the sampling method is also

used as the concentration technique, as is the case with microcolumn SPE, SPE, and SPME (56-60). Depending upon the nature of the sample, direct sampling or headspace sampling may be necessary. SPE is often used for water samples, however, SPME and single-drop microextraction (SDME) are capable of both direct and vapor or headspace sampling. Concentration techniques like single- or double-sided membrane introduction (SS-MIMS or MIMS) are capable of collecting explosives from vapor, with SS-MIMS having a lower associated detection limit (61). While stir-bar sorptive extraction (SBSE) is only used for liquid samples, it is advantageous because the coating can be altered as needed for ideal extraction (52). As the name implies, a coating can be place on numerous items which allows for both vapor and direct sampling. Common coatings include: polydimethyl siloxane (PDMS), carbowax, or polyethylene glycol (PEG) (62,63). Contact surface sampling often uses Teflon strips, filter paper, or swabs to collect and concentrate the particles from the entirety of an object into a smaller area for testing.

Separation of the collected and concentrated material is most commonly performed via a gas or liquid separation technique depending upon the prior techniques used. Gas separation techniques separate the sample when it is in a gaseous state through the interaction with a column surface coating, the size to charge ratio, or the mass to charge ratio. Gas separation techniques for explosive detection include: gas chromatography (GC), ion mobility spectrometry (IMS), and direct injection mass spectrometry (MS). MS techniques can be further delineated by their ionization method into secondary ion MS (SIMS), desorption electrospray ionization (DESI), desorption atmospheric pressure chemical ionization (DAPCI), and direct analysis in real time (DART), for example. MS

separation techniques, in their most basic description, can be used to separate compounds by first ionizing the sample and then separating the ions based on their mass to charge (m/z). IMS functions similarly to MS but the IMS separation is dependent on size to charge and often the ions move as clusters.

Liquid separation techniques use a solvent system to separate the sample based on polarity and interaction with the stationary phase. Liquid separation techniques for explosives include: liquid chromatography (LC), high performance liquid chromatography (HPLC), thin layer chromatography (TLC), capillary electrophoresis (CE), and other electrochemical techniques like microelectromechanical systems (MEMS) and microcantilevers (64,65).

Once separated, the identification and quantification is then conducted using a detector. Depending on the state of the compound after separation, detection can be performed by detecting chemiluminscence (CL) using beads, thin films, nano-clusters, or quenching amplifying fluorescent polymers (AFP) (66,67). Optical techniques such as colorimetry, light detection and ranging (LIDAR), differential absorption LIDAR (DIAL), or ones based in spectroscopy like ultraviolet/visible (UV/VIS), infrared (IR), Fourier transformed infrared (FTIR), Raman, surfaced enhanced Raman scattering (SERS), surface enhanced resonance Raman scattering (SERRS), and laser induced breakdown spectroscopy (LIBS) also have current detection niches from contact samples (65,68,69). The previously mentioned laser based techniques are advantageous because the sample can be analyzed in any state (solid, liquid, gas). Depending upon the technique, the vibrational (IR, LIDAR, DIAL), light absorption (cavity ringdown spectroscopy), light shifts (Raman, SERS, SERRS), and light emissions (LIBS) can be

used for detection. Rather than exhibiting peaks or emission lines specific to the explosive itself, these laser based techniques provide structural and elemental composition information of the explosive. Colorimetry and chemiluminescence can also be used for in-place sampling and in such instances no concentration or separation technique is used. In place sampling using chemiluminescence can be achieved through luminol, which is a reagent that emits light around 425 nm when in the presence of $NO_2$ (67). Vaporization of a contact sample can be achieved and detected through the use of strobe, thermal, or acoustic (surface acoustic wave (SAW)) techniques.

Detection can also be achieved using non-contact means by performing stand-off or near field detection. Optical techniques previously described, along with photoacoustic and terahertz (THz) have been used successfully used for stand-off detection (70). Near field detection can be accomplished through gas separation, electrochemical, CL, spectroscopy, immunochemical techniques, or biosensors (67). CL is the emission of electromagnetic radiation (UV, visible, IR) resulting from a chemical reaction to detect the presence of nitro and nitrate groups present in explosive materials. This allows for a simple sample preparation while also allowing for sensitive detection (1-10 pg) in complex matrixes (67). The rudimentary principle of CL is used in thermal energy analyzers (TEA) in which nitric oxide and ozone form an excited species that emits light as it relaxes back to the ground state, Equation 2.

$$NO + O_3 \rightarrow NO_2^* + O_2$$

$$NO_2^* \rightarrow NO_2 + h\nu$$

**Equation 2. Chemiluminescence reaction of nitrogen containing explosives**

However, CL detectors have disadvantages in that they are only capable of detecting nitrogen containing explosives and lack selectivity. To combat CL's selectivity issues, the technique is often used in conjunction with a chromatographic technique.

Electrochemical detection of explosives is advantageous because it can be performed in the field with high sensitivity, selectivity, wide linear range, and low cost. These advantages are a result of the microelectronics and microfabrication which allow for the delicate detection of electricity changes during a chemical reaction. Depending upon the electroanalytical technique used, measurements can be made which correspond to current, potential, and charge. Since the nitro groups within nitroaromatic explosives easily undergo redox reactions, they are suitable for electrochemical detection. Typically the reduction of a nitroaromatic explosive occurs in multiple steps, the first being a reduction to the formation of a hydroxylamine and the second being the formation of an amine (67). Microcantilevers also take advantage of microfabrication as their premise of detection is based on the resulting displacement of the cantilever beam when an analyte adsorbed onto its surface. The surface is typically composed of a monolayer, polymer, metal oxide, or single-stranded DNA which can be used for selective adsorption. Depending upon the detector used the detection limits of trace explosives can range from the low parts per trillion (ppt) to grams or larger quantities. Published detection limits of various analysis techniques can be found in Table 3.

**Table 3. Published Detection Limits for Explosives Detection**

| | *LOD (pg)* | *LOD (ppt)* | *Reference* |
|---|---|---|---|
| ***Bioluminescence detector (BL)*** | | 0.25 | (71) |
| ***Field ion spectrometer*** | | 10 | (72) |
| ***Gas Chromatography/Electron Capture Detector*** | | 10 | (72) |
| ***Gas Chromatography/Mass Spectrometry*** | 0.001 | 100 | (72,73) |
| ***Lab on a chip High Performance Liquid Chromatography*** | | 215 | (74) |
| ***Chemiluminesence (CL)*** | | 1000 | (73) |
| ***Gas Chromatography/Surface Acoustic Wave*** | | 1000 | (73) |
| ***Nonlinear dependence of ion mobility*** | | 1000 | (73) |
| ***Thermo-redox*** | | 1000 | (73) |
| ***Amplifying Fluorescent Polymer*** | 0.001 | | (74) |
| ***Atmospheric Pressure Ionization/Time-Of-Flight Mass Spectrometry*** | 0.01 | | (71) |
| ***Ion Mobility Spectrometry*** | 0.05 | | (74) |
| ***Atmospheric sampling-glow discharge ion trap MS/MS*** | 0.5 | | (71) |
| ***Quadrupole ion trap-time of flight (QitTOF MS)*** | 0.9 | | (74) |
| ***Fluorescent*** | 1 | | (75) |
| ***Gas Chromatography/Chemiluminescence*** | 1 | | (73) |
| ***Gas Chromatography/differential ion mobility spectrometer*** | 1 | | (73) |
| ***Ion trap ion mobility spectrometer*** | 1 | | (73) |
| ***Infrared spectroscopy*** | 10 | | (71) |
| ***Electron-capture negative-ion Mass Spectrometry*** | 20 | | (71) |
| ***Gas Chromatography/Ion Mobility Spectrometry*** | 500 | | (72) |
| ***Color*** | 1000 | | (73) |
| ***Electrochemical*** | 1000 | | (75) |
| ***Piezoelectric*** | 10000 | | (75) |
| ***Spectroscopic*** | 1000000 | | (75) |

### 2.4.3 Biological Detectors

Biological detectors consist of any detector with an inherent biological driving force, which includes a wide range of organisms such as: canines, pigs, rats, bees, plants, and various microorganisms. Elephants and birds are also among the newest additions to the team of biological detectors. Similar to the other detection techniques, biological detectors represent a viable tool for presumptive detection and location of illicit materials, both bulk and trace. Depending upon the need, these biological detectors can provide rapid and direct responses or slow responses. Plants for example provide a slow detection response as certain plants may exhibit color or morphological changes when in the presence of an explosive (76). While other animal detectors can produce rapid trained responses such as swarming, sitting, or digging.

Great advances in the detection of trace explosives have been made over the years; however, the primary biological detection method continues to be the use of detection canines. Detection canines exemplify a rapid, real-time, illicit substance detector capable of working in a variety of environments (77). Canines have been used as a detection tool for centuries; however, they are more commonly used for military and/or law enforcement purposes. More recently, detection canines have been used in the detection of a variety of substances including: agricultural material, contraband (for example: cell phones, tobacco, alcohol, and prescription drugs), pests, and insects (78). Court cases, such as *U.S. v. Place* and *U.S. v. Race,* have challenged the validity of using a detection canine as a reliable substance detection tool in past years; nevertheless, the review article by Kenneth G. Furton and Lawrence J. Myers and the subsequent creation of the Scientific Working Group on Dog & Orthogonal detector Guidelines (SWGDOG)

have abated these concerns and scientifically validated that canines can be used to reliably detect the odors to which they are trained (77-80).

Previous studies have shown that canines primarily use olfaction to detect the odors of which they are trained (81,82). Although the exact mechanism of olfaction in the canines' nose is still under debate, it is accepted that canines possess unusually high olfaction capabilities which dominate over their use of sight for detection (82-84). Canines have an olfactory repertoire of approximately 1300 genes, containing nearly 20 times more olfactory receptors than humans, with an olfactory system designed for efficient sampling of inhaled molecules and odors. The numerous amount of olfactory receptors allows for canines to be trained on a diverse number of odors with enhanced sensitivity compared to humans (85).

Several theories of olfactory activation in the canine's nose have been proposed (85), however basic olfaction in canines begins with the odorants entering the olfactory system via sniffing (86). The shape of a canine's nose is crucial for olfaction as the eternal nares direct air flow for both the inhalation and expiration of air (87). This structure has three main advantages including the maintenance of the scent source as the expired air is directed back towards it, the expiration of air stirring up particles that can then be inhaled and detected, and creating an additional thrust which vectors the air toward the nares (87). The inspired air then flows through the nasal vestibule which humidifies and warms the air via the maxilloturbinate which filters and distributes the air within the lower respiratory tract. The olfactory portion of the nose is posterior to the respiratory tract and contains the ethmoturbinates which provide a large surface epithelium for odorant transfer (88). It is believed that the odorant then binds with

receptor proteins embedded in the phospholipid bilayer of the membrane. Three theories of odorant binding have been developed including vibrational, steric, and weak shape theory (89). The vibrational theory of olfaction identifies intramolecular vibrations such as stretching, scissoring, rocking, wagging, and twisting resulting in the detection of the odorant. In the steric theory of olfaction, detection can be described as a lock and key fit, in which the overall shape and size of the odorant is responsible for the initiation of the signal. The weak-shape theory is similar to lock and key, however, in this theory, only a portion of the odorant needs to bind for signal transduction. After, in a domino effect, the binding activates a G protein which activates adenine cyclase and converts ATP to cATP, a messenger that binds to a cyclic nucleotide-gated ion channel.

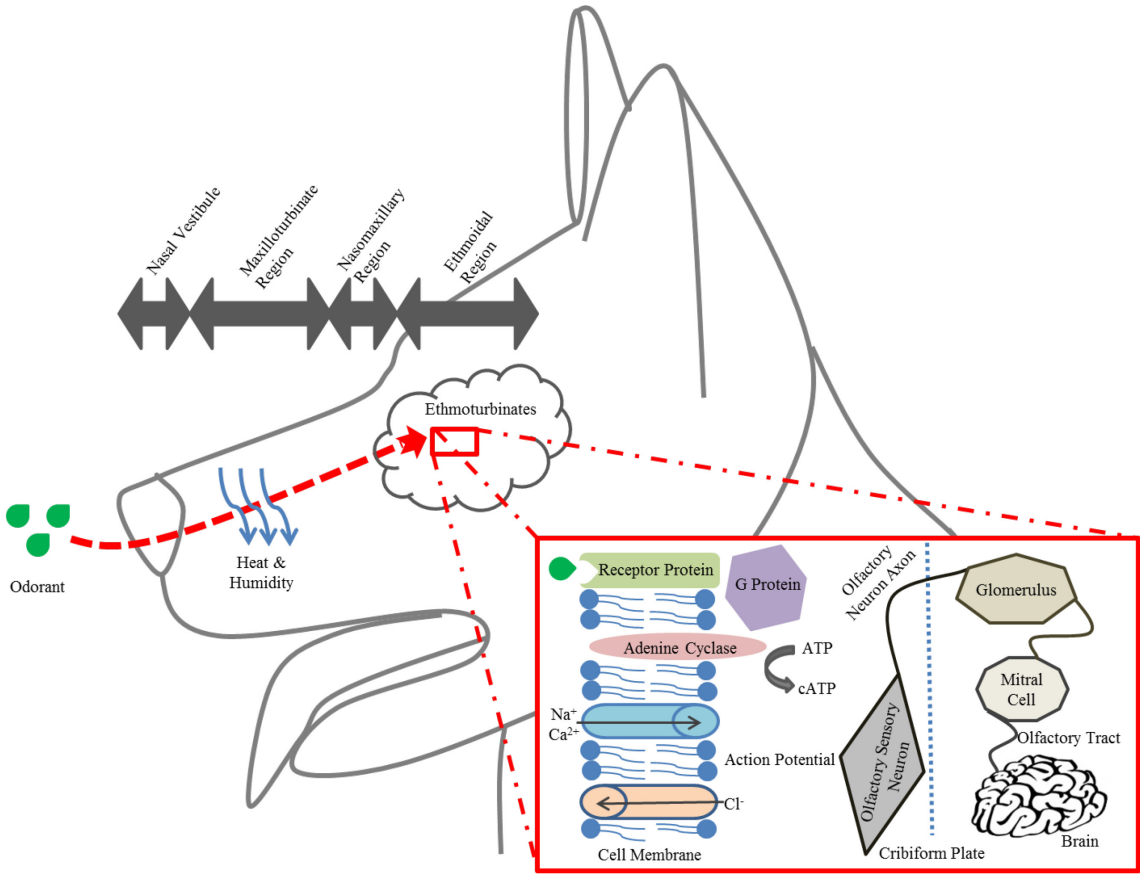



**Figure 8. Olfaction in the canine**

The arrival of free $Ca^{2+}$ and $Na^{+}$ cations at the cyclic nucleotide-gated ion channel increases the membrane potential resulting in the propagation of an action potential from the olfactory sensory neuron along the axon, through the cribiform plate, into the glomerulus and mitral cells, and finally through and olfactory tract which terminates in the brain where the signal is deduced (77,88,90). Multiple odorants are capable of activating a single olfactory receptor protein and single odorants have also been shown to activate multiple olfactory receptors, indicating that olfaction is a combinatorial process, allowing for canines to theoretically be capable of completing approximately one billion odor discriminations (91).

While canines can be trained to detect a number of odors, there is no universally accepted training method. In order for a canine to be trained to an odor, first selection of the ideal canine must be made. Four categories, designated by Panksepp, have been used to describe the emotion command systems of canines which closely correspond to the drives of a canine which can be used for selection of the ideal detection canine (92). These categories include: seeking, panic, fear, and rage. Drives in a canine cannot be learned, but are rather inherent motivational characteristics of the canine. Several drives seen in canines have been designated and include: hunt, prey, retrieve, air scent, tracking, rank, subordinate, pack, play, activity, fight, guard, protection, and survival (93,94). When selecting a canine for detection work, an ideal canine will have a high hunt drive to persistently search, a high prey drive to continue the chase, and a high play drive to retrieve and play with a reward after the task is complete.

Once the canine has been selected, an association between locating the desired material and receiving the reward must be established. Depending upon the organization,

the reward can be verbal ("Good boy"), physical (petting), a toy, or food. Multiple reward schemes can be used. The association between locating the desired material, an explosive, and receiving the reward is known as imprinting. There are two methods of imprinting. The first theory is the separation method in which all of the odors that the canine is to be trained on are kept separate throughout the entirety of training. This can be further subdivided into single compound training, in which the canine is imprinted on one individual odor for a specified time period with additional odors being imprinted one at a time in series, or multiple compound training in which the odors are kept separate, but the canine is imprinted on all of the odors separately at one time. In the combined odor method, the canines are initially imprinted on a "soup" of all of the odors where all of the odors are allowed to mix and then after a specified time period are separated. Once the odors are separated, they are never mixed again.

Once imprinted on the desired materials, the canines must perform regular maintenance training to maintain a satisfactory level of detection. While there are few commonalities within the detection canine training community, there is consensus between SWGDOG and the detection community that canines must be exposed to a variety of environments, scenarios, and material weights (78). Variety is necessary so that the canine will be able to perform reliably during an actual deployment scenario. For instance, if canines are only trained on large weights of material, they will develop a threshold for the substance and will likely miss lower weights of material, or vice versa. Varying the training environments and scenarios is necessary to familiarize the canine with multiple, potential deployment scenarios as the canines are known to perform better when they are working within their normal working parameters and comfort zone.

Varying the environment may also reveal potential limitations of the canine such as fear of slippery floors.

#### 2.4.3.1 Training Aids

While canines are capable of being trained to numerous odors, research has shown that canines typically respond to the most volatile compounds present in an illicit material (77,95,96). The observation has allowed for past researchers to determine the dominant odor signatures of various explosives (1,53,95,97). Dominant odor signatures are composed of the odor responsible for inducing an alert response in a detection canine, which may or may not be the explosive material. For example, it has been observed that canines will more commonly alert to 2-ethyl-1-hexanol, a plasticizer, rather than the explosive material (RDX) in plastic explosives (1,53,95,97). Knowledge of canine behavior has been applied to five classes of explosives, which has led to the development of a prototype surrogate explosives kit. The prototype surrogate explosives kit, manufactured by the International Forensic Research Institute (IFRI), is composed of the dominant odor compound for plasticized, TNT-based, nitroglycerin-based, and tagged explosives, as well as smokeless powders (1,5). The explosives kit is composed of non-controlled substance mimics, which exempts the kit from Alcohol, Tobacco, Firearms and Explosives (ATF) regulations and control. Validation of this explosives kit is therefore necessary for future implementation and standardization within the field.

Surrogate continuation aids (SCAs) can be defined as a training aid material used as positive controls for detection canine training and maintenance. Several types of SCAs have been developed over the years; however, the determination of an optimal design has

yet to be identified. Criteria for the ideal SCA include: inertness for safe handling, harmlessness to the canine, generation of detectable levels of key odorant(s) with high effectiveness relative to real explosives, and must possess a suitable longevity with minimal storage considerations. Three types of SCAs are currently available for use and purchase. The first is the actual illicit (explosive) material. These types of SCAs require an ATF license with strict adherence to protocols, are dangerous to maintain, difficult to obtain, and pose a health and security risk. When possible, explosives detection canines should be trained using these materials, however, great care must be taken when selecting explosive material for training. The reason for this is that several brands of explosives may only contain one energetic material and not all explosives class requirements put forth by SWGDOG may be met if the explosives are not selected carefully (78,90,98). The second type of SCAs uses highly diluted illicit material. In the case of explosive surrogates, these consist of explosives in a non-explosive state typically composed of a highly diluted energetic material mixed on a substrate (99-101). The diluted SCAs typically do not require an ATF license for use, however, there is limited scientific study on the effectiveness of these continuation aids and they can also be quite expensive to procure (3,102). The third type of SCA consists of mimics. This type of continuation aid mimics the odors associated with the illicit material while containing no illicit material, making them non-hazardous. Mimics can be produced in varied ways, but, the use of one such example, Controlled Odor Mimic Permeation Systems (COMPS) allows for a reliable, consistent, and controllable permeation of the odor (103). The prototype surrogate explosive kit currently employs COMPS for the odors mimicked within the kit.

The selection of the proper storage system is necessary for the maintenance of potency, efficacy, and functional integrity of canine SCAs as the cross-contamination of the SCAs are always of great concern. Currently canine handlers and trainers use a variety of containment systems (glass, plastic, cloth, etc.) for SCA storage; however, an in-depth and systematic study was required to determine the optimal containment system taking into consideration different factors that potentially play important roles in the potency, efficacy, and contamination ease of the SCAs. Maintenance of the integrity of the SCA odors is imperative to ensure standardization of training, increasing the reliability of the canine to detect the various illicit odors.

#### 2.4.3.2 Reliability

With the advent of the National Research Council's report: *Strengthening Forensics Science in the United States: A Path Forward*, in 2009, great concern and scrutiny has recently been placed on several disciplines of forensic science (104). While not directly addressed in aforementioned publication, the declaration of the shortcomings of other forensic disciplines was soon applied to detection canines as well. This realization was not novel, as the Scientific Working Group on Dog & Orthogonal detector Guidelines was formed in 2004 to improve the consistency and performance of detection canines for improved reliability, accuracy, and courtroom acceptance (78). SWGDOG has identified several areas of continued research in the document *SWGDOG SC7*: identification/quantification of target odorants, research on olfaction, and studies to determine which odorants are of particular interest (105). While SWGDOG has identified these areas of continued research, the effects of containment systems on odor availability

and the development of methods to monitor the levels of contamination of SCAs have been identified as critical research topics. While SWGDOG works diligently to produce best practices for detection canines, the SWG's greatest achievement also reveals its greatest downfall. Akin to the issues observed in the other forensic disciplines, the documents produced are merely best practice guidelines with no formal organization enforcing their use in the field. SWGDOG has been working meticulously to develop such an organization, but until the organization comes to fruition, there are few ways refute the growing concern over the reliability of detection canines.

The reliability of a detection canine has recently come under increased scrutiny as case law supports the use of well-trained animals; however, the determination for what constitutes a well-trained animal is vague (79,80). SWGDOG maintains that the reliability of the detection canine is defined by having a fair probability that the target odor is present while having a low probability of the canine alerting to anything other than the canine's trained odors (78). The reliability of the canine can further be demonstrated through the canine's training and deployment logs. However, even with the canine's deployment and training records, a true assessment of the canine's reliability can be difficult. Often in deployment, and even some training situations, a canine may alert where no illicit material has been placed. Frequently this alert is classified as an alert to residual odor indicating that the canine may have a very low false alert rate. However, there is little scientific backing to currently support such a claim, and while residual odor on a surface is not impossible in every instance, this belief has led to the common misbelief that detection canines are infallible. As per Justice Souter's dissent *in Illinois v. Caballes*, the belief that a detection canine is infallible is "a creature of legal fiction"

because there are a multitude of factors contributing to its reliability (106). This belief is further shown by Myers and the application of Bayes' Theorem which calculates that even proficient canines have relatively small probabilities of an alert response being a true alert (107).

## 2.5 Calibration of Detection Canines

Detection canines represent a valuable tool, however, unlike laboratory instruments; there are no set practices to ensure that a biological detector is working at a reliable and suitable standard on a daily basis. The deficit has led to the development of a Universal Detector Calibrant (UDC) for which the reliability of both biological detectors and instrumental detectors can be studied and improved (108). The development of a UDC has practical and legal benefits for both canine handlers/trainers and laboratory personnel. Similarly to the daily calibration of laboratory instruments, a UDC for which biological detectors can be calibrated would ensure the detector is working within acceptable limits, thus making the biological detector more like a laboratory instrument. As a result, the value of the detection canine's responses is further increased. Calibration, for this study, is defined as the process of measuring the actual quantity of odor the canine is detecting that corresponds to an indicated quantity on the scale of an instrument.

The implementation of a UDC will allow for the detection canine handler to have additional documentation detailing the daily working parameters of the canine including the number of alerts and misses allowing for the accuracy, robustness, and error rate of the canine to be determined in a more controlled setting. By determining these working factors, the detection canines' responses to their respective odors will withstand greater

scrutiny from the legal system. In addition their use will conform greater with Daubert rules for admissibility of scientific evidence (109). Upon training and implementation of the UDC into to the detection canine's daily routine, the resulting documentation will aid in the standardization of canine training, allowing for the comparison of detector canines spanning the detection categories, while simultaneously making detection canines as objective and reliable as a laboratory instrument.

## 2.6 Instrumental Analysis of Surrogate Continuation Aids (Within this study)

While several means of detection have been previously discussed within this study, headspace analysis using solid phase microextraction (SPME) coupled with gas chromatography with either electron capture or mass spectrometry detection was used to identify and quantify the odorant emanating from the samples. This detection scheme was selected as it has become known, peer reviewed, and accepted as an analysis techniques for explosives.

### 2.6.1 Solid Phase Microextraction (SPME)

Solid phase microextraction (SPME) was developed in 1990 by Janusz Pawliszyn as a rapid extraction technique that requires minimal sample preparation (110). SPME is a pre-concentration technique that is used to extract volatiles and semi-volatiles from a sample. Unlike other extraction techniques, SPME has found a niche in onsite testing as the device is a modified syringe making it portable. The SPME device, Figure 9, consists of a holder and the SPME fiber. The holder includes the plunger and barrel which are the mechanical workings that allow for the fiber to be exposed. The SPME fiber screws into the screw hub and is protected by the metal fiber sheath. Within the fiber sheath is the

fiber which is a 1 cm long solid fused silica rod coated with a polymer film. This configuration is advantageous because it allows for the direct insertion of the SPME fiber into a GC inlet for the desorption of the adsorbed or absorbed analytes. With only slight modification of the inlet, SPME can also be used in conjunction with IMS and HPLC (57,110). Automated SPME has also been developed in which a specialized autosampler hold and expose the fiber to the sample for a specified time controlled by instrumental software.

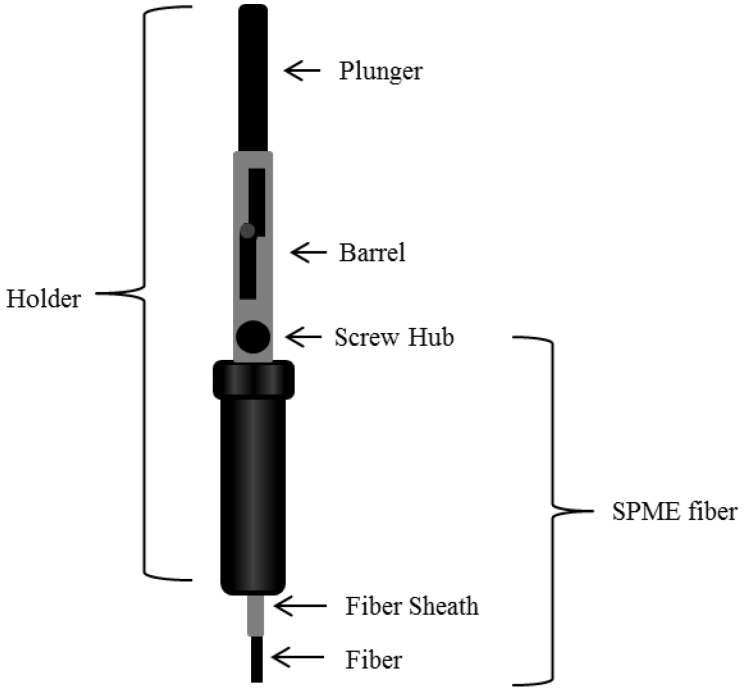



**Figure 9. SPME device**

There are a variety of coatings that can be placed on the fiber which allow for the selective absorption or adsorption of analytes of interest. Currently, Supelco is the only commercial provider of SPME fibers, developing six different fiber coatings in a variety of thicknesses, Table 4. As a general rule, the thicker the coating the more analyte will be

extracted. However, for large molecular weight compounds that have high distribution constants, a thin fiber coating is advantageous because migration in and out of the fiber is slow, thus larger compounds are better retained. Thin fiber coatings are also advantageous when a rapid extraction time is required, although, there may also be a reduction in the linear range. In addition to fiber thickness, SPME fibers can also be classified by polarity. SPME fibers come in three different polarities: nonpolar, bipolar, and polar. On the basis of the theory that "like attracts like," the polarity of the fiber typically defines its end use, with bipolar fibers being a relative catch-all when the sample is mixed. As a general rule, the more polar the fiber, the more rigid the coating, the longer the extraction time, and the hotter the desorption temperature.

The fiber's stability is determined by the coatings ability to crosslink and bond. Nonbonded coatings such as PDMS contain no crosslinkers, but are stabilized; however, they are not solvent resistant which causes swelling of the fiber in the presence of organic solvents. Nonbonded coatings are also less thermally stable resulting in lower possible desorption temperatures. More stable coatings contain crosslinking agents, which cause the coating to crosslink within itself. Crosslinked fibers are disadvantageous in that the coating, while crosslinked with itself, does not link to the fused silica core which may result in fiber stripping from swelling. To overcome these issues, bonded coatings have been developed which contain crosslinkers, but also bond directly to the fused silica core. This allows for the minimal swelling of the fiber even when exposed to organic solvents, good thermal stability, and thinner coating thicknesses.

**Table 4. Commercially available SPME fibers**

| Polarity | Coating | Stability | Sorption | Applications |
|---|---|---|---|---|
| Nonpolar | Polydimethylsiloxane (PDMS) | Nonbonded | Absorbent | Nonpolar and semipolar compounds: aromatics, esters, pesticides |
| Bipolar | Polydimethylsiloxane /Divinylbenzene (PDMS/DVB) | Crosslinked | Adsorbent | Moderately polar compounds: amines, nitroaromatics, volatiles, MW 50-300 |
| Bipolar | Divinylbenzene/ Carboxen/ Polydimethylsiloxane (DVB/CAR/PDMS) | Crosslinked | Adsorbent | Nonpolar and polar compounds, trace analysis, MW 40-275 |
| Bipolar | Carboxen/ Polydimethylsiloxane (Carboxen/PDMS) | Crosslinked | Adsorbent | Highly volatile compounds: vinyl chloride, sulfur gases, MW 30-225 |
| Polar | Polyacrylate (PA) | Crosslinked | Absorbent | Polar compounds: phenols, esters, MW 80-300 |
| Polar | Polyethylene Glycol (PEG) | Crosslinked | Absorbent | Polar compounds: alcohols |

The different SPME coatings are capable of collecting the analytes of interest via absorption or adsorption, Figure 10. If the coating is absorptive, then the analyte of interest will go into the coating. Coatings that are adsorptive do not internalize the analyte, but rather collect the analyte on the surface of the coating. Adsorptive coatings may also function with pores which increase the collection surface area. Micropores are the smallest of the pores, with mesopores being slightly larger, and macropores having the largest size of the pore structure, Figure 10. The shape and size of the pore affect the

adsorption and desorption times as the analytes must first enter the pore and then exit the pore. This activity is known as throughput. Pores with low throughput do not readily adsorb and desorb, making carryover of the analyte to the next sample a concern. Low throughput often occurs if the analyte condenses within the pore, known as hysteresis. This often occurs with midsize volatiles that get trapped in the mesopore section of tapered pores. Adsorptive fiber coatings with low throughput may also result in peak tailing as the analytes do not instantaneously desorb off the fiber, however, this can be overcome by raising the desorption temperature.

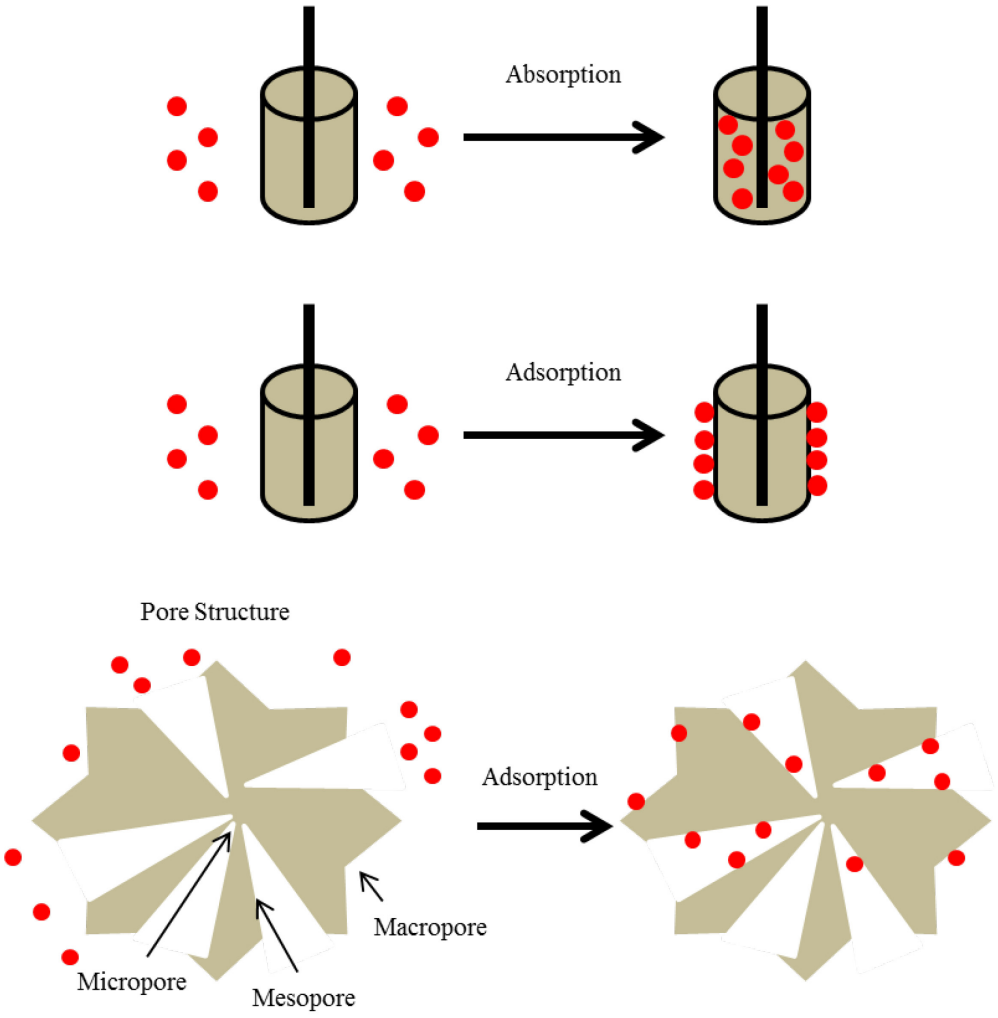



**Figure 10. Types of analyte sorption**

Regardless of the fiber coating, the basic theory of SPME involves two steps. In the first step the analytes partition between the sample and the fiber coating with the second step allowing for the now concentrated analytes to desorb off of the fiber and into an instrument. The partitioning of analytes from the sample to the fiber coating occurs due to the fact that SPME is an equilibrium technique that can be used to non-exhaustively extract analytes from the sample. Within a closed vial, the SPME extraction occurs on the overall equilibrium of the three phases. The first phase is the equilibrium between the fiber coating and the aqueous phase of the sample. The second phase of equilibrium occurs between the headspace and the aqueous phase. The third and final phase is the equilibrium formed between the fiber coating and the headspace. As the concentration of the analyte does not change during the extraction, the distribution of the analyte between the phases can be seen in Equation 3.

$$C_o V_s = C_h^{\infty} V_h + C_s^{\infty} V_s + C_f^{\infty} V_f$$

**Equation 3. Equilibrium distribution in SPME. Where $C_o$ is the initial concentration of analyte in solution, are the equilibrium concentrations of analyte in the headspace, solution, and fiber coating, respectively; and $V_h$, $V_s$, and $V_f$ are the volumes of the headspace, solution, and fiber coating respectively (110)**

The partitioning coefficients between the three equilibria can be seen in Figure 11. In the instance of direct liquid sampling, $K_{fs}$ represents the distribution constant between the fiber coating ($C_f$) and the aqueous phase ($C_s$) which describes the fiber coatings selectivity towards an analyte. The partition ratio (k') describes the relationship between the amounts of analyte in the fiber coating compared to the solution, Equation 4.

SPME gains its sensitivity since the $K_{fs}$ values are quite large for targeted organic analytes.

$$k' = \frac{C_f V_f}{C_s V_s} = \frac{n_f}{n_s} = K_{fs} \frac{V_f}{V_s}$$

**Equation 4. Direct liquid SPME partition ratio. Where $n_f$ and $n_s$ represent the number of moles in the fiber coating and solution, respectively; and $V_s$, and $V_f$ are the volumes of the solution, and fiber coating respectively (110)**

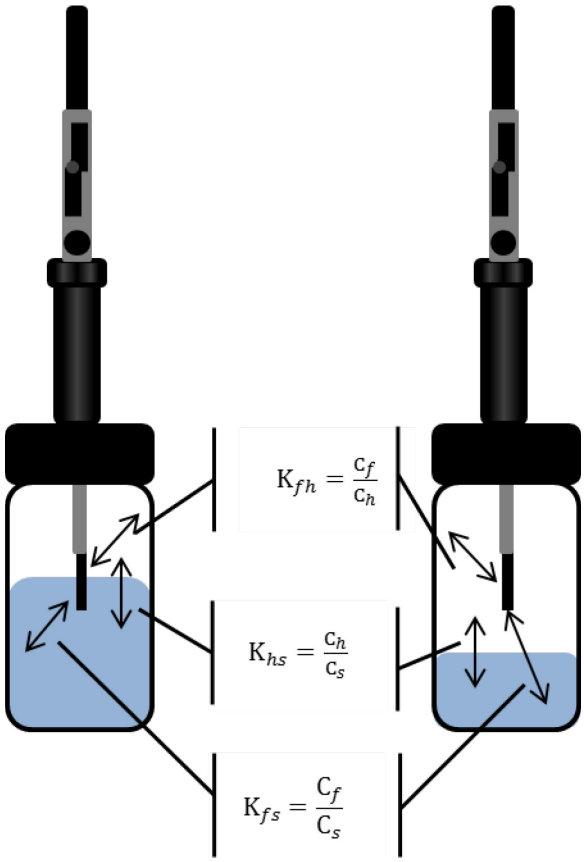



**Figure 11. Partitioning coefficients observed with SPME sampling**

Depending on the sample volume, the equations representing the number of moles of analyte extracted by the fiber coating varies, Equation 5.

$$n_f = K_{fs} V_f C_o \quad \textbf{(a)}$$

$$n_f = \frac{K_{fs} V_f V_s C_o}{K_{fs} V_f + V_s} \quad \textbf{(b)}$$

**Equation 5. Determination of the amount of analyte absorbed by the SPME fiber using direct sampling. (a) When the volume of the sample ($V_s$) is significantly larger than the volume of the fiber ($V_f$) the equation can be reduced. (b) in the instance where the sample is finite, the amount of analyte collected by the fiber is dependent upon the distribution constant ($K_{fs}$), volume of the fiber ($V_f$), volume of the solution ($V_s$), and the initial solution concentration ($C_o$)**

Similar to direct liquid sampling, headspace SPME maintains the three phase equilibrium between the fiber and the headspace ($K_{fh}$), solution and the headspace ($K_{hs}$), and fiber and the solution ($K_{fs}$), Figure 11. Therefore the amount of analyte absorbed onto the fiber is represented by Equation 6.

$$n_f = \frac{K_{fs} V_f V_s C_o}{K_{fs} V_f + K_{hs} V_h + V_s}$$

**Equation 6. Determination of the amount of analyte absorbed by the SPME fiber using headspace testing where the amount of analyte collected by the fiber is dependent upon the distribution constants between the fiber and solution ($K_{fs}$) and the headspace and the solution ($K_{hs}$); volume of the fiber ($V_f$), volume of the solution ($V_s$), volume of the headspace ($V_h$); and the initial solution concentration ($C_o$)**

From these equations, at equilibrium, the amount of analyte extracted by the fiber is independent of the sampling location (direct immersion or headspace). Therefore as long as the SPME fiber retains the same thickness of fiber coating throughout the experiment the detection limits are maintained for both direct immersion and headspace sampling.

### 2.6.2 Gas Chromatography

Gas Chromatography (GC) was first developed in 1941 by Martin and Synge and uses a gas as the mobile phase to separate analytes as they partition in and out of the stationary phase (111). While it was developed in the 1940s, GC did not garner widespread use until the 1950's when its resolution, selectivity, and sensitivity were proven to be reliable. The design of a typical GC can be seen in Figure 12, where the carrier gas enters the system at a defined flow rate determined by a flow regulator. The sample is then introduced into the system in the inlet where it mixes with the carrier gas and enters the column. Once in the column, the analytes separate and are then detected using a detector.

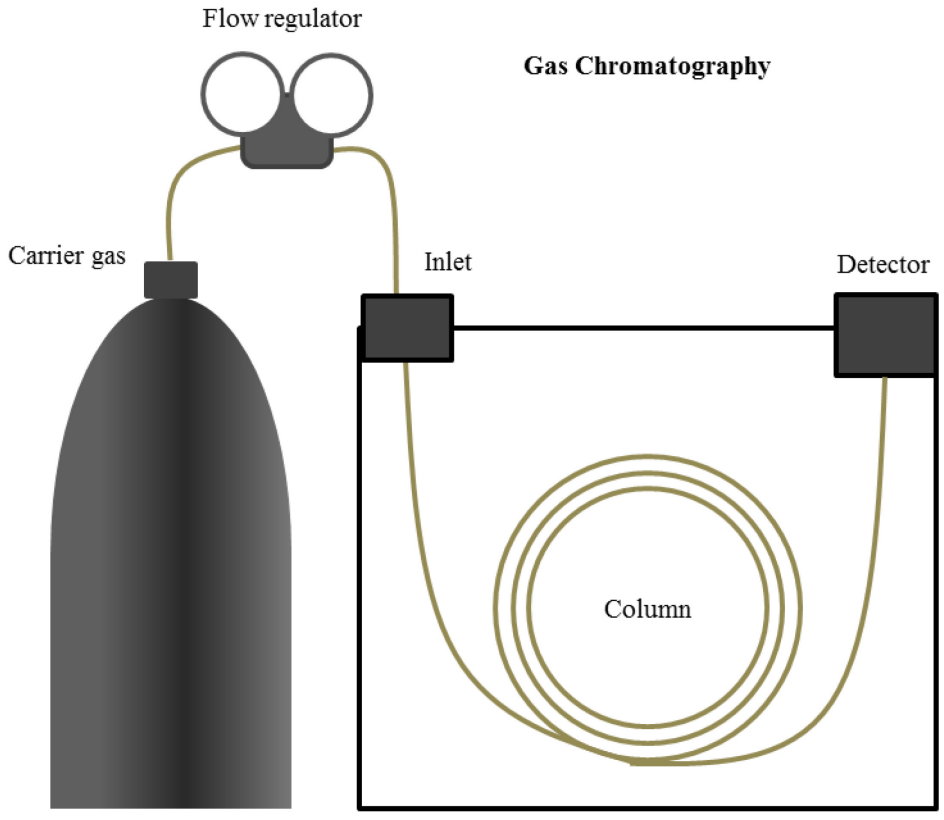



**Figure 12. Diagram of a GC**

The mobile phase (carrier gas) in GC is a gas that is preferably nonreactive, non-flammable, and inexpensive. Taking into account these considerations and the fact that the gas can influence the resolution through its effect on column efficiency determining solute diffusion rates, helium, hydrogen, and nitrogen are among the most popular mobile phases selected for GC. Selection of the carrier gas can be determined by looking at the van Deemter curves for the various gases. At high flow rates, helium and hydrogen perform better with only minor losses in efficiency. However, nitrogen as the carrier gas has the most efficient separations, but a slower flow rate resulting in longer analysis time. A delicate balance must be maintained between efficiency and flow rate so that an optimal separation is achieved in the shortest amount of time.

The inlet is where the sample is introduced into the system. There are three different injection modes including: split, splitless, and on-column. The ideal inlet will have the sample delivered to the column reproducibly, provide instant and complete volatization to increase surface area, produce no decomposition of the sample upon injection, ensure that the sample enters the column in a tight plug, and assure that the sample does not overload the column resulting in ghost peaks. A split injection uses a very fast flushing to allow for only a small amount of sample to enter the column. The split can be designated such that a predetermined amount of sample will enter the column. The use of a split, however, can increase the error associated with the analysis as it is not always accurate. Split injections use a high temperature to volatilize the sample within a non-reactive liner for the best injection parameters. An ideal split injection must also be linear without any discrimination of the sample entering the column based on molecular weight.

A splitless injection is ideal for trace analysis because the entirety of the sample will enter the column, typically one to two microliters of a very dilute sample. Ideal splitless injection occurs when the injector is hot (to volatilize the sample), but the column is cold (to create a tight plug of sample entering the column). Splitless injections should not be performed with concentrated samples because it can damage the column and create ghost peaks. Cold on-column injections require a special needle which is directly inserted into the column. This type of injection is ideal for analytes which are thermally liable and may decompose in the other injection modes.

The stationary phase or GC column determines the selectivity and efficiency of the separation. The oldest GC columns had stationary phases were liquid stationary phase coated into an inert material and packed into a column. Packed columns were eventually replaced by open tubular columns (capillary columns) which have more efficient separations. With open tubular columns a general rule is that, as the sample capacity increases, the film thickness increases, but the efficiency decreases. There are three different types of capillary columns that are designated by the way the stationary phase is placed in the column. Wall-coated open tubular (WCOT) columns are capillaries coated with a thin layer of stationary phase. Support-coated open tubular (SCOT) columns are liners with a thin layer of support material, such as diatomaceous earth, which allows for a higher sample capacity. The most common capillary columns are fused-silica wall-coated (FSWC) which have much thinner walls than WCOT columns. FSWC columns are coated in a polyimide coating, which allows for them to be flexible and can be curved allowing for much longer column links as the column can be coiled.

The selection of film coating used as the stationary phase includes the following parameters: low volatility with a boiling point ideally 100°C higher than the maximum operating temperature, thermal stability, chemical inertness, and provide suitable resolution for the analytes of interest (111). For resolved analyte peaks, the distribution constants must be different for the analytes, but not so different that the elution time of the analytes is excessively long. Similar to SPME, the selection of the coating can to be reduced to "like attracts like," therefore the best analyte separations can be achieved when the stationary phase has a similar polarity to the analytes. Polar compounds can be easily separated by coatings functionalized with –CN, -CO, and –OH groups, whereas hydrocarbon and dialkyl siloxane groups are ideal for nonpolar separations. For samples containing analytes of mixed polarity, portions of the methyl groups in the polysiloxanes can be replaced with phenyl groups to increase the polarity of the column.

### 2.6.3 Detectors

Once separated in the GC, the analytes are then detected by a detector. Instrument specific, a wide variety of detectors can be coupled to a GC, however, mass spectrometry (MS) and electron capture detectors (ECD) are commonly used for explosives detection.

#### 2.6.3.1 Mass Spectrometry

Mass spectrometry (MS) found its first application in the 1940s for petroleum analysis. Since then MS has become a widely accepted analytical technique because it provides information about the elemental composition of a sample, structure of the molecules, qualitative and quantitative composition of mixtures, structure and

composition of solid surfaces, and isotopic ratios of atoms in samples. MS occurs in three basic steps: ionization of the sample, separation of the ions, and detection of the ions.

Ionization of the sample can be described as hard or soft. Hard ionization techniques result in the transfer of a large amount of energy to the analyte resulting in the analyte entering a highly excited state. As the analyte relaxes, bonds within the molecule break producing fragment ions with a mass to charge ratio lower than that of the molecular ion (ion corresponding to the actual molecular weight of the molecule). Hard ionization results in a multitude of fragments produce that give valuable structural information as the bonds break in fairly predictable manners. Soft ionization techniques impart less energy into the molecule resulting in ionization of the sample, but little or no fragmentation. Soft ionization techniques are advantageous because they can give accurate mass information associated with the molecule being analyzed. Examples of ion sources include: electron impact, chemical ionization, field ionization, field desorption, electrospray ionization, matrix-assisted desorption-ionization, plasma desorption, fast atom bombardment, secondary-ion mass spectrometry, and thermospray ionization.

Once ionized, the sample is then separated in a mass analyzer. While there are a variety of mass analyzers, the basic functions of the mass analyzer are the same. The ions enter the mass analyzer through an inlet which allows for only a small amount of the sample to enter in its gaseous form. Depending upon whether the mass analyzer is run in negative or positive mode, the desired ions will then be accelerated into the mass analyzer and separated base upon their mass-to-charge (m/z) ratios. This separation is obtained because the interaction between the ions and magnets/radio frequencies or alternating currents which are specific to the mass analyzer. The separation of ions

requires a vacuum, $10^{-4}$ to $10^{-8}$ torr, to reduce the number of possible ion collisions with atmospheric components, which would convolute the spectra. Examples of a few commonly used mass analyzers are: quadrupoles, time-of-flight, and ion traps. Within the present study a quadrupole mass analyzer with an electron impact ionization source was used for the ionization and separation of the samples.

In some instances, rather than the separated ions moving into the detector, tandem MS or $MS^n$ is used to provide additional conformational information about the analyte of interest. In $MS^n$ experiments, the sample is ionized and the ions are separated. An ion or ions with specific m/z ratios are then selected for further fragmentation. These selected ions, or parent ions, enter a collision cell where additional energy is added resulting in bond breaking. The new ions, daughter or secondary ions, then reach the detector. $MS^n$ experiments are capable of giving a wealth of structural and confirmatory information as known energies are imparted unto the parent ions, resulting in predictable fragmentation patterns.

Once ionized and separated, the ions must then be detected and produce a consumer read-out of the information. Most detectors accomplish this task by converting the ion beam into an electrical signal which can be processed and then turned into a chromatogram and spectra read-out on the computer. Similar to the separation portion of the mass analyzer, the detector must also be under vacuum to reduce the frequency of atmospheric collisions. The ions first enter the detector through a slit, which is specifically set such that only a select range of m/z ratios are detected. The ions then hit the surface of the detector, which produces electrons that are sequentially multiplied into an electrical signal. These detectors are known as electron multipliers and typically use

discrete-dynode electron multipliers or continuous-dynode electron multipliers (electron horns). Additionally, detectors can be arranged such that only a small and specific m/z ratio is detected through either the use of a faraday cup, which is placed in the flight path of the selected ions, or with an array detector, which uses multiple faraday cups or microchannel plates to detect multiple resolution elements.

#### 2.6.3.2 Electron Capture Detector

Electron capture detectors (ECD) are highly sensitive and selective detectors used for the detection of electronegative compounds. An ECD functions through the use of a radioactive source, commonly nickel-63, which is a constant β emitter. The β emission interacts with a carrier gas, such as nitrogen, which results in the production of electrons which are then detected. Since the carrier gas and source are constant, a steady stream of electrons is produced creating a baseline signal. When an electronegative sample enters the detector, the electrons produced from the carrier gas are captured by the sample resulting in a drop in the output signal. Since only compounds such as halogens, peroxides, quinones, and nitrogroups readily capture electrons, an ECD is both selective and sensitive. However, one disadvantage of the detector is that the linear response of the detector is limited to about two orders of magnitude because the detector measures a drop in the signal, which can only go so low. This can be slightly overcome by pulsing the detector, however, the sensitivity is only ideal for trace samples. While an ECD is ideal for explosives detection, known standards must be used since the computer generated output has peaks with only retention time information causing issues with co-eluting interferences. Therefore, with the recent improvements in MS, ECD is commonly used as

a presumptive identifier and the presence or absence of a compound is confirmed using MS.

## 2.7 Research Objectives

The main objective of this research is to improve detection canine handling and training through the use of scientifically validated surrogate continuation aids and the employment of a calibration compound. The content of this report discusses the laboratory and field testing performed. Six different tasks were designated for the completion of this project starting with the development of a universal detection canine standard compound for calibration. This compound will aid in the standardization between detection canines through the careful selection of an ideal compound which meets the designated mandatory and desirable qualities. Through laboratory, field testing, and finally implementation into the field, the calibration compound will in theory make the detection canine as objective as a laboratory instrument. The second task focused on the development of a surrogate continuation aid for peroxide based explosives. Peroxide based explosives are the IED of choice since they can be easily prepared using common household chemicals. By testing the headspace of various peroxide based explosives samples a surrogate continuation aid can then be developed and tested. By creating a training aid that is composed of non-controlled and non-explosive chemicals, the training aid can safely be implemented into the daily training regimen of the canine.

A prototype surrogate explosives training aid kit has already been developed for detection canine training which covers five classes of explosives. This kit needs validation of its reliability and usefulness so that it can be deemed a reliable training

alternative. Validation of the kit will occur through a series of canine trials using trained and untrained detection canines. The last test within validation of the prototype surrogate explosives kit was a comparison test in which the training aids within the kit were compared to other commercially available training aids and their effectiveness was evaluated using canines. The next task was the determination of the optimal storage parameters of the surrogate continuation aids within the prototype surrogate explosives kit. By evaluating a variety of containment vessels, an optimal containment scheme was developed to reduce the potential for contamination.

Since the bulk of this research focused on detection canines, a comparison of the currently used imprinting method was conducted to determine the optimal training protocol for detection canines. Through field testing and imprinting of the detection canines, a reliable evaluation was made between the two training methods such that a recommendation can be given to canine trainers. Finally, the last task was the determination of the optimal type of surrogate continuation aid. By comparing various commercially available surrogate continuation aids, a recommendation of the best training aid option can be given to canine handlers.

# 3 TASK 1: THE DEVELOPMENT OF A UNIVERSAL DETECTION CANINE STANDARD COMPOUND FOR CALIBRATION

## 3.1 Introduction

This study presents the development of a Universal Detector Calibrant (UDC) for which the reliability of biological and instrumental detectors can be studied. Training a biological detector to alert to a safe, non-target, rare compound before each working day provides the handler with documentation detailing the working parameters of the canine, allowing for the canine's responses to withstand greater scrutiny from the legal system. The handler will be able to provide documentation that the detection canine was working within acceptable limits when the tests were completed, thus making the detection canine as objective and reliable as a laboratory instrument. Several compounds meeting the selection criteria have been tested and the best potential calibration compounds are compared in the present study. One compound, 1-Bromooctane, has met the selection requirements of the study and has been chosen as the compound with the greatest potential for use as both a biological and instrumental calibrant. In order to complete this task, several sub-tasks were determined including: the determination of mandatory and desired qualities, compound selection process, laboratory testing, field testing, development of a final training aid device, and implementation into daily detection canine training.

## 3.2 Materials

Potential calibration compounds selected in this study include: Perfluorotributylamine (Supelco, Bellefonte, PA), Perfluorooctyl bromide (Matrix

Scientific, Columbia, SC), 1-Bromooctane (Sigma-aldrich, St. Louis, MO), and Perfluoro-n-heptyl iodide (Matrix Scientific, Columbia, SC). Gauze pads used were IMCO Sterile Gauze Sponges 2x2, 8-Ply (Independent Medical Co-op, Daytona Beach, FL).Polymer bags (Veripak, Atlanta, GA), Barrier Foil Ziplock bags (Ted Pella, Inc., Redding, CA), and glass vials (Supelco, Bellefonte, PA) were purchased.

## 3.3 Methods

On the basis of the selection criteria, a method for potential compound selection was developed. The first step was a comprehensive literature search. Literature searches were performed to determine potential calibration compounds previously used in the literature that may meet the selected requirements. Literature searches were also used to determine the chemical properties of potential calibration compounds as related to the selection requirements. Literature searching of the potential UDCs was a continuous tool used to narrow potential calibration compounds throughout the entirety of the selection process. The second step was to determine if the potential UDC is readily available. Further investigation on the availability of purchasing the potential UDCs was then conducted to determine if the compound could be purchased directly, purchased through special order, manufactured only in house, or has no published synthesis route. Compounds easily and affordably obtained were selected for further investigation. The third step was the determination of health hazards posed by the potential UDC compounds. Health hazards posed to the biological detector and the handler are of the greatest concern and are one of the first qualities of the UDCs that are taken into consideration when making the selection. Compounds were selected for further testing if

they were classified only as irritants with no special handling or disposal requirements. The next step was the determination of the scarcity of the potential UDC in the environment. The UDC must be rarely seen in the environment to ensure that when the canine alerts, it is not alerting to a commonly seen environmental odorant. Compounds were selected such that they had very few environmental uses. As it is impossible to test all potential UDCs, perfluorotributylamine (PFTBA), perfluorooctyl bromide (PFOB), 1-bromooctane (1-BO), and perfluoro-n-heptyl iodide (PFHI) were selected for further testing.

Headspace sampling analyses were performed at equilibrium using 100µL of headspace gas injection or solid phase microextraction (SPME) fibers (Supelco, Bellefonte, PA). Gas chromatography/mass spectrometry (GC/MS) analyses were performed on the four potential UDC compounds (PFTBA, PFOB, 1-BO, PFHI). GC/MS analysis was performed using an Agilent 6890N GC coupled to a 5973Network mass selective detector (Santa Clara, CA) with an HP-5 MS 30m x 250µm x 0.25µm phase thickness capillary column and a helium flow rate of 1 mL/min (J&W Scientific; Rancho Cordova, CA). HP Chemstation was used for instrument control and data analysis. GC separation parameters were as follows for direct headspace injections: the injector port was maintained at 250 °C; all runs were performed with a 10:1 split ratio; and a solvent delay of 0 min was used. An initial oven temperature of 40 °C was held for 2 min, the temperature was then increased to 250 °C at 20 °C/min, and held for zero minutes. GC separation parameters were as follows for SPME injections: the injector port was maintained at manufacture's specifications for SMPE fiber injections; all runs were performed with a 50:1 split ratio; and a solvent delay of 2 min was used. An initial oven

temperature of 70 °C was held for 2 min, then increased to 115 °C at 5 °C/min, increased to 240 °C at 20 °C/min, and held for zero minutes.

Potential delivery devices were manufactured using Controlled Odor Mimic Permeation Systems (COMPS) (103). Devices were constructed via placing a known amount of selected calibrant into a permeable device. Devices include: polypropylene (PP) bags, low density polyethylene (LDPE) bags (4 mil and 2 mil thicknesses), 4 mL glass vials with PTFE/Teflon septa, and 4 mL glass vials with 4mil LDPE septa. The dissipation rates were determined though gravimetric analyses whereby the weights of the COMPS were recorded over a series of days. Replicates along with corresponding blanks were constructed for each potential delivery device. Laboratory testing of the selected calibrant was performed to determine the compound's stability and if a constant permeation rate of odorant could be achieved. Both gravimetric and GC/MS measurements were used to make the aforementioned determinations.

Field testing of the first generation delivery devices were completed under the direct supervision of an International Forensic Research Institute (IFRI) canine trainer and conformed to SWGDOG best practice guidelines (78). The delivery device was hidden within a search pattern that fell well within the test canines capabilities. The detection canine teams were asked to perform a search of the requested area and the responses were recorded. Training the detection canines to the UDC was completed using an IFRI certified trainer following their standard operating procedure (SOP) for imprinting canines on new odors. Once the canine trainer ascertained that the detection canine was imprinted on the UDC odor, the UDC was then placed out for confirmation using the search previously described. Additional canine tests were performed in the same manor

described for field testing of the second generation UDC delivery devices. Implementation of the final delivery devices were then put into daily training practices. Training records were collected from the agencies and analyzed. A current Institutional Animal Care and Use Committee at Florida International University approved protocol was used for all detection canine testing. All canines within this study were maintained by local police departments.

## 3.4 Results

Selection of the proper UDC is integral for proper calibration. UDC compound selection is determined on the basis of a dozen selection criteria including both mandatory qualities and desirable qualities. Mandatory qualities include: (1) The UDC must pose minimal health hazards to canine and handler team. Since the calibration compound will be used daily, it must pose no danger to both the handler and canine, limiting the compounds to those having no or minimal health hazards as determined by the chemical's Material and Safety Data Sheet (MSDS). UDCs were deemed potentially acceptable for selection if they are classified only as irritants with no special handling or disposal requirements. (2) The UDC must be stable. Since the UDC has the potential to be used daily, it therefore needs to remain essentially the same from day to day to provide reliable results. The UDC should have a long half-life to ensure that the detector is training on the parent compound and not a decomposed product. Also, the UDC should be thermally stable over a range of temperatures as most biological detectors are not trained in climate controlled situations. In addition not all delivery devices are stored in strictly climate controlled situations, making compounds which breakdown at high or low

temperatures unsuitable. The calibration compound preferably has 1 to 20 carbon atoms and can be linear or branched to keep within the required vapor pressure and ideal boiling point. In some cases, the calibration compound is halogenated with at least one halogen, and more preferably with two or more halogens for ease of detection. (3) The UDC must be scarce in the natural environment. The UDC must be rarely seen in the environment to ensure that when the canine alerts, it is not alerting to a commonly seen environmental odor. (4) The UDC must be a non-target odorant for biological detectors. The UDC must be unique for all detectors to ensure there is no cross detection between classes of biological detectors. For example, If the UDC was found to be an odorant that explosive detection canines use to determine the presence of an explosive, but a narcotics detection canine is trained to the same calibration compound, every time the narcotics detection canine alerts it could be a drug or potentially and explosive. (5) The UDC must be detectable by biological detectors (i.e., detection canines can be trained to detect the UDC). The main purpose of the UDC is for its use with biological and instrumental detectors. Therefore, biological detectors must be able to be trained to alert to the odor of the compound. Compounds with odorants that the biological detector cannot distinguish from a community of additional odorants or ones that the biological detector does not alert to are unsuitable as a UDC. (6) The UDC must be readily available or conveniently prepared. The UDC should consist of a chemical that is easily obtained or readily manufactured. Compounds not readily available or ones having specialized manufacturing processes are not appropriate as universal calibration compounds because they pose additional and unnecessary challenges in the development of the delivery device. (7) The UDC must be volatile. Compounds are commonly classified as volatile,

semi-volatile, and non-volatile based upon the compound's vapor pressure. Compounds designated as volatile are selected as potential UDCs because they will readily move into to the gaseous state making the compound available for detection. The calibration compound preferably has a vapor pressure of at least $10^{-7}$ mmHg and/or a boiling point of less than 325°C. (8) The UDC must have low chemical reactivity. Compounds should be selected such that they have low chemical reactivity, allowing for few limitations on the delivery device manufacturing parameters, storage parameters, and testing and training parameters. For example, a compound that is highly corrosive to the delivery device or causes corrosion/damage/discoloration to surfaces that it comes into contact with would not be a suitable UDC because an optimal UDC should have few limitations on how and where the compound is placed.

Desirable qualities include: (1) the UDC should be readily detected instrumentally. Since the compound is intended to be universal, it should be easily detected instrumentally as well as biologically. The UDC should be selected such that it has a capacity factor indicating an optimal separation with no sample preparation. An optimal UDC should be detectable on a variety of instrumental detectors and preferentially should have a distinct mass spectral fragmentation pattern if mass spectral detection is used. For quantification, the UDC should be selected such that it is easily dissolved in common solvents which pose little health hazard to the laboratory personnel performing the test. (2) The UDC should be affordable. Budgets are always a concern with any organization, so a compound which can be purchased in bulk for a reasonable price to make a large number of delivery devices is desirable. (3) The UDC should be detectable by other animals including humans. Selection of a compound that is odiferous

is a desirable quality because it adds one more stage of quality control. For example: If the trainer placing the aid notices a change in the odorant, or lack of the odorant in the delivery device, he/she can discard the aid and place a fresh aid out for training, whereas if the aid is odiferous only to canines, the trainer may not recognize if the aid has lost potency. (4) The UDC should be able to provide a consistent rate of odorant. The UDC must permeate at a constant rate, through selection of the compound itself or through the manufacture of the delivery device, to provide a standardized delivery device that can reliably and reproducibly permeate a known rate of odorant over the lifespan of the delivery device.

Completion of literature searching revealed some potential UDCs in the field. For example, n-amyl acetate was used as a threshold determination compound and perfluorotributylamine (PFTBA) was used as a calibration standard to compare biological detectors and instruments (112-114). Upon completion of the initial literature searches performed for compound selection, it was found that several compounds have potential as UDCs and are readily available. Using the available Material and Safety Data Sheets (MSDS), the health hazards of the potential UDC compounds were determined. Several classes of compounds were found to meet the requirements at this stage including, but not limited to: halogenated alkyl compounds, halogenated aryl compounds, halogenated vinyl compounds, thiols, ethers, epoxides, ketones, esters, or aldehydes. Several potential UDCs were eliminated as options after determining the prominence of the compound in the environment since literature searching revealed they had several environmental uses increasing the likelihood of false alerts in the field. This round of selection allowed for a

smaller set of compounds to be selected for further analysis. The environmental uses of a select few potential UDC compounds can be found in Table 5.

**Table 5. Potential UDC compounds and environmental uses**

| Compound | Environmental Use | |
|---|---|---|
| ***n*-amyl acetate** | Cements and glues<br>Lacquers and paints<br>Flavoring<br>Perfume<br>Nail enamels | Paper coatings<br>Leather finishes<br>Textile sizing and finishes<br>Printing compounds<br>Photographic film |
| **Perfluorotributylamine (PFTBA)** | Mass spectral calibration compound<br>Blood substitute<br>Cooling agent for small transformers | |
| **Perfluorooctyl bromide (PFOB)** | Blood substitute<br>CT, MR, ultrasounds contrast medium<br>Partial liquid ventilation | |
| **1-bromooctane (1-BO)** | Solvent used for organic syntheses | |
| **Perfluoro-n-heptyl iodide (PFHI)** | Organic synthesis reactions | |

Direct headspace testing was performed to determine the ease in which a common GC/MS could detect the potential UDCs (115). All four compounds tested were found to be instrumentally detected (Figure 13-Figure 16), however, PFTBA, PFOB, and PFHI had retention times falling within a typical solvent delay and capacity factors indicating poor separation on an HP-5 MS column. On the basis of the retention time, $R_t$=7.400 min, and capacity factor, k'=4.04, 1-BO was the only compound selected to move forward through the selection process. A SPME fiber study was performed, in triplicate, to determine the optimal SPME fiber for sampling 1-BO, with the 1 min and 10 min extraction time results shown in Figure 17. From this study, SPME fibers containing a PDMS-DVB coating were selected for future experiments because the PDMS-DVB fiber collected the largest quantity of 1-BO with low variation in comparison to the other SPME fibers tested. While the CAR-PDMS SPME fibers collected the largest quantity of 1-Bromooctane with a 10 min. exposure time, there was a large deviation associated with this fiber negating its usefulness. SPME was the extraction technique selected for this study because the sampling procedure is simple and can be performed easily in the field.

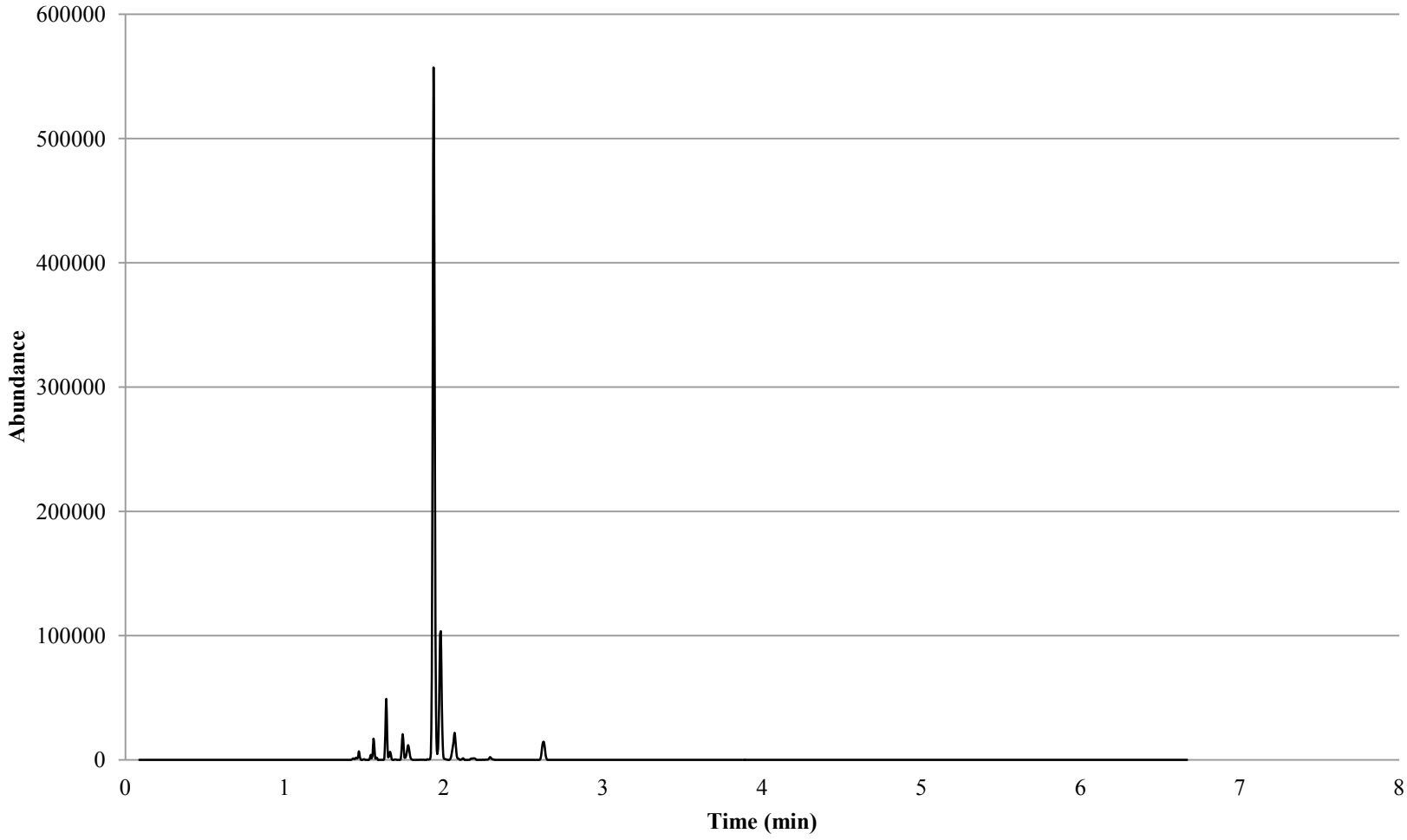



**Figure 13. Direct headspace analysis of potential UDC compounds: PFTBA (Rt=1.938 min, k'=0.32)**

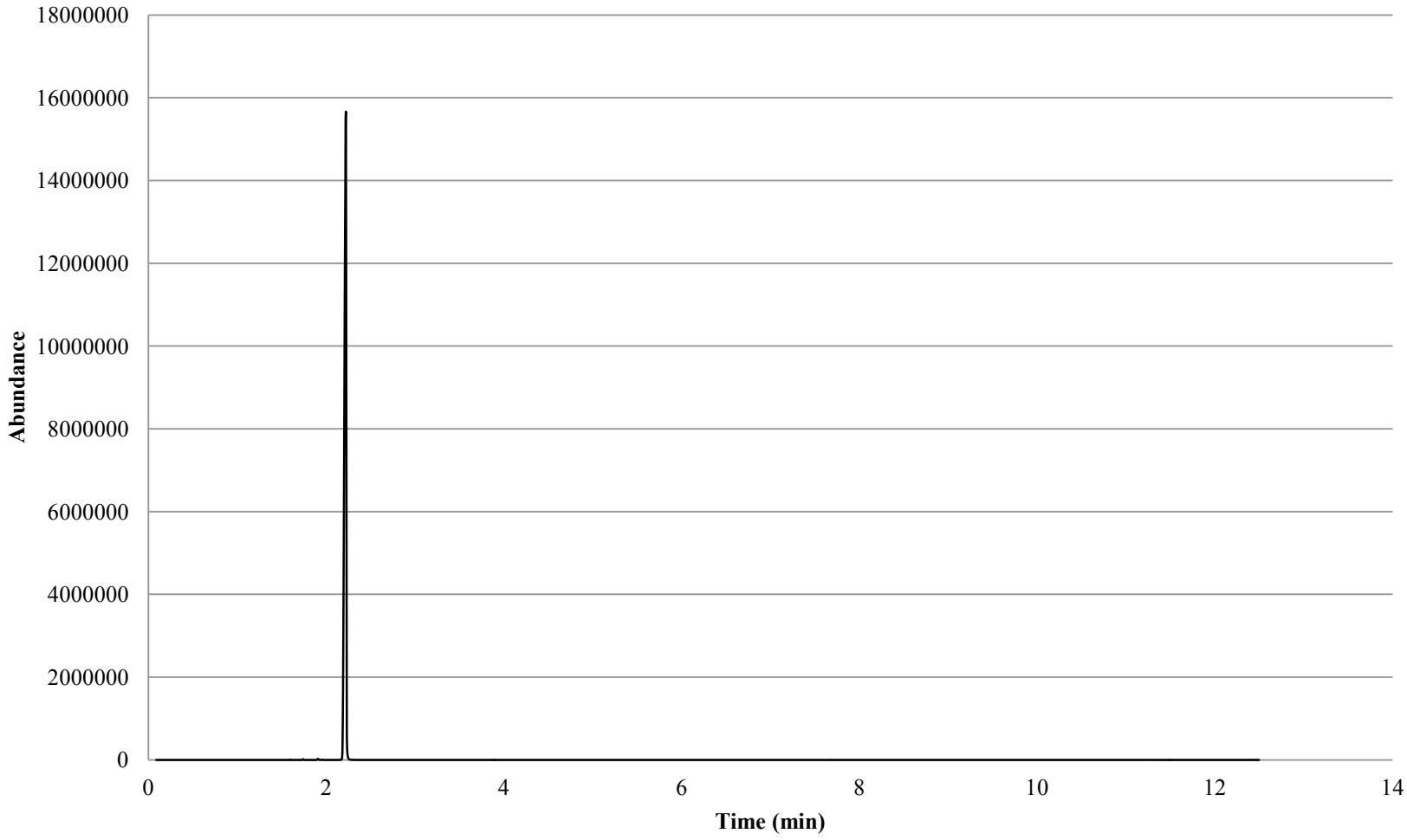



**Figure 14. Direct headspace analysis of potential UDC compounds: PFOB (Rt=2.217 min, k'=0.51)**

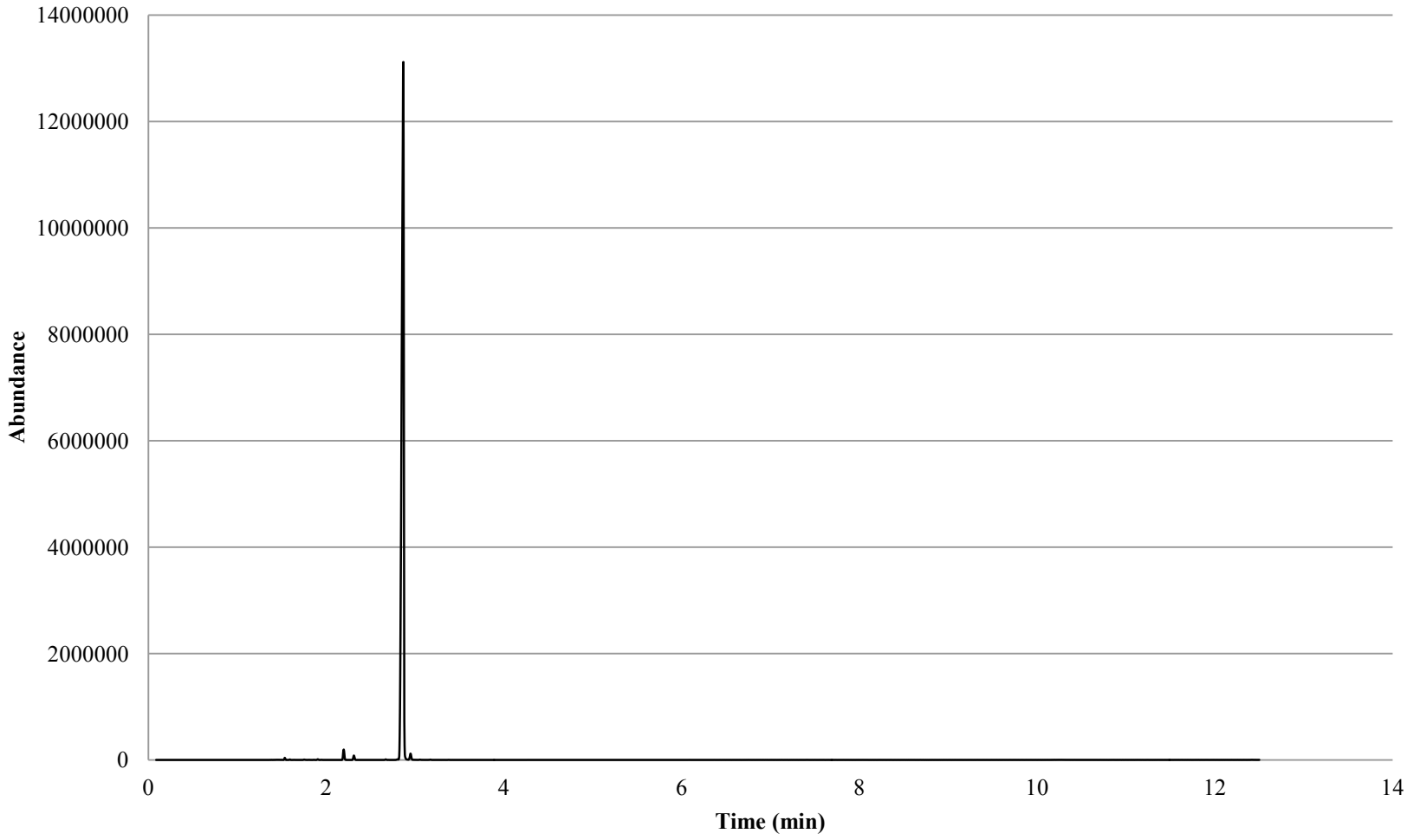



**Figure 15. Direct headspace analysis of potential UDC compounds: PFHI (Rt=2.863 min, k'=0.95)**

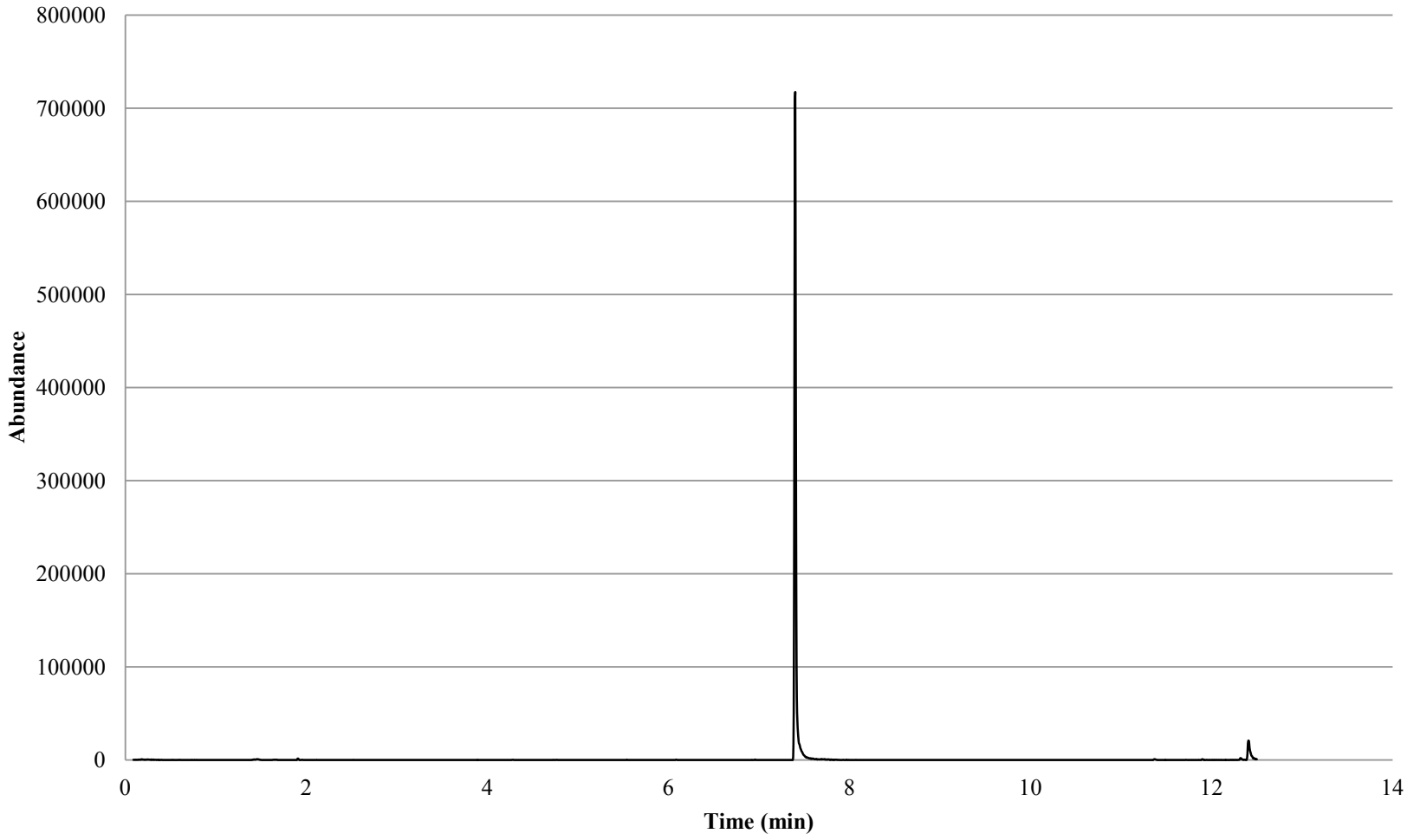



**Figure 16. Direct headspace analysis of potential UDC compounds: 1-BO (Rt=7.400 min, k'=4.04)**

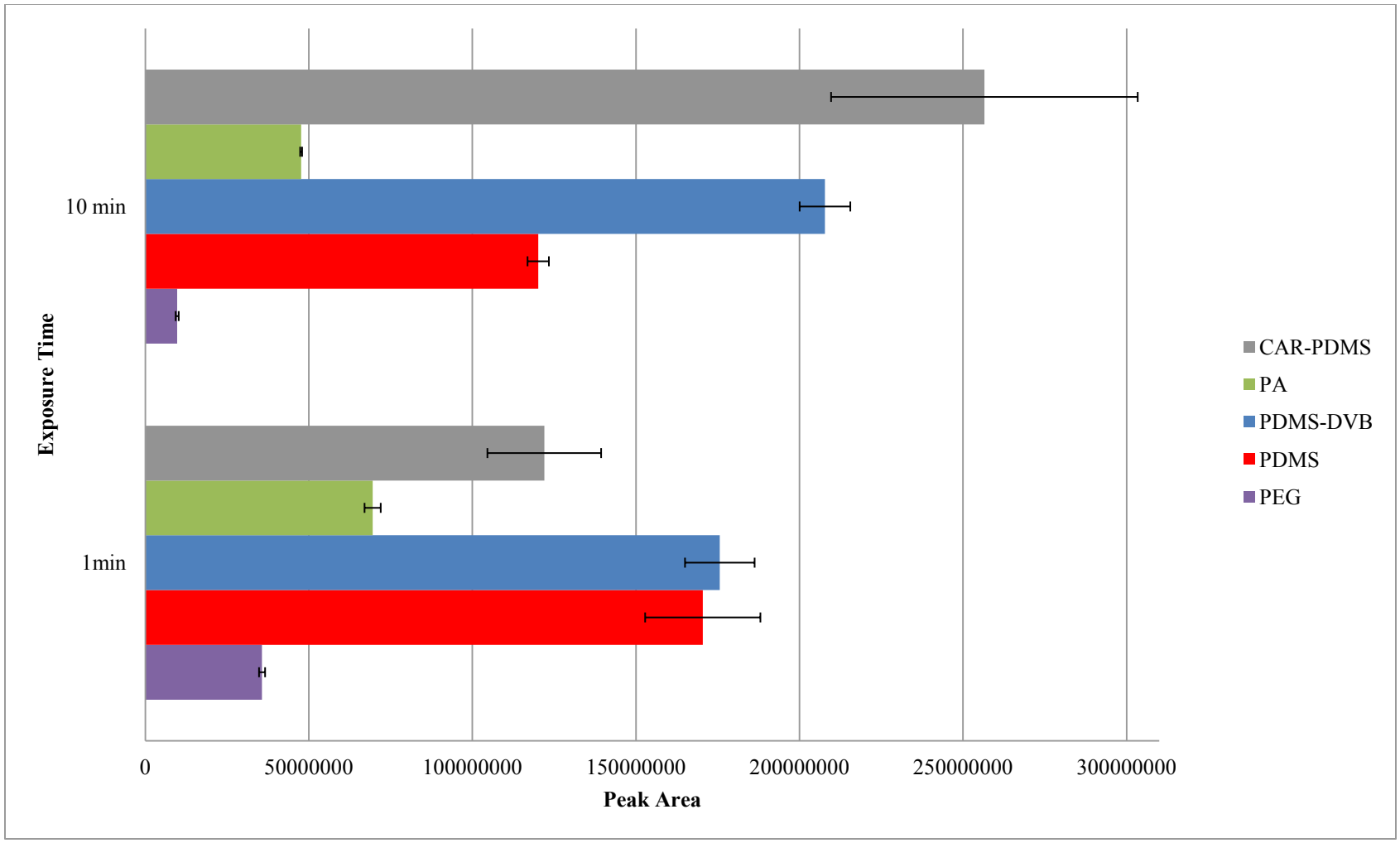



**Figure 17. 1-BO SPME fiber extraction study**

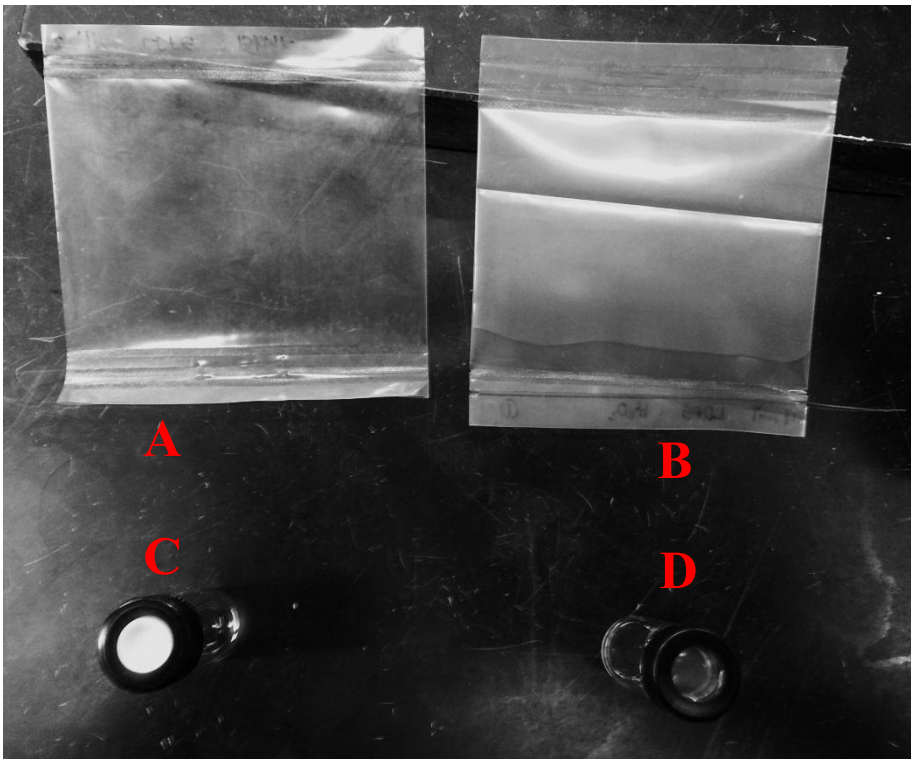



**Figure 18. Potential COMPS devices. (A) 2 mil LDPE bag, (B) 4 mil LDPE bag, (C) 4 mL glass vial with PTFE/Teflon septa, (D) 4 mL glass vial with 4mil LDPE septa**

Several potential delivery devices were constructed, however, the majority of the devices showed little promise for a long lasting training aid. COMPS devices, Figure 18, constructed using PP bags and 4 mL glass vials with PTFE/Teflon septa showed no evidence of permeation, while COMPS devices constructed of 2 mil or 4mil LDPE bags permeated too rapidly for long term use (complete dissipation of 1-BO within 2 days), Figure 20. In order to slow the rate of permeation, the surface area of a permeable polymer was reduced in a first generation device using a 4 mL glass vials with 4mil LDPE septa replacing the manufacturer's PTFE/Teflon septa, Figure 18 D. By reducing the surface area of the permeable polymer to 2% of the original permeating surface area (as seen in Figure 18B), the dissipation rate can be reduced to a more desirable rate. A

dissipation study was conducted to determine the effect of altering the surface area of the permeable polymer using second generation devices, Figure 19. From this study, a linear relationship was observed between the surface area of the permeable polymer and the dissipation rate of 1-bromooctane, Figure 21.

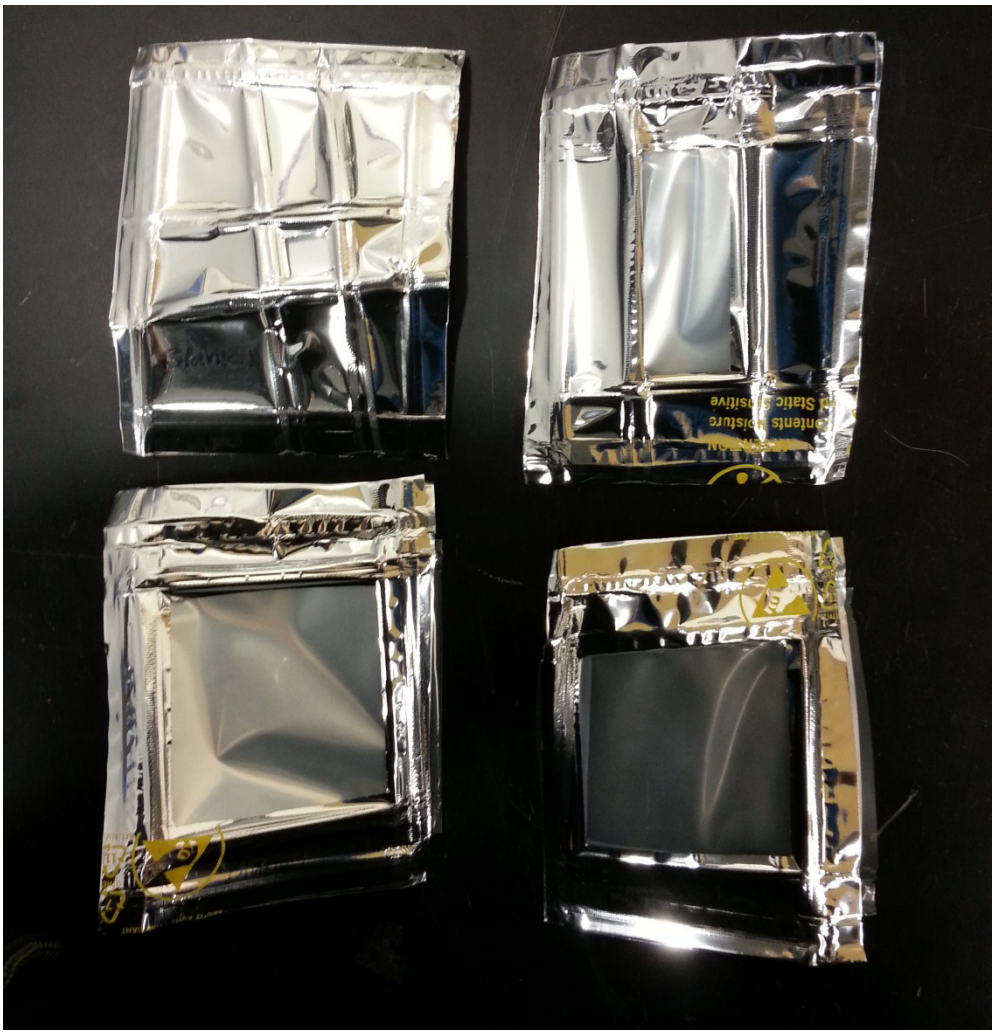


**Figure 19. Altered surface area COMPS. (A) 1cm2 permeating polymer area, (B) 10 cm2 permeating polymer area, (C) 25 cm2 permeating polymer area, (D) 50 cm2 permeating polymer area**

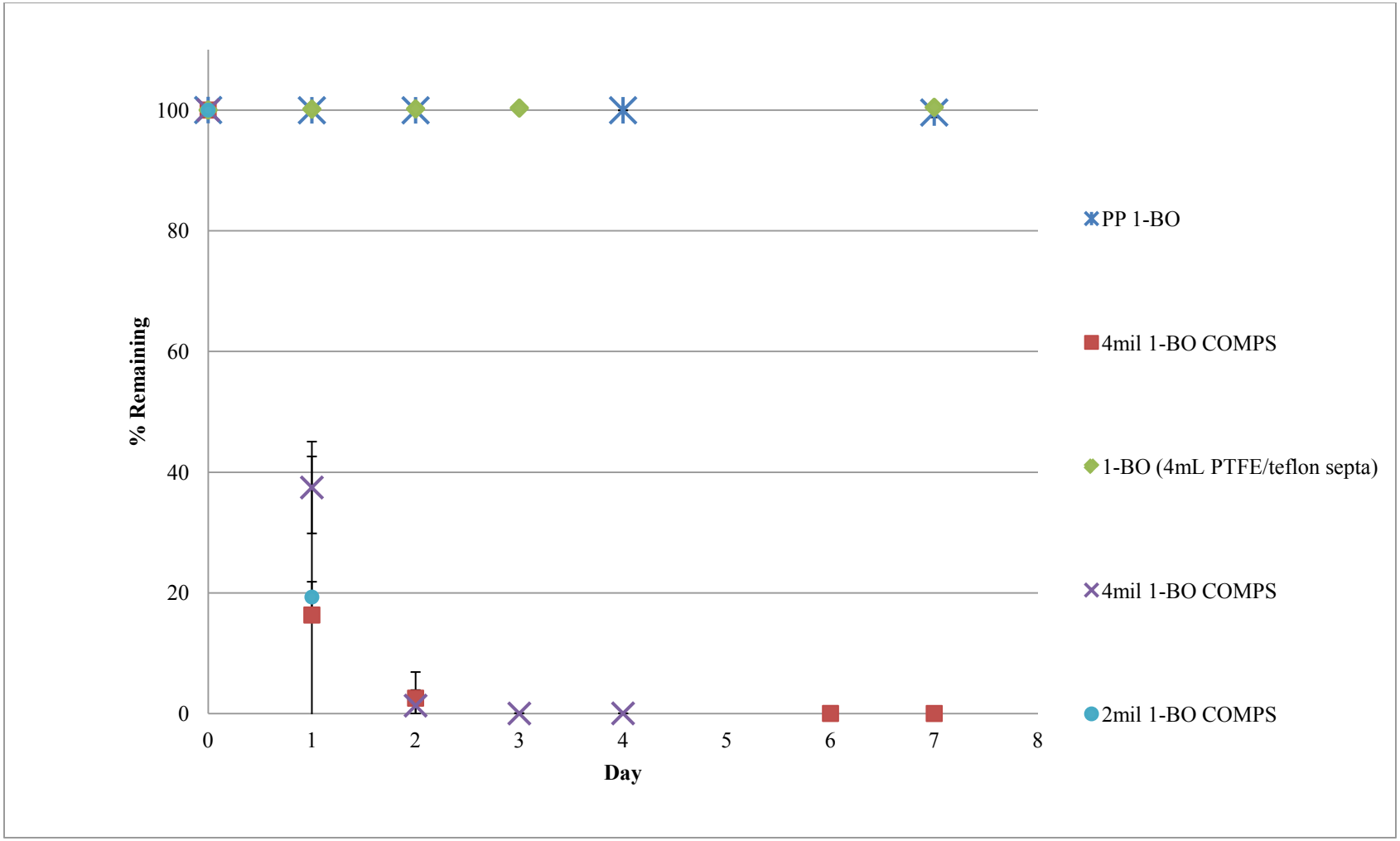



**Figure 20. Permeation rate of potential UDC delivery devices**

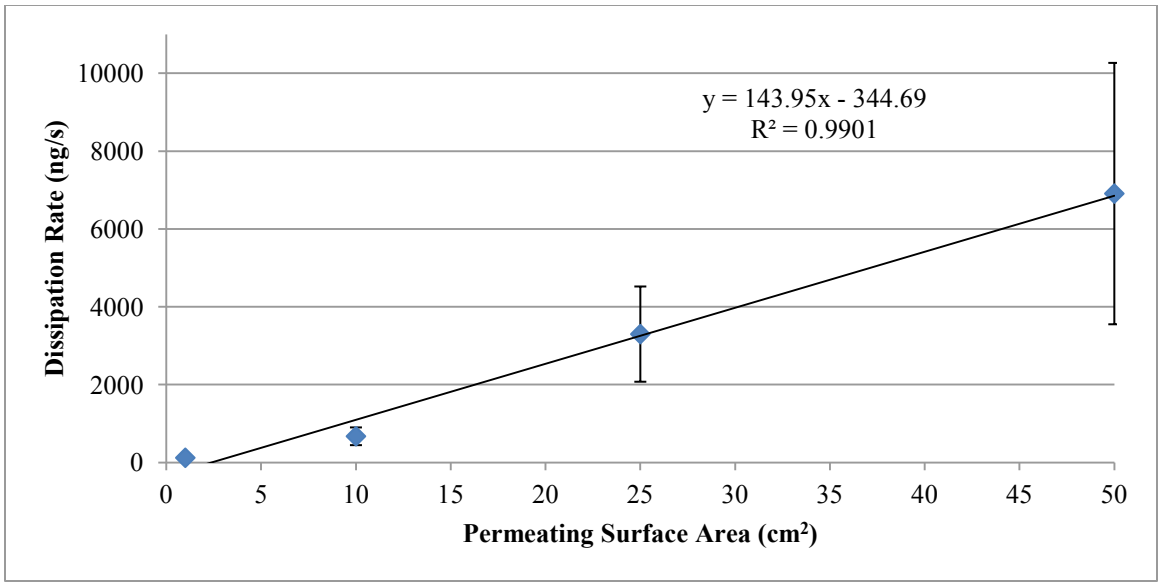



**Figure 21. Effect of permeating surface area on the dissipation rate of 1-bromooctane**

Laboratory testing of the potential deliver devices revealed that 1-BO is stable within the permeation device over the devices lifetime. Additionally, through manipulation of the permeable polymer's surface area, a reproducible, yet changeable permeation of odorant can be achieved. While 1-BO was the only compounds tested at this stage because it conforms to the desirable quality of lacking additional processing steps, other compounds have the potential to become a UDC, as long as the parameters mentioned above are met. Field testing of the UDC in a first generation delivery device was three fold. Preliminary canine testing was completed to determine if 1-BO was a unique odorant for all detectors to ensure that there is no cross detection between classes of biological detectors. A UDC which induces an alert response in scent discriminated canines is unsuitable as an alert response indicates that the UDC is an odorant associated with whichever class of detection the canine is associated with (i.e., narcotics or explosives, etc.). In the first canine trial, an odor recognition test was performed to determine if 1-BO is a dominant odor compound for which biological detectors use to

formulate an alert response. Within this test, 22 explosives detection canines, 13 drug detection canines, and two accelerant canines were tested, Table 6.

**Table 6. Odor recognition test 1: proof that 1-BO is not a dominant odor compound for detection canines**

| Class of Detection Canine | Alert (%) | Interest (%) | No Alert (%) |
|---|---|---|---|
| **Explosives (n=22)** | - | 10* | 90 |
| **Drug (n=13)** | - | - | 100 |
| **Accelerant (n=2)** | - | - | 100 |

***** Explosives detection canines showing interest in the UDC was not scent discriminated

From the canines' responses, it was determined that 1-BO is not a dominant odor compound used by biological detectors within the detection categories tested. The second stage of canine testing was to determine if biological detectors could be trained to alert to 1-BO. Within the second stage nine canines were 100% successfully imprinted and capable of searching and alerting on 1-BO. Since 1-BO is a novel compound for detection canines, care was taken to ensure that no undue stress or irritation was seen in the canines imprinted since 1-BO is listed as an irritant. Throughout the imprinting process no additional stress or irritation was observed in the detection canines imprinted on 1-BO.

The last stage of field testing the UDC is putting the UDC into practice. In this stage five canines have been imprinted and trained using the calibration compound daily. Three training aids were given to the canine handler and the handlers were asked to

present each training aid to the canine over a series of fourteen days. All of the canines in this test were capable of finding the training aids over the course of the test period, Table 7.

**Table 7. Odor recognition test 2: implementation of UDC into daily training (n=5)**

| Day | Low Training Aid % Alert | Medium Training Aid % Alert | High Training Aid % Alert |
|---|---|---|---|
| **1** | 100 | 100 | 100 |
| **2** | 100 | 100 | 100 |
| **3** | 100 | 100 | 100 |
| **4** | 100 | 100 | 100 |
| **5** | 100 | 100 | 100 |
| **6** | 100 | 100 | 100 |
| **7** | 100 | 100 | 100 |
| **8** | 100 | 100 | 100 |
| **9** | 100 | 100 | 100 |
| **10** | 100 | 100 | 100 |
| **11** | 100 | 100 | 100 |
| **12** | 100 | 100 | 100 |
| **13** | 100 | 100 | 100 |
| **14** | 100 | 100 | 100 |

## 3.5 Discussion

Proper selection of a UDC is integral to its functionality. Since the potential of possible compounds for use is essentially infinite with the production of new chemicals each year, it is essential to maintain the described mandatory and desirable qualities for the best possible outcome. Other compounds not meeting these requirements have been published in literature for calibration and/or determining the detection limits of the

canine, however, these compounds are commonly encountered in the environment making them unsuitable for mainstream use (112-114). While literature searches revealed a number of viable compounds, four compounds were selected for further testing since they represented compounds with the most potential. 1-Bromooctane was the only compound selected for implementation into field studies as it required no additional manipulation for instrumental detection. While only designated as a desirable quality, compounds that are not easily instrumentally detected by a variety of detectors would not likely find permanent use in the field since most people are unwilling to take on not only an additional task, but one that requires additional instrumentation.

The use of COMPS technology was selected for the preparation of training aids because they have previous successful implementation in the field with other biological detectors and odors (53). Previous laboratory experiments using odors associated with explosives confirmed this belief, however, successful UDC prototype training aids proved problematic. COMPS devices function on the manipulation of four properties: the compound contained, the polymer selected, the thickness of the polymer selected, and the permeable surface area. UDC training aid prototypes were developed manipulating the polymer and polymer thickness, nonetheless a successful prototype lasting longer that two days was not accomplished. Prior to this study a comprehensive study of the manipulation of all four described properties had not been completed. Manipulations of the compound, polymer, and polymer thickness have been conducted resulting in viable training aids functioning within their respective necessary parameters; therefore manipulation of the surface area of the permeating polymer had not previously been necessary. In order to study the manipulation of the permeating polymer, new COMPS

devices were developed in which a specified surface area of permeating polymer was heat sealed within a non-permeable polymer. Using these new COMPS devices, a successful UDC training aid was developed and further manipulation of the surface area of the permeating polymer allowed for the development of a calibration set of aids representing low to high detection amounts (121 ng/s, 673 ng/s, and 3300 ng/s). Manipulation of the permeating surface area also showed a linear relationship between the permeation rate and permeating surface area. This knowledge will allow for further manipulation of surrogate continuation aids for future requirements deemed necessary by the employing agency.

Upon completion of the laboratory testing, canine testing was performed to determine the feasibility of the laboratory selected UDC. In the first detection canine trial three different, yet commonly used, detection canine categories were used to determine if the compound was a dominant odor compound associated within these categories. Human scent and cadaver detection canines were not examined in this stage because of limited access to these canines (116). Of the 37 detection canines tested only two canines showed interest in 1-BO. Further investigation of the two canines showing interest in the UDC revealed that they were not scent discriminated (canines having a change in behavior in response to a strong odor regardless of whether the odor is not a detection odor). The success of the first test led to the second canine trial in which nine canines were imprinted on 1-BO. The second canine trial served two purposes: to prove that canines could be successfully trained to the odor and to prepare the canines for piloted calibration testing. With the aid of a trained canine trainer all the canines were successfully imprinted on 1-BO with several of the canine handlers annotating in their training records

that the canines had no trouble locating the UDC and showed enthusiasm in searching for the it.

Daily implementation of the UDC into the normal working parameters of the canine resulted in no alteration of the canines' capabilities to locate their target odors. Handlers noted that the canines easily found the UDC regardless of the selected permeation rate used in this test, Table 7. However, the greatest amount of information was collected from the handlers' utilized opinions of the UDC. The handlers tested collectively agreed that a calibration compound which is a non-target odor for all detection canines would be an ideal tool to aid in determining the accuracy of the canine. Additionally, the handlers were all willing to use the calibration compound each working day on a daily basis because it would strengthen their deployment records in court. Depending on the detection area of the canine, court appearances will vary, however, the greatest interest in the UDC came from the narcotics detection canine handlers as the reliability of their canines are routinely questioned in court cases.

## 3.6 Conclusions

Selecting a UDC presents many challenges; however, the implementation of a UDC into regular detection canine training will have several favorable consequences. Unlike any other currently available aids, the UDC represents a universal point of comparison allowing for the standardization of canine training across the detection categories. For example, once trained to the UDC, one would be able to compare a narcotics detection canine with an explosives detection canine even though the canines have been trained to detect different substances. Moreover, the universal calibration

compound can be used throughout the employment of the biological detector as a way to determine continued ability, and sensitivity of the biological detector, as well as for reinforcement training. With a universal point of comparison a standard can be developed universally to demonstrate the reliability, robustness, and error rate of the canine. Knowing these figures of merit allows for the use of detection canines to meet the previously lacking Daubert rules for admissibility. Additionally, knowing the detection canine's figures of merit allows for the canine to be calibrated prior to testing which ensures that the canine is working within prescribed limits, thus bringing the use of detection canines closer to the ideal objectivity and reliability found in laboratory instruments. One will also have the ability to compare one detection canine to another regardless of the detection substance, allowing for more comprehensive statistics to be performed on the accuracy, detection limits, and possibly reveal a superior breed of detection canine.

This compound can be used for the selection of biological detectors by determining the time it takes to train the canine to alert to the compound and the threshold of detection the canine can achieve. Selection of detection canines in using the UDC is also fiscally advantageous because training the canine to the compound prior to purchase may indicate that the canine does or does not have the qualities the purchasing group is looking for in a biological detector. This allows for funds and training efforts to be spent only on canines that meet the buyer's requirements. Using the UDC, the training of the detection canines can be streamlined for initial training. The trainers can begin the training of any biological detector (e.g., on learning search patterns, learning how to alert to an odor, and other general training tasks) regardless of end use of the biological

detector since the UDC is not a dominant odor compound used within the detection categories.

# 4 TASK 2: THE DEVELOPMENT OF A SURROGATE CONTINUATION AID FOR PEROXIDE BASED EXPLOSIVES

## 4.1 Introduction

Peroxide based explosives represent a particularly challenging group of explosives to train biological detectors to find. As discussed in the literature review section, peroxide based explosives have no commercial use due to their instability and the ease in which they detonate. It is because of this that detection canine trainers and handlers do not often have access to these explosives. In some instances, a federal canine trainer may have access to peroxide based explosives such as TATP and HMTD, however, accessibility and coordination between local law enforcement agencies and the federal agency may pose challenges since the federal canine trainer may be responsible for servicing a large area, resulting in sparse training opportunities. It is in this deficit that detection canine training aid manufacturers have begun developing surrogate continuation aids for peroxide based explosives.

Literature supports that canines can be trained to TATP and HMTD through the use of cotton balls that have been spiked with a very low concentration of the dilute explosive or through adsorption of explosive vapors onto a cotton ball when placed in close proximity to the explosive for a period of time (117,118). These types of training aid materials are limited by their lifespan which is typically less than a day, and their need to be in close proximity to a licensed explosive manufacturer. As these limitations,

again, pose challenges to the average detection canine trainer, alternative training aid materials are required and have therefore been developed by commercialized companies. These training aids are typically very expensive with limited lifespans, they may require refrigeration or other specialized storage considerations, and little peer reviewed literature has been published determining the efficacy of the training aids (119,120).

To overcome these challenges, the purpose of this study is to develop a surrogate continuation training aid for peroxide based explosives that is reliable and scientifically evaluated. This required, first, the laboratory testing of peroxide based explosives that were manufacture both to laboratory grade standards and through clandestine manufacturing processes. Once the headspace odors were classified, the dominant odor(s) which induces an alert response in the canines was determined. Through this determination a surrogate continuation aid was then developed and validated through laboratory and field trials using explosive detection canines.

## 4.2 Materials

Compounds used within this study include: acetone (Sigma-aldrich, St. Louis, MO) and 30 % wt./wt. hydrogen peroxide (Sigma-aldrich, St. Louis, MO). Gauze pads used were IMCO Sterile Gauze Sponges 2x2, 8-Ply (Independent Medical Co-op, Daytona Beach, FL) or Dukal Sterile Gauze sponges 4x4, 8-Ply (Independent Medical Co-op, Daytona Beach, FL). Polymer bags (BagBarn, Hanover, IN), Barrier Foil Ziplock bags (Ted Pella, Inc., Redding, CA), glass vials (Supelco, Bellefonte, PA), and polydimethylsiloxane/divinylbenzene (PDMS/DVB) solid-phase microextraction (SPME) fibers (Supelco, Bellefonte, PA) were also purchased.

## 4.3 Methods

TATP and HMTD samples were prepared off site and by licensed professionals. The volatile organic compounds (VOCs) in the headspace were evaluated using a number of techniques including: direct headspace SPME sampling, indirect static proximity testing with gauze and then subsequent SPME analysis, and indirect dynamic sampling with gauze and then subsequent SPME analysis. Direct SPME analysis was performed by placing approximately 0.5 g of explosive material into a 4 mL headspace vial that was then capped. A SPME fiber was then inserted and exposed for 1 or 30 minutes. As the sampling was performed off site, the SPME fibers were then placed on ice or in the freezer until analysis was performed. Static headspace collections were performed using 2" x 2" gauze pads. Five minute exposure times were selected in which the gauze pad was placed directly over a loose powder sample of TATP (approx. 500 mg). A quart size aluminum paint can was then placed over the samples for safety purposes as seen in Figure 25. At the end of the exposure time the gauze pads were then placed in 10 mL vials and transported to the lab for analysis using SPME-GC-MS. PDMS/DVB SPME fibers were used to extract the headspace components collected through static sampling and then sealed in the vial. Indirect dynamic sampling with gauze was performed by using the Human Scent Collection System (HSCS). The HSCS is essentially a vacuum than pulls air through the gauze sponge placed at its opening for a pre-determined amount of time and air flow speed. Dynamic headspace collections were performed using 4" x 4" gauze pads. A variety of collection speeds and times were selected to perform the HSCS extraction of the compounds emanating from a loose (approx. 500 mg) powder sample of TATP. The HSCS was placed two inches from the top of the sample and held in place

using ring stands for reproducibility. At the end of the exposure time the gauze pads were then placed in 40 mL vials and transported to the lab for analysis using SPME-GC-MS. PDMS/DVB SPME fibers were used to extract the headspace components collected through dynamic sampling and then emanated into the vial. SPME sampling was conducted directly over the gauze pad in a closed vial with selected exposure times of 1 and 30 minutes.

SPME analysis was performed using an Agilent 6890N GC coupled to a 5973Network mass selective detector (Santa Clara, CA) with an HP-5 MS 30m x 250µm x 0.25µm phase thickness capillary column and a helium flow rate of 1 mL/minute (J&W Scientific; Rancho Cordova, CA). HP Chemstation was used for instrument control and data analysis. GC separation parameters were as follows: the injector port was maintained at 110 °C for all PDMS/DVB SPME fiber injections; all runs were performed in splitless mode; and no solvent delay was used. An initial oven temperature of 50 °C was held for 3 minutes. The temperature was then increased to 180 °C at 8 °C/minute and held for zero minutes.

Based on the results of the headspace testing, a combined yet separated theory of odor introduction using acetone and hydrogen peroxide was developed. Attempts to create permeation devices for acetone proved problematic due to the high solubilizing power of acetone. Upon inspection of other potential permeable plastics, polypropylene was selected for testing. A small dissipation study was designed in which 1.2 mil and 3.0 mil polypropylene bags were tested as potentially viable COMPS. This test was carried out gravimetrically, by placing appropriate amount of acetone (99%) or hydrogen peroxide (30% w/w) in respective polypropylene bags followed by triple heat sealing to

ensure closure. Five replicates were made for each training aid along with a set of five blank training aids containing no material. Weights of the bags were recorded over a series of days.

Since polypropylene bags were found to be unsuitable COMPS, an alternative permeation device was investigated in which 500µL of acetone or hydrogen peroxide was pipetted into a 4 mL glass vial with PTFE/Teflon septa or a 4 mL glass vial with a #42 Whatman filter paper septa. Three replicates were made for each sample along with corresponding blanks.

A small dissipation study was designed in which 2 mil and 4 mil LDPE bags were tested as potentially viable COMPS. This test was carried out gravimetrically, by placing appropriate amounts of acetone (99%) or hydrogen peroxide (30% w/w) in respective polypropylene bags followed by triple heat sealing to ensure closure. Five replicates were made for each training aid along with a set of five blank training aids containing no material. Weights of the bags were recorded over a series of days.

Canine field trials were conducted to determine if this combined yet separate training aid of acetone and hydrogen peroxide would be a viable peroxide explosive training aid. Training aids were prepared by soaking a 2" x 2" gauze pad in acetone or 30 % w/w hydrogen peroxide. The soaked gauze pads were then placed in two clean sterilized glass and stainless steel toped salt shakers (one for each odor). The two salt shakers where then hidden together in a room for a certified explosive detection canine to search. All of the canines used were trained to detect TATP and HMTD.

From the success of this initial small trial, 5 explosives detection canines were imprinted on the IFRI peroxide based explosives training aid. The canines have

completed and passed the IFRI certification test for the detection of explosives excluding peroxide based explosives. As actual TATP and HMTD are difficult to obtain for testing, a canine training aid provided by Signature Science using dilute TATP on a matrix was placed out to confirm the use of the IFRI peroxide based training aid for these canines. The canine's responses were recorded upon completion of the test.

## 4.4 Results and Discussion

Five peroxide explosive samples were obtained off site by a licensed professional. From the headspace analyses performed on these peroxide explosive samples, no consistent non-explosive compounds were identified in the headspace that could be tested as a possible training alternative for peroxide based explosives. Headspace samples of TATP made to laboratory specifications showed predominantly triacetone triperoxide (TATP), diacetone diperoxide (DADP, the dimer of TATP), acetone, and acetaldehyde. From the direct SPME extraction (Figure 22 and Figure 23), TATP and its dimer diacetone diperoxide (DADP) were the largest contributors to the odor of TATP in this experiment as seen in Figure 24.

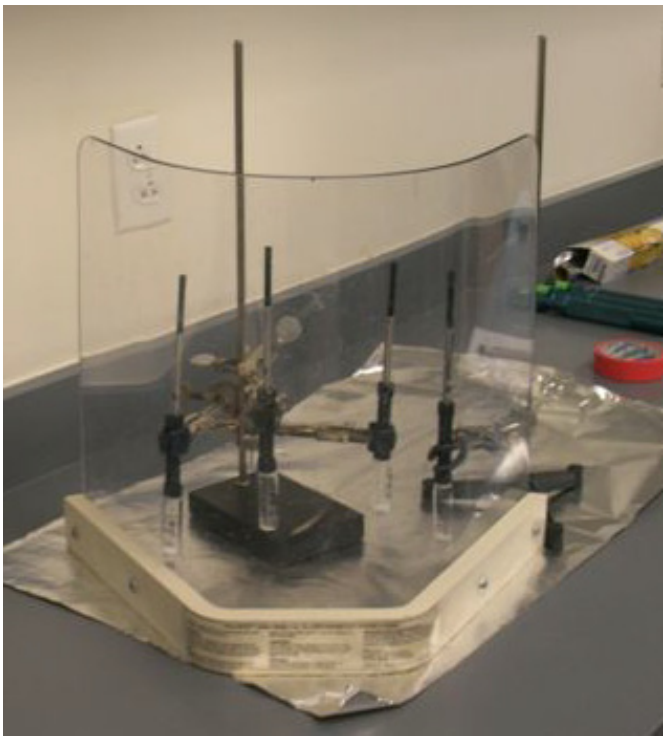


**Figure 22. PDMS/DVB SPME fiber headspace sampling of TATP and HMTD for 1 or 30 minutes**


**Figure 23. Direct SPME headspace sampling of TATP**

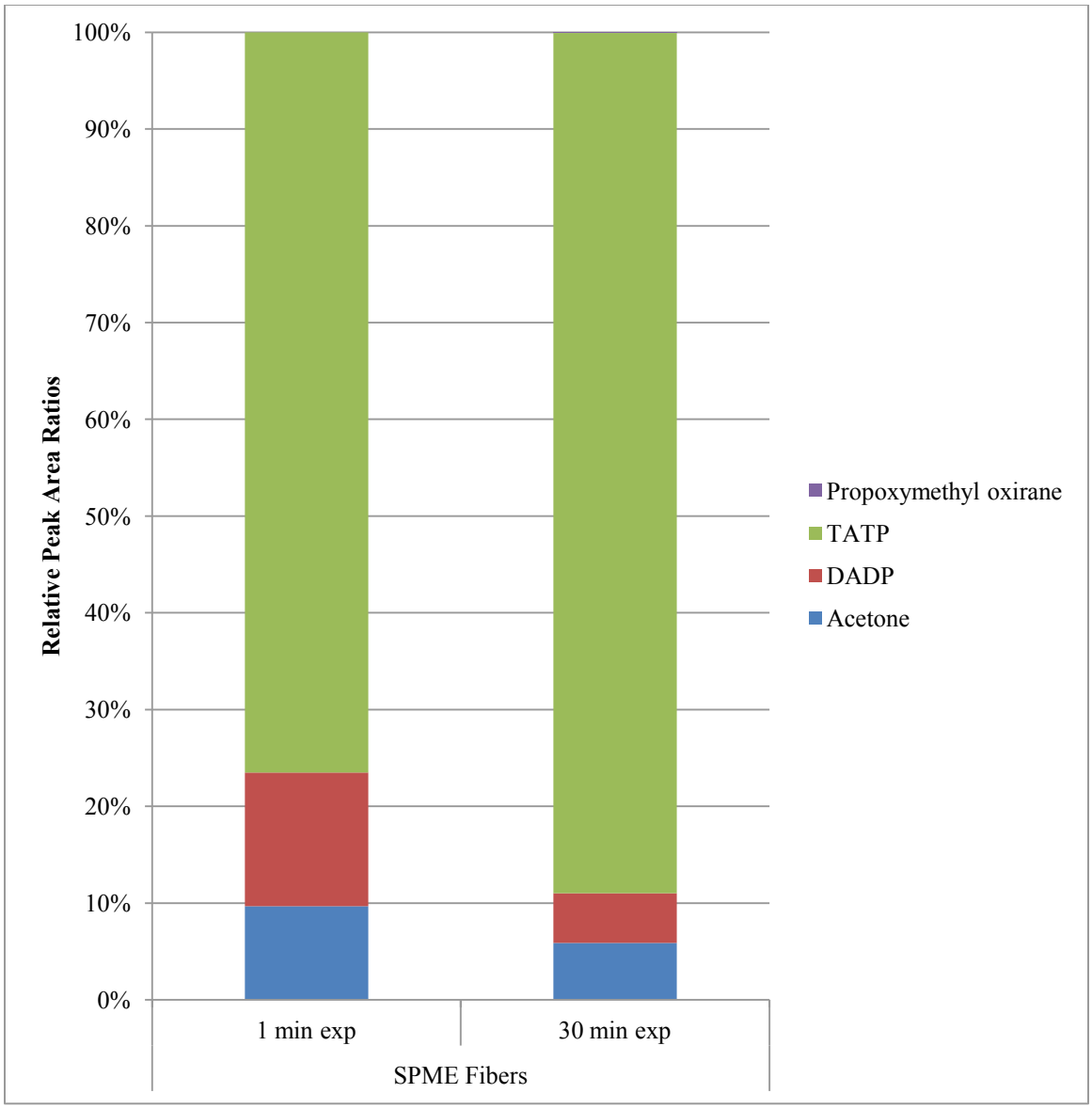



**Figure 24. Direct PDMS/DVB SPME Fiber Extraction of TATP**

From the indirect static gauze extraction (Figure 25), only TATP and methylene chloride (environmental contaminant of the extraction location) were observed in the headspace Figure 26.

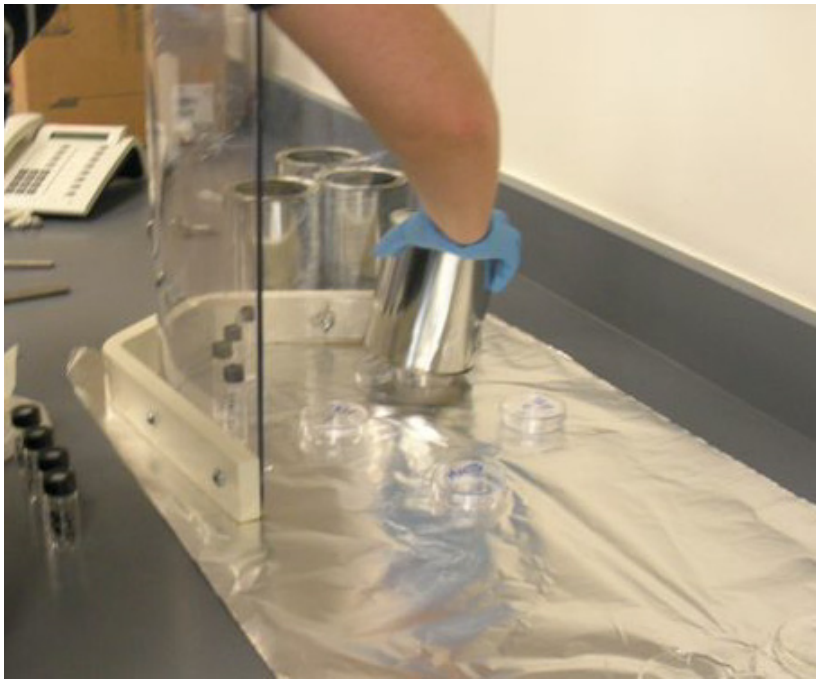


**Figure 25. Static collection of headspace odors of TATP and HMTD**

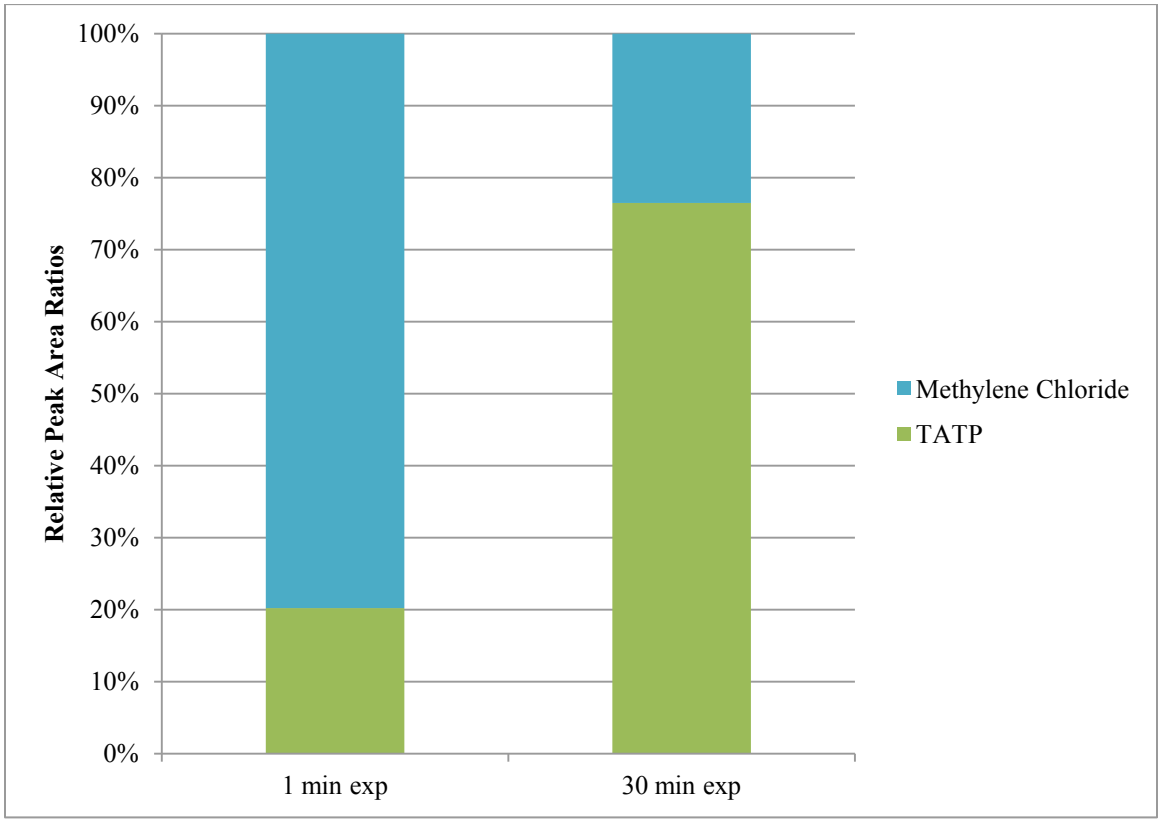



**Figure 26. PDMS/DVB SPME fiber extraction of TATP statically collected on gauze pads**

From the indirect dynamic sampling, methylene chloride (an environmental contaminant of the extraction location) was observed in every sample including the blanks (Figure 27). TATP and toluene were also observed in two of the headspace collections, Figure 28.

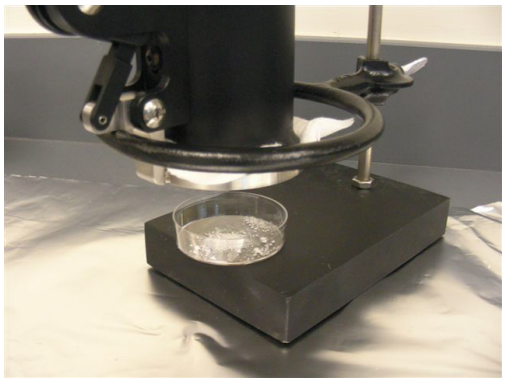


**Figure 27. HSCS dynamic sampling of TATP**

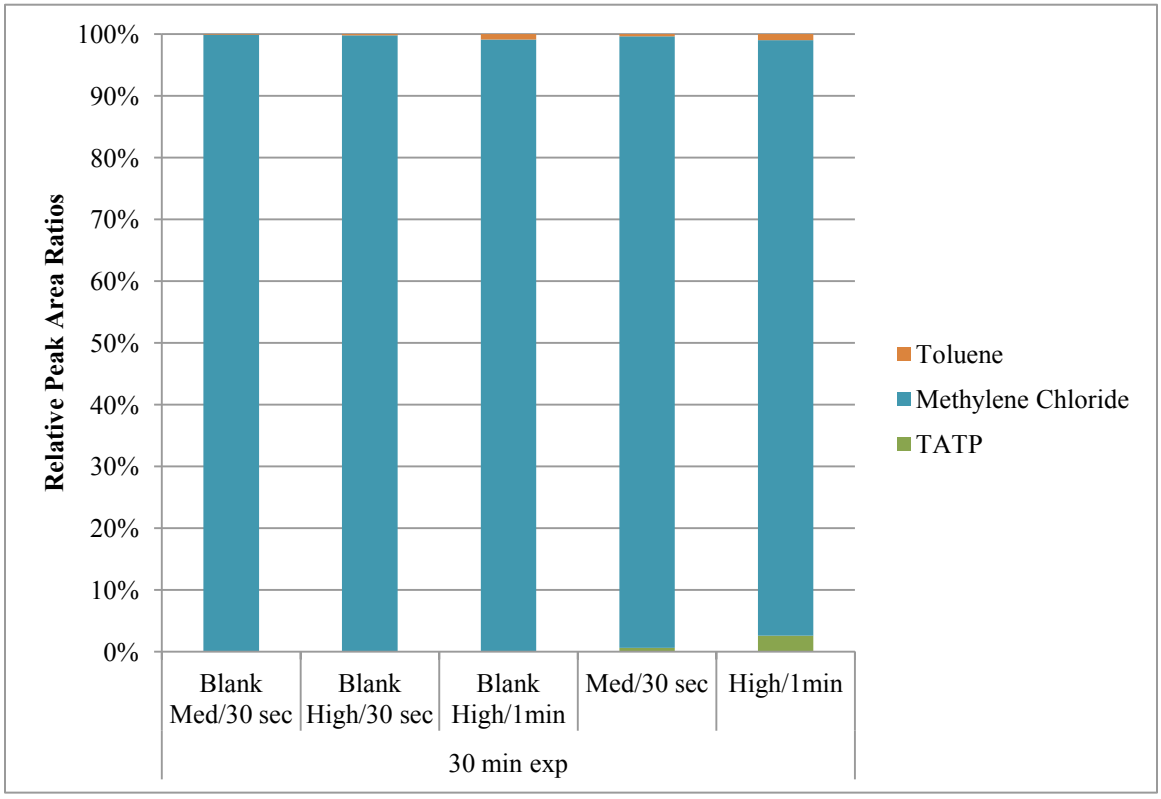



**Figure 28. PDMS/DVB SPME fiber extraction of TATP dynamically collected on gauze pads using the HSCS**

TATP samples which were made using a clandestine manufacturing process showed TATP, DADP, acetone, and various byproducts believed to be the result of the impurities in the acetone used in the synthesis process. However, an increase in abundance of DADP was seen in the TATP samples made using a clandestine manufacturing process (TATP 2 and 3, Figure 29) when compared to the TATP samples made using only laboratory grade chemicals (TATP 1, Figure 29). This is thought to be the result of diluted chemical concentrations and the impurities in the chemical precursors used in the clandestine manufacturing process resulting in the reduced synthesis of TATP. When testing the headspace of HMTD via headspace SPME-GC-MS and indirect gauze pad sampling with subsequent analysis using SPME-GC-MS, no identifiable volatile organic compounds were observed.

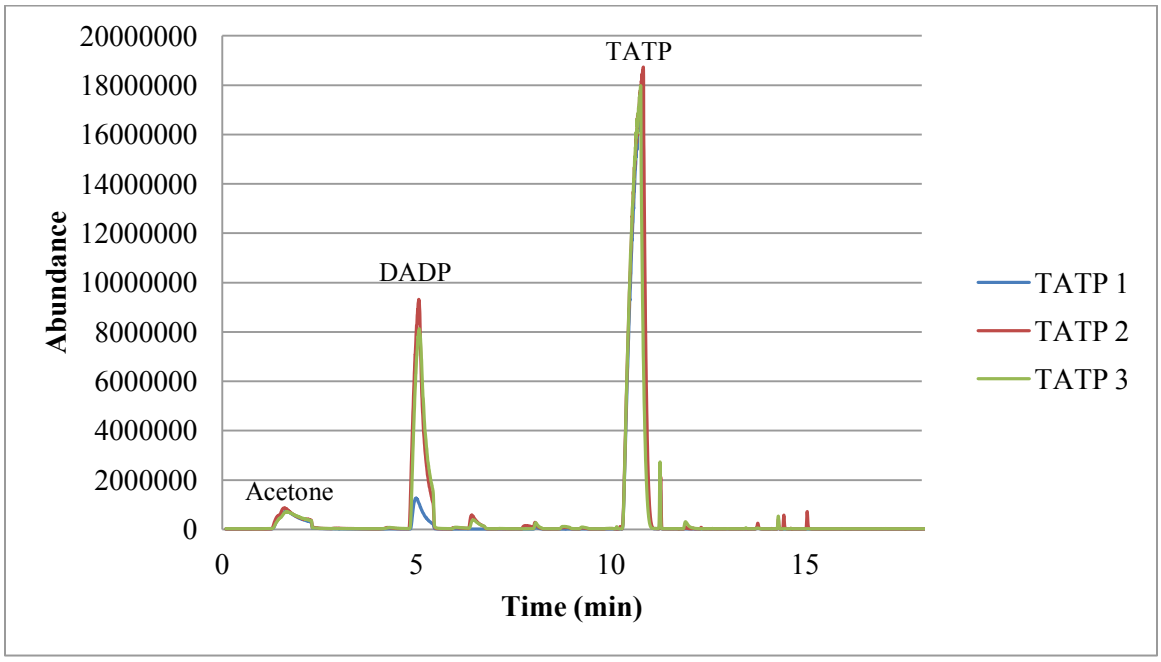



**Figure 29. Chromatogram of TATP samples made using laboratory grade chemicals and clandestine manufacturing processes. TATP 1 represents a sample made using laboratory grade chemicals. TATP 2 and TATP 3 samples were made using a clandestine manufacturing process**

These observations of only the explosive in the headspace lead to the theory of utilizing a dual training aid for peroxide based explosives, where both acetone and hydrogen peroxide would be used. As the use of acetone alone as a training aid would create the probability of high false alerts to acetone containing compounds, a dual training aid consisting of acetone and hydrogen peroxide would reduce the possibility of false alerts by training the canines to alert to these compounds only in combination. Hydrogen peroxide was selected as the secondary component of the training aid because it is a precursor for the production of peroxide based explosives and is an UV decomposition product of peroxide based explosives (121). Each compound would be separated from each other to alleviate safety concerns, but always be used in combination.

Attempts to create permeation devices for acetone proved problematic due to the high solubilizing power of acetone. Polypropylene bags were selected for permeation rate testing, it was concluded that both the thicknesses of polypropylene bags were unsuitable for the development of COMPS. The dissipation rates were not reproducible for either acetone or hydrogen peroxide in either thickness of polypropylene bag used. The polypropylene bags also showed noticeable inflation and corresponding rupture of the bags after two weeks for both the acetone and hydrogen peroxide samples.

Since the polypropylene bags were found to be unsuitable COMPS, an alternative permeation device were investigated in which 500µL of acetone or hydrogen peroxide was pipetted into a 4 mL glass vial with PTFE/Teflon septa or a 4 mL glass vial with a #42 Whatman filter paper septa. The acetone samples using the filter paper for permeation resulted in a training aid that lasted less than 24 hours, which is undesirable.

The hydrogen peroxide and filter paper training aids lasted longer than 24 hours; however, the permeation rate could be altered easily by wetting the filter paper which increased the dissipation rate through a wicking effect resulting in an uncontrollable dissipation of the odorant. The acetone and hydrogen peroxide placed within the 4 mL vials with septa intact were tested as Teflon is known to have minimal permeability; however, in this study none of the training aids produced a gravimetrically observable permeation of odor. From this study it was concluded that the use of a Teflon septa or #42 Whatman filter paper as COMPS devices were unsuitable.

Low density polyethylene (LDPE) bags were originally through to be unsuitable as acetone would disrupt the integrity of the bag; however, they provided the most training aid potential, Figure 30. Both the 4 mil and 2 mil LDPE COMPS showed constant dissipation of hydrogen peroxide, indicating that either of these COMPS are

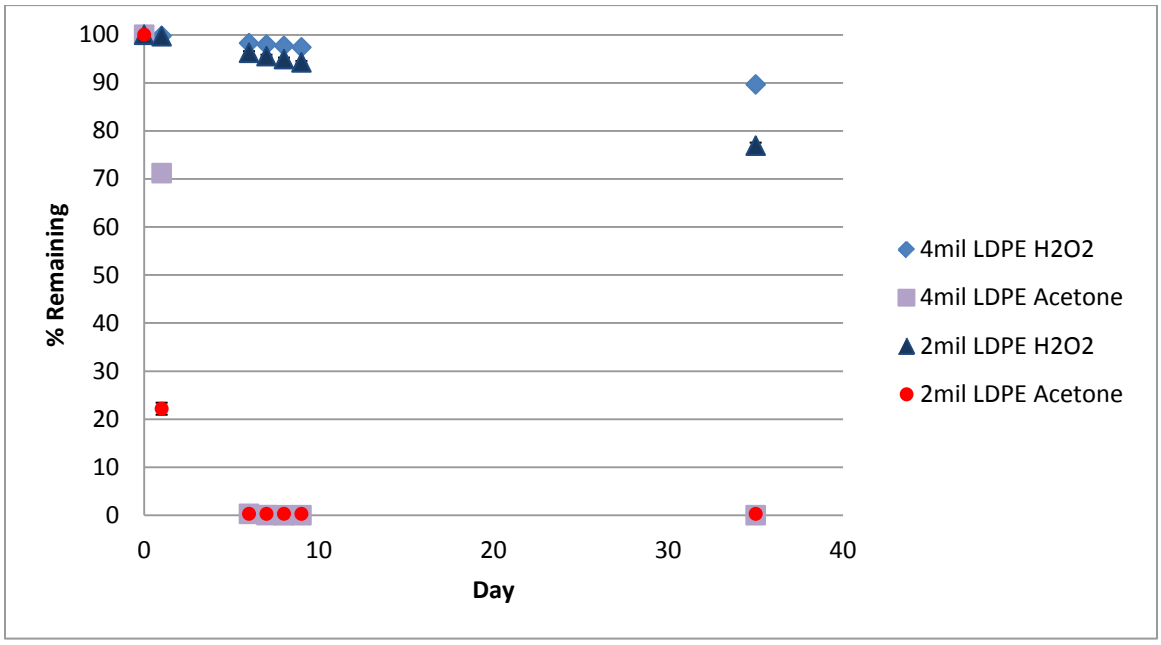



**Figure 30. Average percent remaining of the peroxide training aid using 1mL of acetone or H2O2 in 2 mil or 4 mil LDPE COMPS**

viable for hydrogen peroxide portion of the training aid. Similar to the dissipation rates observed in Task 1, the acetone COMPS permeated rapidly and was gone within 1-2 days. However, the dissipation rate can be controlled by varying the surface area of permeable polymer. Therefore a viable separate yet combined surrogate canine training aid was developed for peroxide based explosives.

Canine field trials were conducted to determine if this combined yet separate training aid of acetone and hydrogen peroxide would be a viable peroxide explosive training aid. Training aids were prepared by soaking a 2" x 2" gauze pad in acetone or 30 % w/w hydrogen peroxide. The wetted gauzes were then placed in individual clean salt shakers which were hidden together. Ten canines participated in the test, Table 8. All of the canines were trained to detect TATP and HMTD. An 80% combined rate of detection was observed which is lower than the SWGDOG best practice alert rate of 90%. As the majority of the canines used for testing did not have regular access to peroxide based explosives for training, the 80% alert rate was an encouraging sign.

**Table 8. Odor recognition test 1: peroxide explosive training aid with previously trained and certified explosives detection canines (n=10)**

| Training Aid | Alert Rate (%) | Interest Rate (%) | No Alert Rate (%) | Combined Rate of Detection (%) |
|---|---|---|---|---|
| **IFRI: Peroxide Explosive Training Aid** | 60.0 | 20.0 | 20.0 | 80.0 |

The successful detection of the IFRI peroxide based explosives training aid in odor recognition test 1, led to five explosives detection canines being imprinted on the IFRI peroxide based explosives training aid. Once imprinted to odor in accordance with the canine trainer's requirements, the canines were then asked to find actual TATP

manufactured by Signature Science. Upon the completion of this canine trial, Table 9, all 5 of the canines were capable of finding the IFRI peroxide based training aid. However, only four canines were capable of locating the Signature Science TATP, with one canine showing no interest and did not alert to the Signature Science TATP training aid. As canines are not infallible, an 80% combined alert rate for actual TATP explosive material is highly indicative of a viable TATP training aid alternative.

**Table 9. Odor recognition test 2: confirmation of the viability of the IFRI peroxide based explosives training aid (n=5)**

| Training Aid | Alert Rate (%) | Interest Rate (%) | No Alert Rate (%) | Combined Rate of Detection (%) |
|---|---|---|---|---|
| **IFRI: Peroxide Explosive Training Aid** | 100.0 | - | - | 100.0 |
| **Signature Science TATP** | 80.0 | - | 20.0 | 80.0 |

## 4.5 Conclusions

Developing a peroxide based explosive training aid for biological detectors presents several challenges since the explosive material is so difficult to obtain and maintain. Upon completion of this study, only VOC's with explosive properties or compounds known to be laboratory environmental contaminants could be confirmed in the headspace, revealing that the development of a non-hazardous, non-controlled training aid mimic poses several challenges. Based on the synthesis starting components and published literature, a combined yet separate training aid mimic was developed for TATP. While, ideally this mimic should be a feasible mimic for HMTD also, this practicality could not be confirmed as no actual explosive HMTD material was obtained for canine testing.

The use of the combined yet separate training aid mimic is necessary for training TATP, because the odors selected for imprinting themselves are quite common. As an explosives detection canine that regularly alerts to common household chemicals would be problematic, training the canine to the odors only in combination alleviates this concern. Since the training aids odors are always used together, the canine learns that they should only alert when both odors are present. This was confirmed, as all five of the canines imprinted on the IFRI peroxide training aid did not alert to hydrogen peroxide, acetone, or products containing either component during training. Additionally, through a serendipitous accident, if acetone and hydrogen peroxide (30 % w/w) become mixed, TATP will form even in the absence of an acid catalyst. In response to this accident, a controlled test was performed in which either acetone or 30 % w/w hydrogen peroxide were contained separately within a single headspace container, allowing the headspace VOCs from each component to mix (combined yet separated). It was discovered that after 10days TATP was found in the headspace of the combined yet separated odors and TATP formed in the headspace two days within the mixed test. As a result, the combined yet separate odor theory used in the IFRI peroxide based explosives training aid is a safe alternative to training with and maintaining peroxide based explosives.

Upon completion of this study, a reliable peroxide based explosive training aid has been developed which alleviates many of the hazard concerns associated with these types of explosives. The IFRI peroxide based training aid can be placed out in a variety of situations through the use of COMPS or gauze sponges soaked in either acetone or hydrogen peroxide. As long as the odors are used in combination, there is minimal risk of training the canine to detect common household chemicals. Additionally, there have

been no instances of canines imprinted on the IFRI peroxide based explosive training aid to date alerting to common household chemicals. While a larger population of canines needs to be tested for full confidence in the IFRI training aid, the results of this study indicated that the training aid is ready for large scale canine trials for validation and to be put into practice in daily use.

# 5 TASK 3: VALIDATION OF THE PROTOTYPE SURROGATE EXPLOSIVES TRAINING AID KIT

## 5.1 Introduction

To ensure the maintenance of the necessary detection capabilities of explosives detection canines, the canines must be trained regularly with the odors they are expected to detect. Due to the implicit nature of explosives, this obligatory training can be problematic. However, this issue can be overcome through the introduction of an appropriately validated prototype surrogate explosives kit which provides a less hazardous yet more controlled delivery of explosive odorants. This study outlines the step- by- step methodology for the validation of the prototype surrogate explosives kit, including a proof of concept study. The validated prototype explosives kit will provide a viable alternative to the commercially available kits currently being used. The new explosives kit will not only reduce the potential health hazards for the canines and their handlers but also increase canines' performances by exposing them to an increased number of odors.

Field tests were conducted with explosives detection canines and included a proof of concept study testing the viability of the surrogate continuation aids (SCAs). This was

completed by imprinting green explosives detection canines on the prototype surrogate explosives kit and then testing the proficiency of the canines alerting to actual explosive material. All canine tests in this research endeavor were conducted with strict adherence to the current Florida International University Institutional Animal Care and Use Committee (IACUC).

Detection canines for this study were grouped into two different categories based on detection experience. Green canines selected for the imprinting of the prototype surrogate explosives kit had only obedience training and no exposure to or experience with explosives. Experienced explosives detection canines used in this study were required to show proficient explosives detection skills at a detection rate of 90% or higher for actual explosive material prior to being selected for testing and preferentially have a current detection canine certification from a SWGDOG recognized certifying body. Proficiency tests were administered prior to testing the prototype SCAs which consisted of a SWGDOG guideline based certification test (78). Canines unable to meet the 90% detection rate were excluded from the study. Canines meeting the detection rate requirement were often used for multiple repetitions of testing.

## 5.2 Materials

The prototype surrogate explosives kit was manufactured in a reproducible manor using chemicals purchased from Sigma-Aldrich (St. Louis, MO) and Natchez Shooters Supplies (Chattanooga, TN). Additionally, 2” x 2” sterile cotton gauze pads (Independent Medical Co-op, Inc.; Daytona Beach, FL), and 2 mil, 3” x 3” low density polyethylene (LDPE) bags (Bagbarn.com; Hanover, IN) were also purchased.

## 5.3 Methods

A proof of concept study testing the viability of the SCAs within the prototype surrogate explosives kit was conducted using previously trained explosives detection canines. In this test, the SCAs were placed in a familiar search pattern to the detection canine with appropriate blanks and distractors as deemed necessary by the canine trainer present. All tests were conducted double blind. The canines' responses, as confirmed by the canine handler, were recorded.

Green explosives detection canines were imprinted on the prototype surrogate explosives kit following the standard imprinting protocol of the canine trainer. Once the canine trainer deemed the canine proficient on the SCAs, a proficiency test was conducted following the SWGDOG guidelines for proficiency testing using actual explosive material. During this test, the detection canines had no exposure to actual explosive material prior to the proficiency test. All tests were conducted double blind. The canines' responses, as confirmed by the canine handler, were recorded.

## 5.4 Results

The proof of concept test, Table 10, was conducted with 180-200 previously trained and certified explosives detection canines. From this odor recognition test, a combined rate of detection of over 93.5% was observed for all of the IFRI explosives kit SCAs. A 90% or higher combined rate of detection is preferable for novel SCAs and since all of the IFRI kit's SCAs achieved this response, the aids were accepted as valid odors within the repertoire of explosives detection canines.

The second odor recognition test was used to validate that the SCAs within the IFRI explosives kit are viable training aids in comparison to actual explosive material. From this test, Table 11, 18 green canines were trained exclusively on the SCAs within the IFRI explosives kit. These canines were then subjected to a certification test following SWGDOG best practice guidelines for detection canine certification (122). Of the 18 canines trained in this manner, only one canine showed difficulty in locating the actual explosive material, C4.

**Table 10. Results of the odor recognition test using previously trained and certified explosives detection canines to find the SCA within the IFRI explosives kit**

| **Odor Recognition Test: Explosives Kit with Previously trained and Certified Explosives Detection Canines** | | | | | |
|---|---|---|---|---|---|
| **Surrogate Continuation Aid** | Alert Rate (%) | Interest Rate (%) | No Alert Rate (%) | Combined Rate of Detection (%) | |
| **TNT** | n= 187 | 98.4 | 1.1 | 0.5 | 99.5 |
| **Nitroglycerin** | n= 186 | 93.0 | 0.5 | 6.5 | 93.5 |
| **Plasticized** | n= 186 | 95.2 | - | 4.8 | 95.2 |
| **Tagged** | n= 180 | 97.8 | 0.6 | 1.7 | 98.3 |
| **Smokeless Powder 1** | n= 200 | 93.5 | 2.5 | 4.0 | 96.0 |
| **Smokeless Powder 2** | n= 183 | 95.6 | 2.2 | 2.2 | 97.8 |

**Table 11. Results of the odor recognition test using green canines trained only on the IFRI explosives kit and then certified following SWGDOG best practice guidelines using actual explosive material**

| Odor Recognition Test: Green Canines Trained Only on Explosives Kit and Certified on Actual Explosives (n=18) | | | | |
|---|---|---|---|---|
| **Surrogate Continuation Aid** | Alert Rate (%) | Interest Rate (%) | No Alert Rate (%) | Combined Rate of Detection (%) |
| **TNT** | 100.0 | - | - | 100.0 |
| **Slurry** | 100.0 | - | - | 100.0 |
| **Dynamite** | 100.0 | - | - | 100.0 |
| **C4** | 94.4 | - | 5.6 | 94.4 |
| **PETN Det. Cord** | 100.0 | - | - | 100.0 |
| **Single Base Smokeless Powder** | 100.0 | - | - | 100.0 |
| **Double Base Smokeless Powder** | 100.0 | - | - | 100.0 |

## 5.5 Discussion

Field testing of the prototype surrogate explosives kit proved to be the most challenging aspect of this study as it was difficult to find detection canine teams willing to participate. A large number of participants were gained after a seminar was given to law enforcement agencies in the state of Florida explaining the kit and how their participation will aid in the advancement of explosive detection canine research. Upon completion of the seminar 34 prototype surrogate explosives kits were given to 17 different law enforcement agencies in attendance. Over the next three months training records associated with the kit were returned, resulting in the high number of canines able to be tested in the first trial, Table 10. Due to the success of this trial, the SCAs within the kit were accepted as viable mimics for the selected groups of explosives. The combined

rate of detection was higher than expected as there is little uniformity in the field as to how many and which explosive groups a detection canine will be trained to detect.

Canine trainers have been known to imprint their canines on as high as (in our field experience) 26 explosive odors, however, upon closer inspection, several of the odors contained the same composition under a different name or manufacturer. In some instances the moniker associated with an explosive was confounding to the canine trainers as the name does not always correspond to the ingredients. For example, in one of our canine trials the canines were trained to detect nitroglycerin using dynamite, however closer inspection of the dynamite training aid revealed that it was a TNT based dynamite rather than nitroglycerin based. This confusion is also observed in selecting smokeless powders for training. There are several different brands of smokeless powders available on the market and if selected improperly, a detection canine may inadvertently be trained to detect only a single brand of smokeless powder rather than all smokeless powders. Previous research of the odors found in the headspace of smokeless powders has shown that while there is variability in the mixtures, smokeless powders typically have additives of ethyl centralite or diphenylamine (53). Therefore, canine trainers selecting single, double, and triple based powder from a single brand can result in the canines missing a different brand of smokeless powder containing the other additives. This conclusion was observed in our testing. In some instances the canine would easily locate one of the IFRI smokeless powder SCAs while showing no interest in the other. The confusion and challenges associated with selecting explosives to train a detection canine highlight the need for a uniform training system in which odors for training are

selected such that all explosives are included while the overall number of training aids is minimal. It is from this need that the prototype surrogate explosives kit was conceived.

The second canine test, in which green canines were imprinted solely on the SCAs within the prototype surrogate explosives kit, also presented challenges as it was difficult to find canine trainers willing to imprint their canines on the kit, Table 11. Through the success of the first canine trial 18 canines were imprinted in the manner previously described. As the canines trained in this test had no exposure to actual explosives until their certification, the combined rate of detection was higher than expected. The canines exhibited no problems locating the actual explosives, with the exception of one canine not alerting to a C4 hide. As the plasticized SCA within the kit dissipates a large quantity of odor, the plasticizer within the C4 used in certification may have been below the canine's trained threshold detection limit. Since detection canine thresholds are known to be low, but vary with between canines, future research will be conducted to build SCAs representing "high" and "low" amounts of explosive odor. However, care will still need to be taken with training as Lotspeich et. al. determined that the amount of odor available for the canine does not always correspond to the weight of material present; but is rather a function of the material itself, the container volume, vapor pressure, temperature, and concealment (123).

## 5.6 Conclusions

As a result of this study the IFRI prototype surrogate explosives kit has been proven to be a viable alternative for explosives detection canine training when actual illicit material is unavailable or cannot be used. The canine data collected supports that

the SCAs within the kit are odors used by canines to form an alert response which can be used to both train and maintain explosive detection canines in the field. As the kit currently only covers five classes of explosives, additional explosive mimics can be added to the kit as their dominant odor compounds become known.

# 6 TASK 4: DETERMINATION OF THE OPTIMAL STORAGE PARAMETERS OF THE SURROGATE CONTINUATION AIDS WITHIN THE PROTOTYPE SURROGATE EXPLOSIVES KIT

## 6.1 Introduction

The prototype surrogate explosives kit, manufactured by the International Forensic Research Institute (IFRI), is composed of the dominant odor compound for plasticized, TNT-based, nitroglycerin-based, and tagged explosives, as well as smokeless powders (1,5). The selection of the proper storage system is necessary for the maintenance of potency, efficacy, and functional integrity of canine SCAs as the cross-contamination of the SCAs are always of great concern. Currently canine handlers and trainers use a variety of containment systems (glass, plastic, cloth, etc.) for SCA storage; however, an in-depth and systematic study was required to determine the optimal containment system, taking into consideration different factors that potentially play important roles in the potency, efficacy, and ease in which the SCA become contamination ease of the SCAs. The goal of this study is to determine the optimal secondary containment system for storing various explosive detection canine training aids. The determination of the proper secondary containment system is a critical step in the validation of various explosive training aids, developed to offer a less hazardous and

more controlled delivery of explosive odorants. A cross-contamination study was performed to determine which secondary containment system demonstrates the least permeation of the explosive odorants out of the containment system. Headspace analyses using SPME-GC-MS or SPME-GC-ECD was used to identify and quantify the explosive odorant contaminating the tertiary containment system over a series of weeks. Headspace analyses of the training aids were also performed to determine if cross-contamination of the training aids held within the containment vessel was also occurring. Permeation rate comparisons, through gravimetric analyses, were made between various containment media to determine if the containment vessel affects the effective life-span of the aid. Airtightness tests were also performed on the secondary containment systems since permeation out of the containment system will be reduced if the system is found to be airtight. Maintenance of the integrity of the SCA odors is imperative to ensure standardization of training, increasing the reliability of the canine to detect the various illicit odors. This study reduces the current inconsistencies in knowledge in the field, allowing for a reliable system of SCA containment in a stream-lined and validated kit to be implemented.

## 6.2 Materials

The prototype surrogate explosives kit was manufactured in a reproducible manor using chemicals purchased from Sigma-Aldrich (St. Louis, MO) and Natchez Shooters Supplies (Chattanooga, TN). 2” x 2” sterile cotton gauze pads (Independent Medical Co-op, Inc.; Daytona Beach, FL) and 2 mil, 3” x 3” low density polyethylene (LDPE) bags (Bagbarn.com; Hanover, IN) were also purchased. Sorbent materials were tested

including: 2” x 2” sterile cotton gauze pads (Independent Medical Co-op, Inc.; Daytona Beach, FL), sorbent clothes (Wal-Mart; Pembroke Pines, FL) and Johnson & Johnson Surgipad* combine dressing (Ethicon, Inc.; Arlington, TX). Containment systems include: aluminum lined bags (Ted Pella, Inc.; Redding, CA), spice jars (IKEA; Sunrise, FL), canning jars (Publix; Miami, FL), 1Qt double zipper closure plastic bags (Wal-Mart; Pembroke Pines, FL), twist top plastic containers (Wal-Mart; Pembroke Pines, FL), plastic containers (Wal-Mart; Pembroke Pines, FL), and clear glass jars with Teflon faced lined caps (SKS-Science; Park Hills, MO). Additional test supplies included: cobalt chloride test strips (Carolina Biological Supply Co.; Burlington, NC), 1450 Pelican® cases (Pelican®; Torrance, CA), canning jars (Publix; Miami, FL), and Suba-Seal® silicone rubber septa (Sigma-Aldrich; St. Louis, MO). Headspace testing was performed using: polydimethylsiloxane/divinylbenzene (PDMS/DVB) and polyethylene glycol (PEG) solid phase microextraction (SPME) fibers (Supelco; Bellefonte, PA).

## 6.3 Methods

The effective shelf-life of the prototype surrogate explosives kits’ SCAs were determined via gravimetric analysis over a series of months. The aids were constructed following the established COMPS method (103) with varied compound weights added specifically for each test completed. The COMPS were suspended in a fume hood and placed such that no two COMPS were touching. Preliminary tests were completed to determine the variance in porosity/dissipation rate of the COMPS and the effect of varying the weight of material added to the COMPS. These two preliminary tests were completed using the plasticized and smokeless powder 1 mimics. The variance in

porosity/dissipation rate was carried out gravimetrically, by placing 2 grams of each training aid in a 2 mil low density polyethylene bag (LDPE) followed by triple heat sealing to ensure perfect closure. Five replicates were made for each training aid along with a set of five blank training aids containing no material. Weights of the bags were recorded over a series of weeks. A second dissipation study was then conducted to determine the effect of various weights of training aid placed in LDPE COMPS. This test was carried out gravimetrically, by placing 1gram, 5 grams, and 10 grams of each training aid (plasticized and smokeless powder 1) in a 2 mil low density polyethylene bag (LDPE) and heat sealing in triplicate to ensure closure. Five replicates were made for each training aid along with a set of five blank training aids containing no material. Weights of the bags were recorded over a series of weeks.

A long-term storage study was then conducted using all of the prototype surrogate explosives kit COMPS continuation aids. Using the dissipation rates seen in the two previous studies, weights of training aid material were selected such that the prototype explosives kit would last approximately two years. This test was performed in the same fashion as the two previous dissipation study tests, with the weight selection being 3 grams or 25 grams for the solid material and 10g for the liquid material. This test was carried out gravimetrically, by placing the selected weight of each training aid in a 2 mil low density polyethylene bag (LDPE) and heat sealing in triplicate to ensure closure. Five replicates were made for each training aid along with a set of five blank training aids containing no material. Weights of the bags were recorded over a series of weeks.

The effects of introducing a sorbent material was also studied using the plasticized continuation aid mimic. Three different sorbent materials were tested

including: 2” x 2” sterile cotton gauze pads, sorbent clothes, and Johnson & Johnson Surgipad* combine dressing. These sorbent materials were cut into 2” x 2” pieces for insertion into the LDPE bags. This test was carried out gravimetrically, by placing the selected weight of each training aid (2 grams of plasticized mimic) and selected absorbent material into a 2 mil low density polyethylene bag (LDPE) and triple heat sealing to ensure closure. Five replicates were made for each training aid along with a set of five blank training aids containing no training aid material. Weights of the bags were recorded over a series of three weeks.

The optimal storage parameters of the prototype surrogate explosives kit were determined using two tests. Seven potential secondary containment systems currently used in the field were selected for testing. These containment systems include: aluminum lined bags, spice jars, canning jars, 1Qt double zipper closure plastic bags, twist top plastic containers, plastic containers, and clear glass jars with Teflon faced lined caps. The first test determined the airtightness of each storage container. Six replicates of each potential containment system were washed with a 1% alkaline solution, rinsed with copious amounts of DI water, and placed in a 105°C isothermal oven for no less than 15 minutes (with the exclusion of the 1Qt plastic bags and aluminum lined bags). Once cooled, a cobalt chloride test strip was placed in each vessel. The vessels were sealed and left on the bench top overnight to ensure dryness. Replicates 1-3 of each vessel remained on the bench top throughout the remainder of the experiment and served as control samples. Replicates 4-6 were immersed in dyed water overnight. The vessels were then removed and the cobalt chloride test strips were examined and compared to the control samples. The second test was to determine the effect of the secondary containment

system on the SCA. Prototype Surrogate Explosive Kits were made using secondary containment systems: spice jars, 1Qt double zipper closure plastic bags, twist top plastic containers, and canning jars. Once completed, the vessels were closed and gravimetric analyses were performed on the continuation aids over a series of weeks to determine the effect of secondary containment on the permeation rate of the SCAs.

A cross contamination test was then conducted to verify the optimized storage parameters of the prototype surrogate explosives kit. Four IFRI Prototype Surrogate Explosive Kits were prepared for testing. Kits were created using 1450 Pelican® cases and canning jars with a Suba-Seal® silicone rubber septa inserted through the pelican® case for headspace analyses. Kit 1 was designated as a blank in which empty canning jars were placed for analysis. Kits 2-4 were designated as test kits in which canine SCAs were placed in the secondary containers. The secondary containers in Kit 2 were left open throughout the entirety of the experiment, secondary containers in Kit 3 were opened and closed daily throughout the entirety of the experiment representing everyday use, and the secondary containers in Kit 4 were closed and not opened throughout the entirety of the experiment. Headspace analyses of the SCAs in Kits 1-4 were performed to determine if SCA odor was permeating out of the secondary containment and into the tertiary containment vessel, and within the secondary containment systems to test for cross-contamination of SCA odors

Headspace analyses using a dual system of polydimethylsiloxane/divinylbenzene (PDMS/DVB) and polyethylene glycol (PEG) solid phase microextraction (SPME) fibers (Supelco; Bellefonte, PA) coupled with gas chromatography (GC), with either electron capture (ECD) or mass spectrometry (MS) detection were used to identify and quantify

the odorant emanating from the secondary containment system over a series of weeks using a 3 hour exposure time. GC-MS analysis was performed using an Agilent 6890N GC coupled to a 5973Network mass selective detector (Santa Clara, CA) with an HP-5 MS 30m x 250µm x 0.25µm phase thickness capillary column and a helium flow rate of 1 mL/minute (J&W Scientific; Rancho Cordova, CA). GC-ECD analysis was performed using an Agilent 6890N GC coupled to a 6890 µ-ECD detector (Santa Clara, CA) with a RTX®-TNT 6m x 530µm x 1.5µm phase thickness capillary column and a helium flow rate of 10 mL/minute (Restek; Bellefonte, PA). HP Chemstation was used for instrument control and data analysis. GC separation parameters were as follows: the injector port was maintained at 250 °C for all PDMS/DVB SPME fiber injections and 240 °C for all PEG SPME fiber injections; all runs were performed in splitless mode; and a solvent delay of 3 minutes was used. An initial oven temperature of 60 °C was held for 2 minutes. The temperature was then increased to 115 °C at 10 °C/minute, then to 250 °C at 15 °C/minute, and finally to a temperature of 300 °C at 10 °C/minute, held for zero minutes.

## 6.4 Results

The effective shelf-life of the prototype surrogate explosives continuation aids were determined first through preliminary tests to determine the variance in porosity/dissipation rate of the COMPS and the effect of varying the weight of material added to the COMPS. These two preliminary tests were completed using the plasticized and smokeless powder 1 mimics, Figure 31and Figure 32. A 6.1% Relative Standard Deviation (%RSD) was observed when determining the variance between the

porosity/dissipation rates of the COMPS. This number was deemed an acceptable variance within the LDPE bags and further tests were completed using the same stock of bags.

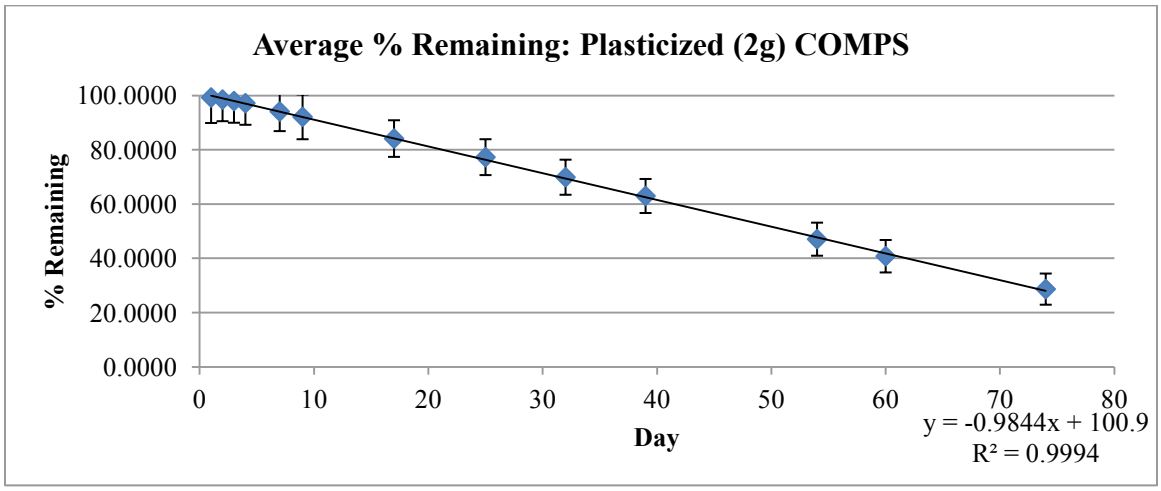



**Figure 31. Variance in porosity dissipation study: the dissipation rates observed with the plasticized SCA within the IFRI explosives kit**

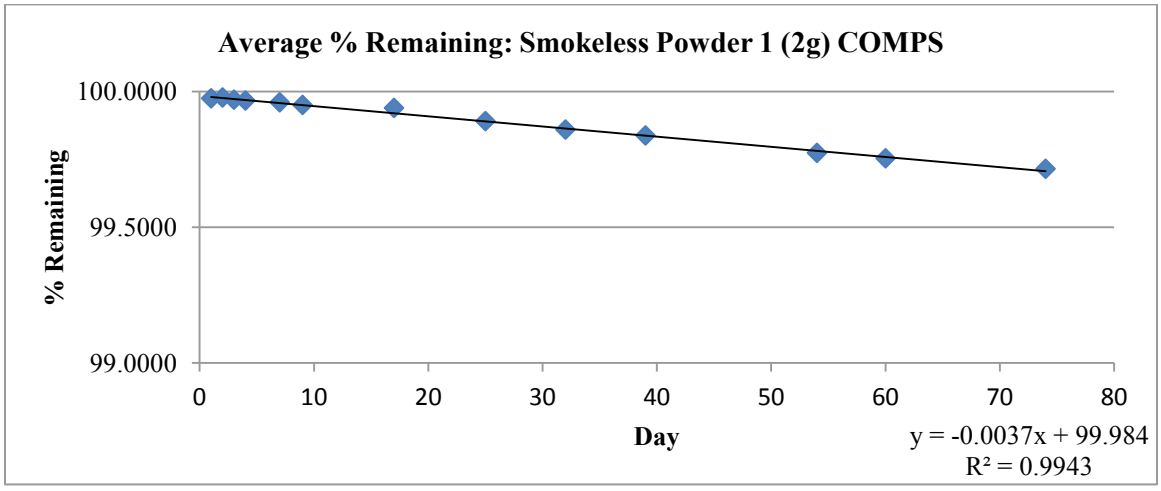



**Figure 32. Variance in porosity dissipation study: the dissipation rates observed with the smokeless powder 1 SCA within the IFRI explosives kit**

When varying the weight of material added to the LDPE bags from 1g to 10g, a 13.5% RSD was observed between the samples. No statistical difference was observed at a 95% confidence interval between the plasticized SCA at the various weights using Student's t-test. From these observations, weights of mimic materials were then selected such that the continuation aid mimic would last approximately two years unconfined. Three grams was selected for the weight of smokeless powder 1, smokeless powder 2, and tagged; 25 grams was selected for the weight of TNT and nitroglycerin; and ten grams was selected for the weight of plasticized SCAs.

Using the aforementioned weights of materials, a long term dissipation study was conducted using all of the SCAs. The results of the long term dissipation study, Figure 33-Figure 38, revealed a steady and predictable dissipation of all of the SCAs, with the exception of the nitroglycerin SCA which exhibited more variation (Figure 38). The observed permeation rates of the SCAs within the IFRI explosives kit can be seen in Table 12.

**Table 12. Observed permeation rates of the SCAs contained within the IFRI explosives kit**

| Surrogate Continuation Aid | Permeation Rate (ng/s) |
|---|---|
| **TNT** | 4.63 ± 0.54 |
| **Nitroglycerin** | 28.0 ± 1.2 |
| **Tagged Explosives** | 2.77 ± 0.50 |
| **Plasticized Explosives** | 355 ± 5.0 |
| **Smokeless Powder 1** | 1.48 ± 1.2 |
| **Smokeless Powder 2** | 7.44 ± 0.72 |

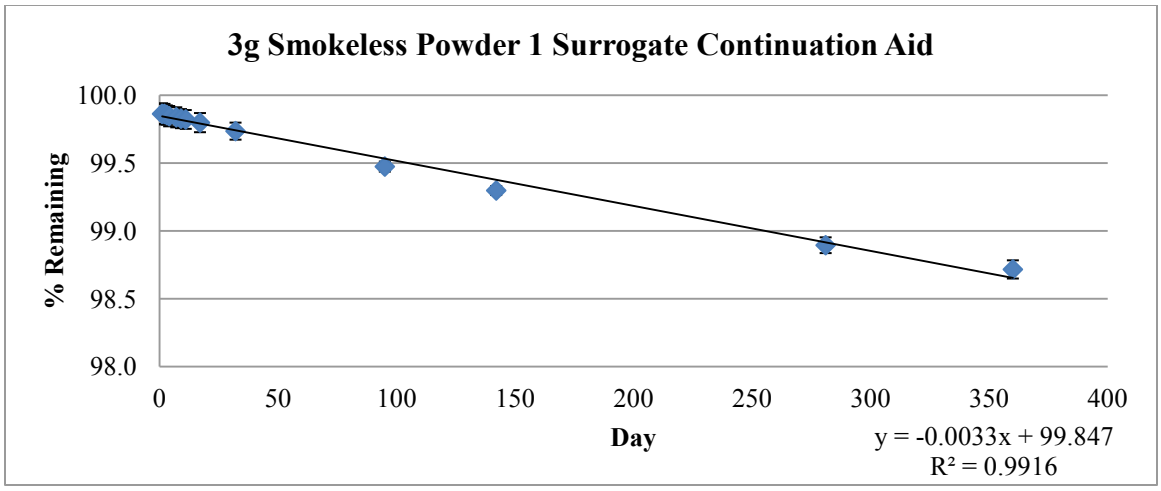



**Figure 33. Long term dissipation study: the dissipation rates observed with the smokeless powder 1 SCA within the IFRI explosives kit**

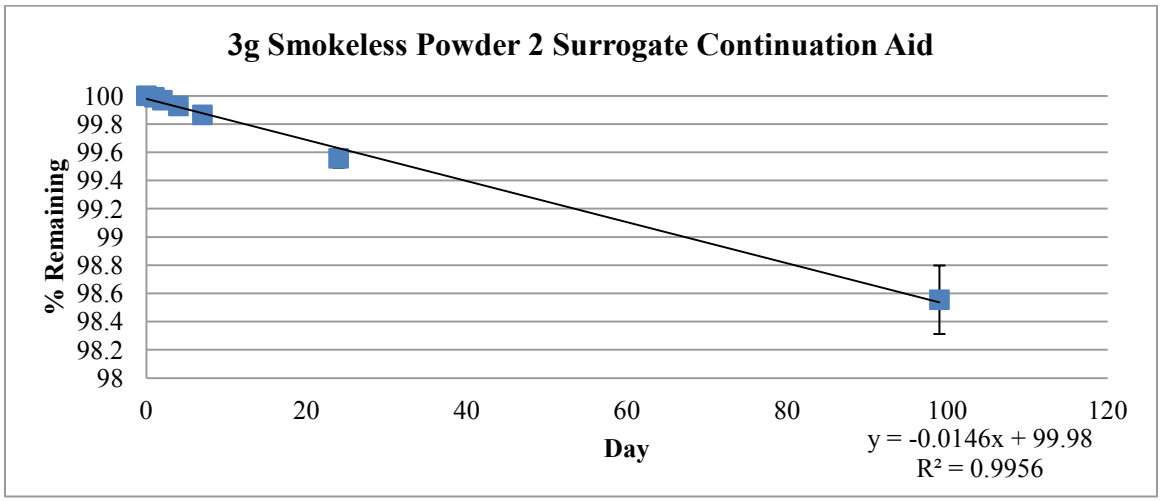



**Figure 34. Long term dissipation study: the dissipation rates observed with the smokeless powder 2 SCA within the IFRI explosives kit**

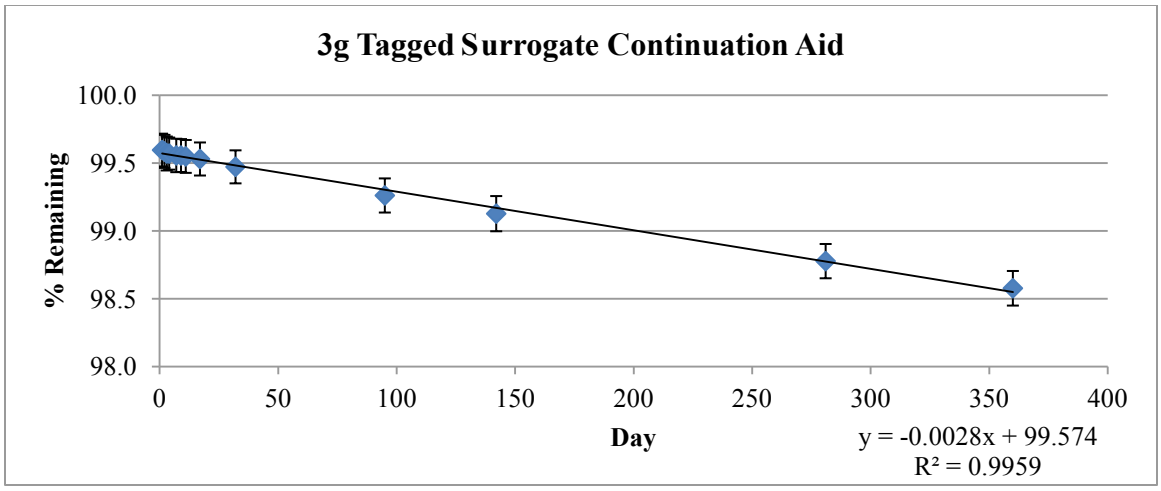



**Figure 35. Long term dissipation study: the dissipation rates observed with the tagged SCA within the IFRI explosives kit**

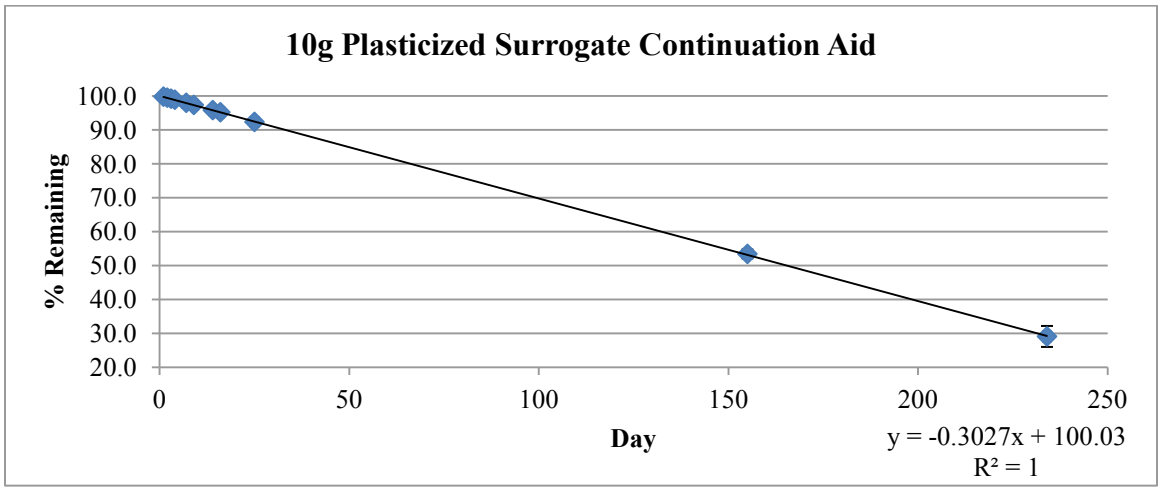



**Figure 36. Long term dissipation study: the dissipation rates observed with the plasticized SCA within the IFRI explosives kit**

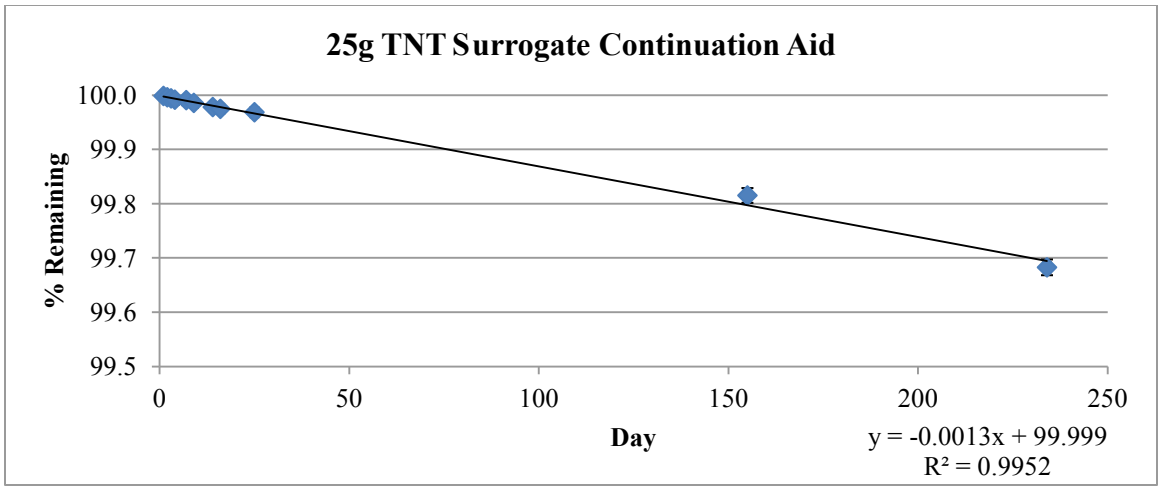



**Figure 37. Long term dissipation study: the dissipation rates observed with the TNT SCA within the IFRI explosives kit**

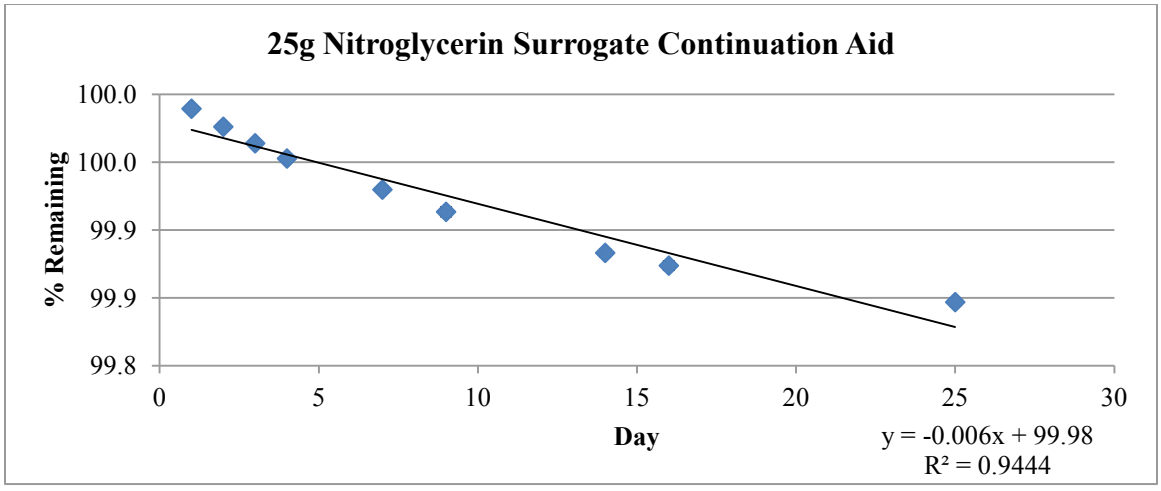



**Figure 38. Long term dissipation study: the dissipation rates observed with the nitroglycerin SCA within the IFRI explosives kit**

Various sorbents were tested to determine their effect on the dissipation rate of the plasticized SCA, Figure 39-Figure 41. No statistical difference was observed at a 95% confidence interval between the plasticized SCA with or without the addition of a sorbent

material. Both ANOVA and Student's t-test were used to perform this analysis. The sterile cotton gauze pads were selected for the construction of future SCAs as they had the lowest relative standard deviation (3.0 %) and the easiest preparation.

The airtightness test resulted with only one of the seven selected secondary containment systems providing viable secondary containment, Figure 42. The aluminum lined bags, Figure 42 A, exhibited inconsistent bag sealing as two of the three replicates had water saturated cobalt chloride test strips after overnight immersion in water. The spice jars, Figure 42 B, had similar results to the aluminum lined bags with two of the three replicates having water saturated cobalt chloride test strips and one jar containing water. The plastic containers, Figure 42 C, resulted in two of the three replicates containing water and the third replicate's cobalt chloride test strip showing high humidity after overnight immersion. The twist top plastic containers, Figure 42 D, were decidedly the worst secondary containment vessel as all three replicates contained water after overnight immersion revealing that the container is not airtight.

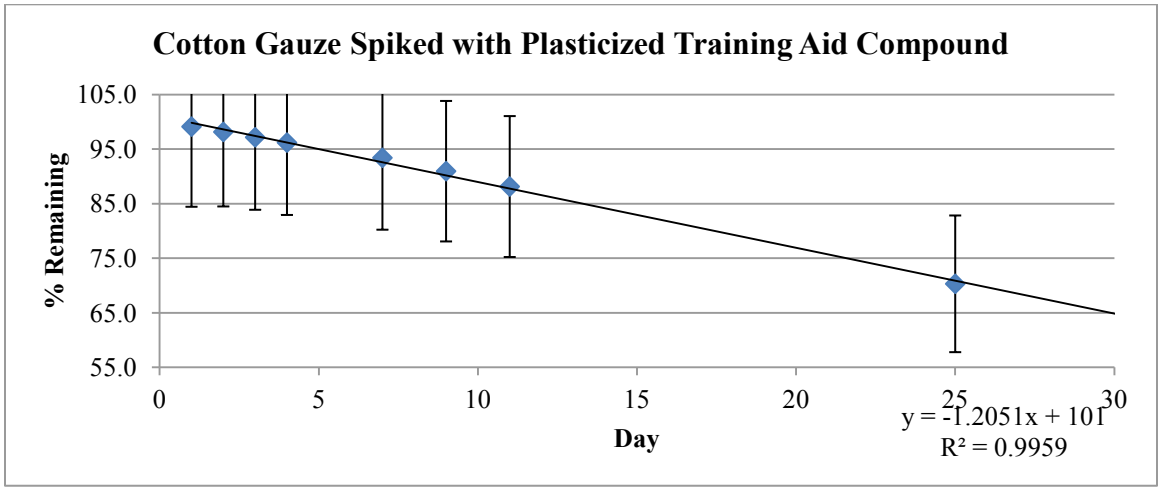



**Figure 39. Sorbent study: the dissipation rate observed with the cotton gauze after being spiked with three grams of plasticized SCA**

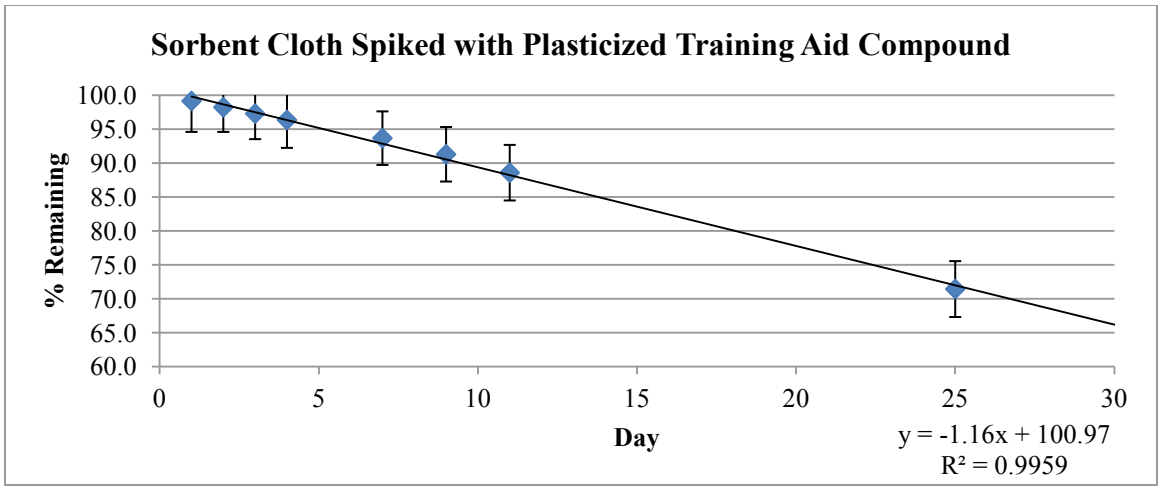



**Figure 40. Sorbent study: the dissipation rate observed with the sorbent cloth after being spiked with three grams of plasticized SCA**

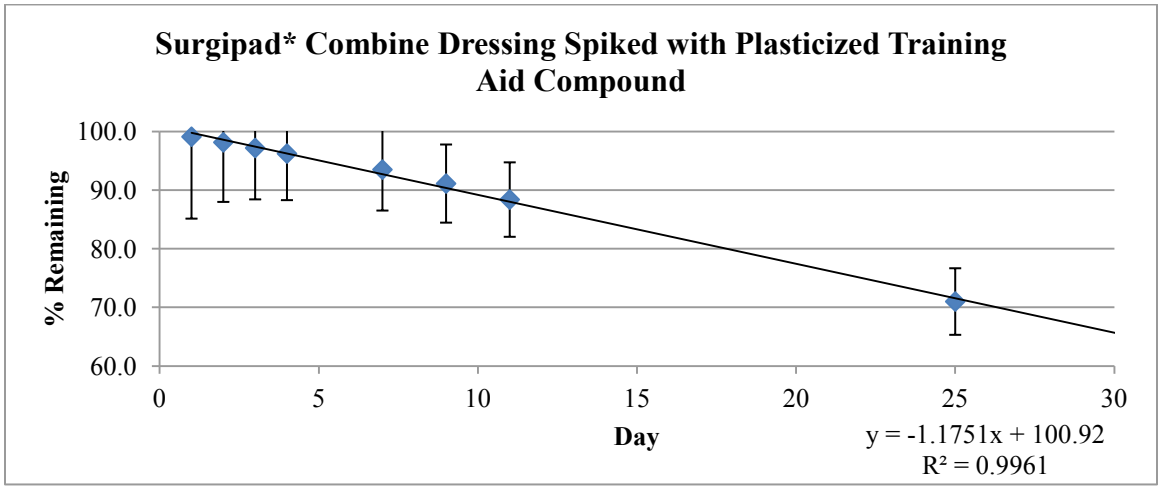



**Figure 41. Sorbent study: the dissipation rate observed with the Surgipad* combine dressing**

The canning jars, Figure 42 G, were the only secondary containment vessels shown to be airtight with reliable jar sealing as all three replicates indicated low humidity which was consistent with the control replicates. Both the 1Qt double sipper closure plastic bags (Figure 42 E) and clear glass jars with Teflon faced lined caps (Figure 42 F) contained no water, however, each of the replicate's cobalt chloride test strip showed high humidity indicating that the containers allowed for permeation and were therefore not airtight.

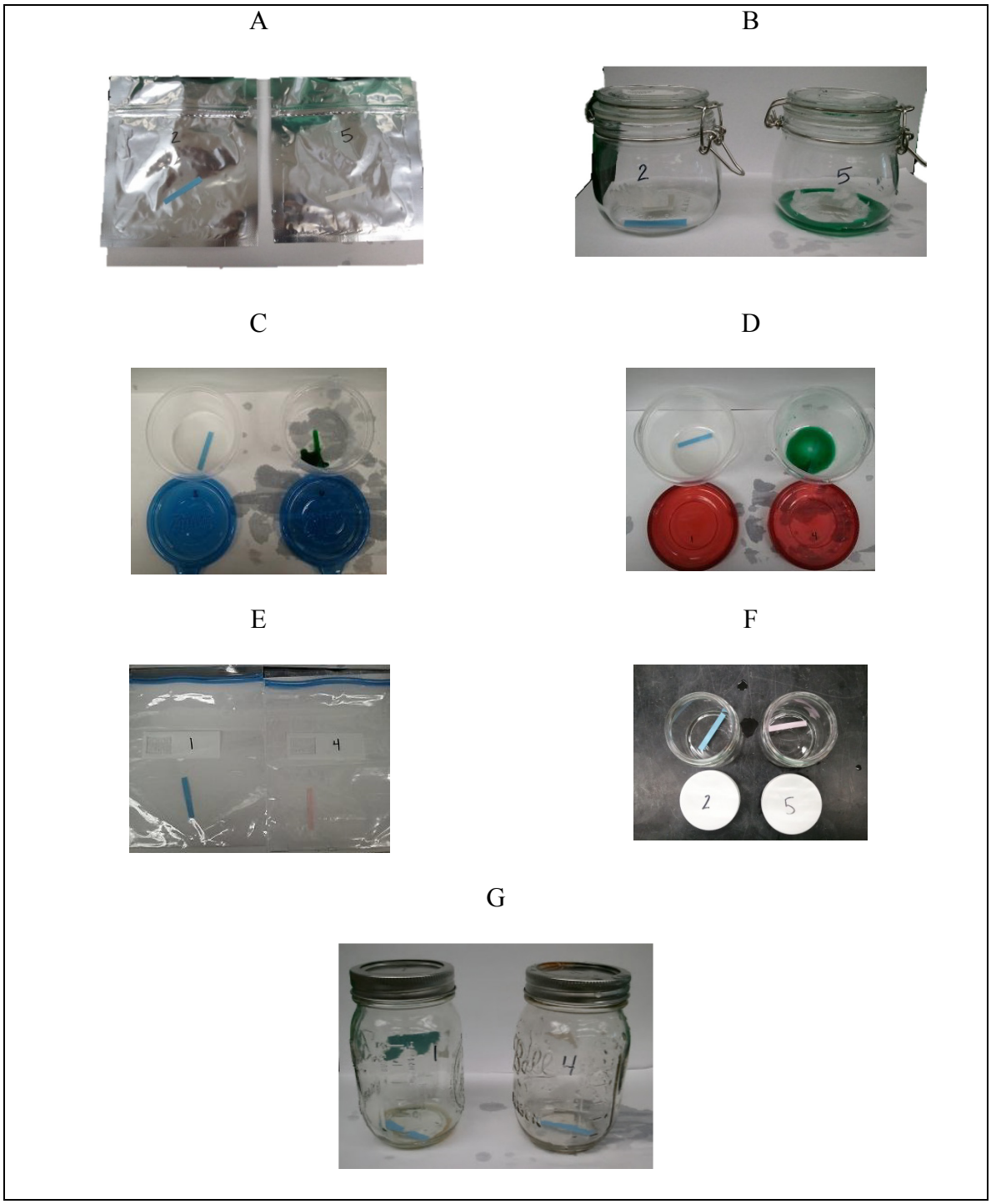



**Figure 42. Airtightness test of the seven selected secondary containment systems. (A) aluminum lined bags, (B) spice jars, (C) plastic containers, (D) twist top plastic containers, (E) 1Qt double sipper closure plastic bags, (F) clear glass jars with Teflon faced**

The effect of the secondary containment system on the SCAs was studied using the plasticized SCA since the dissipation rate is high enough such that the effect can be readily seen. A small number of potential containment systems were selected for this test and compared to plasticized SCAs without containment, Figure 43. The plasticized SCA was found to dissipate at an average rate of 27.0 ± 2.8 mg/day. This dissipation rate was reduced with containment to 9.2 ± 1.6 mg/day in the spice jars, 2.2 ± 1.4 mg/day in the twist top plastic containers, 7.0 ± 1.9 mg/day in the 1Qt double zipper closure bags, and 1.5 ± 0.4 mg/day in the canning jars. The dissipation rate observed in the canning jars represents a 94.0 % reduction in the dissipation rate in comparison to the unconfined plasticized SCA, indicating a longer lifetime of the continuation aid as equilibrium is rapidly reached within the container.

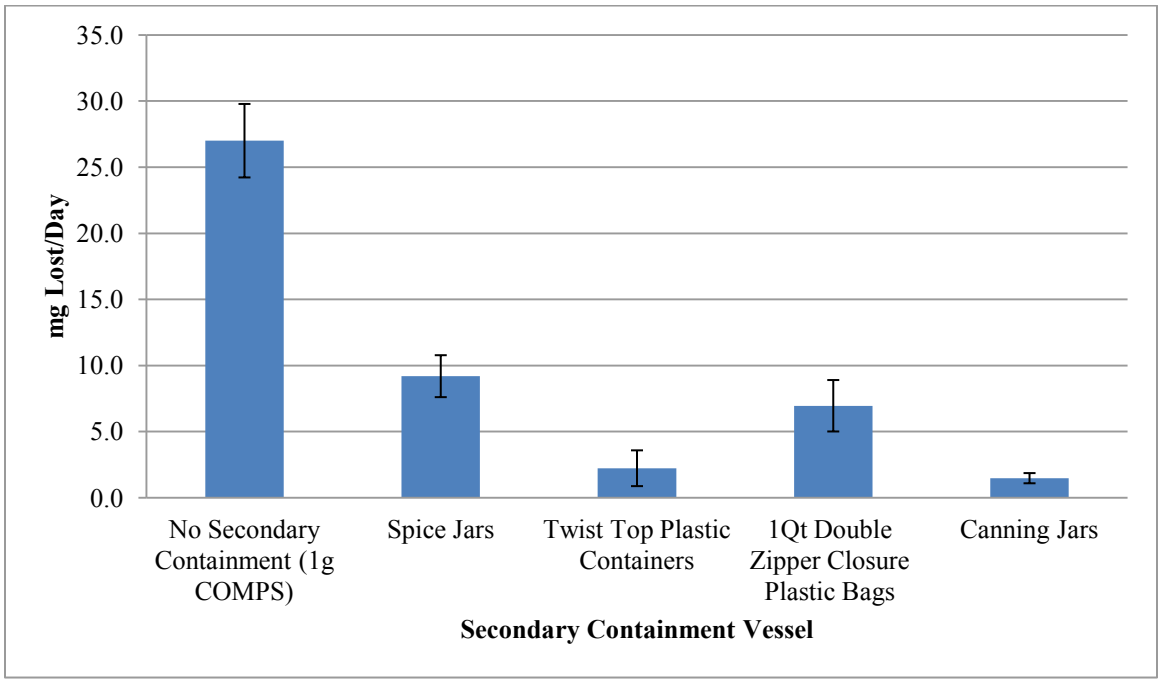



**Figure 43. Permeation rate comparison for various secondary containment vessels (plasticized explosive training aid)**

A bulk headspace analysis method for the SCA's within the prototype explosive kit was then developed. This stage is necessary to ensure continuity between the explosives training aids by using training aid material falling within acceptable parameters. This test was first completed via a fiber selection study in which six different fiber chemistries were studied (polyacrylate, PDMS, carboxen/PDMS, PDMS/DVB, Polyethylene Glycol (PEG), and DVB/Carboxen/PDMS) by exposing each fiber chemistry for 30 minutes, in triplicate, to the headspace of a container holding all six (TNT, NG, plasticized, tagged, smokeless powder 1, and smokeless powder 2) training aids. The results can be seen in Figure 44-Figure 50. It was concluded that a dual fiber extraction including PDMS/DVB and PEG would be used for future testing. This decision was reached because the two fibers in combination yielded the highest recoveries and lowest %RSD of the compounds studied.

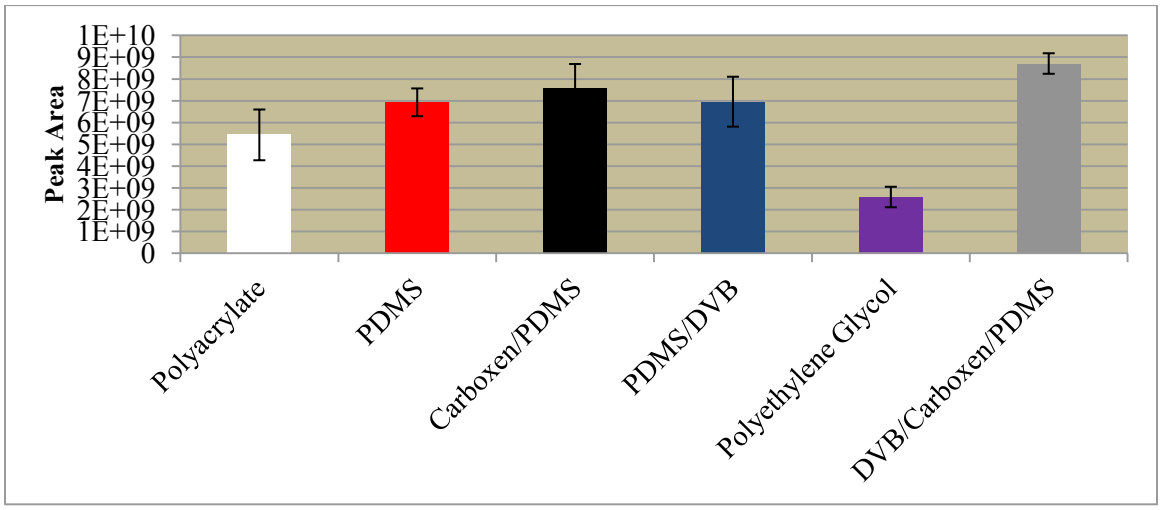



**Figure 44. Fiber study: average plasticized SCA extracted**

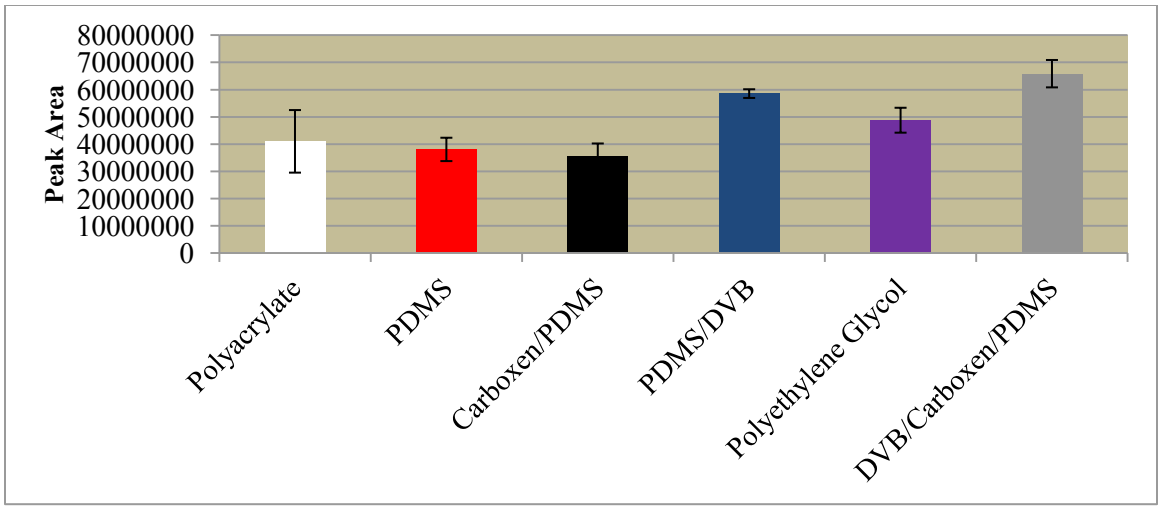



**Figure 45. Fiber study: average tagged SCA extracted (MS detection)**

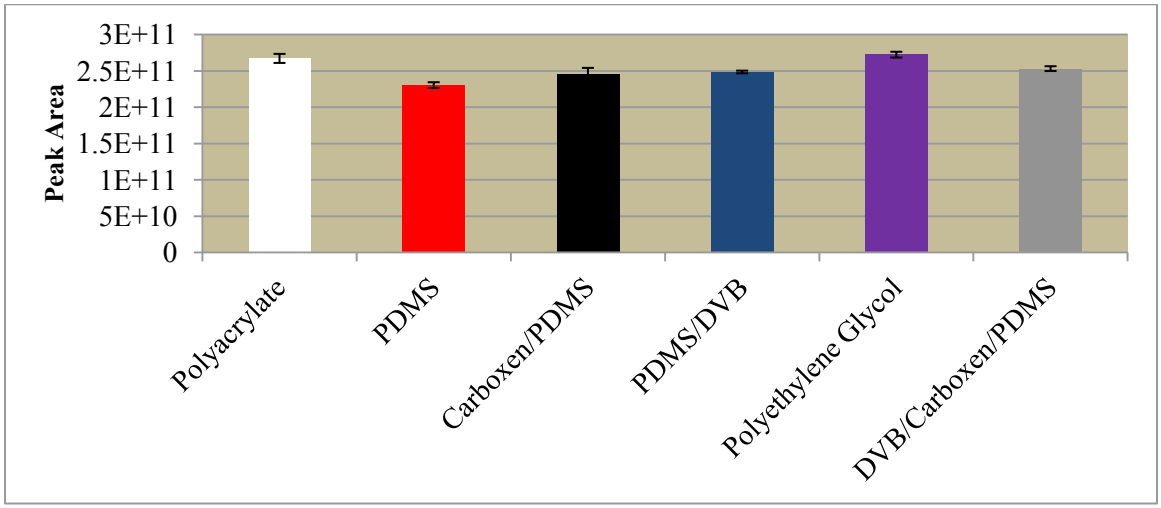



**Figure 46. Fiber study: average tagged SCA extracted (ECD detection)**

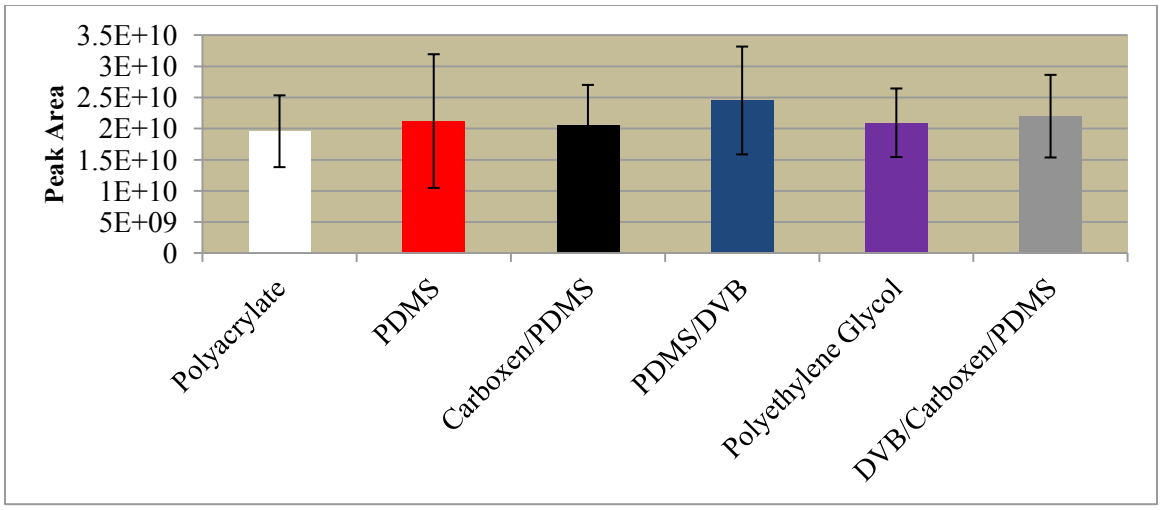



**Figure 47. Fiber study: average nitroglycerin SCA extracted**

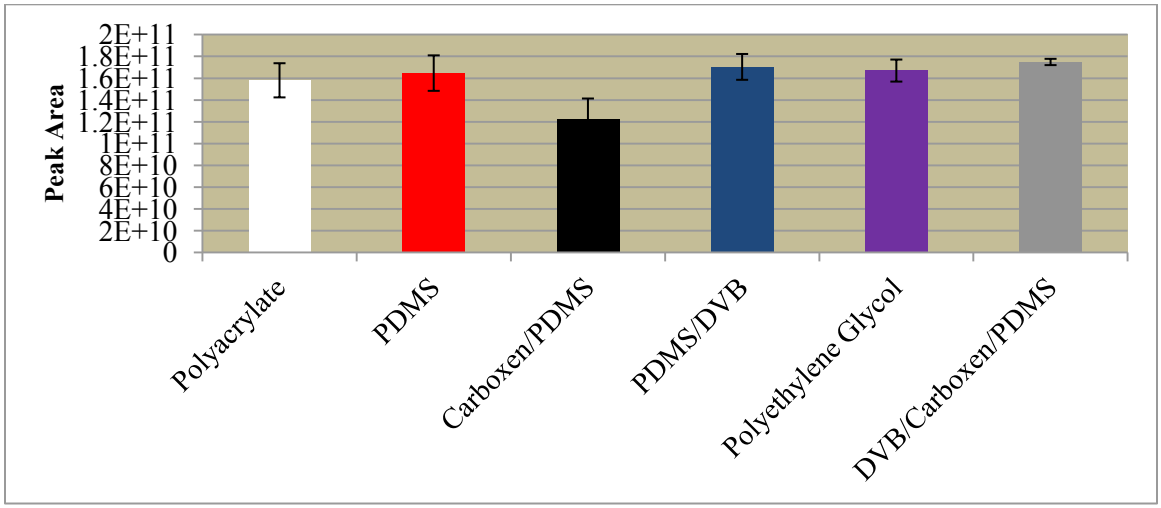



**Figure 48. Fiber study: average TNT SCA extracted**

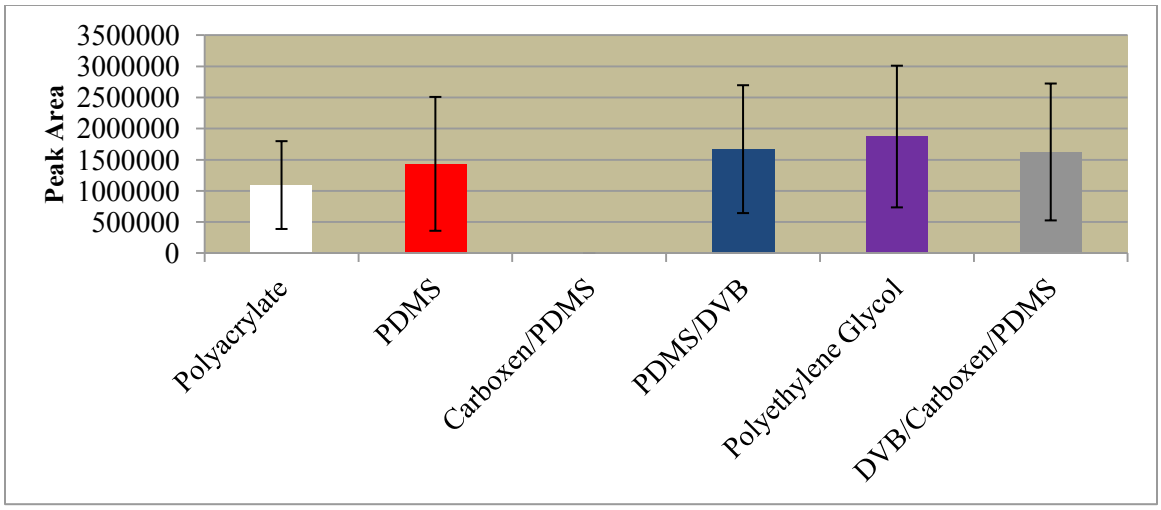



**Figure 49. Fiber study: average smokeless powder 1 SCA extracted**

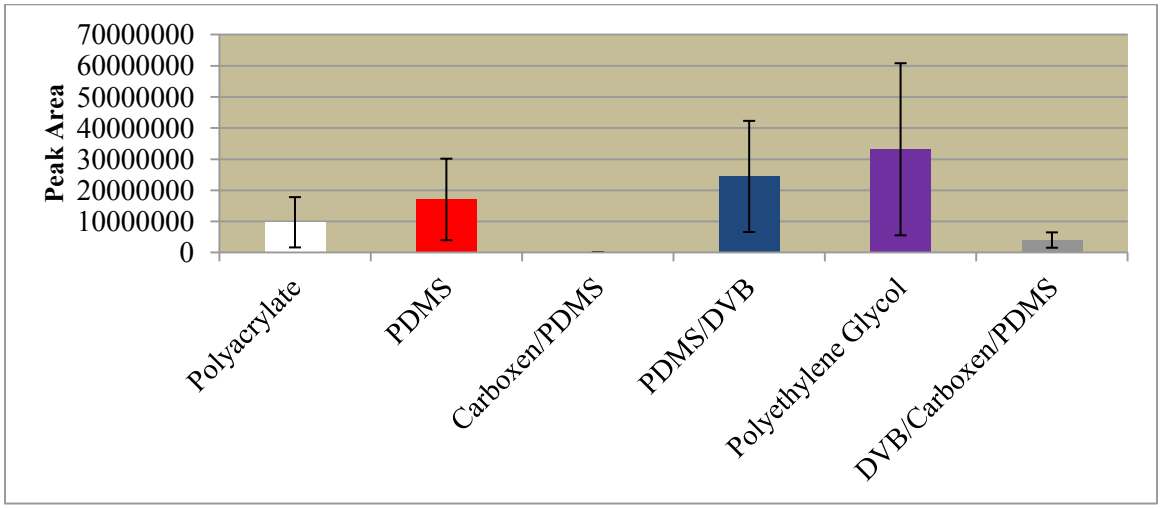



**Figure 50. Fiber study: average smokeless powder 2 SCA extracted**

Upon completion of the fiber selection study, an exposure time study was performed to determine the optimal exposure time for each of the compounds. This study was completed by placing 0.5g of an individual odor compound of the explosives kit

training aids in a 4 mL vial, in triplicate. The headspace was then tested over a specified number of minutes to determine the exposure time in which the maximum recoveries were observed. From this study, an exposure time of 3 hours was selected and used for all future experiments.

Cross contamination studies were conducted using both GC-MS and GC-ECD to determine the effect of using the canning jars as secondary containment systems. Four different kits were compared including: Kit 1- blank, Kit 2- unlidded secondary containment system (open), Kit 3- lidded secondary containment system which was opened daily representing daily use, and Kit 4- completely closed and lidded secondary containment system. The first contamination test qualitatively determined which SCA odors were escaping from secondary containment and were collected from within tertiary containment, Figure 52-Figure 53. From this test, only the compound associated with the tagged SCA was detected after a three hour SPME extraction in Kits 3 and 4. The SCA odors corresponding to the six explosives kit SCAs were observed in Kit 2, however, this is expected as the secondary containment system was left open. The second test was to quantitatively determine the cross contamination occurring *within* the secondary containment system. Since the contaminants were of interest in this test, the chromatogram peaks corresponding to the specific SCA contained within the jar were ignored and only the chromatogram peaks corresponding to contamination were used for this analysis. Results of the second test, Figure 51, showed that Kit 2 exhibited the highest contaminant collected which was to be expected as the secondary containment was left open. Through the use of canning jars as the secondary containment system there was an 86.1% reduction of collected contaminant collected in Kit 3 and 87.3% reduction

of collected contaminant collected in Kit 4. The plasticized SCA was responsible for the most observed contamination in Kits 2-4 followed by the tagged SCA. Kit 4 also was found to have smokeless powder 2 SCA contamination.

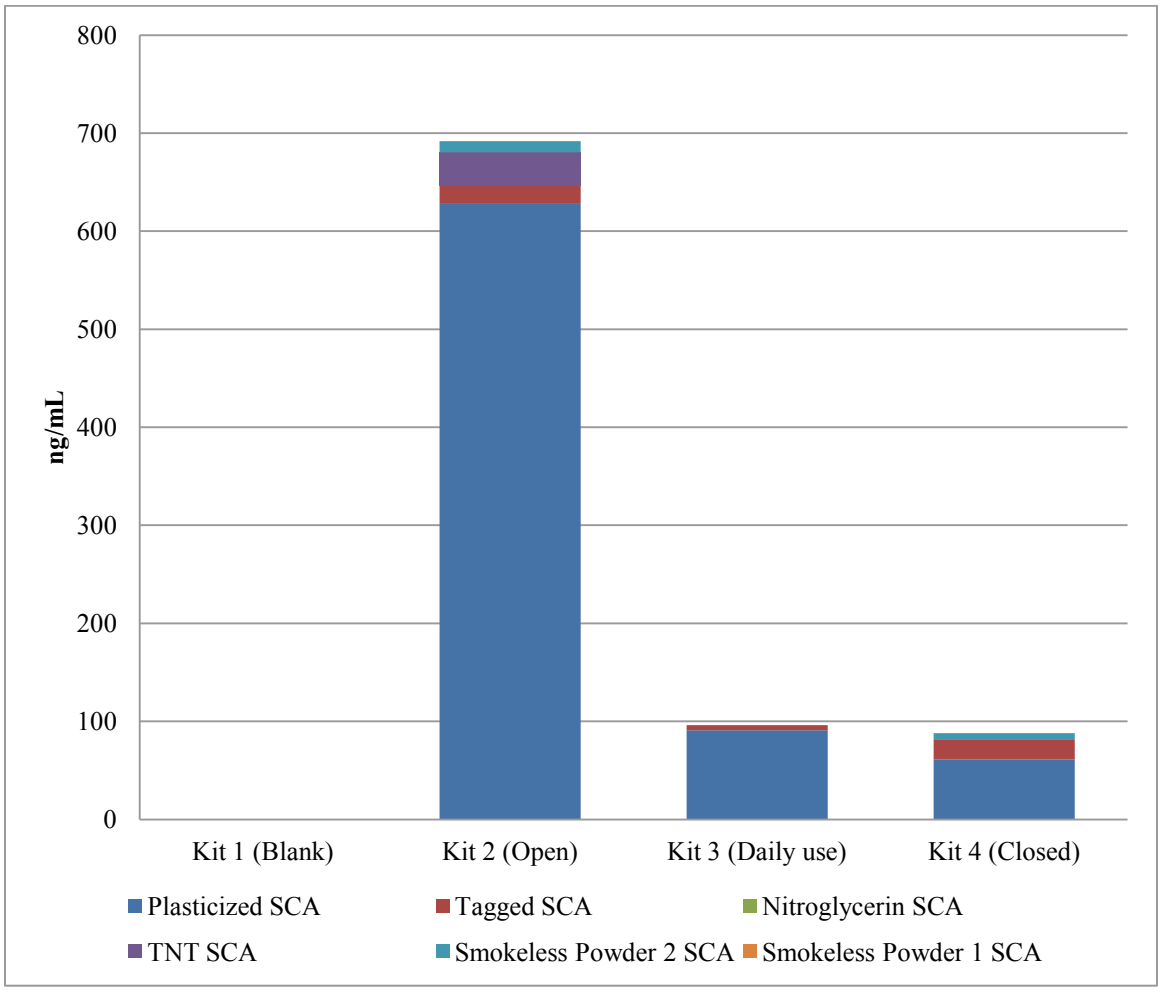



**Figure 51. Average odorant collected from within the secondary containment system**

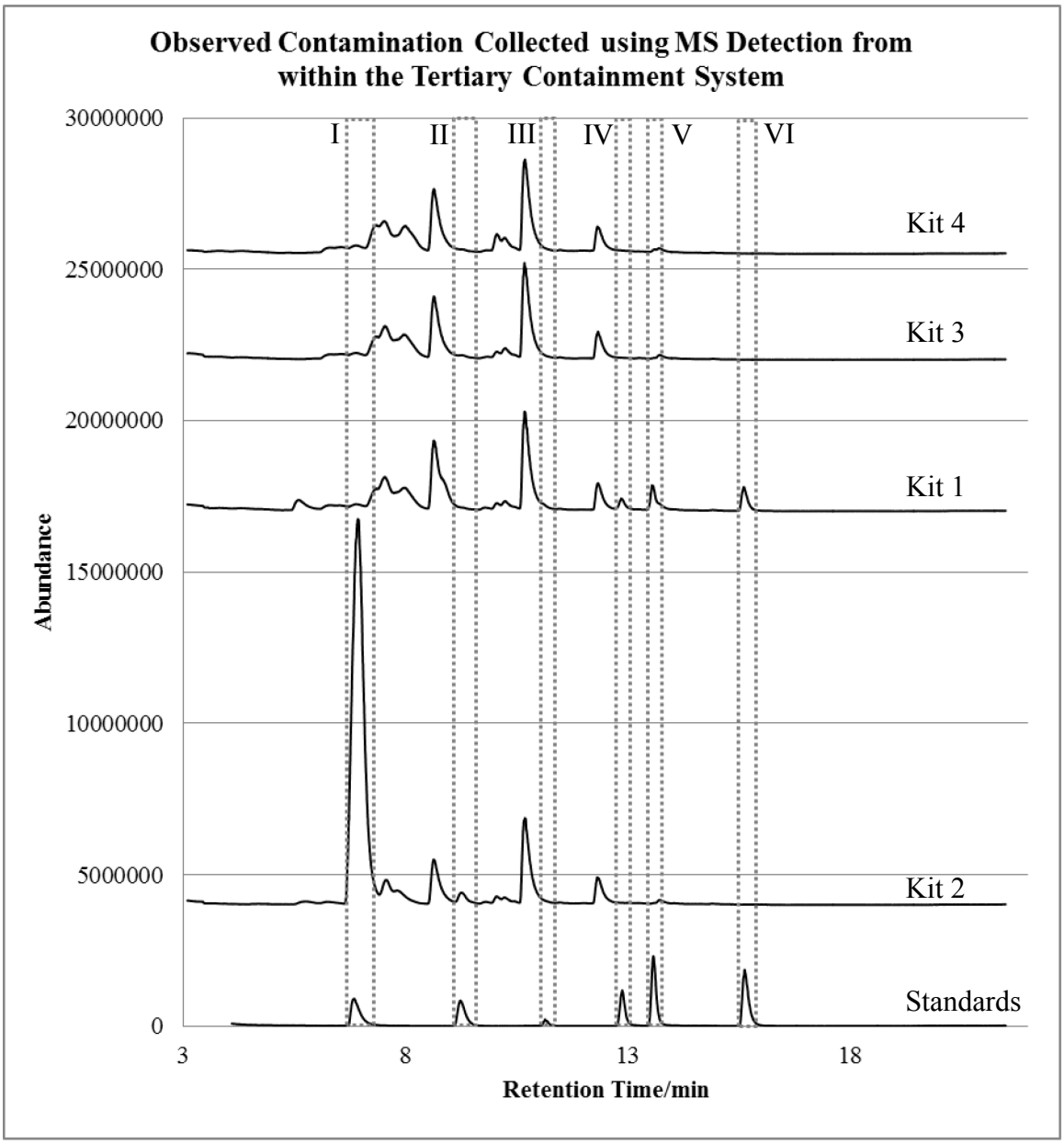



**Figure 52. The observed contamination collected using GC-MS from within the tertiary containment system. Kits compared in this test included: Kit 1- blank, Kit 2- unlidded secondary containment system (open), Kit 3- lidded secondary containment system which was opened daily representing daily use, and Kit 4- completely closed and lidded secondary containment system. Contamination peaks of interest correspond to: I- plasticized SCA, II- tagged SCA, III- nitroglycerin SCA, IV- TNT SCA, V- smokeless powder 2 SCA, VI- smokeless powder 1 SCA**

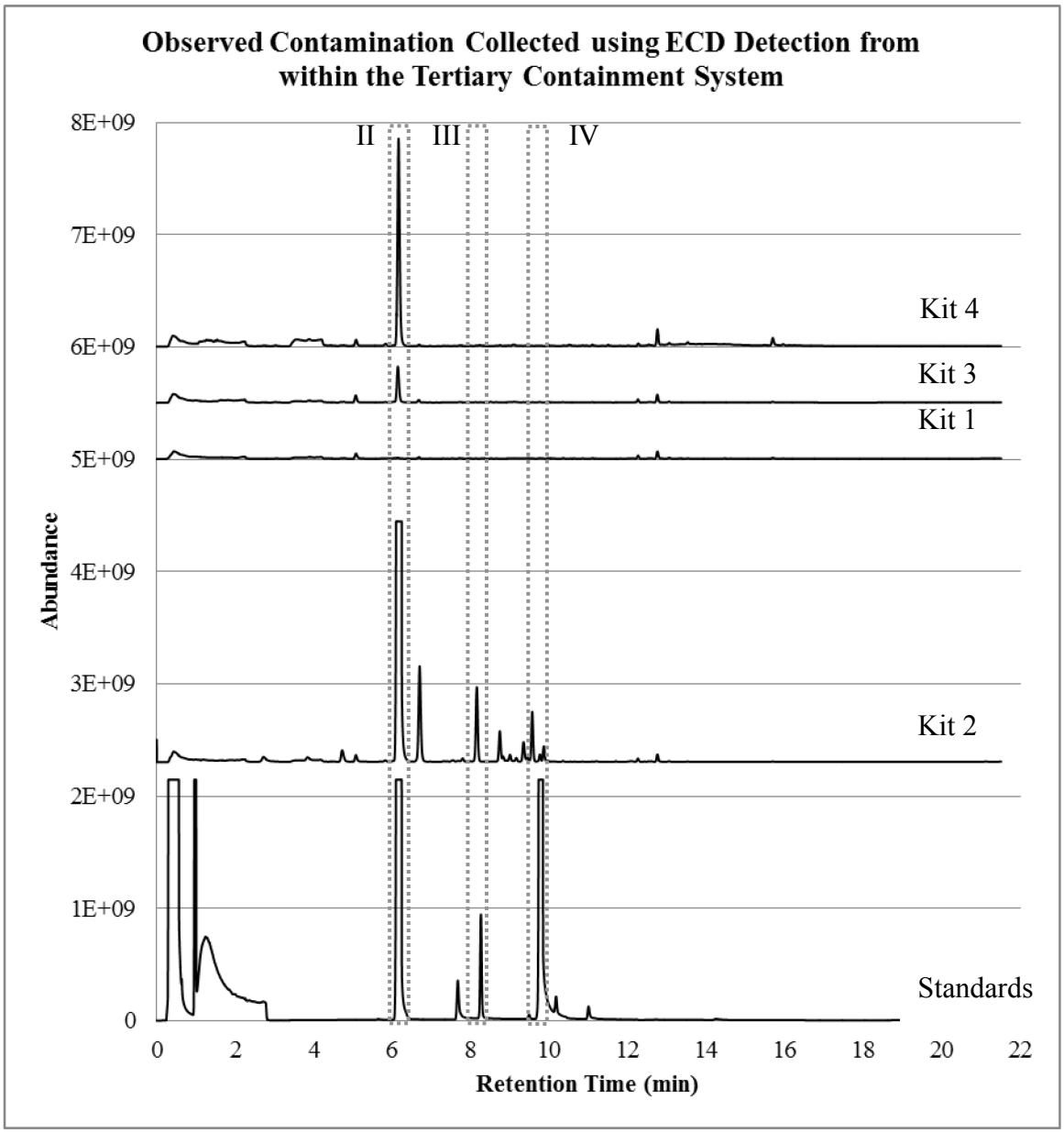



**Figure 53. The observed contamination collected using GC-ECD from within the tertiary containment system. Kits compared in this test included: Kit 1- blank, Kit 2- unlidded secondary containment system (open), Kit 3- lidded secondary containment system which was opened daily representing daily use, and Kit 4- completely closed and lidded secondary containment system. Contamination peaks of interest correspond to: I- plasticized SCA, II- tagged SCA, III- nitroglycerin SCA, IV- TNT SCA, V- smokeless powder 2 SCA, VI- smokeless powder 1 SCA**

The ruggedness of the SCAs within the IFRI prototype surrogate explosives kit were monitored during regular field use to determine whether extremes in temperature would affect their performance. A minimum temperature of 2.5°C (negative temperatures were recorded during the device shipping, not while sampling the kit) and a maximum of 35°C was recorded. No decline in performance was reported, Figure 54.

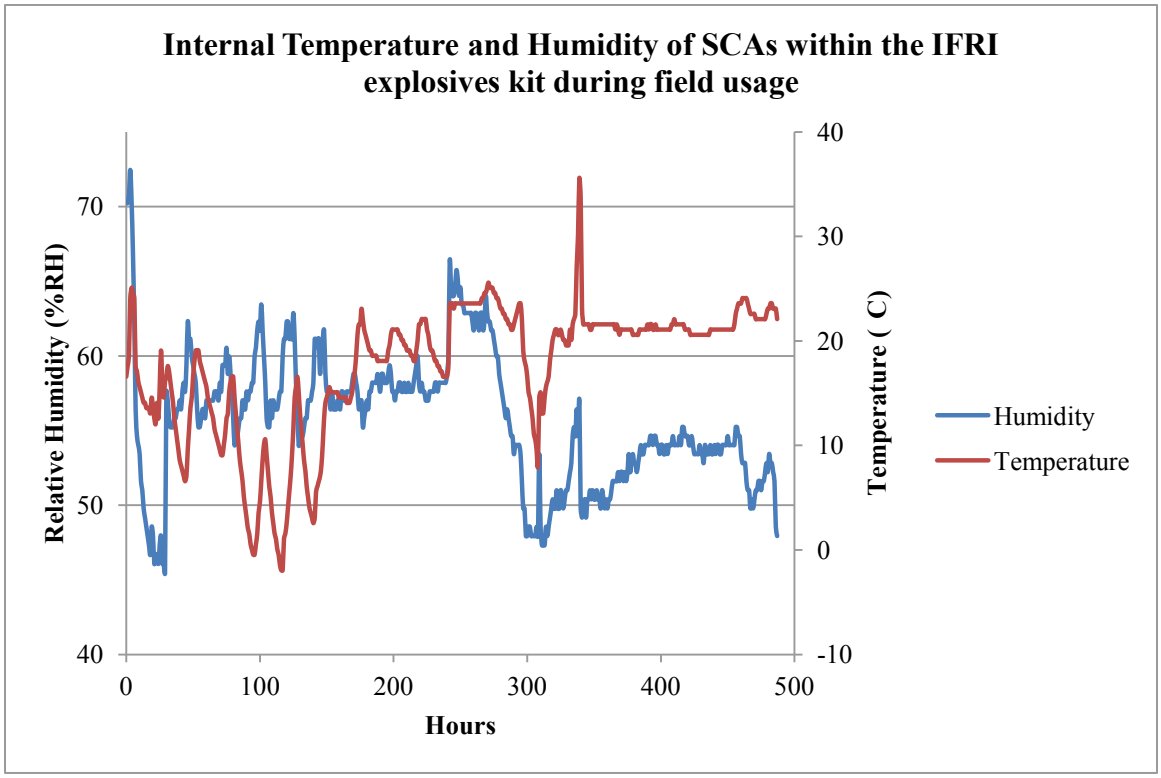



**Figure 54. Temperature and humidity fluctuations monitored of COMPS devices**

## 6.5 Discussion

Explosive detection canines are used daily to perform routine searches for illicit material. As these canines are charged with securing the safety of the population, it is imperative that the detection canine is properly trained and maintained such that their responses can be accepted as accurate. Unlike the other detection canines in the field, a

false negative with an explosive detection canine could have deadly results. This requires the explosive detection canines to have training aids that garner the highest likelihood of accurately locating explosive material in the field. As there are several types of SCA materials for a canine handler to choose from, a scientifically validated and reliable explosives kit containing a collection of explosive odors is indispensable. While training with the actual illicit material is ideal in most cases, selection and storage of the proper explosives can be challenging. In these instances organizations employing detection canines will seek out SCAs.

The goal of this study was to validate the prototype surrogate explosives kit developed by IFRI through controlled tests. In order to complete this task, the SCAs using odors previously described as dominant odor compounds were first studied (1,3,53). As the SCAs within the explosive kit are constructed using the COMPS method, focus was placed on determining the reliability of the training aids produced in this fashion (103). The results of the dissipation studies revealed that there is little variation in the dissipation rate regardless of manufacturing differences in the polymer bags or the weights of compounds placed within the bag. Changing the polymer, polymer thickness, or surface area of the permeating polymer were found to have the greatest effect on the dissipation rate of the SCAs and has been noted as an area of research for future studies. While the three previously stated factors were found to produce the greatest effect on the SCAs, smaller contributing factors (humidity and temperature) were found to interfere with gravimetric analysis of the SCAs.

The test environment for the SCAs represented a harsh environment in which the SCAs were left in the open to permeate. Initial experiments revealed that the dissipation

rate is constant for the SCAs in the explosive kit, however, in the TNT and nitroglycerin SCAs the dissipation rate was found to initially increase in the starting weight and then show slight variations corresponding to humidity changes in the test environment. While most of the materials within the IFRI explosives kit are pure chemical compounds, the TNT and nitroglycerin SCAs are mixtures, which exhibit hydroscopic tendencies. The initial weight gain can therefore be attributed to the presence of moisture in the test environment. The slight variations corresponding to humidity changes can be diminished by increasing the weight of material in the polymer bag. By increasing the weight of material (TNT and nitroglycerin SCA), the weight gains associated with water gains were reduced while the dissipation rate was found to be steady. It was not until 1.5 years into the dissipation study using larger weights of TNT and nitroglycerin that SCA were found to begin showing a slowed dissipation rate. Since this raised concern that the odors were no longer permeating, headspace analyses were performed and revealed similar concentrations of TNT or nitroglycerin SCA were found in each respective headspace as to headspace samples collected at the start of the experiment.

The smokeless powder 2 SCA also presented challenges in determining the permeation rate due to the testing environment. Unlike the IFRI smokeless powder 2 used in the field, oxidation of the SCA was found to be an issue in the laboratory environment. As the SCAs used in the field are sealed within jars, their exposure to moisture and air are limited, unlike the dissipation studies performed in the laboratory where the SCAs were completely and constantly exposed to moisture, air, and light. Discoloration due to oxidation of the smokeless powder 2 SCA occurred within one week of the start date and within approximately two months all of the material within the COMPS exhibited

discoloration, which corresponded to a drastic slow in the observed dissipation rate. As this oxidation was not observed in the field, analyses and additional studies were performed to determine the cause. Dissipation studies were conducted controlling the smokeless powder 2 SCA exposures to light and humidity. Smokeless powder 2 SCA permeating in the dark was found to have a dissipation rate of 3.31 ± 0.41 ng/s and exhibited a similar slowing of the observed dissipation rate after about two months. Smokeless powder 2 SCA permeating in the presence of a desiccant was found to have a dissipation rate of 7.44 ± 0.72 which was maintained throughout the entirety of the study. Slight discoloration was observed in the smokeless powder 2 SCA in the presence of desiccant, however, complete oxidation was not observed during the experiment. Literature supports that in the presence of water and light the chemical contained within smokeless powder 2 SCA will undergo an oxidation reaction that produces additional water. This is believed to be the cause of the slowed dissipation rate observed in the oxidized SCA since the weight of water gained was nearly equal to the dissipation of the SCA (124). Headspace testing of the oxidized smokeless powder 2 SCA revealed only a single chromatographic peak, confirmed through standards and MS fragmentation pattern as diphenylamine (smokeless powder 2 SCA).

Feedback from beta testing of the prototype surrogate explosives kit revealed that the canine handlers were hesitant to use a SCA filled with liquid, as in the case of the plasticized SCA. To abate this concern, the sorbent study was conducted such that the odor is absorbed onto a sorbent, which then dissipates. The sterile cotton gauze pads were selected as the sorbent of choice because they are easily prepared and were found to have no effect on the dissipation rate of the plasticized SCA. Because most persons in the field

training detection canines would like training aids that last approximately two years, the plasticized SCA required a large weight of material to compete with the rapid dissipation rate observed. Continued studies are in progress to reduce the dissipation rate of the plasticized SCA through variations in the polymer, polymer thickness, and surface area of the permeating polymer.

Three levels of containment were employed for the IFRI prototype surrogate explosive kit. The primary containment level is the containment of the training aid material. The primary containment vessel requires the delivery of a known and controllable amount of odor and that the vessel must be permeable. COMPS were selected as the primary containment vessel for the prototype surrogate explosives kit. Secondary containment vessel requirements include: airtightness, sufficient size to hold the SCAs in primary containment, portability, and have no effect on the training aid. Glass canning jars with metal two part locking lids have been selected as the optimal secondary containment vessel for the kit. Tertiary containment vessel requirements include: airtightness, sufficient size to hold all the secondary containment vessels, and portability. Airtight hard plastic cases have been selected as the tertiary containment vessel.

Selection of a secondary containment system for the SCA within the kit was necessary to prevent contamination of the SCAs within the kit and to start a precedence of the best containment system for field use. As there is currently no standard among canine handlers for storage of training aid materials, a wide variety of vessels were selected for testing that are currently used in the field. Several organizations using plastic containers, similar to the ones tested in this study, which are not airtight and are known to

permeate odor have been encountered. An ideal containment system should be airtight and made of a material that is impervious to odor permeation in order to reduce the availability for contamination. Of all the containments vessels tested, the canning jars showed the most promise. As rust is a concern with the canning jars, which may be a limiting factor for the lifetime of the prototype explosives training aid kit, regular examination of the lids must be conducted. Lids showing evidence of rust and/or substandard condition should be immediately changed. Other secondary containment systems are currently used in the field and from the results of this test, a revised method of storage is needed since the training aids are likely becoming contaminated which has detrimental effects in detection canine training. While contamination of the tertiary containment system and SCAs within the kit was observed, the contamination was greatly reduced by using the canning jars. As the plasticized and tagged SCAs represented the majority of the contamination observed in the cross contamination study, future explosives kits can be packaged such that the plasticized and tagged SCAs are separate from the other SCAs and in their own tertiary containment systems.

## 6.6 Conclusions

Completion of this study has shown that the IFRI prototype surrogate explosives kit has been proven to be a viable alternative for explosives detection canine training when actual illicit material is unavailable or cannot be used. As the kit currently only covers five classes of explosives, future work will include the creation of SCAs for additional explosive classes. Additionally, there may also be the need of a future study for the development of “high” and “low” SCA’s for a more comprehensive training aid

kit. While the use of actual explosive material is typically ideal, as a result of this study, it has been shown that regardless of the SCA used, it must be stored and maintained properly for the best possible training outcome. Current methods of SCA storage should be abandoned in favor of airtight low permeable solutions. While canning jars proved to be the most effective secondary containment vessel tested, there are other possible alternatives as long as the requirements are met. Through the use of the IFRI prototype surrogate explosives kit, a streamlined and universal method of training has been developed that will aid in the entirety of explosives canine detection by standardizing the training aids and storage methods.

# 7 TASK 5: DEVELOPMENT OF AN OPTIMAL TRAINING PROTOCOL FOR DETECTION CANINES

## 7.1 Introduction

There are two schools of thought concerning the proper way for training a detection canine. Both methods have the same result. The detection canine will be trained to alert to a predetermined set of materials, however, the time and reliability of each method has yet to be determined. The first method of training is the separation method. Within the separation method, the odors to which the untrained canine is to be imprinted on are kept separate throughout the entirety of the canine's training. There are two variations of the separation method. Within the first; the canines are imprinted on the odors in sequence, only learning an additional odor after mastery of the first odor. The second variation is to imprint all of the odors simultaneously, with each of the odors being kept separate. The second method of training is the combined odor method. Within

this method, all of the odors are combined within a single box creating a "soup" (colloquial term used by canine trainers) with all of the odors available in the headspace. The canine is then imprinted on the "soup" until mastery of the box is achieved (approximately one week of training). Once the canine has mastered the "soup," the odors are separated and the canines are then only exposed to the separate odors for the remainder of the training.

Within this study, the consistency and speed in which the canine can be trained was evaluated. In result, recommendations can then be made to practicing canine trainers such that the canine has the best possible streamlined training protocol that will withstand courtroom scrutiny.

## 7.2 Materials

Field tests were conducted with detection canines using both the separation and combined odor methods. All canine tests in this research endeavor were conducted with strict adherence to the current Florida International University Institutional Animal Care and Use Committee (IACUC). Green canines selected for the imprinting had only obedience training and no exposure to any illicit materials.

## 7.3 Methods

All canines were preselected for detection use for a specific police department and showed similar aptitude for detection work. The canines were housed and cared for by their respective handler; however, all canine training was conducted under the direct supervision of an IFRI certified canine trainer. A single canine trainer was used for all of the training throughout the study to ensure continuity between the test methods. As the

canines were selected for a specific police department's use, the canines were trained and studied as they became available. Since the method of training was being tested rather than the detection substance, both narcotics and explosives detection canines were used in this study.

Four narcotics detection canines were imprinted using the separation method for the detection of five drug odors: cocaine, marijuana, methamphetamine, MDMA, and heroin. The drug odors were placed out individually in Kongs® by splitting the Kong® and placing a bag full of drug within the Kong®. The doped Kong® was then hidden to the trainer's specifications. All five odors were imprinted separately during the same time frame using varied weights of drug throughout the imprinting process. Six explosives detection canines were imprinted using the combined odor method for the detection of eleven explosives: TNT, dynamite, RDX, PETN, AN, smokeless powder (two odors), black powder, C4, tagged explosives, and TATP. Each of the explosive odors were placed into an individual perforated stainless steel container. The eleven containers were then placed into a single stainless steel box with a large circular hole in the top. The explosive odors were combined in the box for one week. After the initial week the odors were separated and each individual odor was hidden to the trainer's specifications.

Regardless of the training method, the canines were instructed and directed to search, put their nose on the odor, and then sit. Upon the sit (the sit response corresponds to an alert), the canines were given their reward (toy). As the canines progressed through the training, they were instructed to search and would then search, locate, and alert to the illicit material odor without prompting. Training sessions were attended throughout the entirety of the imprinting and the canines' progress was noted.

## 7.4 Results and Discussion

Both the separate and combined method for training green canines has been used by handlers for these training aids. Requests were made for training records to determine which method, if either, is superior. Only one canine trainer was willing to share canine training records and use the two different training techniques. A class containing three narcotics detection canines and five explosives detection canines was trained using the two separate methods of imprinting. Records were also obtained for one previously trained narcotics detection canine and one previously trained explosives detection canine. The four total narcotics detection canines were trained using the odor separation method throughout the entirety of imprinting with five drug odors being imprinted at one time. After five days of training all four narcotics canines were capable of finding all five individual odors with no prompting. As per the class schedule, the one previously trained canine was certified to IFRI/NFSTC standards as the end of the six week course with no false alerts and no hide misses. The remaining three canines certified with 100% alert rates for all of their trained odors.

The six total explosives detection canines were trained using the combined odor method for the first week of training and then the eleven explosives odors were separated for the remainder of the canine imprinting. After five days of training all six explosives detection canines were capable of finding the combined odors and on the sixth day of training the odors were separated with the canines having slight difficulty in coming to a full alert on the sixth day of training; however, after the sixth day of training all six explosives detection canines were capable of finding all eleven of the explosives odors with no prompting. As per the class schedule, the one previously trained canine was

certified to IFRI/NFSTC standards as the end of the six week period with no false alerts and no hide misses. The remaining five canines certified with 100% alert rates for all of their trained odors.

From these results no observable difference can be seen between the two training methods. However, this sample of detection canines may not be representative of the population; therefore, more data is necessary before a conclusion can be drawn. Both methods of imprinting produced canines that are capable of reliably finding the odors to which they are trained. On average the canines were capable of locating the illicit materials within a week of commencing the imprinting process. With this sampled population, the six week imprinting class was required not because the canines needed six weeks to recognize the odors, but to train the canines how to search. Training a canine to alert on an illicit material is relatively easy because as soon as the canine associates their reward with an alert response, the canine will respond appropriately to receive the reward. Depending on the canine, the association may be made faster or slower based on the aptitude of the canine. This process is aided by initially hiding the illicit materials in (separation method) or with (combined odor method) the reward. This results in the canine searching initially for the reward which is surrounded by odor. Once the canine learns the game, the illicit materials can be hidden without the reward and the canine will still alert due to the association made between odor and reward.

Training a detection canine to search an object, room, vehicle, and/or open area typically is the most time consuming aspect of canine imprinting. Detection canines that are unfamiliar with the search parameters will often have a difficult time locating a hidden illicit material because the test is too foreign. To overcome this challenge, the

bulk of the imprinting process involves teaching the canine and handler how to direct the search such that all areas are covered in a logical manner that reduces the likelihood of the canine handler team missing any areas. Time and repetition of possible search areas are required so that the canine becomes familiar with several search patterns and can perform reliably in the field.

## 7.5 Conclusions

Completion of this study resulted in no observable difference in the reliability or time in which it took to imprint the detection canine on an odor. While this small sample of canines may not be indicative of the population, the results indicate that both training methods are viable options as long as the canine meets certain requirements. First the canine must be selected with the necessary attributes for detection work. Canines should have high hunt and play drives so that they are inclined for long searches. Secondly, the canine must associate odor, alert, and then reward. Regardless of whether the odors are separate or combined, if the canine does not make this association, the canine will never be a reliable detection tool. Additionally, this study has shown that there is no need to imprint only one odor at a time in the separation method and canines can be imprinted on multiple odors kept separate at the same time. This is beneficial because it reduces the overall training time.

However, there are caveats with this association. Care must be taken to ensure that the canine is only rewarded upon a correct response. Detection canines are continuously learning whether the handler is teaching or not, therefore, improper odors can be easily added to the detection canines repertoire if the handler is not careful. Also,

the canine should be trained to discriminate odor, meaning the canine should only alert to the odors to which they are trained rather than the most odiferous item in the search area. Canines that cannot scent discriminate may have a higher number of false alerts because they locate and will alert to any substance that is odiferous. Upon scent discrimination, the detection canine will only alert to the odors to which they are trained and will ignore competing odors, even ones corresponding to their reward. Third, the canine must be trained and maintained with variation. The weights of illicit material and training scenarios should be continuously altered so that the canine learns to be comfortable in any situation. This allows the canine to implement their trained search pattern in any scenario, resulting in the best likelihood of a correct response.

Additionally, while there was no observable difference between the imprinting methods, the handler and trainer must remember that once the odors are separated in the combined odor method, they should never be combined again. If the materials are "souped" again, the canine will learn the mixed odor as an additional substance in their repertoire and will likely lose the ability to locate the separated odors in the field. This occurs because the canine will learn to associate the presence of all of the odors within the headspace in order to achieve an alert response. This results in detection canines missing single odors in the field which can be extremely hazardous and have deadly consequences. Completion of this study has shown that there is no difference in the consistency and speed in which the canine can be trained when using the two different imprinting methods. In result, either imprinting method represents a viable option for practicing canine trainers, with reliable and streamlined results that will withstand courtroom scrutiny.

# 8 TASK 6: DETERMINATION OF THE OPTIMAL TYPE OF SURROGATE CONTINUATION AID

## 8.1 Introduction

There are several surrogate continuation aids (SCAs) currently available on the market today. Several of these training aids have not been tested to reliable scientific standards, but are rather the concoctions developed by "mom and pop shops," touting effectiveness. An optimal training aid is one that is harmless to the canine, long lasting, and requires no special conditions. As there are several types of SCAs to choose from (COMPS, wax aids, particle aids, polymer aids, commercially available aids), comparisons need to be made between the aids. Aids having the same odor profile can be made or purchased and were tested under various conditions. An optimal SCA will have very little or no significant changes in the odor release or longevity and should be difficult to contaminate over a range of various conditions. But most importantly, the aids should be representative of the odors that they are mimicking. This study used canine field trials testing a variety of explosive SCAs' to determine the optimal training aid when actual illicit material is unavailable for use.

## 8.2 Materials

All canine tests in this research endeavor were conducted with strict adherence to the current Florida International University Institutional Animal Care and Use Committee (IACUC). Experienced explosives detection canines used in this study were required to show proficient explosives detection skills with a detection rate of 90% or higher for actual explosive material prior to being selected for testing. Preferentially, these canines

should have a current detection canine certification from a SWGDOG recognized certifying body. Proficiency tests were administered prior to testing the prototype SCAs which consisted of a SWGDOG guideline based certification test (78). Canines unable to meet the 90% detection rate were excluded from the study. Canines meeting the detection rate requirement were often used for multiple repetitions of testing

The prototype surrogate explosives kit was manufactured in a reproducible manor using chemicals purchased from Sigma-Aldrich (St. Louis, MO) and Natchez Shooters Supplies (Chattanooga, TN). 2" x 2" sterile cotton gauze pads (Independent Medical Co-op, Inc.; Daytona Beach, FL), and 2 mil, 3" x 3" low density polyethylene (LDPE) bags (Bagbarn.com; Hanover, IN) were also purchased. Additional SCAs tested were donated for use and were purchased from NESTT (Non-Hazardous Explosives for Security Training and Testing, (125)) and the National Institute of Standards and Technology (NIST, Gaithersburg, MD).

## 8.3 Methods

A comparison test of the prototype surrogate explosives kit to other commercially available SCAs was conducted using trained explosive detection canines. The SCAs were prepared according to their prescribed directions and placed in an odor recognition line up. The trials were completed double blind.

## 8.4 Results

Seven canine trials involving 52 canines have been conducted to test the NIST and IFRI training aid materials. The first canine trial consisted of 22 canines having a mean age of 3 years, a mean working experience of 1.2 years, and were said to have

recently returned from overseas deployment or in the final preparatory stages for deployment. In this trial a single training aid/ actual explosive material was randomly placed into a five box line-up. A total of 30 double blind line-ups were run spanning three days. The NIST training aid material was loaded 30 minutes prior to the first canine run. Canines were run on-lead throughout the entirety of the test and responses were recorded and analyzed, Table 13. Upon completion of the data analysis, it was determined that the canines did not achieve the 90% alert rate for the positive controls of actual explosive material required for reliable inferences to be made about the efficacy of the training aid materials being tested. The results of this trial have therefore been excluded.

The second canine trial was modified to reduce the overall time required to complete the test. This trial consisted of four canines with a mean working experience of 2.5 years. All canines maintained current IFRI explosive detection certifications following SWGDOG best practices and are currently deployed with local police agencies. In this trial, actual explosive material was placed randomly in foot lockers and the remaining training aids were placed in metal scent boxes along with blanks. A total of 62 pieces were placed out for the canine to run with the positive controls (actual explosive material) being run single blind and the training aids being tested double blind. The NIST training aid material was loaded 60 minutes prior to first canine run. The training aids were run in this manner to reduce discouraging the canine after running several of the pieces with no reward. The training aids tested were run double blind in order to minimize handler influence. The canines completed the test off-lead and all 62 pieces were investigated at one time with canine's responses recorded. The canines were capable of detecting the actual explosive material. The responses to the training aid can

be seen in Table 14. In this test there was some concern that the canines did not have ample access to the particles in the NIST training aids. Therefore in future canine trials the NIST training aids would be placed in such a way that the canines would have ample access to the particles while still concealing the training aid.

**Table 13. Odor recognition test: efficacy of detection between various canine training aids (n=22) canine trial 1**

| Training Aid | Alert Rate (%) | Interest Rate (%) | Combined Rate of Detection (%) |
|---|---|---|---|
| **IFRI Nitroglycerin** | 59.1 | 9.1 | 68.2 |
| **IFRI Plasticized Explosive** | 68.2 | 18.2 | 86.4 |
| **IFRI Smokeless Powder 1** | 50.0 | 9.1 | 59.1 |
| **IFRI Smokeless Powder 2** | - | - | - |
| **IFRI Tagged Explosive** | 77.3 | - | 77.3 |
| **IFRI TNT** | 36.4 | 13.6 | 50.0 |
| **NESTT PETN** | 86.4 | - | 86.4 |
| **NESTT RDX** | 59.1 | 9.1 | 68.2 |
| **NESTT TNT** | 81.8 | 4.5 | 86.4 |
| **NIST 0.01% TNT** | 36.4 | 18.2 | 54.5 |
| **NIST 0.01%C4** | 63.6 | 9.1 | 72.7 |
| **NIST 0.04%Semtex** | 50.0 | - | 50.0 |
| **NIST 0.1% Semtex** | 59.1 | - | 59.1 |
| **NIST 0.1%C4** | 27.3 | 4.5 | 31.8 |
| **NIST 0.1%Semtex** | 9.1 | 13.6 | 22.7 |
| **NIST 0.1%TNT** | 68.2 | 4.5 | 72.7 |
| **NIST 1% Cyclohexanone** | 54.5 | - | 54.5 |
| **NIST 1% DNT** | 54.5 | - | 54.5 |
| **NIST 1% DNT (2)** | 77.3 | 4.5 | 81.8 |
| **NIST 1%2Ethyl-1-hexanol (1)** | 81.8 | - | 81.8 |
| **NIST 1%2ethyl-1-hexanol (2)** | 36.4 | 4.5 | 40.9 |
| **NIST 1%Cyclohexanone (1)** | 45.5 | 13.6 | 59.1 |
| **NIST Blank 2MB** | - | 4.5 | 4.5 |
| **NIST Blank Can** | - | - | - |
| **NIST Blank DCM** | 4.5 | 18.2 | 22.7 |
| **NIST Blank Substrate** | 4.5 | 4.5 | 9.1 |
| **NESTT Blank** | - | 13.6 | 13.6 |
| **Blanks** | 3.0 | 1.8 | 4.8 |

**Table 14. Odor recognition test: efficacy of detection between various canine training aids (n=4) canine trial 2**

| Training Aid | Alert Rate (%) | Interest Rate (%) | Combined Rate of Detection (%) |
|---|---|---|---|
| **IFRI Nitroglycerin** | 100.0 | - | 100.0 |
| **IFRI Plasticized Explosive** | 100.0 | - | 100.0 |
| **IFRI Smokeless Powder 1** | 100.0 | - | 100.0 |
| **IFRI Smokeless Powder 2** | 100.0 | - | 100.0 |
| **IFRI Tagged Explosive** | 100.0 | - | 100.0 |
| **IFRI TNT** | 100.0 | - | 100.0 |
| **NESTT PETN** | 50.0 | - | 50.0 |
| **NESTT RDX** | 75.0 | 25.0 | 100.0 |
| **NESTT TNT** | 75.0 | - | 75.0 |
| **NIST 1% TATP** | 25.0 | - | 25.0 |
| **NIST 0.1% Semtex** | 25.0 | - | 25.0 |
| **NIST 0.1%C4** | - | - | - |
| **NIST 0.1%TNT** | 50.0 | 25.0 | 75.0 |
| **NIST 1% Cyclohexanone** | 25.0 | - | 25.0 |
| **NIST 1% DNT** | 25.0 | - | 25.0 |
| **NIST 1%2Ethyl-1-hexanol (1)** | - | - | - |
| **NIST Blank Can** | 50.0 | - | 50.0 |
| **NIST Blank Substrate** | 50.0 | - | 50.0 |
| **NESTT Blank** | - | - | - |
| **Blanks** | 2.6 | - | 2.6 |

The third canine trial was conducted outdoors in a large open parking lot. This trial consisted of eight canines with a mean age of 6.3 years, mean working experience of 4.1 years,. All canines maintained with current in-house explosive detection certifications and are currently deployed with local police agencies. The in-house certification requires the canines to locate explosives at a 90% rate or higher. In this trial no actual explosive material was available to run as positive controls, therefore, the canine's current certification was used to determine the reliability of the canine. The training aids were

placed in metal scent boxes along with blanks in a large grid pattern with approximately 1.5m distance between each box. The NIST training aid material was loaded 75 minutes prior to the first canine run. A total of 50 pieces were placed out for the canine to run with the training aids being run double blind. The canines completed the test on-lead and all 50 pieces were investigated at one time with canine's responses recorded. Upon completion of the data analysis, the canines in the third trial showed minimal interest in the IFRI training aids and no interest in any of the other training aids. While the trial was conducted in a manner similar to canine trial two, the canines in the third trial had a visibly more challenging time completing the test.

**Table 15. Canines used in third explosives trial**

| FIU Number | Name | Breed | Sex | Age (years) | Training Experience (Years) | Trained on TATP |
|---|---|---|---|---|---|---|
| **163** | Raider | Malinois | Male | 5 | 3 | Yes |
| **164** | Diesel | Malinois | Male | 7 | 5 | Yes |
| **165** | Max | German Shepard | Male | 7 | 4 | Yes |
| **166** | Bo | German Shepard | Male | 7 | 5 | Yes |
| **167** | Five-O | German Shepard | Male | 6 | 3 | Yes |
| **168** | Triton | German Shepard | Male | 4.5 | 3 | No |
| **169** | Zeus | German Shepard | Male | 6.5 | 5 | Yes |
| **170** | Nero | Malinois | Male | 7.5 | 5 | Yes |

Two canine trainers were present during this test and confirmed the test was within the capabilities of the canines, however, upon completion of the test it was noted that typically these canines perform building and vehicle searches, do not train regularly

with box line-ups, and typically train with much larger cardboard boxes. Since this test significantly challenged the canines and no positive controls were available to confirm the reliability of the canines, these results have been excluded; however, the results of this canine trial can be seen in Table 15 and Table 16.

**Table 16. Odor recognition test: efficacy of detection between various canine training aids (n=8) canine trial 3**

| Training Aid | Alert Rate (%) | Interest Rate (%) | Combined Rate of Detection (%) |
|---|---|---|---|
| **IFRI Nitroglycerin** | 37.5 | 25.0 | 62.5 |
| **IFRI Plasticized Explosive** | 12.5 | 50.0 | 62.5 |
| **IFRI Smokeless Powder 1** | 12.5 | - | 12.5 |
| **IFRI Smokeless Powder 2** | 12.5 | 12.5 | 25.0 |
| **IFRI Tagged Explosive** | 37.5 | 25.0 | 62.5 |
| **IFRI TNT** | 12.5 | 12.5 | 25.0 |
| **NESTT PETN** | - | - | - |
| **NESTT RDX** | - | - | - |
| **NESTT TNT** | - | - | - |
| **NIST 1% TATP** | - | - | - |
| **NIST 0.1% Semtex** | - | - | - |
| **NIST 0.1%C4** | - | - | - |
| **NIST 0.1%TNT** | - | - | - |
| **NIST 1% Cyclohexanone** | - | - | - |
| **NIST 1% DNT** | - | - | - |
| **NIST 1%2Ethyl-1-hexanol (1)** | - | - | - |
| **NIST Blank Can** | - | - | - |
| **NIST Blank Substrate** | - | - | - |
| **NESTT Blank** | - | - | - |
| **Blanks** | - | 1.6 | 1.6 |

The fourth canine trial was conducted inside in a large open warehouse. This trial consisted of four canines with a mean age of 6.75 years and a mean working experience of 5.38 years. In addition, three of the canines maintained current in-house explosive detection certifications, one maintained an IFRI explosive detection certification, and all

of the canines are currently deployed with local police agencies. The in-house certification requires the canines to locate explosives at a 90% rate or higher. In this trial actual explosive material was placed for the canine to locate in room searches run prior to the test and also in the electrical junction box line-up. The training aids were placed in metal scent boxes along with blanks along the perimeter of the room to emulate the search pattern typically run by the canines and in two line-ups in the center of the room with approximately 1.5m distance between each box. The NIST training aid material was loaded 60 minutes prior to the first canine run. A total of 50 pieces were placed out for the canines to run double blind. The canines completed the test on-lead and all 50 pieces were investigated at one time with canine's responses recorded. The data collected on the fourth trial indicates that the canines in the fourth trial showed minimal interest in some of the IFRI training aids and no interest in any of the other training aids.

**Table 17. Canines used in the fourth explosives trial**

| FIU Number | Name | Breed | Sex | Age (years) | Training Experience (Years) | Trained on TATP |
|---|---|---|---|---|---|---|
| **171** | Decka | Malinois | Male | 6 | 4.5 | Yes |
| **172** | Finn | German Shepard | Male | 8 | 6 | Yes |
| **173** | Radar | Malinois | Male | 8 | 7 | Yes |
| **109** | Zeus | Malinois | Male | 5 | 4 | Yes |

While the trial was conducted in a manner similar to canine trial two, the canines in the fourth trial had a visibly more challenging time completing the test. One canine trainer was present during this test and confirmed that the test was within the capabilities of the canines and aided in the placement of the aids to emulate the general working habits of the canines tested.

**Table 18. Odor recognition test: efficacy of detection between various canine training aids (n=4) canine trial 4**

| Training Aid | Alert Rate (%) | Interest Rate (%) | Combined Rate of Detection (%) |
|---|---|---|---|
| **IFRI Nitroglycerin** | 100.0 | - | 100.0 |
| **IFRI Plasticized Explosive** | 25.0 | - | 25.0 |
| **IFRI Smokeless Powder 1** | 25.0 | - | 25.0 |
| **IFRI Smokeless Powder 2** | - | - | - |
| **IFRI Tagged Explosive** | 50.0 | 50.0 | 100.0 |
| **IFRI TNT** | - | - | - |
| **NESTT PETN** | - | - | - |
| **NESTT RDX** | - | - | - |
| **NESTT TNT** | - | - | - |
| **NIST 1% TATP** | - | - | - |
| **NIST 0.1% Semtex** | - | - | - |
| **NIST 0.1%C4** | - | - | - |
| **NIST 0.1%TNT** | - | - | - |
| **NIST 1% Cyclohexanone** | 25.0 | - | 25.0 |
| **NIST 1% DNT** | - | 25.0 | 25.0 |
| **NIST 1%2Ethyl-1-hexanol (1)** | - | - | - |
| **NIST Blank Can** | - | - | - |
| **NIST Blank Substrate** | - | - | - |
| **NESTT Blank** | - | - | - |
| **Blanks** | 0.9 | 1.7 | 2.6 |

However, upon completion of the test it was noted that typically these canines perform vehicle searches and building searches, and rarely train with box line-up after the initial imprinting of the canines. It must also be noted that the positive controls used for regular maintenance of the canines used in the fourth canine trial were stored in a "cocktail" box in which all of the explosive material is stored in one box and the odors are allowed to contaminate each other. Since this test significantly challenged the canines, these results have been excluded as it cannot be determined whether the minimal

response rates are due to the training aids or the test challenging the canine beyond their typical working practices. The results of this canine trial can be seen in Table 17 and Table 18.

Upon completion of the fourth canine trial, challenges were observed and mitigation options were identified. A local canine handler was consulted to design the canine trials and develop a test procedure that fell easily within the canine's detection capabilities. The first pilot study using the revised test, canine trial two, was considered a successful one as the canines were capable of completing the test with no visible challenges. Using this as a model, two additional trials were conducted, canine trial three and four, placing the training aids in a similar manner and pattern, however, these results were less successful and proved to be significantly challenging for the canines.

Therefore changes were implemented for future canine trials to increase the likelihood of obtaining viable results. Such changes utilized the SWGDOG SC7 recommended parameters to ensure scientific validity of collected data (126). First local canine handlers were contacted and supplied with standardized 4"x4"x1" metal scent boxes to integrate into their normal training routine. It is believed that some of the challenges observed in canine trial three and four stem from the fact that these canines train sparsely on boxes such that the metal scent boxes used were unfamiliar to the canines, aka outside the canine's training and deployment history. (Training with metal scent boxes was integrated into the training regimen of the canines in canine trial two, which is why it is believed this trial was more successful than the others) This allows the handlers to integrate box line-ups into their training regimen, allowing for the test to fall within the deployment history of the canine. It was determined that more successful trials

would be obtained if the test is less foreign and the canines have been shown capable of locating an explosive material in a box line-up composed of metal scent boxes.

Secondly, a small canine trial (12 canines) in which two odors and two blanks were hidden was conducted in which the metal scent boxes were hidden "in-plain-site" to the handler within the normal search pattern of the canines. All canines participating in this trial have been previously certified with an average age of 5.5 years and training experience of 3.9 years. The data collected from this test trial indicates that the canines were capable of completing the task and all canines showed no evidence of increased stress or lack of interest in the search area. One canine trainer was present during this test and confirmed the test was within the capabilities of the canines and aided in the placement of the aids to emulate the general working habits of the canines tested. Upon completion of the test it was noted that typically these canines perform vehicle searches and building searches, and this new testing strategy emulated their normal working parameters. The results of this trial show a 100% alert rate for the odors placed in the test. Due to the success of this small trial, future canine trials will be modeled after this one in the hope of obtaining accurate results.

Third, a seminar was conducted on October 24, 2011, open to all canine trainers and handlers, funded by NFSTC, in which the development of surrogate continuation aids including the IFRI explosive kit and other training aids available on the market were discussed. There is still some hesitation in the canine community about using surrogate continuation aids for explosives detection and the goal of this seminar was to reduce the gap between research being performed in the lab and work being performed in the field by obtaining feedback and data. This seminar also allowed for multiple trainers to give

input on an optimal test design and surrogate continuation aid design for future canine trials as every trainer does work a bit differently and accounting for these differences is important.

Finally, all future tests were conducted with positive and negative controls following SWGDOG Best Practices to confirm the baseline performance of the canine. Ideally a current certification for the canine handler team would be sufficient for determining the baseline performance of the canine; however, since this test is challenging, positive controls are necessities to determine if the trial falls within the deployment history of the canine. Positive controls should be well maintained uncontaminated explosive odors run both pre and post testing of the training aids to ensure that the canines are capable of performing the test.

The fifth canine trial was conducted indoors in a large animal arena. This trial consisted of two canines with a mean age of 2.7 years and a mean working experience of 1.5 years. All canines were certified to National Narcotic Detector Dog Association (NNDDA) one day prior to testing and are currently deployed with local police agencies. The training aids and blanks were placed in metal scent boxes along the first row of stadium seating within the area with approximately 1.5m distance between each box. The NIST training aid material was loaded 75 minutes prior to the first canine run. A total of 50 pieces were placed out for the canine to run with the training aids being run double blind. The canines completed the test on-lead and all 34 pieces were investigated at one time with canine's responses recorded. From this trial it was observed that the test was well within the detection canines' capabilities. The results can be observed in Table 19. Since this canine trial was found to be within the regular working parameters of the

canines, the results can be accepted as an accurate representation of the tested training aids efficacy.

**Table 19. Odor recognition test: efficacy of detection between various canine training aids (n=2) canine trial 5**

| Training Aid | Alert Rate (%) | Interest Rate (%) | Combined Rate of Detection (%) |
|---|---|---|---|
| **IFRI Nitroglycerin** | 100.0 | - | 100.0 |
| **IFRI Plasticized Explosive** | 50.0 | - | 50.0 |
| **IFRI Smokeless Powder 1** | - | - | - |
| **IFRI Smokeless Powder 2** | - | - | - |
| **IFRI Tagged Explosive** | 100.0 | - | 100.0 |
| **IFRI TNT** | 100.0 | - | 100.0 |
| **NESTT PETN** | 50.0 | 50.0 | 100.0 |
| **NESTT RDX** | - | - | - |
| **NESTT TNT** | - | - | - |
| **NIST 0.1% Semtex** | 50.0 | - | 50.0 |
| **NIST 0.1%C4** | - | 50.0 | 50.0 |
| **NIST 0.1%TNT** | 50.0 | - | 50.0 |
| **NIST 1% Cyclohexanone** | - | - | - |
| **NIST 1% DNT** | - | - | - |
| **NIST 1%2Ethyl-1-hexanol (1)** | 50.0 | - | 50.0 |
| **NIST Blank Can** | - | - | - |
| **NIST Blank Substrate** | - | - | - |
| **NESTT Blank** | 50.0 | - | 50.0 |
| **Blanks** | 3.1 | - | 3.1 |

The sixth canine trial was conducted outdoors at a local canine trainer's facility. This trial consisted of six canines with a mean age of 4.8 years and a mean working experience of 2.5 years. All canines were certified to IFRI certification standards prior to testing and are currently deployed with local police agencies. The training aids were placed in metal scent boxes along with blanks along a fence line and ground set-up with 1.5m between each box. The NIST training aid material was loaded 60 minutes prior to

the first canine run. A total of 50 pieces were placed out for the canine to run with the training aids being run double blind. The canines completed the test on-lead and all 50 pieces were investigated at one time with canine's responses recorded. From this trial it was observed that the test was well within the detection canines' capabilities. The results can be observed in Table 20. Since this canine trial was found to be within the regular working parameters of the canines, the results can be accepted as an accurate representation of the tested training aids efficacy.

**Table 20. Odor recognition test: efficacy of detection between various canine training aids (n=6) canine trial 6**

| Training Aid | Alert Rate (%) | Interest Rate (%) | Combined Rate of Detection (%) |
|---|---|---|---|
| **IFRI Nitroglycerin** | 100.0 | - | 100.0 |
| **IFRI Plasticized Explosive** | 50.0 | - | 50.0 |
| **IFRI Smokeless Powder 1** | 83.3 | - | 83.3 |
| **IFRI Smokeless Powder 2** | 83.3 | 16.7 | 100.0 |
| **IFRI Tagged Explosive** | 100.0 | - | 100.0 |
| **IFRI TNT** | 100.0 | - | 100.0 |
| **NESTT PETN** | - | - | - |
| **NESTT RDX** | - | - | - |
| **NESTT TNT** | - | - | - |
| **NIST 0.1% Semtex** | - | 33.3 | 33.3 |
| **NIST 0.1%C4** | 16.7 | - | 16.7 |
| **NIST 0.1%TNT** | 16.7 | - | 16.7 |
| **NIST 1% Cyclohexanone** | 83.3 | 16.7 | 100.0 |
| **NIST 1% DNT** | 33.3 | 16.7 | 50.0 |
| **NIST 1%2Ethyl-1-hexanol (1)** | 50.0 | - | 50.0 |
| **NIST Blank Can** | 16.7 | - | 16.7 |
| **NIST Blank Substrate** | 16.7 | 16.7 | 33.3 |
| **NESTT Blank** | 33.3 | 16.7 | 50.0 |
| **Blanks** | - | - | - |

**Table 21. Odor recognition test: efficacy of detection between various canine training aids (n=6) canine trial 7**

| Training Aid | Alert Rate (%) | Interest Rate (%) | No Alert Rate (%) | Combined Rate of Detection (%) |
|---|---|---|---|---|
| **IFRI Nitroglycerin** | 100.0 | - | - | 100.0 |
| **IFRI Plasticized Explosive** | 16.7 | 16.7 | 66.7 | 33.3 |
| **IFRI Smokeless Powder 1** | 50.0 | - | 50.0 | 50.0 |
| **IFRI Smokeless Powder 2** | 66.7 | 16.7 | 16.7 | 83.3 |
| **IFRI Tagged Explosive** | 100.0 | - | - | 100.0 |
| **IFRI TNT** | 83.3 | - | 16.7 | 83.3 |
| **NESTT PETN** | 16.7 | 33.3 | 50.0 | 50.0 |
| **NESTT RDX** | - | - | 100.0 | - |
| **NESTT TNT** | 33.3 | - | 66.7 | 33.3 |
| **NIST 0.1% Semtex** | 66.7 | - | 33.3 | 66.7 |
| **NIST 0.1%C4** | 50.0 | 33.3 | 16.7 | 83.3 |
| **NIST 0.1%TNT** | 33.3 | 33.3 | 33.3 | 66.7 |
| **NIST 1% Cyclohexanone** | - | - | 100.0 | - |
| **NIST 1% DNT** | 16.7 | 50.0 | 33.3 | 66.7 |
| **NIST 1% 2Ethyl-1-hexanol (1)** | - | 50.0 | 50.0 | 50.0 |
| **NIST 1% TATP** | - | - | 100.0 | - |
| **NIST Blank Can** | 33.3 | 33.3 | 33.3 | 66.7 |
| **NIST Blank Substrate** | 16.7 | 16.7 | 66.7 | 33.3 |
| **NESTT Blank** | 33.3 | 50.0 | 16.7 | 83.3 |
| **Blanks** | 0.9 | 0.7 | 98.4 | 1.6 |

The seventh canine trial was conducted indoors at school. This trial consisted of six canines with a mean age of 5.9 years and a mean working experience of 4.7 years. All canines were certified to IFRI certification standards prior to testing and are currently deployed with local police agencies. The training aids and blanks were placed in metal scent boxes or lockers along the wall and ground. The NIST training aid material was loaded 60 minutes prior to the first canine run. A total of 116 pieces were placed out for the canine to run with the training aids being run double blind. The canines completed the

test on-lead and all 116 pieces were investigated at one time with canine's responses recorded. From this trial it was observed that the test was well within the detection canines' capabilities. The results can be observed in Table 21. Since this canine trial was found to be within the regular working parameters of the canines, the results can be accepted as an accurate representation of the tested training aids efficacy.

Combining all of the canine trial results, Table 22, high alert rates were obtained for the IFRI training aids in comparison to the NIST and NESTT training aids. Lower alert rates for the IFRI Smokeless Powder training aids are indicative of the challenges faced by handlers to select the proper smokeless powders for maintenance training. These results indicate that the Prototype Explosive Kit training aids are more efficacious than other training aids tested.

NIST and NESTT training aids had lower than expected response rates; however, they also presented the greatest challenge in developing the test due to the nature of the aids themselves. Canine handlers consulted during the preparation of the canine trials anecdotally felt that the NIST samples required more preparation and care taken in comparison to the other training aids, making the canine handlers unwilling to use the NIST training aids in their current state. It is thought that even though changes were made to the test so that canines would have ample access to the particles contained within the NIST training aids, the canines were not getting the necessary exposure to the particles for reliable and consistent alerts. These results indicate that a redesign of the NIST training aids are necessary before implementation in the field will be successful, Figure 55. In this test it was also noted that the canines had a more difficult time completing the third odor recognition test, resulting in lower combined rates of detection

than that of the initial proof of concept odor recognition test. The theories behind this observation will be discussed further in the discussion section. Preliminary results are encouraging for the Prototype Surrogate Explosives Kit; however, a larger sample size of explosives detection canines is required to establish performance superiority of the new training aids.

**Table 22. Odor recognition test: efficacy of detection between various canine training aids (n=18) cumulative corrected results**

| Training Aid | Alert Rate (%) | Interest Rate (%) | No Alert Rate (%) | Combined Rate of Detection (%) |
|---|---|---|---|---|
| **IFRI: Nitroglycerin** | 100.00 | - | - | 100.00 |
| **IFRI: Plasticized Explosive** | 50.00 | 5.56 | 44.44 | 55.56 |
| **IFRI: Smokeless Powder 1** | 66.67 | - | 33.33 | 66.67 |
| **IFRI: Smokeless Powder 2** | 72.22 | 11.11 | 16.67 | 83.33 |
| **IFRI: TNT** | 94.44 | - | 5.56 | 94.44 |
| **IFRI: Tagged** | 100.00 | - | - | 100.00 |
| **NESTT PETN** | 22.22 | 16.67 | 61.11 | 38.89 |
| **NESTT RDX** | 16.67 | 5.56 | 77.78 | 22.22 |
| **NESTT TNT** | 27.78 | 5.56 | 66.67 | 33.33 |
| **NIST 0.1%C4** | 38.89 | - | 61.11 | 38.89 |
| **NIST 0.1%Semtex** | 22.22 | 16.67 | 61.11 | 38.89 |
| **NIST 0.1%TNT** | 22.22 | 22.22 | 55.56 | 44.44 |
| **NIST 1% Cyclohexanone** | 22.22 | 5.56 | 72.22 | 27.78 |
| **NIST 1% DNT** | 33.33 | 22.22 | 44.44 | 55.56 |
| **NIST 1%2Ethyl-1-hexanol (1)** | 16.67 | 5.56 | 77.78 | 22.22 |
| **NIST 1% TATP** | 27.78 | 16.67 | 55.56 | 44.44 |
| **NIST Blank Can** | 30.00 | 20.00 | 50.00 | 50.00 |
| **NIST Blank Substrate** | 22.22 | 5.56 | 72.22 | 27.78 |
| **NESTT Blank** | 27.78 | 22.22 | 50.00 | 50.00 |
| **Blanks** | 1.79 | 0.40 | 97.81 | 2.19 |

**Figure 55. NIST training aids. From left to right: open training aid where particles are placed, closed training aid, standard metal box in which the NIST training aids were hidden for canine trials**

## 8.5 Discussion

The third and final canine test compared the efficacy of detection between the IFRI prototype surrogate explosives kit to other commercially available SCAs, Table 22. The SCAs selected for comparison were based on dilute explosives absorbed onto a matrix of the manufacturer's choosing. Unlike the previous canine tests, this canine test was constructed similar to the Bureau of Alcohol, Tobacco, Firearms and Explosives (ATF) National Odor Recognition Test (NORT) and consisted of a large number of items searched. 52 trained and certified detection canines completed this test in seven canine trials; however, as the test was conducted double blind, canines incapable of finding the positive controls were excluded from the test leaving 18 canines' worth of data. While having to exclude this many canines seems to reflect poorly on the quality of the detection canine community, after consulting with several canine trainers, the testing parameters were altered to better reflect the daily working search parameters of the canines. The canines had a challenging time locating the positive controls in the NORT

based test but were capable of locating the positive controls when they were placed in a familiar test scenario. It is thought that because the testing scenario was so unfamiliar to the detection canines, as most of them are not trained for the NORT test, the canines were incapable of completing the test as initially designed. Unlike the previous two canine tests, the combined rate of detection was lower for the IFRI SCAs; however, this is not to be unexpected. As the likelihood of false positives and false negatives increases, the number items searched increases. In addition, the canines were unfamiliar with the testing scenario (127). Even with the lower combined rates of detection, the IFRI prototype SCAs still out performed the other commercially available training aids in our trials. As this test was not comprehensive to all of the commercially available training aids, future study could include the comparison of a more comprehensive list of commercially available training aids.

## 8.6 Conclusions

As a result of this study the IFRI prototype surrogate explosives kit has been proven to be a viable alternative for explosives detection canine training when actual illicit material is unavailable or cannot be used. The canine data collected supports that the SCAs within the kit are odors used by canines to form an alert response which can be used to both train and maintain explosive detection canines in the field. In comparison to the other available SCAs, the IFRI prototype surrogate explosives kit performs better that the tested commercially available SCAs with the greatest ease of preparation.

# 9 OVERALL CONCLUSIONS

The purpose of this study was to determine the major headspace odors of various peroxide based explosives so that safe, reliable, and long lasting SCA can be developed. The initial theory of creating the peroxide based explosive SCA was that a VOC(s) within the headspace would be a dominant odor compound of the explosive that could be used to mimic the explosive. However, after testing, only VOCs corresponding to the explosive compounds were found in the headspace along with acetone. Since acetone was found in the headspace and hydrogen peroxide is a known starting component and decompositional product, a combined yet separate theory was developed to make the SCA. It was imperative to keep these two chemicals separate because once mixed they form TATP. However, it is important to note that if these chosen odors are not used in conjunction, the detection canine could accidentally be trained to common household chemicals. Through field trials the combined yet separate peroxide based explosive SCA was shown to be a viable TATP training aid alternative.

The development of a universal detection calibrant (UDC) will aid canine handlers and trainers in several facets of training the canine. The UDC has the potential to be used daily, providing a documented record of the canine's functionality for the day which can later be used to substantiate the handler's assertion in court that the canine was working within acceptable limits. The UDC can also be used by canine trainers in the early stages of imprinting the canine to determine how fast the canine learns to alert to the odor as well as the sensitivity the canine can achieve. This may indicate that the canine is better suited for one area of detection over another. Twelve mandatory and desirable qualities were determined for the selection of the UDC with the greatest

emphasis placed on the safety and the scarcity of the chemical. After 1-bromooctane was selected as the UDC, canines were imprinted and the UDC was put into practice. The canine handlers participating in this UDC study were very enthusiastic to use the it because they are interested in any tool that can improve the reliability of their canines in the court system.

While only a small sample of canines was tested comparing imprinting methods, no significant difference was seen between the separation and combined odor method. This result is indicative of the detection canine population, indicating that either method is viable as long as the canine is trained on uncontaminated training aids and is scent discriminated. Using this knowledge, canine handlers and trainers can then implement a method based upon the results to train the detection canines more efficiently.

A large portion of this study was dedicated to validating the prototype surrogate explosives kit. Validation of the kit will provide an additional tool for canine handlers to use, reducing the risk to the detector teams and the number of target odors used for training, introducing a more uniform system to be utilized universally. Through the use of laboratory and field tests, the SCAs within the kit were proven to be reliable over a long period of time under harsh environmental conditions. A containment system using three levels of containment was developed to best store the SCAs with the greatest reduction and contamination potential. As contaminated training aids can be detrimental to the detection canine's reliability, storing training aids in the recommended manner will be beneficial for both mimics and actual illicit material SCAs. The final stage of IFRI prototype surrogate explosive kit validation was comparing it to other commercially available training aids. As a result of this test the IFRI SCAs were found to outperform

the other SCAs tested, indicating that if no actual illicit material is available for testing, then the IFRI prototype surrogate explosives kit is the best alternative. Completion of this research and implementation of the recommendations made will aid in the standardization of biological detectors and increase the number of explosives a detection canine can reliable detect. Future work includes testing the dissipation rate of the training aids by an indirect means other than gravimetric analysis. This will allow for instrumental correlation to the observed gravimetric dissipation rates. Additionally, studies equating the dissipation rates observed in the IFRI SCAs to a corresponding weight of explosive material are necessary such that training scenarios can be designed to mimic desired training scenarios.

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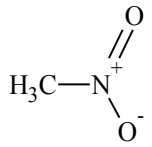
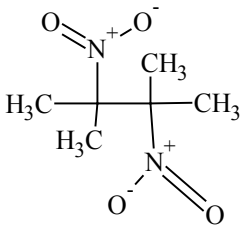
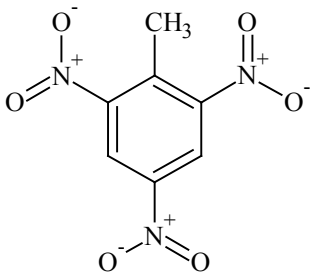
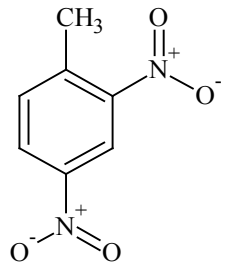
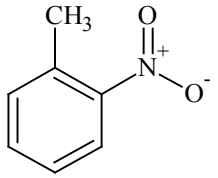
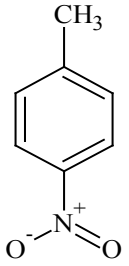
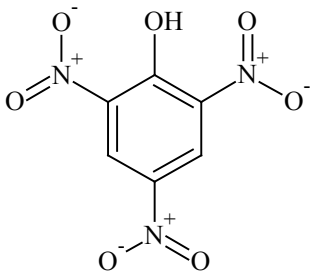
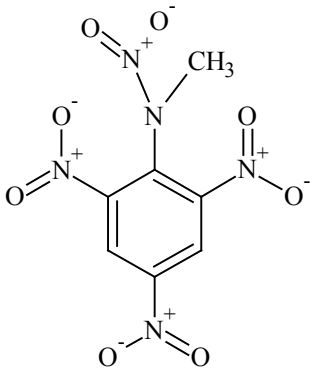
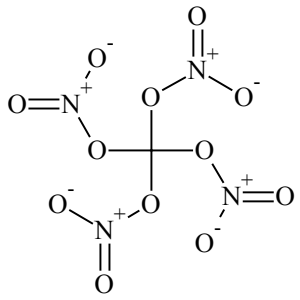
APPENDICES

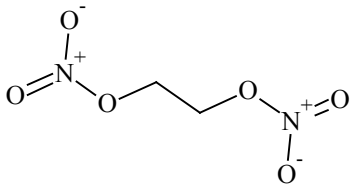
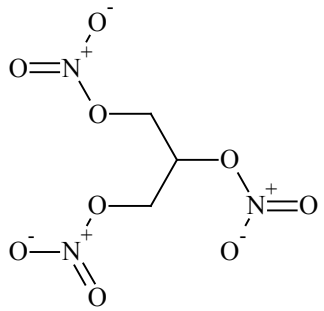
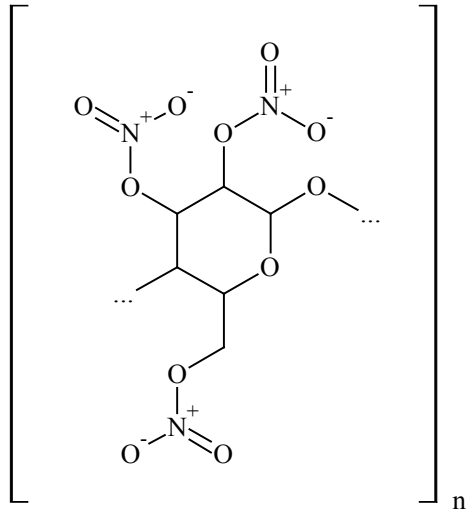
Appendix A Examples of organic explosives and their properties

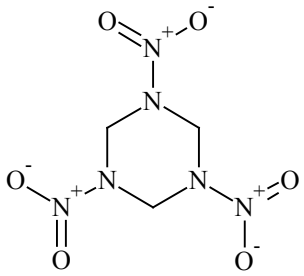
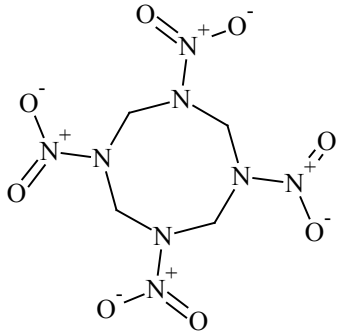
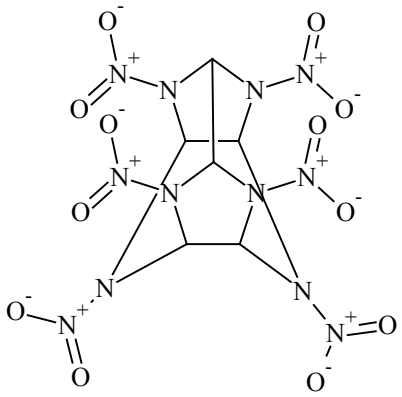
**Table 23**

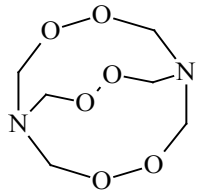
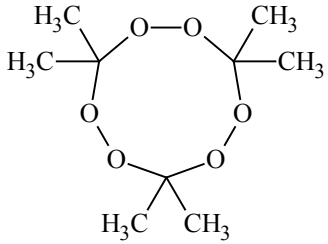
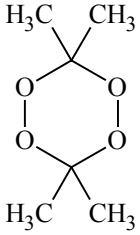
| | *Compound* | *Structure* | *Formula* | *Molecular Weight (amu)* | *Vapor Pressure @ 25°C (torr)* |
|---|---|---|---|---|---|
| **Nitro Alkanes** | Nitromethane (NM) |  | $CH_3NO_2$ | 61.04 | $2.8 \times 10^{1}$ |
| | 2,3-Dimethyl-dinitrobutane (DMNB) |  | $C_6H_{12}N_2O_4$ | 176.17 | $2.1 \times 10^{-3}$ |
| **Nitro Aromatics** | 2,4,6-Trinitrotoluene (TNT) |  | $C_7H_5N_3O_6$ | 227.13 | $5.8 \times 10^{-6}$ |

| | *Compound* | *Structure* | *Formula* | *Molecular Weight (amu)* | *Vapor Pressure @ 25°C (torr)* |
|---|---|---|---|---|---|
| **Nitro Aromatics** | 2,4-Dinitrotoluene (2,4-DNT) |  | $C_7H_6N_2O_4$ | 182.14 | $2.1 \times 10^{-4}$ |
| | 2-Nitrotoluene (2-MNT) |  | $C_7H_7NO_2$ | 137.14 | $1.5 \times 10^{-1}$ |
| | 4-Nitrotoluene (4-MNT) |  | $C_7H_7NO_2$ | 137.14 | $4.1 \times 10^{-2}$ |

| | *Compound* | *Structure* | *Formula* | *Molecular Weight (amu)* | *Vapor Pressure @ 25°C (torr)* |
|---|---|---|---|---|---|
| **Nitro Aromatics** | Piciric Acid (PA) |  | $C_6H_3N_3O_7$ | 229.11 | $5.8 \times 10^{-9}$ |
| | Tetryl |  | $C_7H_5N_5O_8$ | 287.15 | $5.7 \times 10^{-9}$ |
| **Nitrate Esters** | Pentaerythritol tetranitrate (PETN) |  | $C_5H_8N_4O_{12}$ | 314.14 | $1.4 \times 10^{-8}$ |

| | *Compound* | *Structure* | *Formula* | *Molecular Weight (amu)* | *Vapor Pressure @ 25°C (torr)* |
|---|---|---|---|---|---|
| **Nitrate Esters** | Ethylene glycol dinitrate (EDGN) |  | $C_2H_4N_2O_4$ | 152.06 | $7.0 \times 10^{-2}$ |
| | Nitroglycerin (NG) |  | $C_4H_5N_3O_9$ | 227.09 | $3.1 \times 10^{-4}$ |
| | Nitrocellulose (NC) |  | $[C_6H_7N_3O_{11}]_n$ | 297.14 | N/A |

| | *Compound* | *Structure* | *Formula* | *Molecular Weight (amu)* | *Vapor Pressure @ 25°C (torr)* |
|---|---|---|---|---|---|
| **Nitramines** | Trinitro-triazacyclohexane (RDX) |  | $C_3H_6N_6O_6$ | 222.12 | $4.6 \times 10^{-9}$ |
| | Tetranitro-tetrazacylooctane or Octogen (HMX) |  | $C_4H_8N_8O_8$ | 296.16 | $1.6 \times 10^{-13}$ |
| | Hexanitroisowurzlitane (CL-20) |  | $C_6H_6N_{12}O_{12}$ | 438.19 | N/A |

| | *Compound* | *Structure* | *Formula* | *Molecular Weight (amu)* | *Vapor Pressure @ 25°C (torr)* |
|---|---|---|---|---|---|
| **Peroxides** | Hexamethylene triperoxide diamine (HMTD) |  | $C_6H_{12}N_2O_6$ | 208.02 | N/A |
| | Triacetone triperoxide (TATP) |  | $C_9H_{18}O_6$ | 222.03 | $5.2 \times 10^{-2}$ |
| | Diacetone diperoxide (DADP) |  | $C_6H_{12}O_4$ | 148.02 | $1.3 \times 10^{-1}$ |

Appendix B Techniques and detection limits for the analysis of explosives

| Analyte | Separation technique | Detection technique | Detection limit | Time of analysis | Ref. |
|---|---|---|---|---|---|
| TNT; DNB; 2,4-DNT; 2,6-DNT; 4-MNT | Microchip MEKC | Amperometry (screen-printed carbon electrode @ -0.5 V) | ~600 ppb (TNT) | 210 s | (128) |
| TNT; RDX; 2,4-DNT; 2,6-DNT; 2,3-DNT | Microchip MEKC | Amperometry (gold wire electrode @ -0.7 V) | 110 ppb | 400 s | (129) |
| TNT; 2,4-DNT; 2,6-DNT; 2,3-DNT | Microchip MEKC | Amperometry (gold electrode deposited onto channel outlet @ -0.8 V) | 24 ppb (TNT) | 130 s | (130) |
| TNT | µFIA | Amperometry (mercury/gold amalgam electrode @ -0.6 V) | 7 ppb | 30 s | (131,132) |
| TNT; 1,3-DNB; 2,4-DNT | Microchip MEKC | Amperometry (boron-doped diamond electrode @ -0.7 V) | 70ppb (1,3-DNB); 110 ppb (2,4-DNT) | 200 s | (133) |
| TNT; TNB; DNB; 2,4-DNT; 2-Am-4,6-DNT; 4-Am-2,6-DNT | µFIA/microchip MEKC | Amperometry (screen-printed carbon electrode @ -0.5 V) | 60 ppb (TNT & DNB) | 25 s (screening mode); 150 s (fingerprint mode) | (134) |
| TNT, DNT, TNB | µFIA/microchip MEKC | Amperometry (screen-printed carbon electrode @ -0.4 V) | 800 ppb (TNT); 450 ppb (TNB) | 36 s (screening mode); 140 s (fingerprint mode) | (135) |
| TNT; DNB; TNB; NB; Tetryl; 2,4-DNT; 2,6-DNT; NT; 2-Am-4,6-DNT; 4-Am-2,6-DNT | Microchip MEKC | IDLIF, visualizing agent Cy7 | ~1 ppm | 60 s | (136) |
| TNB; TNT; 2,4-DNB; 2-Am-4,6-DNB | Microchip MEKC (using LIDS) | Amperometry (screen-printed carbon electrode @ -0.5 V) | 80 ppb (TNT) | 120 s | (137) |

| Analyte | Separation technique | Detection technique | Detection limit | Time of analysis | Ref. |
|---|---|---|---|---|---|
| TNT; TNB; 2,4-DNT; 1,3-DNB; 2,4-DNP | Microchip immunoassay | Direct LIF | ~1 ppb | 50 s | (138) |
| Post blast explosive residue cations ($NH_4^+$; $Na^+$; MMA) | Microchip CE | Contactless conductivity detection (@ 200 kHz, 10 $V_{p-p}$) | N/A | 60 s | (139) |
| TNT; TNB; Tetryl | Nonaqueous microchip CE | UV-Vis @ 505 nm | Without *ex situ* preconcentration: 160 ppb (TNT); 60 ppb (TNB); 200 ppb (Tetryl) With *ex situ* preconcentration: 340 ppt (TNT); 250 ppt (TNB); 190 ppt (Tetryl) | 20 s | (140) |
| Pre- and post-blast residues ($K^+$; $NH_4^+$; $Na^+$; MMA; $NO_3^-$; $Cl^-$; $ClO_4^-$) | Microchip CE with addition of 18-crown-6 ether | Contactless conductivity detection (@ 200 kHz, 5 $V_{p-p}$) | 3.2 µM ($NH_4^+$); 5.8 µM (MMA); 6.2 µM ($K^+$); 5.6 µM ($Na^+$); 8.7 µM ($Cl^-$); 7.2 µM ($NO_3^-$); 6.2 µM ($ClO_4^-$) | 60 s | (141) |
| Pre- and post-blast explosive residues ($K^+$; $NH_4^+$; $Na^+$; MMA; $NO_3^-$; $Cl^-$; $ClO_4^-$) | Microchip CE with addition of 18-crown-6 ether | Movable contactless conductivity detection (@ 200 kHz, 5 $V_{p-p}$) | N/A | 17 s (screening mode), 45 s (fingerprint mode) | (142) |
| Pre- and post-blast explosive residues ($K^+$; $NH_4^+$; $Na^+$; MMA; $NO_3^-$; $Cl^-$; $ClO_4^-$) | Microchip CE | Movable contactless conductivity detection (@ 200kHz, 10 $V_{p-p}$) | 80 µM ($NH_4^+$); 70 µM ($Na^+$); 150 µM ($Cl^-$); 130 µM ($ClO_4^-$) | 60 s | (143) |

| Analyte | Separation technique | Detection technique | Detection limit | Time of analysis | Ref. |
|---|---|---|---|---|---|
| Post blast explosive residue cations ($NH_4^+$; $Na^+$; MMA) | Microchip CE | Contactless conductivity detection (@200 kHz, 5 $V_{p-p}$) | 50 µM ($NH_4^+$) | 60 s | (137) |
| HMX; RDX; TNB; TNT; 2,4-DNT; 2,6-DNT; NG; PETN; Tetryl; 2-MNT; 3-MNT; 4-MNT; NB; DNB | MEKC using SDS | UV-Vis @ 185, 214, 229, and 254 nm | <1 ppm | 15 min | (144) |
| DBP; DEGDN; 1,3-DNN; 1,5-DNN; 1,8-DNN; EGDN; NG; NGU; 2-MNN; 2-MNT; 3-MNT; 4-MNT; PETN; PA; Tetryl; HMX; TNT; RDX; EC; 2,3-DNT; 2,4-DNT; 2,6-DNT; 3,4-DNT; DPA; 2-nDPA; N-nDPA | MEKC using SDS | UV-Vis @ 220 nm | 5 x $10^{-6}$ M for nitroaromatic compounds; 1 x $10^{-6}$ M for nitroaliphatic compounds; 5 x $10^{-5}$ M for PETN and HMX | 10 min | (145) |
| EPA 8330 explosives | MEKC using SDS | UV-Vis @ 254 nm | N/A | 14 min | (146) |
| NGU; PA; NG; 3,4-DNT; 2,3-DNT; 2,4-DNT; 2,6-DNT; 2-MNT; 4-MNT; 3-MNT; N-nDPA; DPA; 2-nDPA; EC; DBP | MEKC using SDS | UV-Vis (diode array) | N/A | 12 min | (147) |
| TNT; TAT; 2,6-Dam-NT; 2,4-Dam-NT; 2-HADNT; 4-HADNT; 2-Am-4,6-DNT; 4-Am-2,6-DNT | MEKC using SDS | UV-Vis (diode array) | 100-200 ppb | 8 min | (148) |
| TNT; Tetryl; NG; PETN; RDX; HMX; EGDN; NGU | MEKC using SDS | LIF (488 nm excitation; fluorophore, fluorescein, or rhodamine B) | 1 x $10^{-4}$ – 4 x $10^{-4}$ M | 7 min | (149) |
| EPA 8330 explosives | CEC (1.5 µm nonporous ODS silica) or MEKC using SDS | LIF (Cy5) | 1 – 10 ppm | 33 min | (150) |

| Analyte | Separation technique | Detection technique | Detection limit | Time of analysis | Ref. |
|---|---|---|---|---|---|
| HMX; RDX; 1,4-DNB; NB; 1,2-DNB; TNT; 2,4-DNT; 2,6-DNT; 3,4-DNT; 3-MNT; 2,3-DNT; 2-Am-4,6-DNT; 4-Am-2,6-DNT | MEKC using SDS | Amperometry (silver-on-gold electrode @ -0.7 V) | 70 – 110 ppb | 9 min | (151) |
| 2-MNT; 3-MNT; 4-MNT; 1,2-DNB; 1,3-DNB; 1,4-DNB; 2,3-DNT; 2,4-DNT; 2,6-DNT; 3.4-DNT | MEKC using SDS and sulfobutyl ether-β-CDCD | UV-Vis @ 214 nm | N/A | 13 min | (152) |
| EPA 8330 explosives | CEC (1.5 µm nonporous ODS silica) | UV-Vis @ 254 nm | N/A | 2 and 7 min | (153) |
| EPA 8330 explosives | CEC (3 µm nonporous ODS silica) | Amperometry (bare gold electrode @ -1.0 V) | 75 – 170 ppb | 85 min | (154) |
| Blackpowder pipe bomb anions ($Cl^-$; $NO_2^-$; $NO_3^-$; $SO_4^{2-}$; $SCN^-$; $ClO_4^-$; $HCO_3^-$; $HS^-$; $OCN^-$) | CE | Indirect UV-Vis (dichromate ions as visualizing agent @ 205 and 280nm) | N/A | 15 min | (155) |
| Emulsion explosives ($NH_4^+$; $Na^+$; $NO_3^-$; $Cl^-$; $ClO_4^-$) | CE | Indirect UV-Vis (5 mM chromate ions as visualizing agent @ 214 nm) | N/A | 5 min | (156) |
| $K^+$; $NH_4^+$; $Ba^{2+}$; MMA; $Sr^{2+}$; $Na^+$; $Ca^{2+}$; $Al^{3+}$; $Mg^{2+}$; $Li^+$; $Co^{2+}$; $Zn^{2+}$ | CE with addition of 18-crown-6 ether | Indirect UV-Vis (5mM imidazole as visualizing agent @ 215 nm) | 500 ppb | 7 min | (157) |
| $K^+$; $NH_4^+$; $Sr^{2+}$; $Na^+$; $Ca^{2+}$; $Mg^{2+}$; $Br^-$; $Cl^-$; $NO_2^-$; $NO_3^-$; $SO_4^{2-}$; $ClO_4^-$; $SCN^-$; $ClO^{3-}$ | CE with addition of 18-crown-6 ether | Indirect UV-Vis (5mM imidazole (for cations) and 1,3,6-naphtalenetrisulfoni acid (for anions) as visualizing agents @ 215 nm) | 0.8 – 15 ppm | 7 min | (158) |
| HMX, RDX, PETN, Tetryl | Direct infusion | MS (ESI, quadrupole) | 170 fmol/µL | N/A | (159) |
| TNT, RDX, HMX | Direct infusion | MS (ESI-FTICR) | ~1 mg/mL | N/A | (160) |
| Laurylamine acetate | Direct infusion (SPE extraction) | MS (ESI, quadrupole) | 8 pg | N/A | (161) |

| Analyte | Separation technique | Detection technique | Detection limit | Time of analysis | Ref. |
|---|---|---|---|---|---|
| TATP | HPLC (C-18 column (2.1 mm x 150 mm, 3 µm particle size) ) and direct infusion | MS (ESI, positive mode, quadrupole) | 62.5 ng | N/A | (162) |
| RDX | LC (C-18 column (2.1 mm x 150 mm, 5 mm particle size)) | MS (ESI) | 4 x $10^{-8}$ M | N/A | (163) |
| CL-20, TNT, RDX | Direct infusion | MS/MS (ESI, negative mode) | N/A | N/A | (164) |
| CL-20 | HPLC (LC-CN column (4.6mm x 25 cm, 5 µm particle size)) | PDA (ESI) | 100 mg/L | 14 min | (165) |
| RDX, TNT, HMX, PETN | Direct infusion | MS and MS/MS (ESI, quadrupole) | ~20 ppm | N/A | (166) |
| BP substitutes, ascorbic acid | IC (Ion Pac AS18 column (2 mm x 250 mm), Ion Pac AG18 guard column (2 mm x 50 mm) | MS (ESI, quadrupole) | N/A | ~15 min | (167) |
| TNT, RDX, NG, HMX, TATP | ND | MS (EESI, LTQ) | ~0.5-10 pg | N/A | (168) |
| TNT, RDX | N/A | MS (EESI, LTQ) | 1 x $10^{-12}$ M | N/A | (169) |
| TNT, RDX | N/A | MS (nanoEESI, LTQ-XL) | 1 ppt | ~5 s | (170) |
| 21 nitroaromatic, nitramine and nitrate ester explosives | HPLC (C-18 column (3.9 mm x 150 mm, 4 µm particle size)) | MS (APCI, ESI, API, MAT TSQ) | 0.012 ng or higher | ~25 min | (171) |
| TNT, NG, PETN, RDX | Infusion into the LC stream or Direct infusion | MS/MS (APCI, LCQ) | 5 fg (TNT); 200 pg (NG); 250 pg (PETN); 5 ng (RDX) | N/A | (172) |

| Analyte | Separation technique | Detection technique | Detection limit | Time of analysis | Ref. |
|---|---|---|---|---|---|
| DNT, TNT, PETN, RDX, HMX | SFC ($SF_3$ packed column), LC (packed cyanopropyl column (25 cm x 4.6 mm; 5 µm particle size)) | MS (APCI, quadrupole) | >119 ng | ~22 min | (173) |
| HMTD, TATP | HPLC (C-18 column (3.9 mm x 150 mm; 4 µm particle size)) | MS/MS (APCI, TSQ) | 0.26 ng (HMTD); 3.3 ng (TATP) | < 10 min | (174) |
| TNT, RDX | Vapor introduced via proximity of the probe | MS (APCI-CFI, quadrupole) | N/A | < 3 min | (175) |
| TNT, RDX | Vapor introduced via proximity of the probe | MS (APCI-CFI, ion trap) | 10-20 ppt; 0.3 ppt (MS/MS TNT) | < 3 min | (176) |
| TNB; TNT; 2,4-DNT; *m*-DNB; *p*-DNB | Direct infusion or desorption | MS (APCI, DACPI, LCQ) | N/A | N/A | (177) |
| TNT, RDX, PETN | N/A | MS (thermal desorption, APCI, LCQ) | < 10 ng (TNT); < 30 ng (RDX); < 10 ng (PETN) | N/A | (178) |
| RDX, TNT | N/A | MS (DAPCI, LTQ) | < 10 pg | N/A | (179) |
| UN | HPLC (Synergi MAX-RP 80A column (150 mm x 2 mm; 4 µm particle size)) | MS/MS (APCI, ESI, $LCQ_{DUO}$) | 3 µg (APCI); 6 µg (ESI) | ~ 6 min | (180) |
| UN | HPLC (C-18 column (150 mm x 2 mm; 5 µm particle size)) | MS (APCI, $LCQ_{DUO}$) | N/A | ~ 10 min | (181,182) |

| Analyte | Separation technique | Detection technique | Detection limit | Time of analysis | Ref. |
|---|---|---|---|---|---|
| TNT, RDX, HMX, PETN, TATP, C4, DMMP | N/A | MS (DESI (methanol/water/NaCl), LTQ) | 1 m LOD: 1 ng (TNT, HMX, TATP, C4), 0.5 ng (RDX, DMMP), 10 ng (PETN)<br>3 m LOD: 10 ng (TNT, TATP), 4 ng (RDX), 5 ng (HMX, C4), 20 ng (PETN), 3 ng (DMMP) | N/A | (183) |
| RDX, TNT | N/A | MS (LTP, DESI, LTQ) | < 5 pg | N/A | (184) |
| TNT, PETN, RDX, HMX | N/A | MS (DESI (methanol/ water or ethanol/ water), LTQ) | < 1 pg (TNT, RDX), < 10 pg (HMX); < 100 pg (PETN) | 5 s | (185) |
| TNT, RDX. HMX, PETN | N/A | MS (DESI, LTQ) | 5 pg (TNT), 500 pg (RDX), 50 pg (PETN) | ~3 s | (186) |
| RDX, HMX, TNT, PETN | N/A | MS (DESI (methanol/ water), LTQ) | 2.5 ng | < 40 s (250 ms scan time) | (187) |
| TATP | N/A | MS (DESI (methanol/ water doped with ammonium acetate or NaCl), LTQ) | <1 ng | < 5 s | (188) |
| TATP, HMTD, TrATrP | N/A | MS (DAPCI, DESI (methanol/ water doped with ammonium acetate, NaCl, LiCl, or KCl), LTQ) | 1 ng | < 5 s | (189) |

| Analyte | Separation technique | Detection technique | Detection limit | Time of analysis | Ref. |
|---|---|---|---|---|---|
| RDX, TNT, HMX, TNB | Direct or SPE (SDB-RPS) | MS (DESI (methanol/ water), LTQ) | 1 – 10 ppb | < 1 min | (190) |
| TNT | Liquid delivered to ablation surface via a capillary | MS/ MS (DESI (methanol/water/acetic acid), QTrap ($N_2$ curtain gas)) | 10 µg/ mL | N/A | (191) |
| RDX | N/A | MS (DESI (methanol/water/NaCl), QTrap ($N_2$ curtain gas)) | < 15 ng | N/A | (192) |
| DNT, Amino-DNT, TNB, TNT, Tetryl, RDX, HMX | N/A | MS (DART, TOFMS) | ~ 3 ppm | ~ 3 s | (193) |
| 1,3-DNB; 2-am-4,6-DNT; 2,4-DNT; TNT; 1,3,5-TNB, RDX, HMX | N/A | MS (DART (He), TOFMS) | ~ 90 fg | N/A | (194) |
| RDX, PETN | N/A | MS (DESI, homemade field-portable MS) | 1 ng (RDX), 250 pg (PETN) | < 5 s | (195) |
| PETN, TNT | Seeded vapors | MS (SESI; QQQ (older model), QQQ (newer model); QTOF) | > 1.5 ppt (QQQ (older model)); > 0.3 ppt (QQQ (newer model)); 0.6 ppt (QTOF) | > 3 s | (196) |
| TNT, RDX, PETN, Semtex-H, C-4 | Particles placed on silicon wafers | MS (SIMS (carbon cluster primary ion source)) | N/A | N/A | (197) |
| Smokeless powder, Blackpowder | Solution casting onto silicon wafers | MS (TOF-SIMS ($Ar^+$ and $Ga^+$ primary ion sources)) | N/A | N/A | (198) |

| Analyte | Separation technique | Detection technique | Detection limit | Time of analysis | Ref. |
|---|---|---|---|---|---|
| TNT, RDX, PETN | Solution placed on filter paper or a glass slide (in some instances doped with HCl, NaCl, acetic acid, ammonium nitrate, ammonium chloride, or chloroform) | MS (DBDI (negative ion), LTQ) | 10 pg (TNT), 0.1 ng (RDX), 1 ng (PETN) | N/A | (199) |
| TNT, RDX, PETN | Solutions deposited on glass slides | MS (DBDI (negative ion, LTP probe)) | 500 fg (TNT), 1 pg (RDX), 500 fg (PETN) | N/A | (200) |
| RDX; HMX; 3,4-DNT; 2,6-DNT; 2,5-DNT; TNT; TNAZ; DNI; BTTN; NG; TO; NTO; DNP | Inclusion complex with β-CD | MALDI-TOF-MS (Sinapinic acid matrix, $N_2$ laser, 8- 16 laser shots averaged) | N/A | N/A | (201) |
| RDX, HMX, TNAZ | Inclusion complex with CD | IS-MS (5- 10 scans summed, QQQ) | N/A | N/A | (202) |
| RDX, PETN, TNT | Heating with nichrome wire | READ (negative ion MS, 90 Hz) | ~ ppt (expected) | 0.5- 2 hrs | (203) |
| RDX | Laser thermal desorption (Nd:YAG or $CO_2$) | MS (quadrupole) or IMS | N/A | ~ 3s | (204) |
| 1,3-DNB; 2,4-DNT; 2,6-DNT; 1,3,5-TNB; 4-am-2,6-DNT; 2-am-4,6-DNT; TNT; Tetryl; RDX; HMX | HPLC (C18 column (25 mm x x2.1 mm)) | MS (APPI (negative ion), QTOF) | < 0.029 ng | <10 min | (205) |
| DNT; TNT; RDX; PETN; Semtex | N/A | MS (laser ionization, TOF) | N/A | N/A | (206) |

| Analyte | Separation technique | Detection technique | Detection limit | Time of analysis | Ref. |
|---|---|---|---|---|---|
| Nitrobenzene, NT | Laser ionization (Argon ion laser or XeCl excimer pumped dye laser) | MS (TOF) | N/A | < 1 min | (207) |
| NB; 2,4-DNT; 2,6-DNT | GC (10 % OV-351, 80/100 mesh, 1.8 m x 2 mm) | TEA (950° C pyrolysis temperature) | 0.05 mg/L | ~16 min | (208) |
| NG; TNT; RDX | GC | TEA (1000° C pyrolysis temperature) | Low pg | N/A | (209) |
| NG; DNT; TNT; RDX; EGDN; Tetryl | GC (DB-5, 30 m x 0.32 mm x 0.25µm); HPLC (10 µm uBondapak CN, 30 cm x 3.9 mm) | GC-TEA (900° C pyrolysis temperature); HPLC-TEA (550° C pyrolysis temperature) | Low pg | ~16 min | (210) |
| NG; EGDN; TNT; RDX; Tetryl; NB; TNB; 2,4-DNT | Handswab extracts | TEA (500-900° C pyrolysis temperature) | Low ng | N/A | (211) |
| NG; TNT; RDX | GC | TEA (550-800° C pyrolysis temperature) | 5 pg | N/A | (212) |
| NG; EGDN; BTN; TEGDN; TNT; RDX; NB; 4-NT; 2,4-DNT | GC | TEA (625-750° C pyrolysis temperature) | Sub ng | N/A | (213) |
| NG; EGDN; TNT; DNT; PETN; RDX | | TEA (900° C pyrolysis temperature) | pg | N/A | (214) |
| 2-NN; 2,4-DNT; 2,6-DNT; 1-NP; 1,3,5-TNB; NG; PETN; TNT; RDX | SFE/TDM/GC | TEA (800° C pyrolysis temperature) | 2.6 ppb | N/A | (215) |

| Analyte | Separation technique | Detection technique | Detection limit | Time of analysis | Ref. |
|---|---|---|---|---|---|
| NG; TNT; PETN; RDX | | TEA (750° C pyrolysis temperature) | 3.1 ng (NG); 2.9 ng (TNT); 4.0 ng (PETN); 2.3 ng (RDX) | N/A | (216) |
| NG; 2,6-DNT; 2,4-DNT; TNT; PETN | SGC (10 µm ODS-bonded silica particles (80 Å), 75 cm x 250 µm), $CO_2$ mobile phase | TEA (740° C pyrolysis temperature) | Low pg | ~ 5 min | (217) |
| NG; 2,4-DNT; 2,6-DNT | N/A | IMS | 0.3 ng | ~24 ms | (218) |
| NG; 2,4-DNT; 2,6-DNT | GC ((Rtx-1, 30 m x 0.25 mm x 0.25 µm) or (DB-5MS, 15 m x 0.25 mm x 0.25 µm) | TEA (850° C pyrolysis temperature) | <0.2 ng (NG); <0.05 ng(2,4-DNT and 2,6-DNT) | ~8 min | (218) |
| NG; 2,4-DNT | GC (Rtx-1, 30 m x 0.25 mm x 0.25 µm) | TEA (850° C pyrolysis temperature) | 0.1- 1 ng | ~8 min | (219) |
| NG; 2,4-DNT | N/A | IMS | 0.1- 1 ng | ~24 ms | (219) |

# VITA

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|---|---|
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