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Utilizing Headspace Solid-Phase Microextraction for the Characterization of Volatile Organic Compounds Released from Contraband and its Implications for Detector Dog Training

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UTILIZING HEADSPACE SOLID-PHASE MICROEXTRACTION FOR THE CHARACTERIZATION OF VOLATILE ORGANIC COMPOUNDS RELEASED FROM CONTRABAND AND ITS IMPLICATIONS FOR DETECTOR DOG TRAINING

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Kelvin J. Frank

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To: Dean Michael R. Heithaus
College of Arts, Sciences and Education

This dissertation, written by Kelvin J. Frank, and entitled Utilizing Headspace Solid-Phase Microextraction for the Characterization of Volatile Organic Compounds Released from Contraband and Its Implications for Detector Dog Training, 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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DEDICATION

To my parents Kelvin J. Frank Sr. and April Frank.

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I would firstly like to thank God for giving me the strength to successfully complete this degree.

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ABSTRACT OF THE DISSERTATION

UTILIZING HEADSPACE SOLID-PHASE MICROEXTRACTION FOR THE CHARACTERIZATION OF VOLATILE ORGANIC COMPOUNDS RELEASED FROM CONTRABAND AND ITS IMPLICATIONS FOR DETECTOR DOG TRAINING

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Miami, Florida

Professor Kenneth G. Furton, Major Professor

Improving the accuracy and reliability of odor detection dogs is of utmost importance particularly for legal reasons. Field testing in conjunction with headspace analysis of volatile organic compounds (VOCs) has in recent times allowed for these improvements, by providing scientifically based recommendations for optimum training protocols. The current project leveraged on these established capabilities to enhance three areas of odor detection: illicit drugs, explosives and mass storage devices.

With hemp being legalized under the 2018 Farm Bill, legal questions have been raised regarding a dog's ability to ignore hemp if trained to detect marijuana, as both are types of *Cannabis*. Results concluded that most dogs do alert to hemp; however, they can be successfully trained over time to discriminate between hemp and marijuana. Headspace analysis showed marked similarities between sets of both products with minor differences. These differences can be further investigated to determine if characteristic marijuana VOCs

exist that can be included in canine training regimens. Other tests showed that dogs imprinted on current marijuana odor mimics can falsely respond to hemp as the VOC components of these mimics are not specific to marijuana. These mimics should therefore be avoided for further training purposes.

Dogs have been trained to detect and locate explosives such as triacetone triperoxide (TATP) that cannot be detected by most instrumental detectors. Headspace analysis showed TATP consisting primarily of the TATP molecule with relatively smaller amounts of the precursor acetone. Field tests determined that dogs imprinted on TATP may also falsely respond solely to the precursors acetone or hydrogen peroxide and as a result, additional training to ignore these VOCs should be considered.

Detection of mass storage device (MSDs) is a relatively new field with little understanding of optimum training methods for dogs. Headspace analysis of various MSDs showed that they do have characteristic VOCs that can allow for successful odor detection with specificity. Additionally, the validity of 1-hydroxyclohexylphenyl ketone and triphenylphosphine oxide (TPPO) as training compounds were also investigated. 1-hydroxyclohexylphenyl ketone was detected in MSDs but also in other electronic controls while TPPO was not detected in MSD components.

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ACRONYMS AND ABBREVIATIONS

Δ9-THC	Cannabinoid Δ9-tetrahydrocannabinol
AN	Ammonium Nitrate
ANFO	Ammonium Nitrate Fuel Oil
ATP	Adenosine Triphosphate
cAMP	Cyclic Adenosine Monophosphate
CBC	Cannabichromene
CBCA	Cannabichromenic Acid
CBD	Cannabidiol
CBDA	Cannabidiolic Acid
CBGA	Cannabinoid Cannabigerolic Acid
CBRs	Cannabinoid Receptors
CI	Chemical Ionization
COMPS	Controlled Odor Mimic Permeation System
CORT	Canine Odor Recognition Training
CSA	Control Substances Act
CSS	Controlled Substances Staff
CT	Computer Tomography

DEA	Drug Enforcement Administration
DESI-MS	Desorption Electrospray Ionization-Mass spectrometry
DVB/CAR/PDMS	Divinylbenzene/Carboxen/Polydimethylsiloxane
ECS	Endocannabinoid System
EI	Electron Impact Ionization
GC	Gas Chromatography
H2SO4	Sulfuric Acid
HMEs	Homemade Explosives
HMX	octahydro-1,3,5,7-tetranitro- 1,3,5,7-tetrazocine
HNO3	Nitric acid
HPK	1-hydroxycyclohexylophenyl ketone
HS-SPME	Headspace-Solid-Phase Microextraction
IEDs	Improvised Explosive Devices
IMS	Ion Mobility Spectrometry
LDPE	Low-Density Polyethylene
LSD	Lysergic Acid Diethylamide
MDMA	3,4-methylenedioxymethamphetamine
MOE	Main Olfactory Epithelium

MS	Mass Spectrometry
MSDs	Mass Storage Devices
NC	Nitrocellulose
NG	Nitroglycerine
NPV	Negative Predictive Value
NQR	Nuclear Quadrupole Resonance
ORCs	Olfactory Receptor Cells
ORs	Odor Receptors
ORT	Odor Recognition Test
PBEs	Peroxide-Based Explosives
PBXs	Polymer-Bonded Explosives
PC	Potassium Chlorate
PCP	Phencyclidine
PETN	Pentaerythritol Tetranitrate
Picric Acid	Trinitrophenol
PPM	Parts Per Million
PPV	Positive Predictive Value
RDX	1,3,5 trinitro-1,3,5 triazine

SIM	Subscriber Identification Module
SPME	Solid-Phase Microextraction
TATP	Triacetone Triperoxide
TETRYL	2,4,6-trinitromethylnitramine
THC	Tetrahydrocannabinol
THCA	Tetrahydrocannabinolic Acid
TNT	Trinitrotoluene
TPPO	Triphenylphosphine Oxide
UDC	Universal Detector Calibrant
USB	Universal Serial Bus
VNO	Vomeronasal Organ
VOCs	Volatile Organic Compounds

1. INTRODUCTION

Owing to their highly developed olfactory system, dogs have been extensively used by various disciplines for the detection of target odors of interest. These include but are not limited to explosives, narcotics, mass storage devices, firearms, search & rescue, medical detection, pests, ignitable liquid residues, conservation, invasive species, agriculture, currency and tracking/trailing [1]. Their heightened sense of smell allows dogs to detect odors at a level of sensitivity often unrivaled by most instruments [2]. Dogs are also highly selective, possessing the ability to discriminate target odors in a myriad of interfering non-target odors [3], [4]. These factors, in addition to a dog's mobility, independent thinking, and ability to quickly learn new tasks through conditioning, have made detector dogs an intrinsic element of law enforcement, military and private agencies for real-time detection of target odors.

The use of detector dogs however has not gone without scrutiny as traditionally, the methods and rationale for training were often anecdotal rather than guided by tested scientific methods. As a result, there has been increased efforts for standardizing procedures and guidelines for best practices of detector dogs. In the United States for example, the Scientific Working Group on Dog and Orthogonal Detection Guidelines (SWGDOG) was established in 2004 in collaboration with international, federal, state and local partners with the aim of establishing standards and guidelines for best practices for detector dog teams. SWGDOG has now transitioned to the Dogs and Sensors Subcommittee of the Organization of Scientific Area Committees (OSAC) for Forensic Science under the National Institute of Standards and Technology (NIST). Their guidelines

provide proficiency, maintenance, certification protocols for detector dog teams as well as suggestions for key areas of scientific research. The use of analytical chemistry in conjunction with reliable field testing has now allowed for an improved understanding of odor detection dogs and hence enhanced training methods. This study leverages on these already established analytical and field capabilities to set the foundation to explore several limitations in three areas of detector dog training: illicit drugs, explosives and mass storage devices.

Under the Agricultural improvement Act of 2018 hemp was legalized in the United States of America. The legalization of hemp has raised questions regarding the reliability of dogs that have been trained to detect marijuana, another type of *Cannabis* which still remains illegal federally and in most states. There have been reports of dogs not being able to discriminate between the odor of the two substances. Alerts to hemp can have serious legal ramifications since trained law enforcement dogs should respond only to illicit substances as these responses provide the legal basis for probable cause during a search. This study investigated the overall response of marijuana trained dogs to hemp and whether these dogs can be trained to successfully distinguish between the two substances. In addition, the Volatile Organic Compounds (VOCs) of both substances were analyzed in order to determine if any specific markers exists that can potentially be used to improve a dogs' rates of discrimination between the two.

Explosive detection dogs continue to be the gold standard for trace detection of explosives as they provide a superior form of sampling, selectivity, mobility, and versatility compared to instruments and can be quickly trained to deal with new threats. In recent times, the use

of peroxide-based explosives such as triacetone triperoxide (TATP) has provided limitations for most analytical instruments as these instruments are typically calibrated for traditional explosives consisting of nitrogen. Dogs however have been trained to detect these explosives. The second part of this study investigated the VOCs associated with solid TATP samples and their implications for canine training. Also, the VOCs of two TATP commercial training aid "mimics" were also analyzed to determine how they compared to an actual TATP sample and hence its overall efficacy.

The use of dogs for the detection of mass storage devices is relatively new discipline. As a result, many anecdotal and unreliable reports exists regarding methods for successful training. Additionally, the goals of these dogs are highly agency specific which adds an additional layer of complexity for training. Many departments do not perform the initial training but instead purchase pretrained dogs from sellers. It is therefore important for these departments to understand the specific methods used for training these dogs to determine if the dogs are in fact suitable for their needs. In most correctional facilities for example, cellular phones and other electronic devices are considered contraband. Some facilities however allow mp3 players which contain similar components to cellular phones. Other agencies might be concerned with only detecting one particular type of device. Questions have been raised as to the extent of VOC crossover between the many devices that exist and optimal training methods for a successful detection dog. This study looked at VOCs associated with different types of mass storage devices to firstly determine what the dogs might be responding to in order to begin laying the analytical foundation for this area of odor detection. Additionally the validity of two compounds 1-hydroxycyclohexylophenyl

ketone (HPK) and triphenylphosphine oxide (TPPO) as a training tool for detection of mass storage devices was investigated.

As part of the response to increase day-to-day reliability of detector dogs, a patented tool, the Universal Detector Calibrant (UDC) was previously developed. This study also served to further develop the UDC as a calibration device utilizing another patented device: Controlled Odor Mimic Permeation System (COMPS). A series of COMPS were created analyzed to provide varying levels of odor availability for the UDC, effectively mimicking the calibration procedure used for instrumental detectors.

2. LITERATURE REVIEW

2.1 Process of Olfaction in Dogs

Olfaction, the process of odor perception, is a form of chemoreception that allows an organism to receive and process chemical compounds (odorants) from its environment. Olfaction is essential as it provides information for communicating, locating food, mating, and avoiding danger. In vertebrates, including most mammals, olfaction is accomplished through a main olfactory system for detecting volatile chemicals and an accessory olfactory system (e.g., vomeronasal organ (VNO)) for fluid-phase chemicals such as pheromones. The main olfactory system consists of the olfactory mucosa (main olfactory epithelium (MOE) and respiratory epithelium) and the olfactory bulb. Within the MOE are olfactory receptor cells (ORCs) that mediate the olfactory process. The ORC is a bipolar neuron with a dendrite containing hair like cilia immersed in the fluid mucous membrane and an axon that extends to the glomerulus of the olfactory bulb. Embedded in the membrane of the cilia are extracellular portions containing odor receptors (ORs) and intracellular portions coupled to a G-protein. When an odorant binds to ORs, the G-protein, a subunit, breaks away activating adenyl cyclase which catalyzes the conversion of adenosine triphosphate to cyclic adenosine monophosphate that in turn binds to the face of a cyclic nucleotide-gated ion channel. Binding to the ion channel causes a cation influx and change in membrane potential resulting in an action potential that travels along the axon to the glomerulus and mitral cells then on to the brain where the signal is perceived as an odor. A single OR can be activated by multiple odorants and a single odorant can activate several different ORs, providing the basis for combinatorial diversity which allows distinctive

odorant pattern signaling to the brain and significantly expands the discriminatory power of the olfactory system [5],[6]. The process believed to occur in transforming an odorant into a detected odor is illustrated in Figure 1.

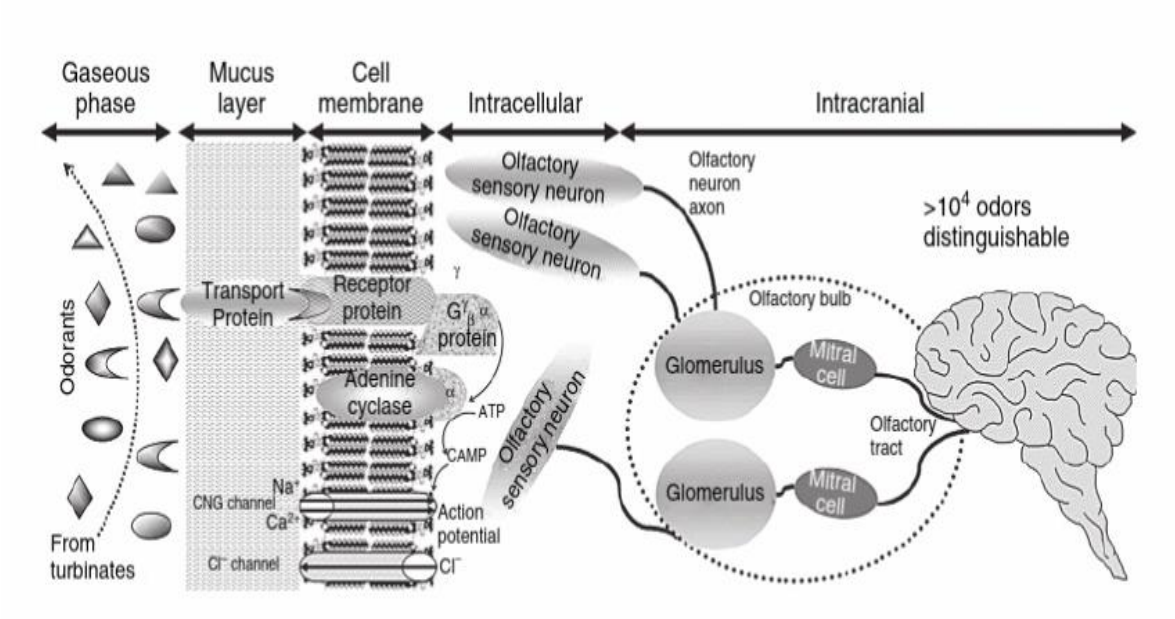


Figure 1. The process of transforming an odorant into a detected odor [7].

Compared to microsmatic species, such as humans, who have evolved to rely more greatly on other senses like sight, macrosmatic animals, such as dogs, have evolved to depend heavily on a keen olfactory system as a basis for survival. As a result of anatomical, physiological and genetic differences, dogs can more efficiently sample and process environmental odorants resulting in a sense of smell many orders of magnitudes greater than that of a human's [8].

Air enters a dog's nasal cavity through the external nostrils or "naris." The nasal cavity is comprised of two bilateral chambers separated by the nasal septum. Within each chamber lie convoluted folds of bone called turbinates or conchae. Air first reaches the

maxilloturbinates where it is warmed, moistened and filtered before flowing into the more posterior ethmoturbinates containing the MOE. The extent of turbinate folding as well as a dog's muzzle length increases the overall surface area of the MOE. In humans, this surface area is approximately 5 cm^2 compared to 70-170 cm^2 in dogs[6],[9]. The number of ORCs in humans is estimated to be approximately 5 million and between 200-300 million in dogs. There is also marked variation in the number cilia within each ORC, with dogs having hundreds per cell while humans approximately 25. All of these differences allow for an overall larger olfactory receptor repertoire in dogs permitting the discrimination of numerous odorants at lower odorant concentrations. A dog's olfactory brain components such as the olfactory bulb, tract and stria also constitutes a much larger area relative to total brain size when compared to humans [10]. Figure 2 shows the sagittal cross section of a dog's skull and the location of some of these key components of the olfactory system

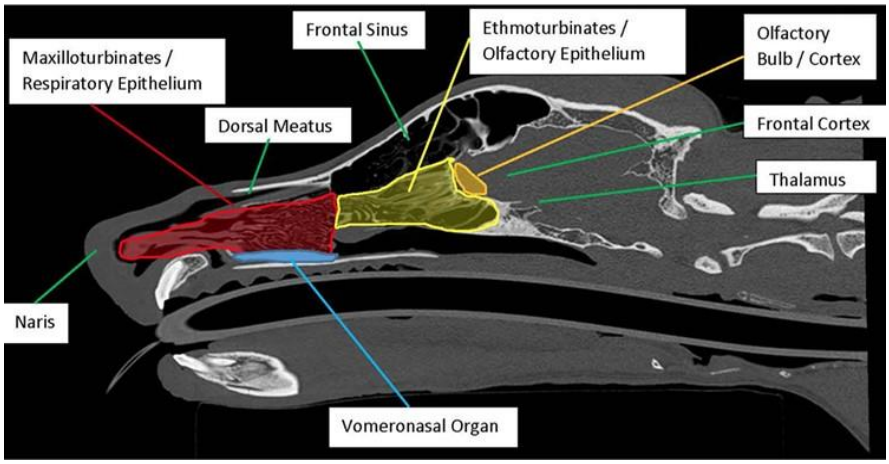


Figure 2. Sagittal cross section of a dog's skull with key components of the olfactory system [1].

A dog's nose is a highly efficient sampling system. Unlike humans, where there is a single pathway for both olfaction and respiration, dogs have a separate olfactory recess that is excluded from the respiratory path by a bony plate, the lamina transversa. During respiration, it is estimated that 12-13% of air is separated via the lamina transversa and travels to the olfactory recess while the remaining is directed to the respiratory tract [11]. The process of active sniffing however produces improved airflow with short sharp sniffs at a frequency of 4-7 Hz, equivalent to 240-420 sniffs per minute, generating larger volumes of high velocity air to the olfactory recess, after which it flows back over the turbinates [11]. The average dog takes in approximately 30 mL of air per nostril per sniff equating to 3.6 L/min of sampled air. The aerodynamics of active sniffing is further facilitated by the morphology of the nares (Figure 3). Inspired air within a spatial distance or "reach" of approximately 1 cm is drawn into each nostril to the nasal cavity while expired air exits via ventral-lateral slits. This inspiration-expiration pattern minimizes re-inspiration of expired air subsequently promotes inspiration of fresh odorants. The lateral expiration also creates a vortex that stirs surrounding air drawing ambient odorants towards the nose effectively increasing the aerodynamic reach. Expiration of warm, moist air may also promote the volatilization of latent odorants for inhalation [11]. In addition, during the expiration phase, no air enters or exits the olfactory region which allows for prolonged exposure of odorants. The estimated aerodynamic reach of 1cm is smaller than the inter-nostril separation indicating that inspiration by each nostril occurs from spatially separate regions [12]. The bilateral odor sampling is believed to assist in localization of odor source by dogs.

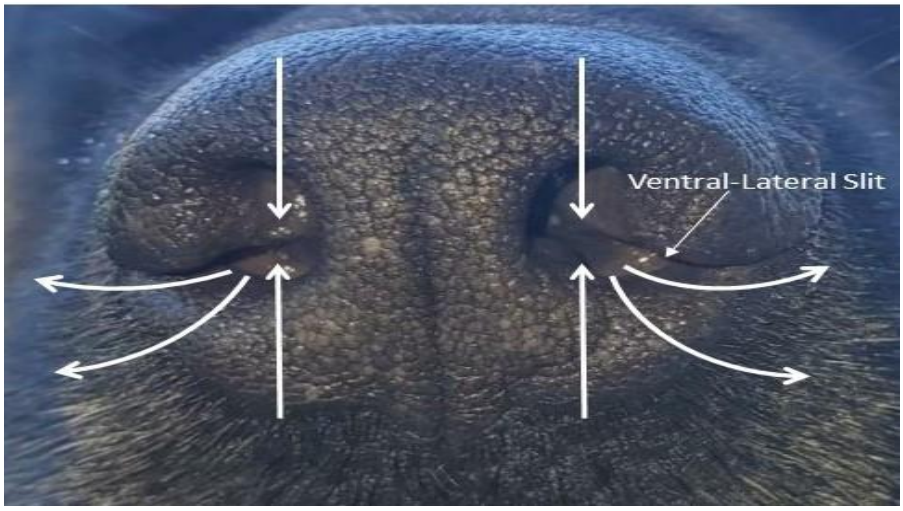


Figure 3. The morphology of a dog's external nares and the pathways for inhalation and expiration.

Since the identification of OR gene transcripts by Buck and Axel in 1991, OR genes have been studied in several species including dogs. The OR gene repertoire in dogs has been reported to contain 1,094 genes [13], approximately 2.5 times more than a human [14]. In dogs as much as 20% of these genes have been estimated to be inactive pseudogenes with percentage varying among breeds. The number pseudogenes is significantly lower however compared to humans where it was determined to be almost 50% [15]. Although there is debate, it is assumed that the overall larger gene repertoire and active genes might allow for a wider range of detected odorants in dogs.

2.1.1 Training a Dog for Odor Detection

Prior to training dogs in any area of odor detection, the "ideal" dog must be selected. Selection is determined by certain traits deemed necessary for the continued success of the dog-handler team. The first of these traits and if not the most important is high drive, meaning that the there is something (e.g., a reward) that the dog badly desires and as such

is willing to continuously work to obtain it. Other traits include but are not limited to intense focus, the ability and desire to cooperate with a handler and athleticism. It is important to note that handlers must also possess the necessary skill to understand and quickly interpret a dog's behavior as well as be able to influence the dog's actions to a certain extent [16]

After selecting a dog, the trainer may opt to continue improving certain traits such as search drive and obedience prior to odor detection training. Once this is completed, the trainer begins to make an association between the desired odor and positive reinforcement such as a reward which can be in the form of food, toy, petting/verbal praise. This association is known as imprinting and centers around the concept of classical conditioning. In classical conditioning, two stimuli, a conditioned stimulus and an unconditioned stimulus are repeatedly paired to elicit a conditioned response. Eventually, the unconditioned stimulus can be removed with the conditioned stimulus being sufficient to elicit the response. A typical example of this is making a whistling or kissing noise while giving food to your dog. Here, the noise becomes the conditioned stimulus which is paired to the food which is the unconditional stimulus and elicits an overall response of happiness and anticipation of food which now becomes a conditioned response. Eventually, the use of the noise alone will be sufficient for the dog to anticipate the food. In the case of imprinting, the odor becomes the conditioned stimulus and the reward the unconditioned stimulus. The conditioned response can take several forms including salivation, barking, scratching and searching depending on the unconditioned reinforcer that was used.

Classical conditioning, however, does not require the dog to engage in any specific behavior in order to receive the reward. Therefore, the process of operant conditioning is used to build upon classical conditioning. Operant conditioning centers around the relationship of a voluntary behavior and its consequence. This relationship is achieved via reinforcement which can be positive or negative. Reinforcement serves to ensure repeatability of the desired behavior. In operant conditioning the stimuli that comes before the behavior and determine a reward is referred to as discriminative stimuli. In detector dog training, this stimuli is the target odor of interest where the desired behavior is trained (e.g., to sit) which results in the dog consequently being rewarded by the handler. Figure 4 shows a typical setup for conditioning a dog to respond to a target odor. The dog is first made to stick its nose inside the box containing the target odor by visually placing a reward such as a toy in the box. When the dog sniffs and searches for the toy, the wanted behavior (e.g., to sit) is conditioned which is then followed by an external reward.

Figure 4. A typical scent box that is used for odor detection training [17].

2.2 Drugs

2.2.1 History of Drugs

In simple terms, a drug refers to any natural or synthetic substance capable of producing a psychological or physiological change in an organism. The discovery and development of drugs is by no means a new phenomenon with an extensive history dating back thousands of years. Derived mainly from plant products enhanced by animal materials and minerals, drugs found use in ancient civilizations for religious, medical and recreational purposes and continued over the course of history [18]. The use of drugs like alcohol, *Cannabis* and opium precedes written history while those such as cocaine and heroin being relative newcomers dating to the late 19th century. The historical birth of the renaissance period (14th-17th century AD) provided the platform for scientific thought and advances in the use of drugs for medical treatments [19]. From the 16th century and onward, scientists sought to isolate active ingredients from these plant materials to achieve improved and/or desired properties ushering in the beginnings of the modern pharmaceutical industry by the 19th century. The extraction of organic alkaloids, glycosides and glucosides for example, proved a major landmark in the history of pharmacology. Morphine, a powerful painkiller and an alkaloid of the opium plant was isolated by French scientist Freidrich Serturner in 1805. Serturner discovered that morphine's effect was ten times stronger than processed opium. Cocaine, another alkaloid and a stimulant was extracted from coca leaves in 1859 by German chemist Albert Niemann who coined it a "magical" substance. Glycosides such as digoxin was later isolated for treatment of heart conditions. Other notable extracts included aspirin from willow trees and quinine from the cinchona tree. The chemical

structure of these organic extracts provided the base for later synthetic and semi-synthetic drugs. Heroin for example, was synthesized from morphine in 1874 and used as an alternative pain killer. In the last century, improvements in science and technology has allowed increase in drug potency and the creation of new synthetics with many having limited medical application. Some studies have shown the increase in purity of drugs like cocaine and heroin with others like marijuana seeing increases in the percentage of Tetrahydrocannabinol (THC) [20]. Synthetic compounds such as 3,4-methylenedioxymethamphetamine (MDMA) and methamphetamines have become widely available being branded as "party drugs." Additionally, "designer drugs" which are chemical analogs of existing drugs can easily be created to mimic pharmacological effects while simultaneously circumventing legal issues. These factors have all led to a significant increase in drug abuse which continues to be a growing problem. Today, drugs can be divided into four general categories depending on how it interacts with an individual's brain and the effect on the person's mindset and behavior (Table 1)

Table 1. The four drug classifications based on its effect on the user.

Drug classifications by Effect on the User

Category	Effect	Examples
Opioids	Pain relief	Heroin, Morphine, Fentanyl
Hallucinogens	Mind altering causing changes in mood, thought process and perception of reality	Marijuana, Lysergic acid diethylamide (LSD), Phencyclidine (PCP)
Stimulants	Increase central nervous system activity.	Cocaine, Caffeine, MDMA
Depressants	Depress central nervous system activity.	Alcohol, Barbiturates

2.2.2 History of drug use in the United States of America and the War on Drugs

The use of drugs for recreational and medicinal purposes has been a part of the United States since the country's inception. Opium was legally imported for more than a hundred years [21]. Used in its raw form for pain relief, several of its alkaloids such as morphine and codeine would be utilized for not only the treatment of pain but also other conditions such as diarrhea and coughing. It is estimated that by 1858, over 300,000 pounds of opium was entering America annually [22]. According to historians, the Civil War was a major driving force for the beginning of widespread abuse of opioids, as soldiers quickly turned to morphine for relief from both physical pain and mental illness. Additionally, the rise of Chinese laborers saw the establishment of opium dens particularly on the west coast. Opioid addiction increased from approximately .72 addicts per 1,000 people to 4.59 per

1,000 in the 1890s [23]. By the late 19th century, America entered its first drug and opioid epidemic and the need to confront this problem became evident. Laws to ban or regulate drugs were first implemented on a local, city or state by state basis but in 1890 the first congressional act to levy taxes on morphine and opium took place [24]. It was during this period, that heroin quickly rose to fame being marketed as a "safer" and "less addictive" alternative to morphine. By the beginning of the 1900s however, abuse of heroin became yet another opioid issue. Cocaine abuse also spiked in this period after being widely used as an energy boosting supplement and an active ingredient in other products such as Coca-Cola and margarine. It was even touted by many as a miracle drug for a wide range of ailments and also a potential treatment for morphine addiction [25] Sources estimate that by 1902 there were nearly 200,000 cocaine addicts in America. This increasing addiction led to the Pure Food and Drug Act of 1906 that mandated full disclosure to customers of specific ingredients contained in products as this information was often kept proprietary. Some of these ingredients included morphine, heroin, cocaine, *Cannabis* and even alcohol. The Opium Exclusion Act soon followed in 1909 allowing its use for medical purposes only with a ban on the importation, possession and the use of opium for smoking. This act became the first federal law to ban the non-medical use of a substance. In 1914, congress passed the Harrison Act which levied taxes on anyone importing, manufacturing and distributing opium or cocaine. The Heroin Act in 1924 also prohibited manufacturing, importation and distribution of heroin even for medical use. During the First World War, the use of cocaine and opioids also became popular drug on the frontline with soldiers often receiving them as packages from family and friends [26]. Post-World War 1 and the Great Depression that followed lead to another rise in the use and abuse of drugs. This rise

resulted in an increased number of legislations such as the 1922 Narcotic Drug Import and Export Act, 1927 Bureau of Prohibition, 1932 Uniform State Narcotic Act, 1937 Marijuana Tax act and the 1938 Food, Drug, and Cosmetic Act, all aimed at curtailing the issue [27]. The second World War saw the rise of amphetamines with soldiers accounting for the largest number of users between 1939 and 1945 [26] It is estimated that the Pentagon issued between 250 million to 500 million Benzedrine pills to American troops during this period. Others such as dextroamphetamine became common during the Korean war that followed. Consumption and addiction also increased amongst civilians at home. It became critical at this point for the United States to enforce more stringent measures to control and regulate the use of illicit drugs.

In 1951, Congress passed the Boggs Act, which became the first Act to establish mandatory minimum prison sentences for drug offences. Under the Boggs Act, the possession of cocaine, heroin or *Cannabis* imposed two to five years for a first offense along with a fine up to $2,000, 5 to 10 years for a second offense, and 10 to 15 years for any subsequent offenses [21]. Maximum criminal penalties were also imposed for violations of import and export. In response to a 1955 nationwide investigation by a senate subcommittee into the trafficking, addiction and treatment of drugs, the Narcotics Control Act of 1956 was passed. This act increased sentences to a five-year mandatory minimum sentence for the first offense and between 10-40 years for a second offence with no possibility of probation, parole, or suspension of sentence [21].

However, these new laws had very little impact on the growing epidemic and drug use continued to soar. The 1960s and 70s ushered in the era of counterculture and youthful

rebellion strongly influenced by the music of that time. Americans began to experiment with hallucinogenic drugs such as marijuana and lysergic acid diethylamide (LSD) that would allow creativity mind altering experiences. This period also saw the resurgence in the use of cocaine since its decrease after the 1914 Harrison Tax Act and the drug now became an integral part of popular culture and trendy amongst the elite. By 1982 cocaine use had peaked with an estimated 10.4 million users [28].

With the drug culture now exploding, President Richard Nixon signed the Controlled Substances Act (CSA) regulating the manufacture and distribution of certain drugs and substances used in its production. The CSA also placed all substances that was federally regulated into one of five schedules depending on the substance's medical use, potential for abuse and dependency [29].

In 1971 the 'War on Drugs" was officially declared by President Nixon stating that the number one public enemy was drug abuse. The war led to the formation of the Drug Enforcement Administration (DEA) to combat trafficking and use of illicit drugs in the United States. The DEA also took the responsibility of administering and enforcing the Controlled Substances Act.

2.2.2.1 DEA Scheduling of Drugs

As stated above, the CSA created five schedules with different criteria for each substance to be included with the rate of abuse being the main factor for scheduling [30]. Currently, this process of scheduling is facilitated by the Controlled Substances Staff (CSS) The CSS provides expertise to the Food and Drug Administration centers, Center for Drug

Evaluation and Research Offices and Divisions and the Department of Health and Human Services as part of the review process in assessing or reassessing drugs for abuse potential and dependence liability. The CSS also serves as a liaison with the DEA and mandates the Department of Health and Human Services to notify the Attorney General via the DEA of any new drugs having a stimulant, depressant, or hallucinogenic effect on the central nervous system[30].

2.2.2.1.1 Schedule I

Schedule I drugs have no currently accepted medical use and a high potential for abuse. Examples of drugs in this category are: heroin, LSD, marijuana, methaqualone, peyote and MDMA [31].

2.2.2.1.2 Schedule II

Schedule II drugs have a high potential for abuse, with use potentially leading to severe psychological or physical dependence. Examples of drugs in this category are: Combination products containing less than 15 milligrams of hydrocodone per dosage unit (e.g. Vicodin), cocaine, methamphetamine, methadone, oxycodone and fentanyl [31].

2.2.2.1.3 Schedule III

Schedule III drugs have a moderate to low potential for physical and psychological dependence. Its abuse potential is less than Schedule I and Schedule II drugs but more than Schedule IV. Examples of drugs in this category are: Products with less than 90 milligrams of codeine per dosage unit (e.g. Tylenol with codeine), ketamine, anabolic steroids, testosterone [31].

2.2.2.1.4 Schedule IV

Schedule IV drugs have a low potential for abuse and low risk of dependence. Examples of drugs in this category are: Xanax, Soma, Darvon, Darvocet, Valium, Ativan, Talwin, Ambien, Tramadol [31].

2.2.2.1.5 Schedule V

Schedule V drugs have lower potential for abuse compared to Schedule IV. These drugs consist of preparations containing limited quantities of certain narcotics and are typically utilized for antidiarrheal, antitussive, and analgesic purposes. Examples of drugs in this category are: cough preparations with less than 200 milligrams of codeine or per 100 milliliters (Robitussin AC), Lomotil, Motofen, Lyrica, Parepectolin [31].

2.2.2.2 Drugs in 21st Century America

Today, the demand and use of illegal drugs in the United states exceeds that of almost every other nation in the world [32]. Grappling to fight the drug trade since 1971, the United States government has spent over 1 trillion dollars since the beginning of the war on drugs and the implementation of the DEA, Figure 5 displays the allocation of the 2020 Federal Drug Control budget with approximately 45% alone toward treatment.

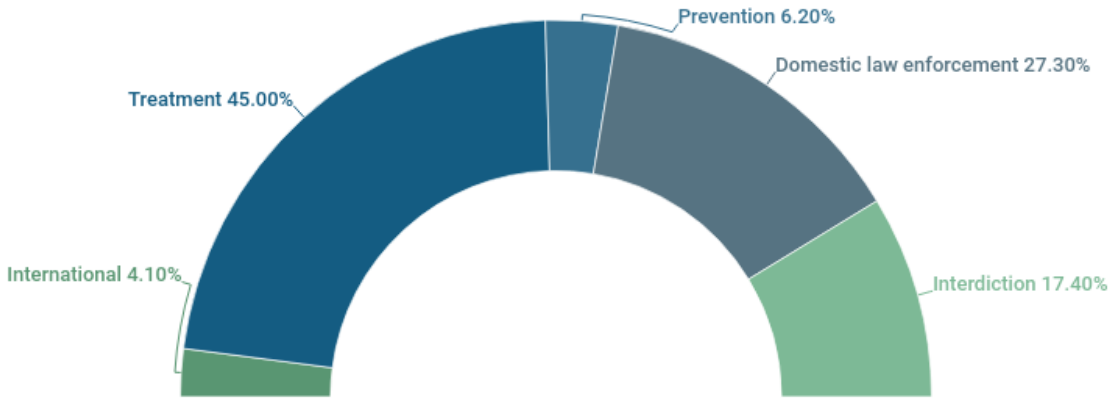


Figure 5. Distribution of federal drug control spending in the United States in fiscal year 2020 [33].

2.2.3 *Cannabis*

2.2.3.1 *Cannabis* and its constituents

Cannabis is a genus of the flowering plants belonging to the Cannabaceae family. The plants can be divided into three basic species: *Cannabis* sativa, *Cannabis* indica and *Cannabis* ruderalis. As depicted in Figure 6, *Cannabis* sativa plants are characterized by long, narrow leaves, a fibrous stalk and can grow up to 3 meters tall. They are typically grown in equatorial regions with warmer climates and can take between 9 to 12 weeks for flowering. The *Cannabis* indica plant is shorter in height with leaves that are wider and shorter with a tougher stalk. Due to their height, they tend to be more suitable for balcony or indoor growing with a shorter flowering period of 7 to 9 weeks. *Cannabis* ruderalis plants are short in height with small bushy leaves and relatively short with flowering periods. They have grown and adapted to cooler northern environments where the amount

of light can often be much less compared to southern climates As a result of crossbreeding, a monotypic classification *Cannabis Sativa* L. has been adopted which encompasses the different species [34].

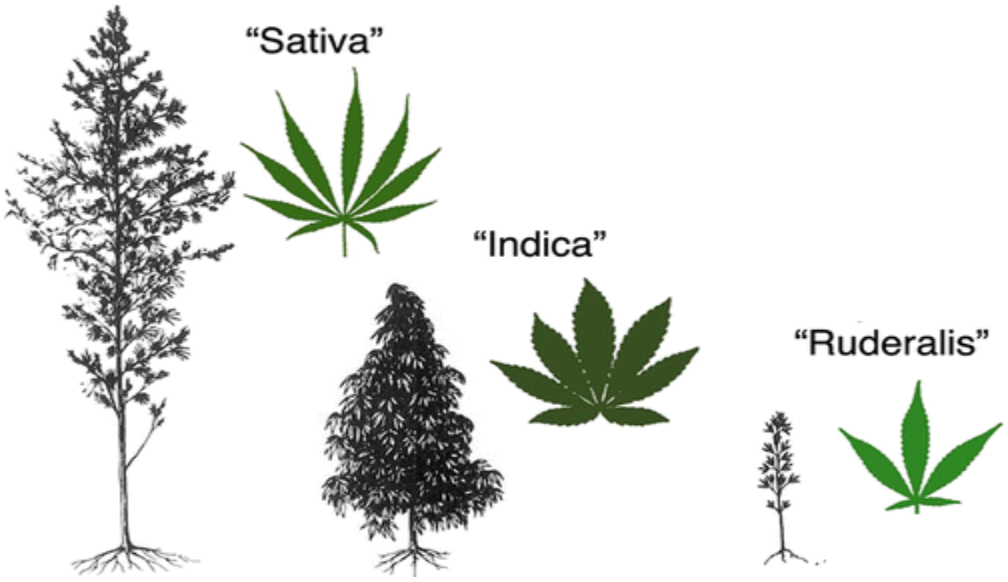


Figure 6. The appearance of Cannabis sativa, Cannabis indica and Cannabis ruderalis[35].

For millennia, *Cannabis* has been used for fiber products (e.g., textiles, plastics and construction materials), oils, edible seed products and other recreational uses (e.g., smoking) [36]. *Cannabis* is characterized by a series of chemical compounds including terpenes, carbohydrates, fatty acids and their esters, amides, amines, phytosterols, phenolic compounds, and unique class of terpenophenolic compounds referred to as cannabinoids [34]. More than 100 cannabinoids have been isolated from *Cannabis* sativa L. all originating from the "grandfather" cannabinoid cannabigerolic acid (CBGA) (Figure 7)

[37]. From this cannabinoid, plant enzymes that are unique to strains convert CBGA into three major cannabinoid precursor compounds, tetrahydrocannabinolic acid (THCA), cannabidiolic acid (CBDA) and cannabichromenic acid (CBCA). These eventually become tetrahydrocannabinol (THC), cannabidiol (CBD) and cannabichromene (CBC) respectively. Although not common, in some strains CBGA may convert to CBG. Collectively, the presence of and variations in the different classes of chemical compounds contributes to the overall effect of *Cannabis*.

On the basis of their cannabinoid profiles, *Cannabis* can be classified into five different chemotypes: chemotype I which consists of drug plants containing high levels of the psychoactive cannabinoid tetrahydrocannabinol (THC); chemotypes III and IV are fiber-type plants that contains very low amounts of psychoactive cannabinoids but high levels of nonpsychoactive cannabinoids (e.g., CBD); chemotype II is an intermediate between drug-type and fiber-type plants chemotype V is composed of fiber-type plants which contains almost no cannabinoids.

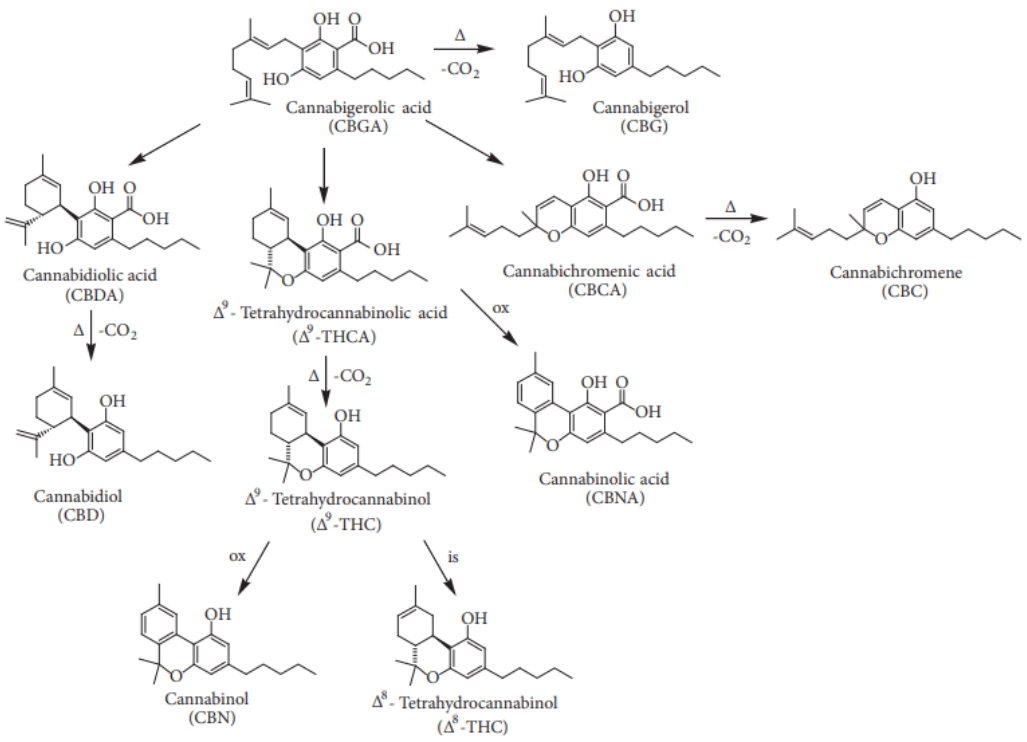


Figure 7. Chemical structures of main cannabinoids present in Cannabis sativa L. Abbreviation: Δ = heating; ox = oxidation; is =isomerization [34]

2.2.3.2 *Cannabis* as a Drug and its Effects on the Body

For recreational purposes, *Cannabis* as a drug is normally used in three different forms: herbal *Cannabis* obtained from dried leaves and flowers, also referred to as weed, ganja, marijuana, pot, dope among others; *Cannabis* resin, a pressed concentrate form of the plant; and *Cannabis* oil from plant distillates or extracts. The herbal form is the most widely used worldwide with resin being used mainly in Europe and oil the least used of the three [38]. Herbs and resins are commonly smoked as opposed to ingesting, as this provides the fastest mechanism for chemicals to reach the brain and produce the desired effects. Smoking may take the form of hand-rolled cigarettes (joints), pipes, water pipes (bongs) or rolled in cigar wraps (blunts). Its use as a drug is mainly due to the presence of the psychoactive

compound Δ9-THC that contributes to the “high” effect of the user. Although THC has found several applications in the medical field for treatment of various diseases and illnesses [39], its negative effects via smoking still remains significant [40], [41]. For this reason it continues to be illegal for recreational use in the majority of the world. *Cannabis*, however, still remains the number one produced, used and trafficked illicit drug globally.

2.2.3.2.1 THC and the Endocannabinoid System

The endocannabinoid system (ECS) consists of a network of natural endogenous lipid messengers (endocannabinoids), cannabinoid receptors (CBRs) and enzymes for their biosynthesis and degradation [42]. The system functions to maintain homeostasis within the body thus allowing optimal functioning. Endocannabinoids function as neurotransmitters throughout the nervous system binding to receptors (CBR1 and CBR2). These receptors are distributed throughout the brain but more concentrated in the hippocampus, cerebellum, prefrontal cortex and amygdala which are areas that influence, memory, pleasure, reward, thinking, concentration, movement, coordination, pain perception and sensory and time perception[41]. These CBRs are often activated by the endocannabinoid anandamide. Tetrahydrocannabinol, an exocannabinoid, due to having a similar chemical structure to anandamide (Figure 8) can also bind to CBR1 receptors. CBR1 receptors are known to moderate the release of neurotransmitters, such as gamma-aminobutyric-acid, glutamate, and dopamine [42]. When *Cannabis* is smoked, THC enters the lungs into the bloodstream then on to the brain where it attaches to the CBR1 receptors effectively altering the mental and physical functions of the body.

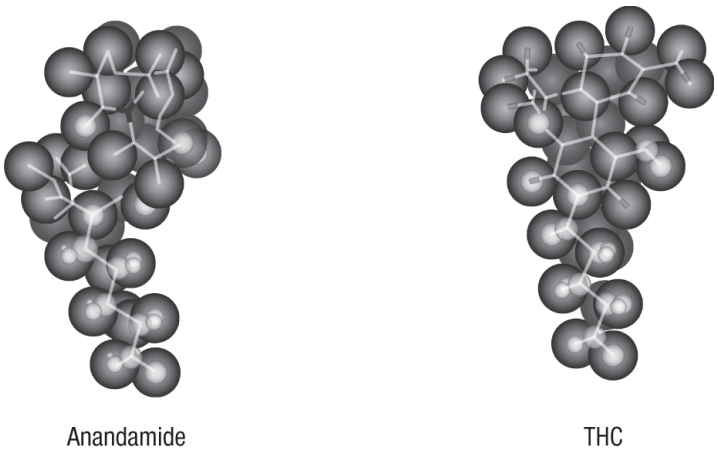


Figure 8. The structure of Anandamide and THC [43].

These effects can occur almost immediately often marked by an increase in heart rate, enlarged bronchial passage and expansion of blood vessels in the eyes causing them to become red. Behavioral effects can range from feelings of euphoria, relaxation, sleepiness, depression, anxiety, paranoia, psychosis etc. Tetrahydrocannabinol also activates the brain's reward system that is responsible for pleasure (e.g., sex and eating). This activation releases dopamine at much higher levels resulting in the pleasurable "high" as we know it.[38]. Tetrahydrocannabinol can alter the functioning of the hippocampus and orbitofrontal cortex regions of the brain resulting in memory loss, impaired thinking, inability to focus and lack of ability to learn and perform difficult tasks. Other regions like the cerebellum and basal ganglia can also be altered, affecting balance, posture, coordination, and reaction time. These negative effects are the reasons why it is dangerous to drive after consuming *Cannabis*. Li and Brady (2014) for example determined *Cannabis* to be the leading non-alcoholic drug amongst drivers killed within 1 hour of a vehicular crash in six US states (California, Hawaii, Illinois, New Hampshire, Rhode Island, and West Virginia) [44]. Other large European studies determined that drivers with traces of

THC in their blood were twice as likely to be responsible for fatal crashes compared those who used no drugs or alcohol [45]. In addition to the immediate effects listed above, long term cognitive effects of THC are also possible among *Cannabis* users.

2.2.3.3 *Cannabis* in the United States of America

The use of *Cannabis* in the United States can be traced back to the colonial era. During the 17th century, the use of hemp (fiber-type *Cannabis* that contains very low amounts of psychoactive cannabinoids) was encouraged by the government for the production of fuel, ropes, paper, fabric among other products. Until after the civil war, when it was replaced by imports, the production of hemp thrived. The drug form of *Cannabis*, like other drugs such as opium and cocaine, became popular throughout the 19th century for its use in medicine as tinctures and extracts, and was commercially available in pharmacies. The arrival of Mexican immigrants after The Mexican Revolution of 1910 ushered in the increased use of *Cannabis* drug for recreational purposes. It then became widely known as marijuana (originally marihuana). By the early 1930s, states began regulating its use particularly after passage the 1932 Uniform State Narcotic Act. By 1937, congress passed the Marijuana Tax Act which criminalized the possession and sale of not only marijuana but all forms of *Cannabis* including hemp [46]. Marijuana's use however, as with other drugs, continued to increase, as it was also heavily associated with the counterculture movement of the 1960s and 1970s. This increased use led to *Cannabis* being classified as a schedule I drug under the Controlled Substances Act. Since that time, there have been conflicting attitudes at the state and federal level regarding its use. By 1972, eleven states

had decriminalized *Cannabis* after a report by a bipartisan committee appointed by President Nixon suggested that personal use be decriminalized. However, after the "war on drugs" began federal penalties for *Cannabis* possession increased under the 1986 Ant-Drug Abuse Act [47]. In 1996, California passed proposition 215 becoming the first state to legalize *Cannabis* for medical use. To date, 32 other states including Washington, D.C have followed suit [48]. In 2012, Colorado and Washington became the first states to approve its recreational use. It has now been approved in a total of 18 states including the District of Columbia.

Marijuana continues to be the number one used illicit drug in the US. In 2017 alone there was a reported 37.6 million users. More concerning, 2018 saw 11.8 million young adults reporting using marijuana [41]. A 2019 Monitoring the Future survey noted a significant increase in young users (13-16 age group). The 13-14 age group had an 11.8% reported marijuana use within the year while the 15-16 group 28.8%. The 17-18 group continued to remain the highest users with a 35.7% reported use [49]. The use among young adults is a cause for concern as it has been established scientifically that the brain, specifically the prefrontal cortex does not fully develop until the mid-20s making the brain more susceptible to the adverse effects of drugs [50]. Vaping of THC oil is also becoming increasingly popular amongst teens as well. 20.8% of high school seniors reported marijuana vaping, almost the same (19.4%) as the 15-16 age group [51]. These percentages represented the second largest one-year increase in the use of a drug in the survey's 45-year-old history. Since there are few studies on vaping, the possible effects of vaping THC versus smoking presents many concerning questions.

As a result of the concerns mentioned above, marijuana still remains illegal under federal law. This law applies to marijuana offenses committed on federal property which includes Capitol grounds, national parks, military grounds and other federal land. Federal law also governs commerce between states as well as trafficking in and out of the country. Offenses for simple possession range from 1-3 years in jail and up to $5000 in fines while growing and selling can result in 5 years to life in prison and $250,000-$1,000,000 in fines [52].

2.2.3.4 The 2018 Farm Bill (Hemp vs Marijuana)

Under the Agricultural Act of 2014, institutes of higher education and agriculture departments, under a pilot program were allowed to grow "industrial hemp" for research purposes to investigate the market potential for hemp and hemp derived products. This act also legally defined hemp as the plant *Cannabis* sativa L. with a THC content of no more than 0.3 percent by dry weight. The 2018 Farm Bill, (Pub. L. 115-344) went one step further, federally legalizing Hemp production for all purposes and effectively removing it and its derived products from Schedule I of the Controlled Substances Act [53]. The Farm Bill was the first time that hemp was legally distinguished from marijuana, which remains a controlled substance to date. Since the bill, there has been a significant increase in the production of hemp across the US. According to the 2019 U.S hemp License Report, over 510,000 acres of hemp were licensed across 34 states, which represented a 455% increase compared to 2018 [54]. In addition to industrial use, hemp flowers (buds) are now becoming very popular for recreational use with the number of online stores increasing. Despite being low in THC content compared to marijuana, hemp contains high levels of

CBD, which can allow for a more relaxed feeling. Studies have in fact suggested that CBD may assist in treating anxiety as well as falling and staying asleep. It has also been widely suggested as a potential treatment for epileptic seizures and types of chronic pain[55] [56],[57],[58]. The increasing potential health benefits of CBD has encouraged increased hemp production as CBD can be extracted and used in oils, tinctures etc.

2.2.3.4.1 Legal Issues of the Farm Bill and Detection of Marijuana

In February of 2019, the Idaho State police pulled over a truck and seized almost 7000 pounds of hemp under the premise that it was marijuana. This resulted in the cultivators, Big Sky Scientific filing a lawsuit against the police and state. This was not an isolated incident, as later that year New York Police Department boasted of a huge 106-pound drug bust to later realize that it was a shipment of hemp. Marijuana and hemp looks and smells similar making it difficult to tell the difference. Additionally, the main presumptive color screening test for marijuana, the duquenois-levine test, is geared towards detecting the presence of THC with an indicated purple color change. The presence of THC in hemp consequently allows for false positive results due to lack of specificity. As a result, many researchers are now investigating tests that can differentiate between hemp and marijuana. One research group for example discovered that a color test based on 4-aminophenol can be used to differentiate the two using the ratio of THC to CBD. [59]

Dogs have also been used as a screening tool to locate illicit drugs such as marijuana. Now, as a result of this regulation, many agencies are either not training new dogs on marijuana or contemplating removing dogs currently trained on marijuana due to concerns of the dogs

not being able to differentiate between the two substances. The main reason for this move is that a search and seizure executed on probable cause such as an alert by a dog to legal substances such as hemp, is now essentially in violation of a person's 4th amendment rights. Therefore, there is much liability associated with having dogs trained on marijuana because of the risk of alerting to what may well be an allowable substance.

2.3 Explosives

An explosive refers to any chemical compound or device that can function by explosion. An explosion occurs when potential energy is converted to kinetic energy and suddenly released. The energy can be released as blast waves, propulsion of debris or by the emission of thermal and ionizing radiation. There are three fundamental types of explosions: atomic explosions, physical explosions and chemical explosions.

Atomic or nuclear explosions occur due to fusion or fission of atoms releasing large amounts of energy in the form of shockwaves. The energy produced from these shockwaves can be a million to a billion times greater than the energy produced from a chemical explosion resulting in fatalities to anyone in proximity. Intense gamma, ultraviolet (UV) and infrared (IR) radiation are also emitted, capable of producing adverse health effects that can become fatal in weeks or many years [60]. The World War II bombings of Hiroshima and Nagasaki that killed over 200,000 people were both examples of atomic bombs used as weapons of war [61].

A physical explosion results from high pressure build-up of a substance within a contained system. This is usually a result of heating the system causing potential energy to rapidly

convert to kinetic energy, rupturing the container and producing a shockwave. A famous example was the Krakatoa volcano explosion of 1883, estimated to be the loudest explosion ever recorded on earth. According to one theory, eruption of lava over time resulted in the opening of an underground chamber where sea water entered and turned to steam, building up pressure in the walls of the volcano, eventually causing the blast. The shockwave produced, traveled around the earth seven times and was heard almost 3000 miles away [62].

Chemical explosions are caused by rapid chemical reactions or change of state generating high-pressure gases and large quantities of heat, releasing energy in the form of a blast wave. To function, these explosives require the mixing of two components: a fuel and an oxidizer. The types of explosives discussed herein are defined by the chemical reactions of these components.

2.3.1 History of Chemical Explosives

Black powder, also referred to as gunpowder, was possibly the first explosive composition. It is believed that around 220 BC, black powder was accidentally made by Chinese alchemists. It consists of powdered charcoal and sulfur that acts as a fuel mixed with a potassium nitrate (also known as saltpeter (KNO_3)) oxidizer. Initially used for fireworks, by the end of the 13^{th} century, black powder was widely used in mining and building operations as well as military applications such as breaching of walls and propelling projectiles via tubes. In 1425, an improved version of black powder, “corned black powder” was introduced. The manufacturing process during corning allowed for the

components to be ground and pressed together for a more intimate fuel and oxidizer mixture, resulting in an explosive that was more uniform and ballistically superior [60]. Corned black powder eventually found use in guns, hand grenades and for blasting purposes in the 16th and 17th century.

By the 19th century however, with the advent of the industrial age, the search for new and improved explosives was on, as the many limitations of black powder became apparent for advanced mining and blasting operations. In 1846, Italian Professor Ascanio Sobrero discovered liquid nitroglycerine (NG), a mixture of nitric acid (HNO_3), sulfuric acid (H_2SO_4), and glycerol but did no further studies after realizing its explosive properties. A few years later, Immanuel Nobel, a Swedish inventor resumed investigations on NG developing two methods for its manufacturing, eventually opening a manufacturing plant in 1863 with his son Alfred. The explosive however was susceptible to accidental initiation resulting in several accidents, one of which killed Alfred's brother, Emil and another that destroyed the Nobel factory in 1864. This led Alfred to create an improved, less sensitive version of the explosive known as dynamite in 1867, which was created by combining NG with a clay like absorbent called Kieselguhr making it much safer for storage, use and transport. In 1875, Nobel also developed a more powerful gelatin dynamite, a mixture of nitroglycerin and nitrocellulose. This mixture would also serve as the base for the first smokeless powder, ballistite, in 1888. The reduced sensitivity of dynamite however, made it relatively difficult to initiate an explosion leading to Nobel's other invention, the metal 'blasting cap' detonator that consisted of mercury fulminate. Mercury fulminate, originally discovered in the 17th century by Swedish–German alchemist, Baron Johann Kunkel von Lowenstern found little use due to its extreme sensitivity before being rediscovered in 1799

by Edward Howard of England and proposed as an initiator for black powder. These advancements by Nobel provided reliable, much-needed explosives for the expansion of the world economy in the latter part of the 19th century [63],[60].

Nitrocellulose (NC,) also referred to as guncotton was discovered during this same period by German-Swiss Chemist Christian Schonbein in 1846. Like many other explosives, it was accidentally discovered after wiping a spilled mixture of nitric acid and sulfuric acid with a cotton cloth, which subsequently exploded as it dried. Both NC and NG were ground-breaking discoveries as it became apparent that nitric and sulfuric acid allowed for the introduction of oxygen and nitrogen directly into the molecule of the fuel (nitration chemistry) creating a stronger explosive. Figure 9 shows the reaction mechanism for the conversion of glycerin into nitroglycerin using both HNO_3 and H_2SO_4.

As with NG, there were early challenges with the use of NC because of its instability. This was until Sir Frederick Abel in 1865, demonstrated that the stability of NC can be improved by converting it into a pulp. Abel's assistant, E.A. Brown then demonstrated that mercury fulminate can be used to detonate dry NC and a small quantity of dry NC can further detonate pulped NC. This became the basis for the principle of explosive trains and boosters and allowed NC to be adopted for commercial and military use by 1868 [60].

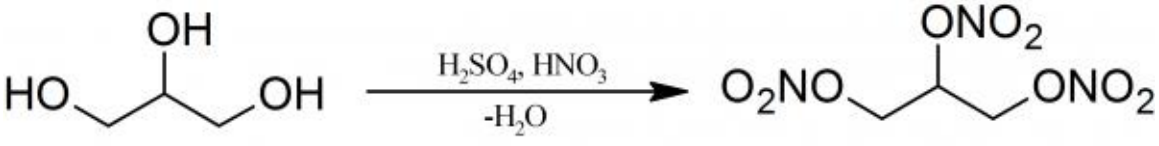


Figure 9. The nitration reaction of glycerol to form nitroglycerin.

The widespread use of these explosives in mining operations resulted in many gas and dust explosions with a great number of casualties [60]. After recommendations by European scientific commissions, ammonium nitrate (AN) based explosives replaced NG and NC under the Coal Mines Regulation Act of 1906. Originally discovered in 1654 by German chemist Johann Glauber, considerations for AN use in explosives began in the 19th century. It was first suggested as a replacement for potassium nitrate in black powder and later discovered that its addition improved the explosives properties of dynamite. By 1917, in Britain alone, 92% of all explosives used for coal mining were AN-based. For improved performance and safety, AN was eventually combined with fuels, most notably fuel oil (ANFO). This combination served to increase its waterproofness as holes drilled in mines and quarries for AN explosives often became wet decreasing explosive performance. This eventually led to other forms of ANFO explosives that is used today including water-gel, slurry and emulsion forms that further increase water resistance and optimal performance.

Like commercial explosives, black powder was also the first for military applications. trinitrophenol (Picric acid), first mentioned by Glauber in 1742, was adopted in the late 19th century as an alternative to black powder and accepted worldwide as the basic military explosive [60]. During this same period, 2,4,6-trinitromethylnitramine (tetryl) was first prepared by Mertens in 1877 and by the early 20th century was used as the base charge for blasting caps. Experiments involving trinitrotoluene (TNT) led to the development of the explosive isomer 2,4,6-trinitrotoluene in 1880 by Hepp. The isomer became the standard form of TNT and gradually replaced picric acid which was found to be very sensitive and prone to accidental initiation. By 1914, TNT was the standard explosive employed by militaries during World War I.

Pentaerythritol tetranitrate (PETN) was prepared in 1894 by the nitration of pentaerythritol and was widely available prior to World War II. Pentaerythritol tetranitrate did however suffer from chemical instability and sensitivity to impact and was often combined with TNT in a 50:50 mixture called 'Pentolite.' Originally prepared in 1899 by Henning for medicinal purposes, explosive properties of 1,3,5 trinitro-1,3,5 triazine (RDX) was discovered by Herz in 1920. Two types of RDX, Type A and Type B were eventually synthesized with the former being pure RDX and RDX with 8-12% impurities [60] As with PETN, RDX was not utilized alone but combined with TNT during World War II. Torpex for example is a combination of TNT, RDX and Aluminum. The impurities from Type B RDX was later used to develop octahydro-1,3,5,7-tetranitro- 1,3,5,7-tetrazocine (HMX). HMX was also combined with TNT in a 75% HMX and 25% TNT mixture referred to as 'Octol' also used during the second world war. Figure 10 lists the chemical structures of Picric acid, Tetryl, TNT, PETN, RDX and HMX.

As research continued for more reliable explosives, polymer bonded explosives (PBXs) also referred to as plastic bonded explosives were developed in the 1950s. In PBXs, the explosive material is embedded in a rubber or plastic like polymer (typically 2-10% by mass) [64]. The use of a plasticizer allows for a less sensitive explosive with improved mechanical properties and processability [60]. Polymer bonded explosives typically consist of RDX, PETN or combinations which can also include explosives such as TNT. Currently, two of the most common plastic explosives are Composition C-4 (RDX + plasticizer) and SEMTEX (RDX + PETN + plasticizer). Currently, many different explosive formulations exist. Table 2 provides an extensive list of explosives and their respective formulations. These formulations have been selected in order to achieve desired performance.

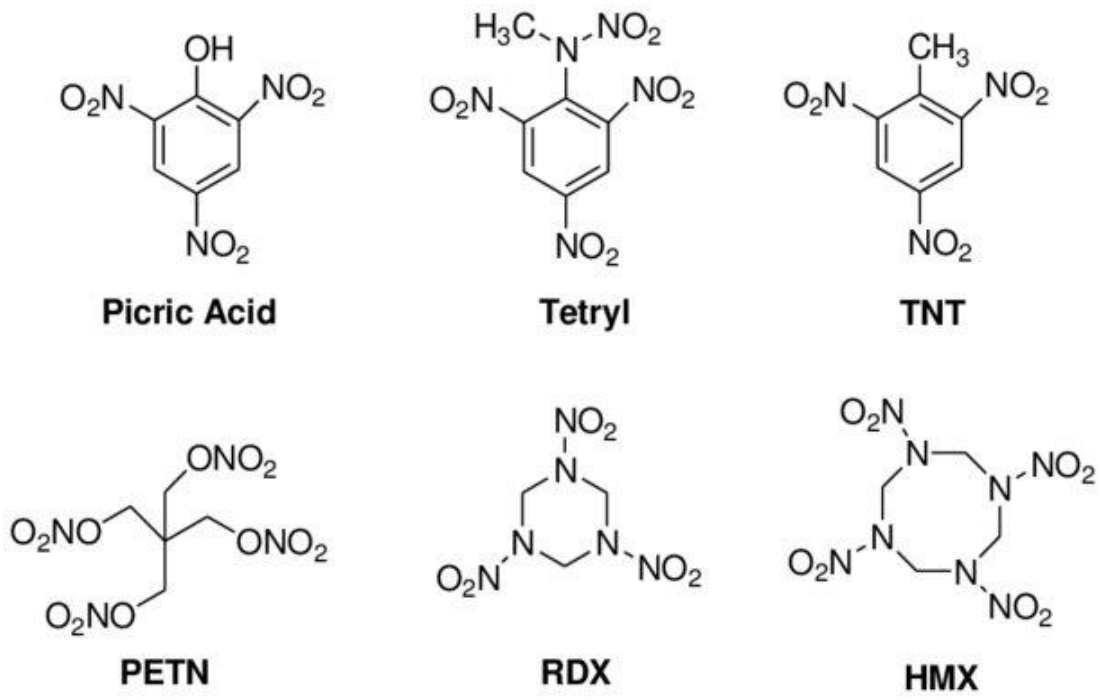


Figure 10. Chemical Structures of Picric Acid, Tetryl, TNT, PETN, RDX and HMX [65].

The majority of chemical explosives contains the elements nitrogen and oxygen along with a hydrocarbon backbone which act as fuels and can be oxidized. With the exceptions of nitrogen triiodide (NI_3), azoimide (NH_3NI_3) and azides such as lead azide (PBN_6), the oxygen molecule is attached to nitrogen in the form of nitro groups NO, NO_2, and NO_3. Nitro groups are a fundamental aspect of explosive chemistry. Nitrogen which naturally exists as the diatomic molecule N_2 is a stable gas at a very low energy state because of its very strong triple bond. When in an oxidized state such as NO_2, nitrogen enters a significantly higher energy level. During an explosion, N_2 gas is formed which reduces nitrogen to its lower energy state releasing large amounts of energy as heat in a highly exothermic process.

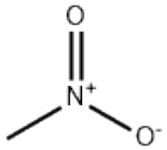
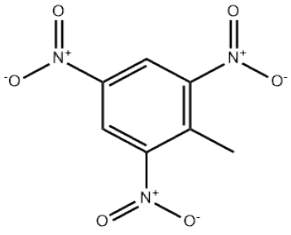
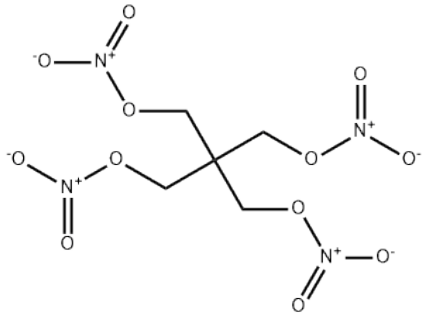
Table 2. Examples of explosives and their components.

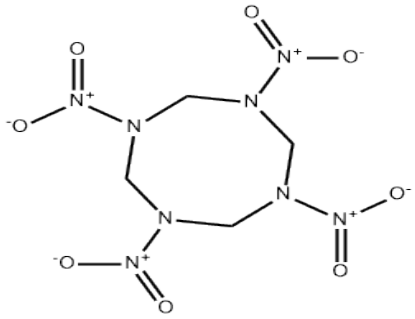
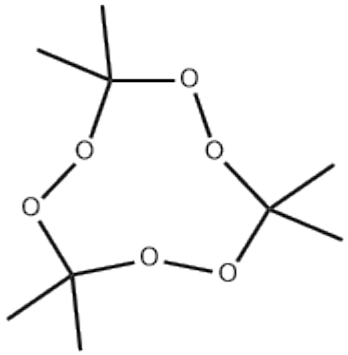
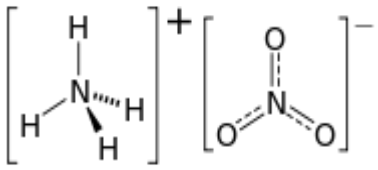
Explosive	**Components**
Amatol	Ammonium nitrate +TNT
Ammonal	Ammonium nitrate +TNT+ Al
ANFO (Amex or Amite)	Ammonium nitrate + fuel oil (Diesel)
Black powder	Potassium nitrate +C+S
Composition A	RDX+ wax
Composition B	RDX+TNT
Composition C-2	RDX+TNT+DNT+NC+MNT
Composition C-3	RDX+TNT+DNT+ tetryl +NC
Composition C-4	RDX+ plasticizers
Composition D	Ammonium picrate
Cyclotol	RDX+TNT
Detasheet (Flex-X)	RDX+ plasticizers
DBX	TNT+RDX+ ammonium nitrate +Al
Demex 200	RDX+ plasticizers
Detonation cord (commercial)	PETN
Detonation cord (military)	RDX or HMX
Dynamite (ammonia)	NG+NC+ sodium nitrate
Dynamite (gelatine)	NG+NC+ ammonium nitrate
Dynamite (military)	TNT
HBX-1	RDX+TNT+Al
Helhoffnite	NB + nitric acid
HTA	HMX + TNT +Al
Nitropel	TNT
Nonel Cord	HMX
PE-4	RDX + plasticizers
Pentolite	PETN +TNT
Picratol	TNT + ammonium picrate
Primasheet 1000	PETN + plasticizers
Primasheet 2000	RDX + plasticizers
PTX-1	RDX + TNT +Tetryl
PTX-2	RDX + TNT + PETN
Red Diamond	NG + EGDN +sodium nitrate + ammonium
Semtex A	PETN + plasticizers
Semtex H	RDX + PETN + plasticizers
Smokeless powder (double based)	NC + NG
Smokeless powder (single based)	NC
Smokeless powder (triple based)	NC + NG + nitroguanidine/TNT
Tetratol	TNT + Tetryl
Time Fuse	Potassium nitrate + C + S
Torpex	TNT + RDX + Al
Tritonal	TNT + Al
Water gel/slurry (aquaspex)	NG
Water gel/slurry (hydromex)	Ammonium nitrate + TNT

2.3.2 Classification of Chemical Explosives by Chemical Structure

Chemical explosives generally fall into six different classes based on chemical structure: nitro aliphatic, nitro aromatic, nitrate esters, nitro amines, peroxides and nitrate salts (Table 3) Peroxide based explosives will be further discussed in section 2.3.5.

Table 3. The six general classes of explosives.

Explosive Class	**Characterization**	**Example**	**Additional Examples**
Nitro aliphatic	Carbon (C) bonded to a nitro (NO_2) group. (**C- NO_2**)	Nitromethane 	Nitroglycerine Nitroguanidine
Nitro aromatic	An aromatic (Ar) ring attached to a Carbon (C) bonded to a nitro (NO_2) group. **(Ar-C- NO_2)**	2,4,6-trinitrotoluene 	Picric Acid
Nitrate ester	An oxygen bonded to a Carbon (C) and a nitro (NO_2) group **(C-O- NO_2)**	PETN 	Ethylene glycol di-nitrate

Nitro amine	Nitrogen bonded to a nitro (NO_2) group. **(N- NO_2)**	HMX 	RDX Tetryl
Peroxide	Two oxygen bonds **(-O-O-)**	Triacetone Triperoxide (TATP) 	Hexamethylene-triperoxide diamine (HMTD)
Inorganic salt explosives	Typically nitrates (NO_3^-), chlorates (ClO_3^-) and perchlorates (ClO_4^-) mixed with ammonium (NH_4^+), Potassium (K) and Sodium (Na) to form oxidizing salts	Ammonium Nitrate (oxidizer) 	Ammonium nitrate/fuel oil mixture

2.3.3 Classification of Chemical Explosives by Performance and Use

Classifying explosives based on chemical structure gives little information regarding its performance. As a result, explosives are often classified based on its performance as either a low explosive or high explosive as described in Figure 11. Figure 11 also shows subclassification of these explosives based on use.

2.3.3.1 Low Explosives

Low explosives, also referred to as propellants, decompose by the process of deflagration, where rapid burning occurs, and combustion waves travel at subsonic speeds (1-350 m/s) often accompanied by flames or sparks and a hissing or crackling noise. They can be easily initiated via flame, spark, friction and high temperature. It is possible however, for low explosives to decompose and detonate if confined in an enclosed container. Confinement allows increased pressure build up accelerating the rate of deflagration allowing for combustion waves to travel at supersonic (above 600 m/s and generally in the 2000–2500 m/s range) speeds [66]. Black powder, smokeless powders, liquid fuels or composites thereof are examples of propellants.

2.3.3.2 High Explosives

High explosives decompose solely by detonation. High explosives can be divided into primary high explosives and secondary high explosives. Primary high explosives are used as an initiating devices for secondary explosives as they are very sensitive, rapidly detonating when subjected to heat or shock, friction, electric spark. Detonation velocities of primary high explosives fall in the range of 3500-5500m/s [60]. Some examples are lead azide, lead styphnate and mercury fulminate.

Secondary high explosives are less sensitive, more powerful explosives with detonation velocities in the range of 5500-9000 m/s [60]. They are very stable and not readily detonated via shock and heat therefore requiring a primary explosives for initiation. Examples of secondary high explosives include military explosives such as TNT, RDX, HMX tetryl, picric acid etc. and commercial explosives such as ANFO, slurries and emulsions.

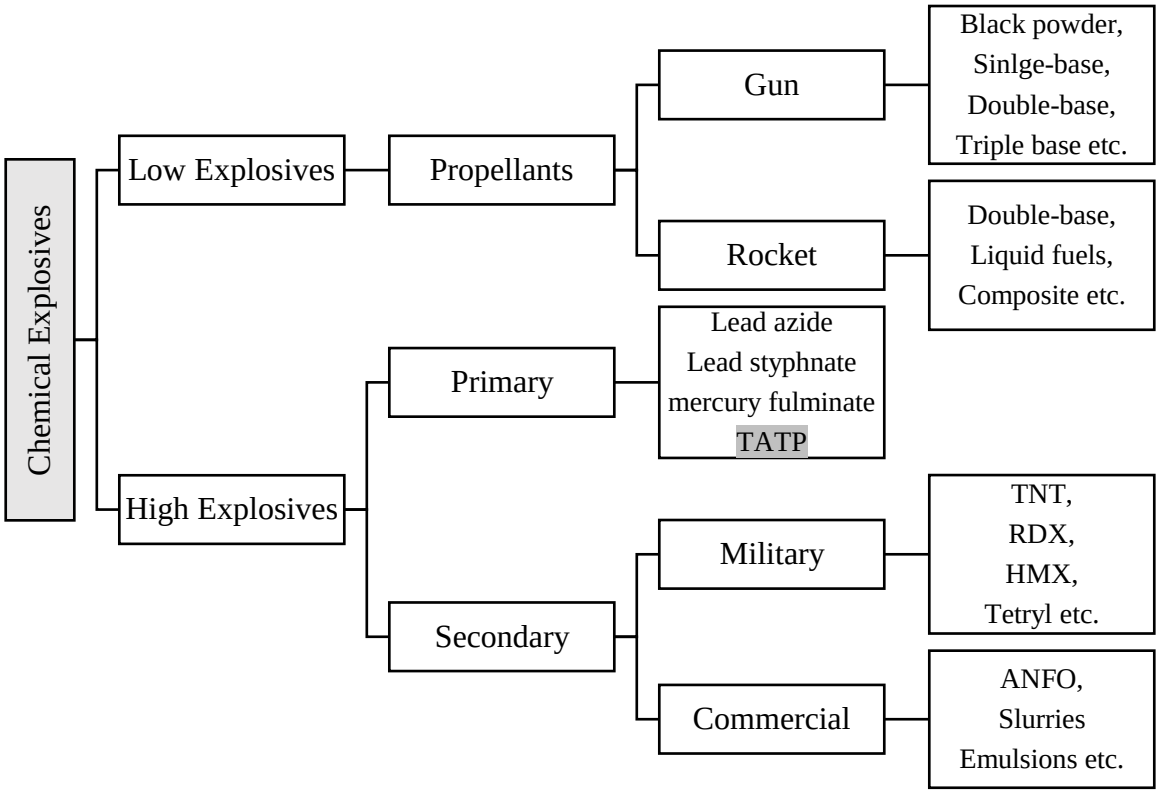


Figure 11. Explosive classification based on performance and use.

2.3.4 Improvised Explosive Devices and Homemade Explosives

An Improvised Explosive Device (IED) refers to any non-industrially produced explosive device. These devices typically consisting of an initiator, switch, main charge, power source, container, and is often packed with “enhancers” such as nails and metal fragments to increase the amount of shrapnel from the explosion. Improvised Explosive Devices rose to prominence in the early 2000’s becoming the predominant weapon among terrorist and insurgent groups in the Middle East as well as domestic terrorism. Since then, IEDs have accounted for the majority of injuries and deaths of civilians and Americans in combat [67],[68]. Improvised Explosive Devices can take many forms, including landmines, roadside bombs, vehicular-borne explosive devices, pipe bombs and person-borne devices. In 2018 alone, there were approximately 12,500 reported deaths worldwide and injuries caused by IEDs, representing 39% of all explosive weapon injuries [69].

In recent Middle East conflicts, as well as increasingly so on U.S. soil, homemade explosives (HMEs) have been the most common type of explosive material utilized for IEDs [70]. The increase in HMEs has been fostered by the ease of legally acquiring and amassing inexpensive explosive precursors, coupled with the simplicity of constructing the devices. Homemade explosives can generally be separated into two categories: fuel-oxidizer mixtures that can simply be combined together to form the explosive and peroxide-based explosives that requires chemical synthesis of the precursors. In the United States, between 2015-2019 there were 203 explosions and 1,180 recoveries involving IEDs containing fuel-oxidizer mixtures. This in comparison to 18 explosions and 188 recoveries of IEDs containing other explosive compounds during the same period [71]. Table 4 presents extracted data from the United States Bomb Data Center (USBDC) Explosives

Incident Report for 2019 depicting explosions and recoveries involving IEDs in comparison other traditional explosives during 2015-2019. Figure 12 shows an example of a home-made IED.

Table 4. Incidents of explosions and recovery involving IEDs and other traditional explosives between 2015-2019 [71].

Explosives 2015-2019	**Explosions**	**Recoveries**
IED-Fuel Oxidizer Mixtures	203	1180
IED-Explosive Compounds	18	188
Military Explosives-Demolition Materials (Ex.C-4)	0	141
Nitroglycerine	0	14
PETN	0	34
TNT	0	69

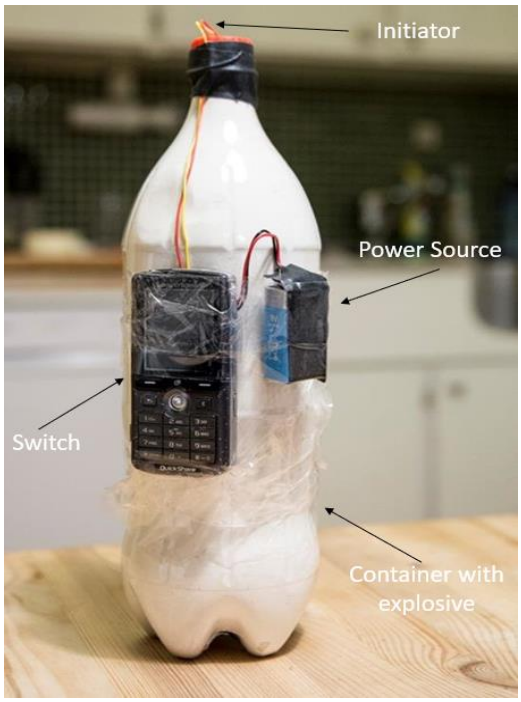


Figure 12. Homemade IED consisting of a power source (battery), initiator (electrical wire), switch (cellular phone) a plastic bottle filled with an explosive. Figure adapted from [72].

2.3.4.1 Fuel-oxidizer Mixtures

Fuel-oxidizer mixtures are composed of a simple mixture of an oxidizing agent and a fuel. The oxidizer in these mixtures is typically fertilizer-based (e.g. ammonium nitrate or urea) or pyrotechnic-based (e.g. chlorate and perchlorate salts). The most prominent of these oxidizers used is AN. Widely available as an agricultural fertilizer, it has become a favorite amongst foreign terrorists [73], [74]. By 2012, 85% of the IEDs seen in Afghanistan contained HMEs of which 70% were AN-based [73]. Ammonium nitrate has also found use in domestic terrorist attacks such as the Oklahoma City bombings in 1995 and the recent New York and New Jersey attacks in 2017.

Increased restrictions on the purchasing of AN in the Middle East in recent times, has resulted in chlorate and perchlorate salts notably potassium chlorate (PC) becoming a viable alternative oxidizer [74] [75]. Potassium chlorate can be purchased from chemical or fireworks suppliers, or simply manufactured from household products. Notable attacks involving PC included the 2002 Bali Nightclub Bombings and 2004 Australian Embassy Attack in Indonesia [76]. The famous Unabomber Ted Kaczynski also used potassium chlorate in some of his bombings. These oxidizers can be combined with many fuels to form explosives. Fertilizer-based explosives are generally thermally stable and insensitive to friction, impact and electrostatic discharge allowing them to be easily manufactured and transported, hence its prominent use by terrorists.

2.3.4.2 Peroxide-based Homemade Explosives

The second category of HMEs is peroxide-based explosives (PBEs), which, like fuel/oxidizer mixtures, are composed of commercially available materials, but require synthesis of those ingredients in contrast to a simple mixture. The most common PBE is triacetone triperoxide (TATP), which is synthesized from acetone and hydrogen peroxide, and has been used in several terrorists attacks, such as the 2015 Paris attacks and the 2016 Brussels bombing [77],[78]. Hexamethylene triperoxide diamine (HMTD), another common PBE, is synthesized from hexamine and hydrogen peroxide, and has also found use amongst terrorists such as the London subway bombings [79]. Peroxide-based explosives are extremely unstable and friction sensitive high explosives hence having no military or industrial use. Due to their -O-O- bonds which are more reactive compared to nitrate groups, the stability is much lower compared to traditional explosives.

2.3.5 Triaectone Triperoxide (TATP)

Triacetone triperoxide (TATP) is also referred to as the “Mother of Satan” because of its very destructive nature. Triacetone triperoxide was first synthesized by Wolfenstein in 1895, and although it was initially investigated as a primary explosive and initiator, it did not find any military or commercial application due to its high instability. As previously stated, the manufacture of TATP requires a simple synthesis of acetone, hydrogen peroxide and an acid catalyst, making it a common HME for IEDs. When synthesized, TATP forms into a white crystal (Figure 13) that is highly sensitive to impact, friction, static electricity, and temperature changes [80].

Figure 13. TATP white crystals [81].

Figure 14 shows the intermediates involved in the reaction of acetone and hydrogen peroxide to form the cyclic trimer TATP. Diacetone diperoxide (DADP), a cyclic dimer can often present in the crystal mixture as a byproduct of TATP degradation over time [82].

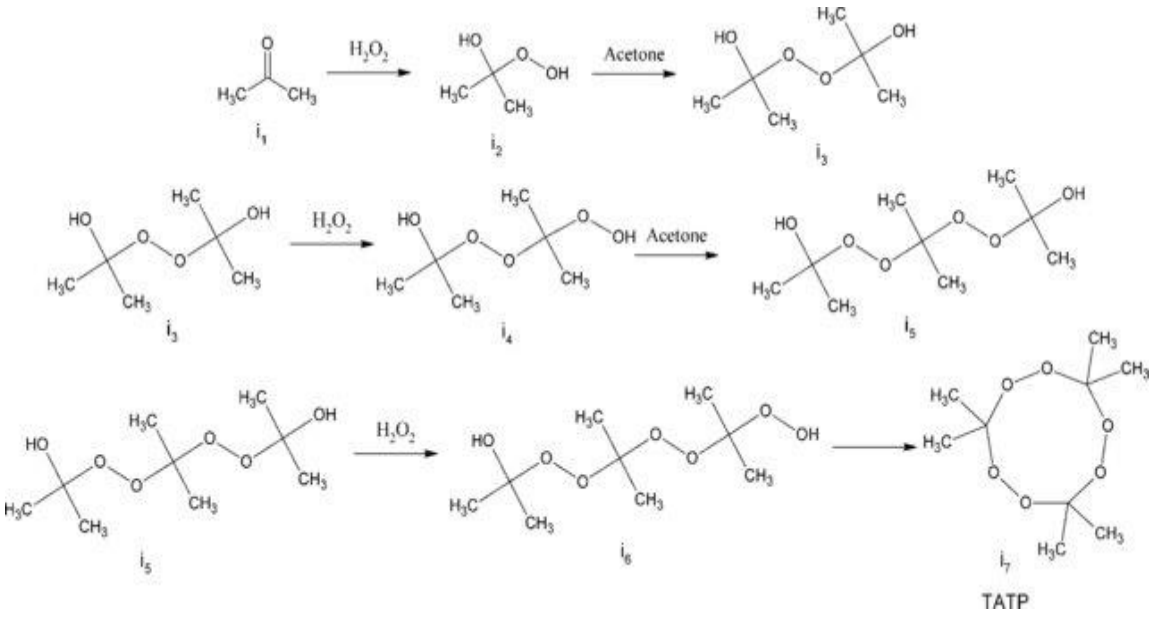


Figure 14. Intermediates involved in the reaction mechanism between acetone and hydrogen peroxide to form TATP [80].

As with other some other peroxide-based explosives, TATP is unique in that its explosion is not a thermochemically highly favored event but rather the result of an entropy burst resulting from the formation of acetone, ozone and other gaseous compounds from one molecule of TATP in the solid state, without the release of heat or flame upon detonation. [83]. This is in comparison to fuels of conventional explosives with nitro groups including nitroaromatics, nitrate esters, and nitramines which are highly energetic compounds that release energy via a fast, exothermic process. It is believed that the three isopropylidene units of the TATP molecule do not function as a fuel that can be oxidized and releasing thermal energy during the explosion. It is however responsible for holding together and properly orienting the three peroxide units for the decomposition chain reaction [83]. Triacetone triperoxide is approximately 80% as powerful as TNT with reported detonation velocities over 5000 m/s [84]

2.3.6 Detection of Explosives

Detection of explosives can be broadly classified into two categories: bulk detection and trace detection. Bulk explosive detection methods utilize a radiation source to remotely monitor physical and chemical properties of an object to determine if it is an explosive material. This is accomplished by imaging techniques such as x-ray (single-energy, dual-energy and backscatter), fluoroscopy, dielectrometry and computer tomography (CT), or nuclear-based techniques such as thermal neutron analysis, pulsed fast neutron analysis, and nuclear quadrupole resonance (NQR.). These techniques explore physical parameters such as material density, geometry and elemental composition of the material. As a consequence of the presence of high nitrogen and oxygen content of explosives, relative amounts of these elements along with hydrogen and carbon can aid in discriminating explosives from non- explosives. Geometric information such as shape, size and volume coupled with pattern recognition of specific devices (e.g., detonators and wires) increase the detection of an explosive with a very high probability[85],[86]. Figure 15 shows the bulk detection of an IED using a typical airport scanner. Figure 15 a) and Figure 15 b) represents 2-D X-ray images, the first in default view and the second at 30 degrees difference in perspective. Figure 15 c) depicts a 3D rotatable CT scan image and Figure 15 d) a cross-sectional 3D image [87].

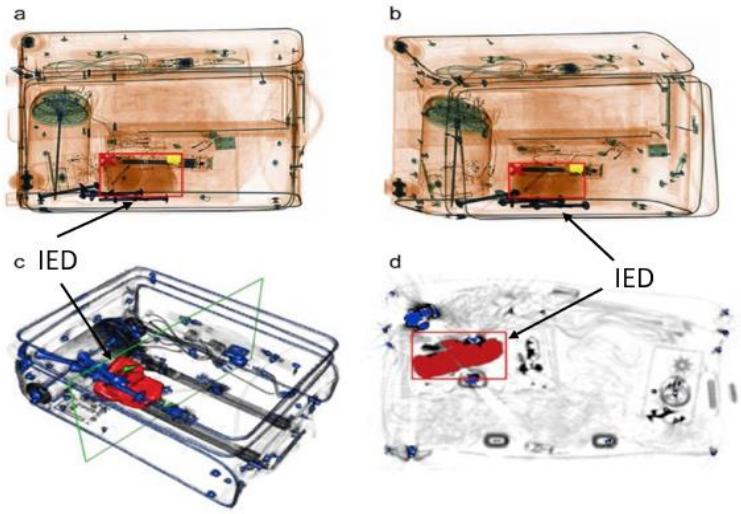


Figure 15. Detection of an IED using a) 2D X-ray default image b) 2-D X-ray image with a 30 degrees difference in perspective c) 3D rotatable CT scan image and d) a cross-sectional 3D image. Figure adapted from [87].

Trace detection in contrast rely on either the chemical identification of either explosive particulates or explosive vapors via 1) sample collection 2) analysis or 3) identification by comparison to a library. Samples are collected by surface removal of particulates (ex. swabbing) or by actively or passively transporting vapors from the environment. Due to having very low vapor pressures at room temperature, many explosives are not detectable by vapor sampling. As a result, more volatile chemical byproducts and taggants are often the chemicals of interest for these vapor detectors. Table 5 presents a list of some of these explosives and their respective identified VOCs. Methods of chemical analysis of trace explosive samples include ion mobility spectrometry, chemiluminescence, thermo-redox, surface acoustic wave (SAW), ultraviolet fluorescence, mass spectrometry and odor detection dogs. Figure 16 lists some of the common methods employed for bulk and trace detection mentioned above.

Table 5. Volatile organic compounds (VOCs) identified from a selection of explosive materials.

Explosive material	Active explosive compound	Identified VOCs	Literature
Composition C-4	RDX	Cyclohexanone, 2-ethyl-1-hexanol, toluene, DMNB (tagged only)	[88],[89], [90]
Detonation cord	PETN (most common), RDX, or HMX	Nitroglycerin, g-butyrolactone	[91]
Deta sheet	PETN with nitrocellulose	2-ethyl-1-hexanol, 1-butanol acetic acid ester, 2-ethyl-1-hexanol acetic acid, acetic acid, 1-butanol, toluene, butyl acetate, g-butyrolactone, tributyl acetalcitrate, DMNB (tagged only)	[88],[89],[91]
Semtex H	PETN and RDX	isophorone, g-butyrolactone, acetone, undecane, dodecane, DMNB (tagged only)	[88],[91]
Commercial dynamite	Nitroglycerine, nitrocellulose, ammonium nitrate	EDGN, ammonia	[90]
TNT	TNT	TNT, 2,4-DNT	[89]
Single-base smokeless powder	nitrocellulose, 2,4-DNT (not present in all brands)	2,4-DNT, diphenylamine, ethyl centralite	[92]
Double-base smokeless powder	nitrocellulose, nitroglycerine	2-ethyl-1-hexanol, 2,4-DNT, ethyl centralite, diphenylamine, nitroglycerine	[89],[92]
TATP	TATP	TATP, acetone, diacetone diperoxide (DADP)	Unpublished data
HMTD	HMTD	formic acid, trimethyl amine, formamide, formaldehyde, hexamine, dimethylformamide	[93],[94]
Ammonium nitrate	requires mixture with a fuel	ammonia	[95]
Potassium chlorate	requires mixture with a fuel	chlorine	[96]
Urea nitrate	Urea nitrate	ammonia	Unpublished data

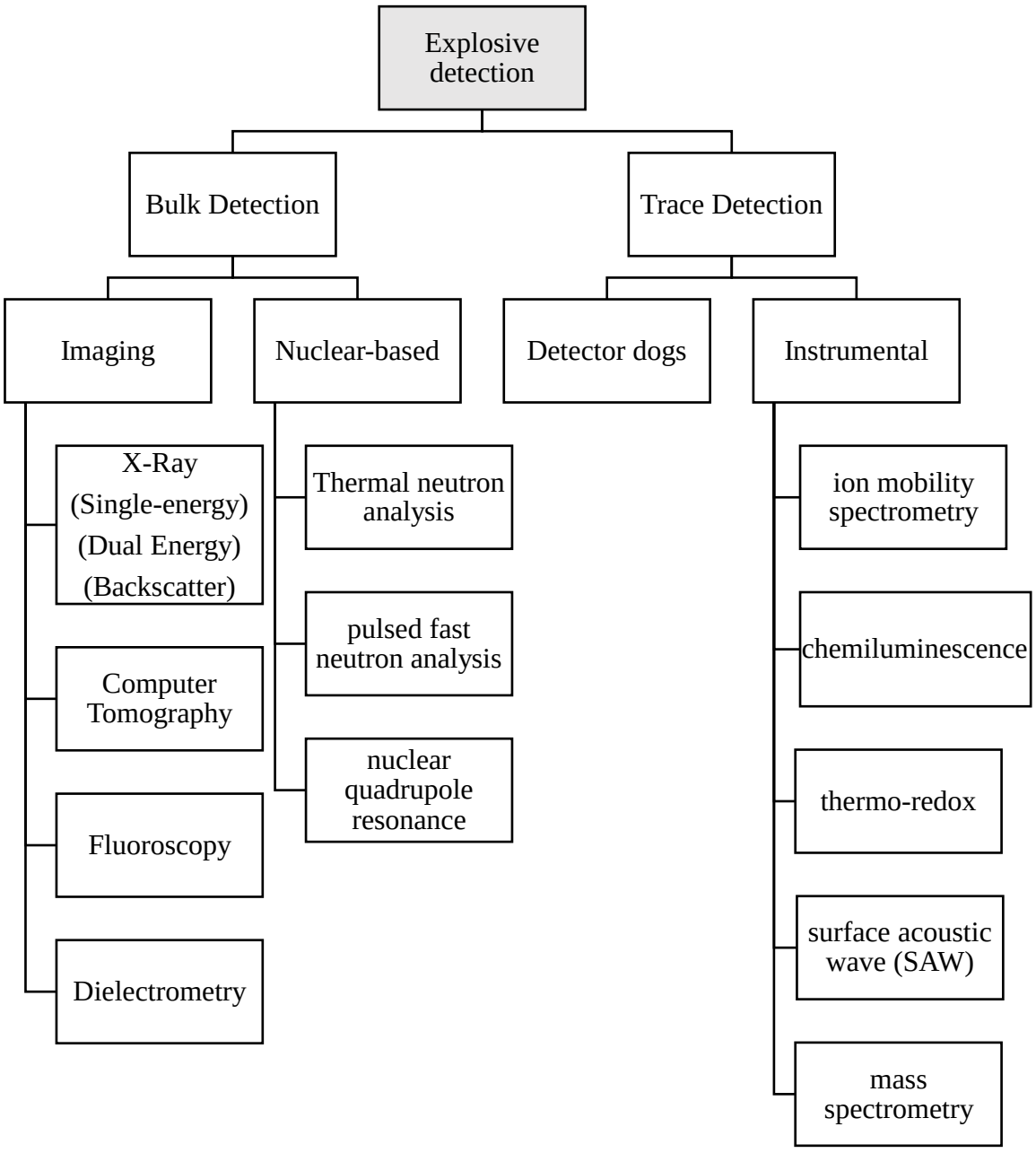


Figure 16. Common methods employed for bulk and trace detection of explosives.

2.3.6.1 Trace Detection of TATP

Unlike traditional explosives, TATP contains neither nitro groups nor metallic elements making its detection by traditional bulk detection scanners difficult. Additionally, TATP possesses no significant absorption in the UV spectrum and does not fluoresce. Most detection methods are limited to IR/Raman spectroscopy or mass spectrometry coupled with chromatography [97]. Other utilized techniques include ion mobility spectrometry (IMS) as well as desorption electrospray ionization-mass spectrometry (DESI-MS). Additionally, researchers have also began to investigate the development of improved bulk methods such as X-ray systems as well as the recalibration of existing instruments algorithms to allow for bulk TATP recognition [98].

In recent times, dogs have been suggested as a reliable trace detector for TATP and other peroxide-based explosives with many anecdotal reports of its success. However, due to the extremely hazardous nature of these explosives, it is highly regulated resulting in the majority of explosive detection dogs not being trained to detect it. Training often requires the presence of an experience bomb technician. Even if there is an opportunity to be imprinted on the odor, maintenance training is problematic and can be accomplished once a year or even less.

2.3.7 Detector Dog vs Instrumental Detection

Instrumental trace detection of explosives continue to evolve utilizing many technologies including ion mobility spectrometry [99], advanced mass spectrometry [100][101], raman spectroscopy [102], nanomaterials [103], calorimetric sensor arrays [104],[105], microcantilevers [106], [107], [108], microfluidics [109], and fluorescence quenching [110] [101]. While recent developments of explosive detection technologies has pathed the way towards limits of detection nearing parts per quadrillion (ppq) , sampling systems of these instruments are less developed in comparison to dogs. Trace detectors generally utilize surface sampling for removal of explosive particles or standoff vapor detection. Vapor based sampling employs either a limited passive approach that relies on the environmental flow of the analyte into a stationary detector or a more versatile suction-based method that continuously draws in surrounding air. The suction-based method, while more efficient, is still limited in its overall aerodynamic reach. These sampling limitations have led some researchers to mimic a dogs active sniffing pattern as electronic noses in hopes of obtaining improved vapor sampling systems. Staymates et al. (2016) for example investigated the use of a bio-inspired sampling inlet using the active sniffing pattern of a dog. It was determined that the inlet, when connected to a commercially available vapor detector, improved analyte detection of the system by a factor of up to 16 [111].

Table 6 highlights some of the advantages and disadvantages of detector dogs and instrument technologies revealing that in an optimized layered approach, dogs can offer a complementary orthogonal detection mechanism. Dogs continue to hold the advantage on selectivity, mobility, sampling, cost and speed. In addition, dogs can be rapidly trained to respond to novel target odors while being highly selective, as they are trained to ignore

non-target odors that may have chemical similarities to the target odors. Instrument detectors on the other hand, might be unable to respond to new target odors or ignore non-target odors without changes to the sampling system, detection system or target library which can be both time consuming and very costly [112]. In the case of HMEs, this becomes even more problematic as these explosives typically contain odors commonly found in the environment which if added to the target library can lead to excessive false positive alarms if instrument calibrations are not conducted effectively. These false positives or false alert rates can have significant economic repercussions ranging from a few tens of thousands to tens of millions of dollars per incident and as a result are weighed equally as heavily as a false negative or missed detections for explosive detection[113],[114].

Table 6. Comparison of detector dog and standoff instrument technologies. Adapted from [3].

Aspect	***Dog***	***Instrument***
Selectivity (from interferences)	**Very good**	*Sometimes problematic*
Mobility	**Very versatile**	*Limited*
Integrated sampling system	**Highly efficient**	*Problematic/often inefficient*
Introduction of novel targets	**Rapid**	*Time consuming*
Capable of remote guidance and integration	**Straightforward**	*Currently limited*
Initial cost	**Approximately $10,000**	*Generally, $20,000- $60,000*
Annual cost	**Approximately $3,000 (veterinary care and food)**	*Approximately $5,000 (service contract)*
Intrusiveness	**Often innocuous (breed dependent)**	*Varies based on mobility and size*
Overall speed of detection	**Rapid (real-time)**	*Varies - rapid detection inversely proportional to detection capabilities*
Duty cycle	*Approximately 1hr search duration (dependent on conditioning and environment)*	**Approximately 24hr/day (theoretically)**
Calibration standards	*Available but novel and not widely used*	**Widely available, can be run simultaneously**
Identification of explosive	*Does not identify explosive type (generic positive alert)*	**Identification possible for specific explosive depending on instrument**
Operator/handler influence	*A potential factor*	**Less of a factor**
Instrument lifetime	*Generally, 6-8 years*	**Varies, up to 10 years or more**
State of scientific knowledge	*Emerging*	**Relatively mature**
Target chemical(s)	*Emerging understanding of target chemicals*	**Parent explosive(s)/well studied**
Degree of standardization	*Variable*	**Consistent standards**

2.4 Mass Storage Devices and Digital Evidence

Digital evidence refers to information and data of value to an investigation that is stored on, received, or transmitted by an electronic device. Digital evidence is acquired when data or electronic devices are seized and secured for examination[115]. The information received can be useful as evidence in a criminal investigation or prosecution. Mass storage devices (MSDs) can include hard drives, removable media, thumb drives, memory cards, handheld devices and other peripheral.

2.4.1 Hard drives

Hard drives consists of an external circuit board external data and power connections; and internal magnetically charged glass, ceramic, or metal platters that store data [115]. These may be internally installed to a computer or externally connected via a universal serial bus (USB) in order to increase storage capacity (Figure 17).

Figure 17. An external hard drive with a USB connection (top) and external hard drive (bottom) [116].

2.4.2 Removable Media

Removable media take the form of cartridges and disk-based data storage devices. Typically, they store, archive, transfer, and transport data along with other information. They allowing sharing of data, information, applications, and utilities among different computers and devices [115]. These include compact discs (CDs) and digital versatile disks (DVDs) which are similar in appearance (Figure 18).

Figure 18. The appearance of a CD and DVD [117].

2.4.3 Thumb Drives

Thumb drives also commonly referred to as flash drives are small, lightweight and removable storage devices that attaches via USB connecting ports. Its size allows for it to be easily concealed as parts of other devices such as watches, pens, knives, and keychains along with other devices (Figure 19).

Figure 19. A typical thumb drive on the left and on the right a thumb drive concealed as a pen [118].

2.4.4 Memory Cards

Memory cards are small devices that can be interfaced with digital cameras, computers, mobile phones, drones, tablets digital music players, video game consoles, hand held devices and other electronic products (Figure 20). [115]

Figure 20. The appearance of a typical memory cards

2.4.5 Handheld Devices

Handheld devices are portable data storage devices that provide communications, digital photography, navigation systems, entertainment, data storage, and personal information management [115]. Today, handheld devices mainly come in the form of mobile phones and tablets (Figure 21).

Figure 21. Image of a tablet (larger device) and a mobile phone (smaller device) [119]

2.4.6 Subscriber Identification Module Cards

Subscriber identification module (SIM) cards are small removable chips that are placed inside of mobile phones and allow a user to connect to a particular mobile network allowing them to make calls, send short message service (SMS) messages and connect to the internet (Figure 22). They can store information such as stored telephone number contacts, call history, internet data usage and SMS messages.

Figure 22. Image of SIM card (left) and insertion of a sim card in a mobile phone[120]

In a crime investigation, all of the above-mentioned devices can lend information regarding e-mail messages, internet browsing history, photographs, financial records, global positioning system (GPS) history, databases, call and SMS records that can be integral to a prosecution.

2.4.7 The Use of Detector Dogs for Locating Mass Storage Devices.

Search and recovery of mass storage devices is typically accomplished by crime scene investigators. In recent years however odor detection dogs have been trained to successfully recognize MSDs. These devices may be very small, as in the case of memory cards, and therefore very difficult to find as they may be hidden in areas not visible to the human eye or cleverly concealed as shown in Figure 19. Dogs, however, can be used to detect these clandestine devices by recognizing the odor VOCs released by these devices. An famous example was at the home of former “Subway” spokesperson, Jared Fogle, where a dog detected a hidden USB drive containing incriminating pornographic material that was not previously found by investigators [121]. Figure 23 shows K9 Bear after being

awarded by the American Society for the Prevention of Cruelty to Animals, for his contribution to this case.

Figure 23. Team of K9 Bear and handler Todd Jordan that recovered the USB device at the home of Jared Fogle [121]

Detection of MSDs by dogs have now found regular usage within various area of law enforcement notably in correction facilities that use them to find contraband devices being smuggled into the prisons. Figure 24 shows an electronic detection dog, K9 Razor after successfully sniffing out contraband mobile phones at the Broward Correctional Institution in Ft Lauderdale Florida.

Figure 24. K9 Razor of the Broward Correctional Institution in Ft Lauderdale, Florida in 2008 poses with several cell phones that he sniffed out hidden in a box [122]

2.5 Reliability of Odor Detection Dogs

Despite a well-established understanding of the mammalian olfactory system and the excellent olfactory capacity of dogs, the use of dogs for odor detection has often been labeled as a "black box technology" as the chemical compounds of a target material to which the dog is responding is often unknown. In the past, the rationale for training dogs have been more anecdotal rather than rooted in scientific principles. As a result, there has been legal scrutiny and challenges regarding a dog's reliability and accuracy such as the 2013 case of Florida vs Harris. In response, the operational and scientific communities have collaborated to develop consensus-based best practice guidelines in an attempt to address previous inconsistencies and improve the proficiency of detector dog teams.

Advancements in analytical chemistry, in conjunction with olfactory testing, has now allowed for an improved understanding of what compounds a dog may detect from a target

sample. Analytical sampling techniques like solid-phase microextraction (SPME) and sorption on other solid sorbents has been successfully used to concentrate and extract VOCs which are otherwise present at very low concentrations in the atmosphere. Post-sampling analysis methods such as gas chromatography (GC) and mass spectrometry (MS) has been employed to identify these compounds [89].

Knowledge of these compounds has subsequently aided in improved scientifically grounded training regimens as well as the development of safe, reliable training aid mimics that can closely replicate the odors of target materials [89].

2.5.1 The Universal Detector Calibrant (UDC)

With dogs continuing to be one of the most effective detection tools in the field, there are limited procedures for evaluating their daily reliability. For instruments, tuning, calibrations and diagnostic checks are completed routinely to ensure proper operation on a regular basis. A patented device called the Universal Detector Calibrant (UDC) has been developed to provide a means by which canines can be tested or calibrated at more frequent intervals, regardless of the substance the canine has been trained to detect [123]. Using a Controlled Odor Mimic Permeation System (COMPS) [124], [125], the UDC offers varying levels of a selected target odorant, 1-bromooctane. The COMPS utilize a permeable polymer in which a target odor is housed and delivered at known and reproducible rates. The thickness of the polymer can be adjusted in order to increase or decrease these rates.

The selection criteria used to choose the 1-bromooctane target odorant are described in Figure 25, using the following parameters: thermal stability, low chemical reactivity, a long half-life, rarely or never occurs naturally in the environment, safe for handling, readily available and volatility. The UDC allows for safe and reliable daily reinforcement and estimation of detection limits prior to the start of any working day. Dog handlers are therefore able to produce additional legal documentation to gauge their olfactory capabilities. The UDC has also been used in research settings for introducing "green" dogs to detection work as well as monitoring their daily capabilities. [126]

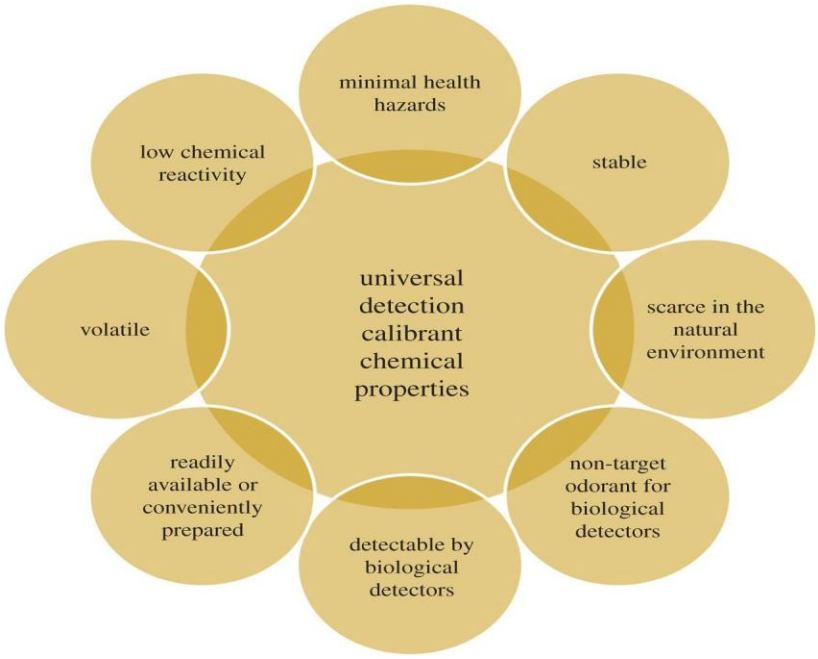


Figure 25. Desired chemical properties of a universal detector calibrant [127].

2.5.1.1 Controlled Odor Mimic Permeation Systems

Figure 26 displays a COMPS device containing a gauze pad inside of a sealed low-density polyethylene (LDPE) polymer bag. Target compounds are spiked onto the gauze pads prior to sealing. The rate of target compound delivery or dissipation for COMPS is measured using gravimetric analysis. Figure 27 shows the gravimetric analysis of 1-Bromooctane housed in 3-inch x 5-inch 4 MIL thick LDPE bag. Rate of dissipation is expressed as the mass loss (mg) of 1-Bromooctane per time (mins)

Figure 26. Image of a COMPS device containing a gauze pad inside of a sealed low-density polyethylene (LDPE) polymer bag. Target compounds are spiked onto the gauze pads prior to sealing [125]

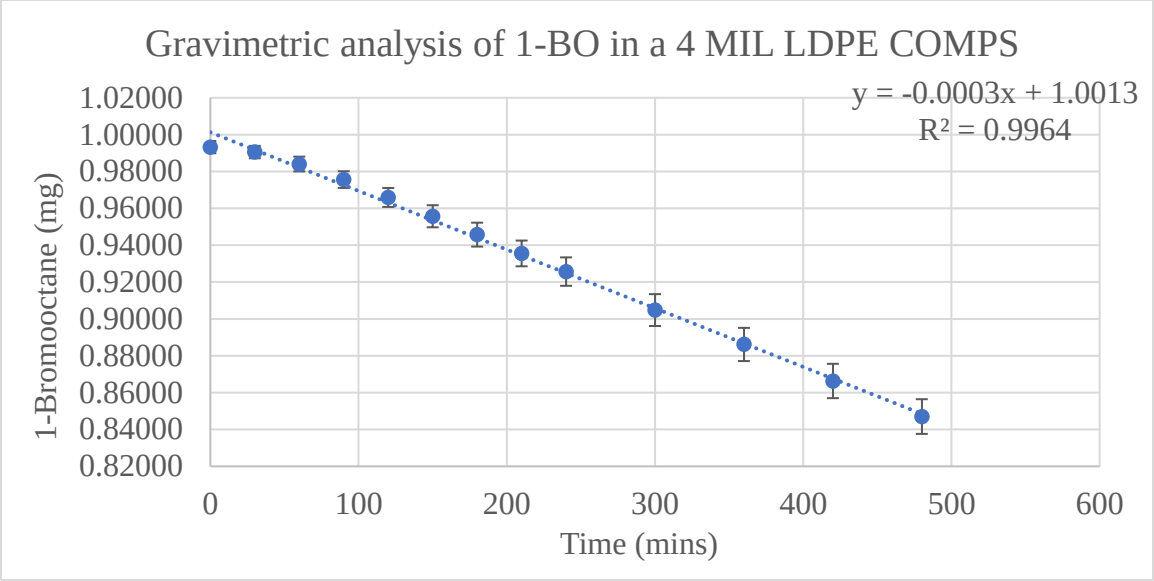


Figure 27. 1-Bromooctane housed in 4MIL thick 3" x 5" LDPE bag.4MIL LDPE bag with an average permeation rate of .31mg/min.

As previously stated, the thickness of the COMPS polymer can be adjusted in order to increase or decrease the rate of odor delivery. Figure 28 shows the effects of adjusting bag thickness for 12 compounds with varying vapor pressures (mmHg at 25 °C) and hence varying rates of odor dissipation. After varying polymer thickness (numbers shown in parenthesis in (B), increased similarities in rates of permeation of the target compound. Obtaining known, quantifiable, and reproducible rates of odor delivery release to subjects during a research study is critical for obtaining uniform, reproducible results. Ignoring uniformity in odor availability can limit the applicability and interpretability of results [125].

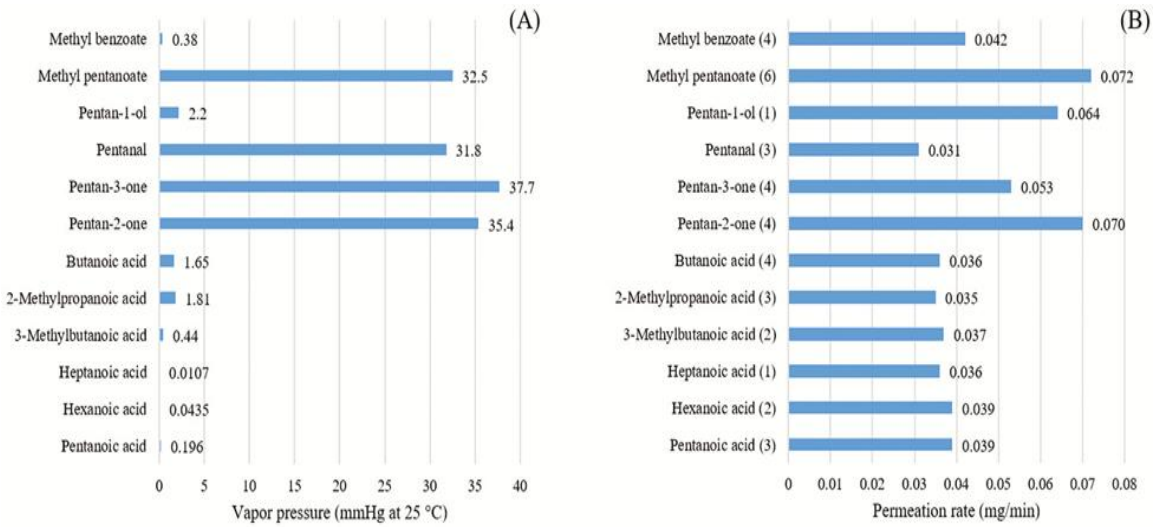


Figure 28. Variation in (A) vapor pressures (mmHg at 25 °C) for 12 tested compounds compared with (B) permeation rates (mg/min) for 12 tested compounds. Numbers in parenthesis (B) show selected COMPS thickness in MIL [125].

2.6 Analytical Methods

Generally, an analytical procedure can be separated into the following steps: sample collection, sample preparation, separation and sample analysis (Figure 29).

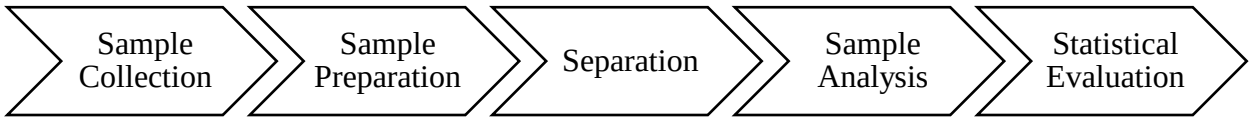


Figure 29. General steps in an analytical procedure.

Each of these steps are integral to increase the throughput of the analytical process and obtain the most accurate results. The sampling step involves deciding how to collect representative samples of the material in question and obtaining them in the right amounts. Sample preparation partitions components from the sample matrix as most analytical instruments are unable to analyze both the sample and the matrix. In addition, samples must be concentrated to a suitable level prior to instrumental analysis to ensure detection. In the separation step, the isolated sample is divided into its respective compounds by a chromatographic procedure such as gas chromatography (GC) or liquid chromatography (LC) where retention time is the basis for identification. The sample then proceeds to a detector that is coupled to the GC or LC instrument. Examples of detectors include Mass Spectrometer (MS), Flame Ionization Detector (FID) and Electron Capture Detector (ECD). The final step involves statistical evaluation that is usually achieved by a calibrated computer software [128].

2.6.1 Solid-phase Microextraction (SPME)

Sample preparation is crucial step because significant loss in analyte can take place if an inappropriate method is employed. Solvent-based sample preparation techniques are often tedious and time consuming, involving a multi-step process that often reduces the amount of collected analytes. As a result, many modern sample preparation methods has focused on high extraction efficiency, decreased analysis time, automation and reduced solvent [129].

Solid-phase microextraction (SPME), developed by Janusz Pawliszyn in 1990 is a non-exhaustive sample preparation method that offers sampling, preconcentration and extraction into one step with the ability to introduce captured analytes directly into analytical instruments. Solid-phase microextraction is advantageous as it allows for a rapid, simple extraction with little to no solvent use and improved sample clean-up. Today, SPME is employed in many different areas of research including but not limited to forensic, environmental, toxicology, biological matrices, pharmaceuticals, natural products, polymers and coating, and agriculture [130].

A SPME device consists of a fused silica fiber approximately 1-2cm in length that is coated with a liquid (polymer), a solid (sorbent), or a combination of both. The fiber is located in a tubing that is housed in a hollow needle like shaft that acts as both a protective barrier for the fiber as well as a septum piercing needle. Figure 30 shows the setup of a typical SPME assembly unit consisting of the SPME device attached to a holder. The unit operates by engaging the plunger to expose the fiber for analyte extraction while locking the plunger

into place by shifting the retaining screw to the side. The reverse procedure is performed to retract the fiber back into the shaft after extraction.

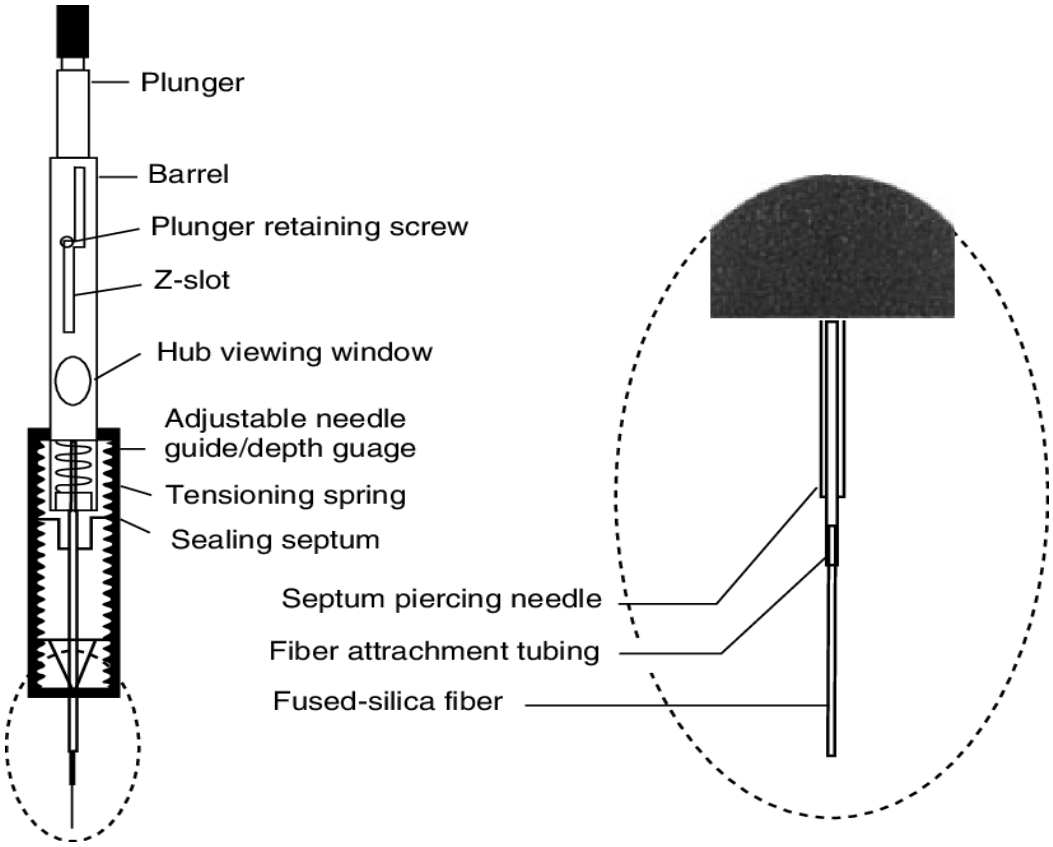


Figure 30. Solid-phase microextraction (SPME) assembly.

Solid-phase microextraction is usually performed in one of three modes: direct immersion SPME (DI-SPME) headspace SPME (HS-SPME) and membrane-protected SPME. In direct immersion, the fiber is immersed into the sample matrix allowing direct transfer of analyte to the fiber. For headspace sampling the fiber is exposed above the sample which is normally contained in a closed container (e.g., glass vial with a cap) allowing sample

distribution among the sample, headspace and fiber. HS-SPME is particularly useful for volatile and semi-volatile compounds DI-SPME utilizes a protective hollow membrane which prevents large molecules from diffusing into the extraction phase, while simultaneously allowing the mass transfer of analytes[129]. Direct immersion SPME is preferred for non-volatile and high molecular weight compounds like proteins and fatty acids. Figure 31 displays the three modes of SPME.

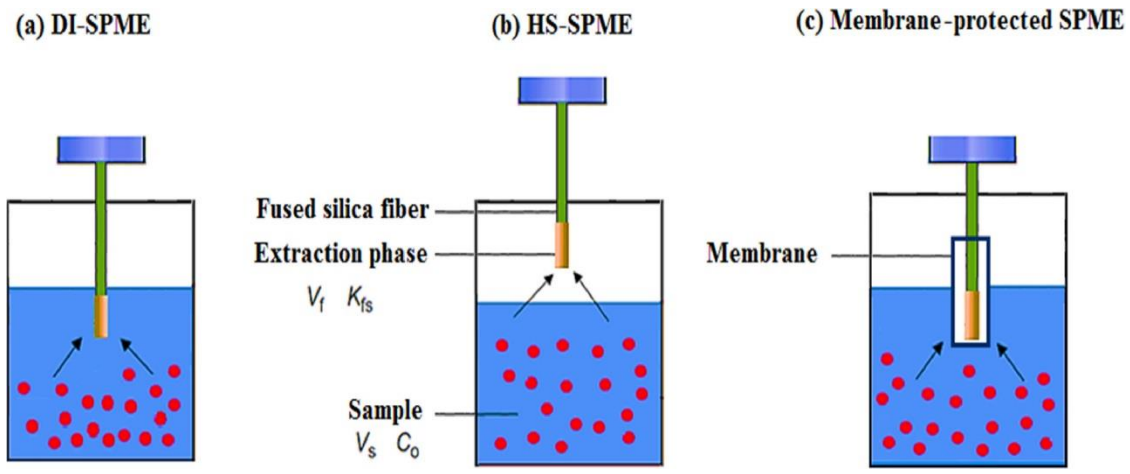


Figure 31. Most common modes of SPME: (a) DI-SPME, (b) HS-SPME and (c) Membrane-protected SPME [129].

Solid-phase microextraction involves a multiphase equilibrium process where analytes are partitioned between the fiber and the aqueous phase or in the case of headspace, the aqueous phase (can also be a solid), the headspace and the fiber. The SPME extraction process is complete once the when the analyte concentration has reached distribution equilibrium between the sample matrix and the fiber coating [131]. Post-equilibrium extracted analyte is independent of further increases of extraction time. Equation 1 describes equilibrium conditions for a two- phase system where C_0: initial concentration

of the analyte in the sample, V_s : volume of sample, V_f : volume of fiber coating, $C^{\infty}{}_f$: equilibrium concentration on the fiber, $C^{\infty}{}_s$: equilibrium concentration in the sample.

$$C_0 V_s = C^{\infty}{}_s V_s + C^{\infty}{}_f V_f$$

Equation 1. Equilibrium conditions for a two-phased system.

The distribution constant K_{fs} of the analyte between the fiber and sample matrix is described by Equation 2

$$K_{fs} = C^{\infty}{}_f V_f / C^{\infty}{}_s V_s$$

Equation 2. Distribution constant of analyte between the fiber and sample matrix.

The total number of moles of analyte *n* that is extracted at equilibrium by the fiber is defined in equation 3 by combining both equations 1 and 2. Equation 3 follows the assumption that the volume of the sample V_s is larger than the volume of the fiber and demonstrates that the amount of analyte extracted by the coating is directly related to the analyte concentration in the sample matrix.

$$n = C^{\infty}{}_f V_f = (K_{fs} V_f V_s C_0) / (K_{fs} V_f + V_s)$$

Equation 3. The total number of moles of analyte extracted at equilibrium by the fiber in a two-phased system.

For a multi-phase system such as HS-SPME the following Equation 4 can be applied for equilibrium conditions where K_{hs} represents the distribution coefficient between the fiber and headspace. Equation 4 also shows that the amount of extracted analyte is not related

to placement of the fiber in the headspace once the headspace, volume of fiber coating and sample is constant.

$$n = C^{\infty}_{f} V_f = (K_{fs} V_f V_s C_0) / (K_{fs} V_f + K_{hs} V_h + V_s)$$

Equation 4. The total number of moles of analyte extracted at equilibrium by the fiber in a multi-phased system.

The amount of analyte that can be adsorbed by a fiber is dependent on both the distribution constant of the analyte and the thickness of the fiber coating. Optimum extraction time is normally determined by the length of extraction time required for analytes with the highest distribution constants. Distribution constants typically increase as molecular weight and boiling point of the analyte increases. For increased selectivity, the type or thickness of the fiber polymer coating can be changed for desired analytes. Generally, thick coatings allow for greater extraction of compounds in the volatile range while thin coatings are more suitable for adsorbing/desorbing semi-volatile analytes. Table 7 below shows a general selection guide for selecting the size and polymer chemistry of a SPME fiber based on both polarity and molecular weight of target analytes.

Table 7. SPME fiber selection guide based on molecular weight (mw) and polarity of target compounds [132].

Analyte of Interest	Recommended Fiber size and Chemistry
Gases and low molecular weight compounds (MW 30-225)	75 µm/85 µm Carboxen/polydimethylsiloxane
Volatiles (MW 60-275)	100 µm polydimethylsiloxane
Volatiles, amines and nitro-aromatic compounds (MW 50-300)	65 µm polydimethylsiloxane/divinylbenzene
Polar semi-volatiles (MW 80-300)	85 µm polyacrylate
Non-polar high molecular weight compounds (MW 125-600)	7 µm polydimethylsiloxane
Alcohols and polar compounds (MW 40-275)	60 µm Carbowax (PEG)
Non-polar semi-volatiles (MW 80-500)	30 µm polydimethylsiloxane
Flavor compounds: volatiles and semi-volatiles, C3-C20 (MW 40-275)	50/30 µm divinylbenzene/Carboxen on polydimethylsiloxane on a StableFlex fiber
Trace compound analysis (MW 40-275)	50/30 µm divinylbenzene/Carboxen on polydimethylsiloxane on a 2 cm StableFlex fiber
Amines and polar compounds (HPLC use only)	60 µm polydimethylsiloxane/divinylbenzene

2.6.2 Gas Chromatography (GC)

The process of chromatography involves the physical separation of a chemical mixture into its individual components. To achieve separation the components are carried by a mobile phase (gas, liquid or supercritical fluid) through a stationary phase (solid or liquid on the carrier or gel) where separation is determined by the affinity of the individual components to the stationary phase. Several types of chromatography exists which include paper chromatography, thin layer chromatography, liquid chromatography, size exclusion chromatography, ion-exchange chromatography affinity chromatography and gas chromatography.

Gas chromatography is used for separating volatile mixtures into individual compounds. The theoretical basis for GC was first described in 1941 by Archer Martin and Richard Synge. The first successful application followed in 1952 by Martin and Anthony James with the separation of fatty acid mixtures using gas–liquid partition chromatography. Today, gas chromatography is used primarily for trace analysis purposes in many applications such as food analysis, quality control, research, air quality control, blood alcohol analysis and Forensic Science, with sensitivities ranging from parts per million (ppm) to parts per quadrillion (ppq) [133],[134].

In GC, the mobile phase used is an inert carrier gas that carries compounds through a specially coated column which acts as the stationary phase. The stationary phase consists of a high molecular weight liquid which is deposited on the surface of an inert adsorbent (packed column) or coated along the walls of a capillary tube. Separation is based on the extent to which compounds partition between both mobile and stationary phases. Compounds with greater solubility in the stationary phase will be retained in the column over a longer period. The extent of the partitioning is described by partition coefficients which is affected by not only the type of stationary phase, but also temperature. Assuming constant temperature this coefficient is defined by Equation 5 where K_D represents the distribution coefficient of compounds, C_L the concentration of compounds in stationary phase and C_G the concentration of compounds in mobile phase.

$$K_D = C_L / C_G$$

Equation 5. Distribution coefficient of a compound in a gas chromatographic system

Figure 32 below shows the general schematics of a gas chromatography instrument.

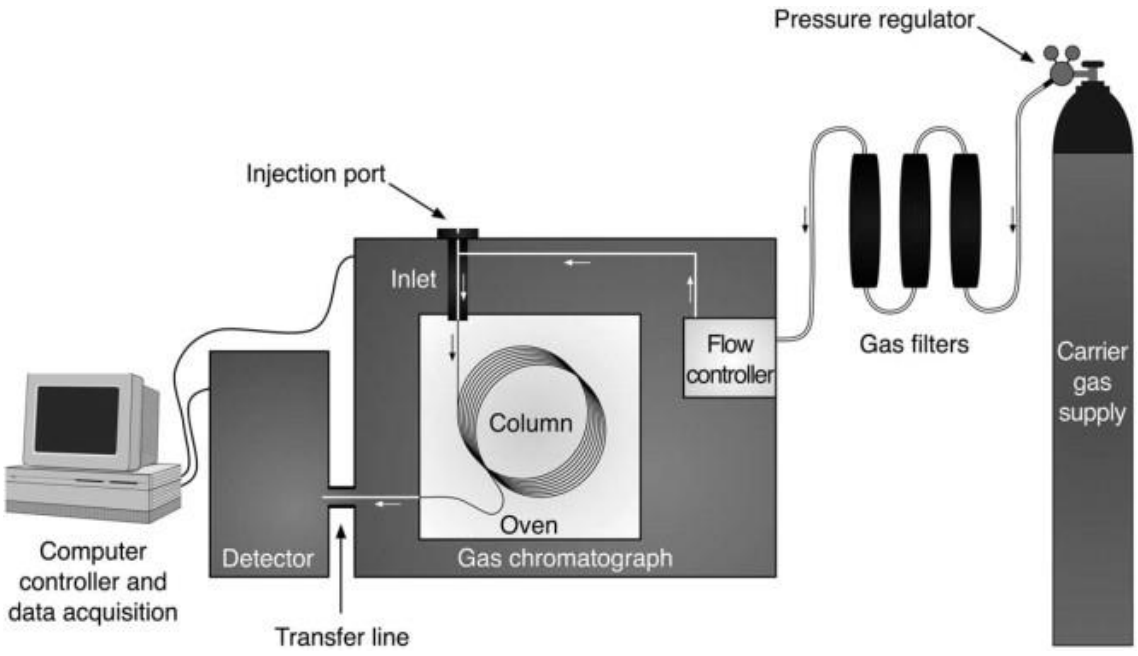


Figure 32.Gas chromatography analytical process [135].

As previously mentioned, the carrier gas serves as the mobile phase for GC experiment. The carrier gas for any GC application should be chemically inert with respect to the sample components and the stationary phase. Common gases used includes hydrogen, helium, nitrogen and argon. Helium, however, is the most widely employed for chromatographic systems as it is unreactive, nontoxic, non-explosive, shows minimal viscosity change under increasing temperature and is compatible with most detectors. The carrier gas flows from the gas supply tank where it is first purified by filtration to remove moisture, oxygen, hydrocarbons and other impurities. After purification, the gas passes through a flow control and/ or pressure regulator which assures consistent flow to the inlet

and the column. In the GC inlet, samples enter via the injection port and is accomplished using a syringe (manual or autosampler) for liquid samples or a device such as SPME that can be interfaced with the port for solid samples. Injection ports can allow either split or spitless injection. For capillary columns where sorption capacity is lower compared to packed columns, smaller volumes may be required for samples with high concentrations. Splitting essentially allows only part of the sample to enter with the remaining ejected out of the inlet. The temperature in the injection port is kept above that of the boiling point of the compounds in the mixture, thus allowing them to vaporize. The vaporized compounds are mixed with the carrier gas then carried to the oven where separation begins in the column. The compounds are then adsorbed by the column then desorbed by fresh carrier gas until it moves to the outlet and is eluted. Order of elution is governed by a combination of two main factors. The first is K_D with the compound having the lowest K_D value would theoretically elute first. The second is the oven temperature where increasing temperature allows compounds with a lower boiling points to be retained for a shorter time in the column. The time taken for a compound to elute is referred to as the retention time t_R.

The dimensions and chemistry of the chromatographic column can significantly affect the quality of analyte separation. A longer column length and smaller column diameter allows for better separation of compounds and increased overall column efficiency. Column efficiency refers to having narrower peaks in the chromatogram which allows for better separation of more compounds in the same timeframe. Efficiency is normally measured by the number of theoretical "plates" *N* where a higher plate count indicates a narrower peak. The concept of theoretical plates derives from an analogy with fractional distillation where the more traps or "plates" within a distillation column allows a narrower boiling range to

be extracted from each plate. The number of theoretical plates is calculated by Equation 6 where t_R represents retention time and $W_{1/2}$ the width of the peak at half height. According to this equation, peak width and N value are clearly inversely related.

$$N= 5.54 (t_R/W_{1/2})^2$$

Equation 6. Efficiency of a GC column as a function of length

Efficiency of a column as a function of diameter is measured in plates per meter (N/m). Smaller diameters therefore allows for larger (N/m) values. With column length, efficiency is described by Equation 7 with H being the height equivalent to a Theoretical Plate (assuming constant stationary phase and carrier gas). Increase in length hence allows for additional theoretical plates and improved column efficiency.

$$N=L/H$$

Equation 7. Efficiency of a GC column as a function of diameter

As mentioned above, GC columns can be divided into either packed columns or capillary columns. Packed columns are typically made from copper, aluminum, stainless steel or glass. Sizes range from 2-6mm in diameter and 1-16m in length with the exception of some micro packed columns that have diameter and length ranges of 0.8mm-1.2mm and 0.5-2m respectively. Packed columns allow for more sample volume but is associated with broader peak shapes and lower separation of compounds. Figure 33 shows the cross-sectional construction of a packed column.

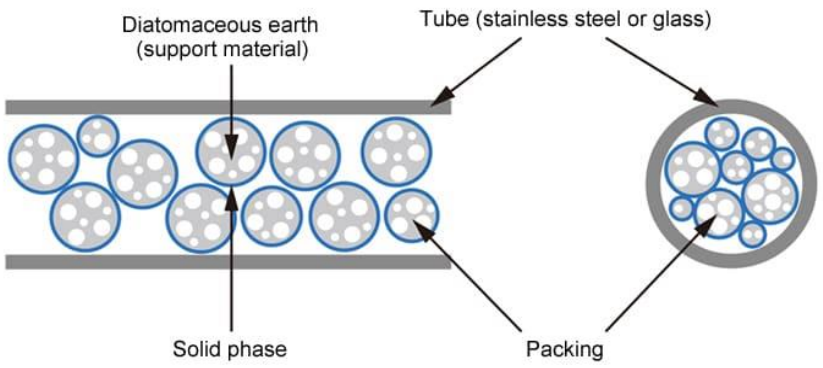


Figure 33. The cross-section construction of a packed chromatographic column [136].

Capillary columns on the other hand consists of fused silica or stainless steel lined with a high molecular weight liquid phase or absorbent material. Sizes range from 0.1-0.6mm in diameter and 10-60m in length. Capillary columns handle less sample volume but has better peak resolution and detection sensitivity. Figure 34 shows the cross-sectional view of a capillary column.

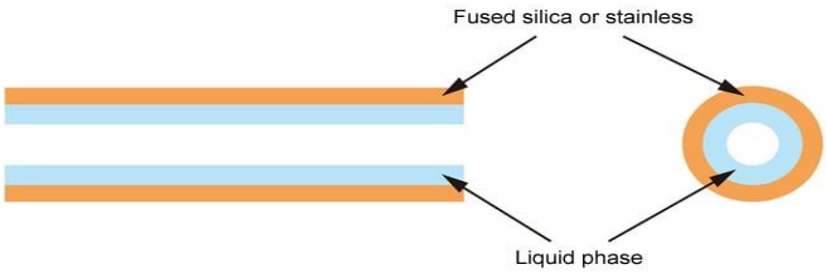


Figure 34. The cross-section construction of a capillary column [136].

Common stationary phases for filling the columns are adsorbents (carbon, silica gels, molecular sieves, porous polymers), and/or liquid stationary phases. Table 8 below provides a comprehensive list of stationary phases and its application for organic compounds.

Table 8. Characteristics of stationary phases and its application for organic compounds Adapted from [16].

Composition of Stationary Phase	Polarity	Max Temp (°C)	Application
100% dimethylpolysiloxane	Low	340–360	Alcohols, aromatic hydrocarbons, esters, flavors and aromas, free fatty acids, glycols, halogenated hydrocarbons, hydrocarbons, ketones, organic acids, oxygenates, polycyclic aromatic hydrocarbons (PAHs), pesticides, polymers, steroids, solvents, sulfur compounds
5% phenyl/95% dimethylpolysiloxane	Low	340–360	Alcohols, amines, hydrocarbons, bile acids, drugs, Environmental Protection Agency (EPA) methods, fatty acid methyl esters (FAME), flavors and aromas glycerides, halogenated compounds, PAHs, polychlorinated biphenyls (PCBs), pesticides, steroids, sterols, sugars, sulfur compounds
5% diphenyl/95% dimethylpolysiloxane	Low	340–360	
6% cyanopropyl-phenyl/94% dimethylpolysiloxane	Mid-polarity/ low	280–300	Organic volatiles and semi-volatiles, aromatics, halocarbons, solvents
14% cyanopropyl-phenyl/86% dimethylpolysiloxane	Mid-polarity /low	300–320	Alcohols, aromatic hydrocarbons, organic acids, PAHs, pesticides, phenols, steroids
50% phenyl/50% dimethylpolysiloxane	Mid-polarity	320–340	Drugs, pesticides
25% cyanopropyl/25% phenyl/50% dimethylpolysiloxane	Mid-polarity /high	260–280	Halogenated compounds, phenols, pyridines
Polyethylene glycol	High	250–260	Alcohols, aldehydes, anesthetics, antidepressants, aromatic hydrocarbons, esters, FAME, flavors and aromas, glycols, halogenated compounds, ketones, nitro compounds, PAHs, phenols, solvents, sulfur compounds
Cyclodextrin	Polar/ Opticall y active	220–250	Separation of enantiomers, optical isomers of acids, alcohols, amino acids, aromatic hydrocarbons, diols, flavors, aromas, ketones, organic acids, phenols

2.6.3 Mass Spectrometry

After compounds are separated and eluted from the chromatographic column, it enters a transfer line to be sequentially identified by a detector which generates an electrical signal to which is then interpreted by a computer software. There are generally two types of detectors: universal detectors that can analyze a wide range of compounds and selective detectors which are sensitive to certain group of compounds (e.g., halogenated compounds or nitrogen compounds). Ideally detectors should possess high sensitivity (i.e., sufficiently low limits of detection) and detectability, short response times, wide linear range and stable baseline and signal indication. Table 9 describes some of the commonly used selective and universal detectors and how they compare with each other.

Table 9. Detectors commonly interfaced with Gas Chromatography.

Detector	**Category**	**Detection Limit (g/s)**	**Linear Range (g/s)**
Flame ionization (FID)	Selective (organic carbon compounds)	10^{-12}	10^{7}
Electron capture (ECD)	Selective (organic halogenated compounds)	10^{-13} - 10^{-14}	10^{2}
Thermal conductivity (TCD)	Universal	10^{-6} - 10^{-5}	10^{5}
Thermal ionization (TID)	Selective (organic nitrogen and phosphorous)	10^{-13} N 10^{-14} P	10^{3}
Mass selective detector (MSD)	Selective	10^{-12}	10^{4}

A mass spectrometer consists of a sample introduction system, ion source, mass analyzer and detector. Samples can be introduced to the mass spectrometer via a transfer line from (e.g. gas chromatography, liquid chromatography) or directly by a solid probe. After introduction, the sample is ionized. The two most common form of ionization is electron impact ionization (EI) and chemical ionization (CI). With EI, the gaseous sample is bombarded with a beam of electrons (normally at 70 eV) resulting in the formation of molecular ions which then undergo fragmentation to form smaller ions. In CI, the analyte is mixed with a reagent gas such as methane, and ammonia. The reagent gas first undergoes EI after which it mixes with the analyte forming analyte ions. Chemical ionization is commonly referred to as a "soft" ionization method as there is less energy applied to the analytes resulting in less fragmentation and hence easier mass spectra interpretation compared to EI. Equation 8 shows the ionization reactions that occur under CI using methane as a reagent gas.

$$CH_4 + e \rightarrow CH_4^{+\bullet} + 2e \quad (8.1)$$

$$CH_4^{+\bullet} \rightarrow CH_3^{+} + H^{\bullet} \quad (8.2)$$

$$CH_4^{+\bullet} \rightarrow CH_2^{+\bullet} + H_2 \quad (8.3)$$

$$CH_4^{+\bullet} + CH_4 \rightarrow CH_5^{+} + CH_3^{\bullet} \quad (8.4)$$

$$CH_3^{+} + CH_4 \rightarrow C_2H_5^{+} + H_2 \quad (8.5)$$

$$CH_5^{+} + M \rightarrow [M + H]^{+} + CH_4 \quad (8.6)$$

Equation 8. Ionization reactions that occurs under CI using methane as a reagent gas.

Other soft ionization techniques include electrospray ionization (ESI) and Matrix Assisted Laser Desorption Ionization (MALDI). Soft ionization techniques are useful for thermolabile analytes such as peptides and proteins.

The fragmented ions are then separated based by a mass analyzer based on their mass-to-charge (m/z) ratio in the analyzer. The most common mass analyzers used today are the quadrupole, time-of-flight (TOF) and the ion trap. The quadrupole comprises of four parallel metal rods with one set of opposite rods connected to direct current (DC) voltage and the other set alternating current (AC) voltage (Figure 35). By alternating the ratio of the applied voltage only ions of a certain m/z ratios will be allowed to reach to the detector. Advantages of quadrupole analyzers include low cost, small size, durability and ease of operation while disadvantages include limited range of mass separation (about 1000 Da).

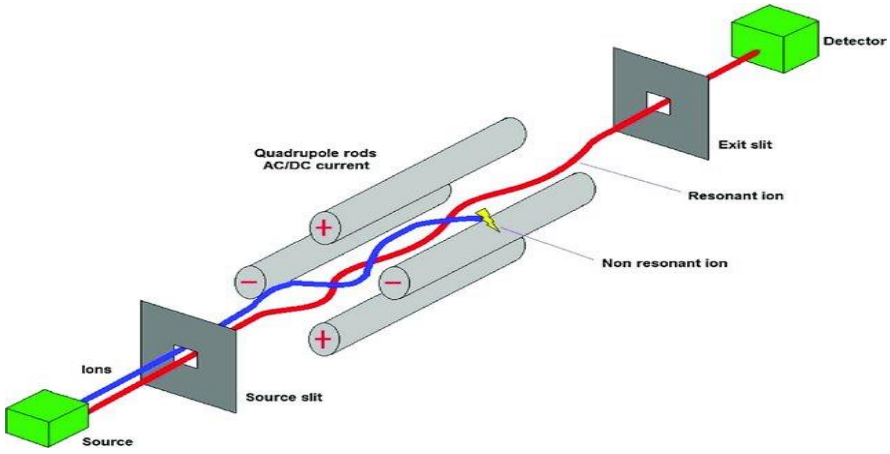


Figure 35. The schematics of a quadrupole mass analyzer [137].

An ion trap consists of two endcap electrodes where DC voltage is applied and a doughnut shaped ring electrode with an RF potential (Figure 36). Combinations of RF and DC voltages are then applied destabilizing and trapping ions within specified m/z ranges. These

ions are then ejected via a hole in one of the endcaps to reach the detector. Noted advantages of this analyzer compared to a quadrupole include higher sensitivity and better resolution while disadvantages include difficulty in interpreting spectra for polar compounds like ketones alcohols and aldehydes [16]

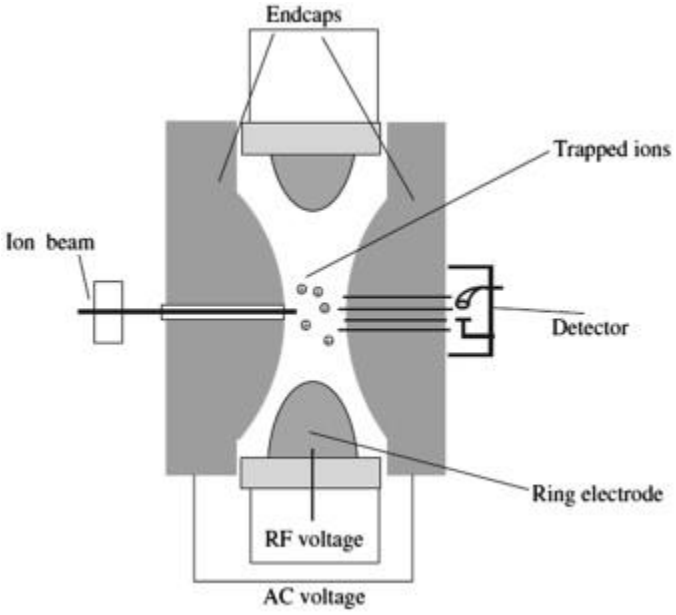


Figure 36. The schematics of an ion trap mass analyzer [138].

The time-of-flight mass analyzer as the name implies, separates ions based on time taken to reach the detector which is based on their m/z value. Ions of lower mass reach the detector faster than those of higher mass. Ions are first generated in the ion source by neutral molecule analytes after which an electrical field is applied, directing them through a drift tube to the analyzer. Advantages of TOF includes high resolution scans and detection of masses above 100,000 Da.

Figure 37 displays an example of a typical mass spectra. The compound here acetone, shows a molecular ion peak m/z =58 and two fragments m/z=43 and m/z=58. A less intense M+1 peak is also observed. This is due to the presence of the carbon isotope (^{13}C) in the compound.

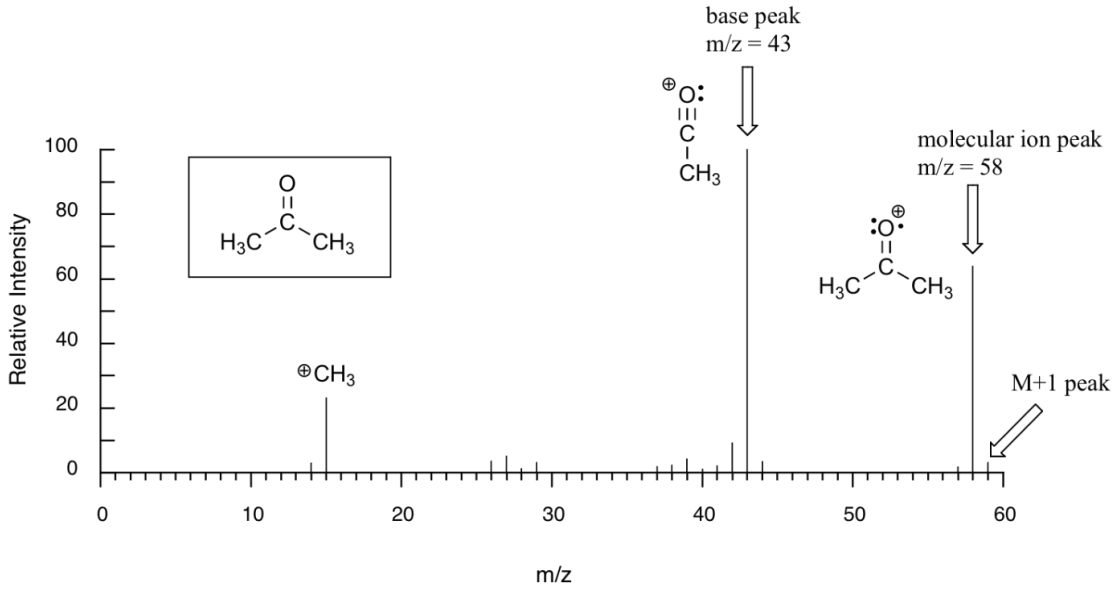


Figure 37. Example mass spectra of acetone showing fragments m/z =11, m/z =43, m/z=58 and m/z= M+1 [139].

2.7 Statistical Analysis

Statistics can be defined as a mathematical science that involves the collection, analysis, presentation and interpreting of data [140][141]. Statistical analysis essentially examines collected data from a sample for the purpose of testing a hypothesis. For data collected in this study, two types of statistical analysis were performed: predictive values and principal component analysis (PCA).

2.7.1 Predictive Values

When conducting field testing for detector dogs, it is important to know whether responses, positive or negative are in fact true responses. A reliable statistical method for measuring this is the Predictive Value test. As the name implies, Positive Predictive Value (PPV) and Negative Predictive Value (NPV), test the likelihood of the responses being a true positive or true negative based on the prevalence, sensitivity, and specificity of the measured values. The closer the value is to 100%, the greater the likelihood that the observed value is true Predictive values are widely used in the medical field to similarly measure the accuracy associated with diagnostic tests [142]. Equations 9 and 10 shows the calculations for PPV and NPV are described below.

$$\text{PPV}=\text{true positive} / (\text{true positive} + \text{false positive})$$

Equation 9. Positive Predictive Value Test

NPV= true negative / (true negative + false negative)

Equation 10. Negative Predictive Value Test

2.7.2 Principal Component Analysis

Interpretation of large datasets can often be a difficult task. Principal Component Analysis (PCA) is a mathematical algorithm that is used to reduce the dimensionality of large data variables into smaller variables while preserving most of the variation [143]. This is done by constructing principal components along which data variation is maximal. The principal components allow for samples to be represented by fewer data points while allowing for similarities and differences between samples to be visually assessed [143], [144].

3. SIGNIFICANCE OF RESEARCH AND OBJECTIVES

The first task of this project involves investigating the response of trained law enforcement marijuana detector dogs to samples of hemp, which is now a legal substance. Currently there are many reports of dogs not being able to distinguish between marijuana and hemp as a result of similarities in smell. As mentioned earlier, some police departments are now avoiding training new dogs on marijuana with some departments contemplating the withdrawal of dogs already trained to detect it. The second part of this task involves the development of a training method to aid dogs in discriminating between both substances. while third part involves VOC analysis of a series of marijuana and hemp samples for comparison and statistical analysis. Additionally, the third part looks at current commercial marijuana canine training mimics and validate its efficacy through field testing as well as analysis of VOCs.

The second task analyzes the VOCs associated with triacetone triperoxide (TATP). Because TATP is a non-traditional (not containing nitrogen), peroxide-based explosive, it is undetectable by most security scanners. Detector dogs however can be used as a trace detector for TATP. By understanding the VOCs associated with this explosive, a more effective training system can be proposed. Also, commercial training aid mimics will also be analyzed through field testing and VOC analysis to make recommendations on its efficacy.

The third task explores the VOCs associated with various mass storage devices. A relatively new field of odor detection, dogs have been trained to locate these devices. Methods for successful training however vary widely with many conflicting reports. By analyzing the VOCs of MSDs, this task aims to lay the scientific foundation for detector dog training by gaining insight into which VOCs might be responsible for dogs alerting to MSDs. In addition, the anecdotal use of two chemical compounds triphenylphosphine oxide (TPPO) and hydroxycyclohexylphenyl ketone (HPK) for training dogs will be validated by looking at their prevalence in MSDs.

The final task surrounds the continued development of a universal detector calibrant (UDC) for dogs. Currently, there are insufficient tools to ensure a dog's reliability prior to the start of the workday. By improving the calibrant, trainers can measure the dog's performance (e.g., sensitivity) to ensure that the dog is working within acceptable parameters. By leveraging on a previously patented odor delivery tool, Controlled Odor Mimic Permeation System (COMPS) a series of calibrants will be developed with measurable rates of odor delivery.

4. DIFFERENTIATION OF MARIJUANA AND HEMP USING DETECTOR DOGS AND HS-SPME-GC-MS

4.1 Introduction

When a dog is trained to respond to a stimulus such as an odor, two processes come into effect: generalization and discrimination. Generalization refers to the tendency to respond not only to a trained stimulus but also stimuli that is similar to that trained stimulus. Discrimination is essentially the reverse of generalization with the ability to not respond to a stimuli that is similar to the trained stimulus. Both of these processes are integral for the success of a detector dogs as there will be scenarios when either generalization or discrimination is desired and times when they are not. Training protocols are therefore paramount in accomplishing generalization or discrimination.

A generalization gradient represents how generalization can be predicted along a stimulus dimension based on the similarities to a conditioned stimulus with the greatest generalization occurring to stimuli that is most similar. Figure 38 depicts this gradient with a Gaussian shaped distribution showing the probability of responding to a stimulus decreasing as the stimulus becomes more dissimilar to the conditioned stimulus. A narrower gradient depicts less generalization (more discrimination) while a broader gradient more generalization These gradients have been observed with several species in different stimulus dimensions such as wavelengths of light [145], sound frequency [146] degrees of rotation [147], spatial location [148] shapes [149], and monomolecular odors [150].

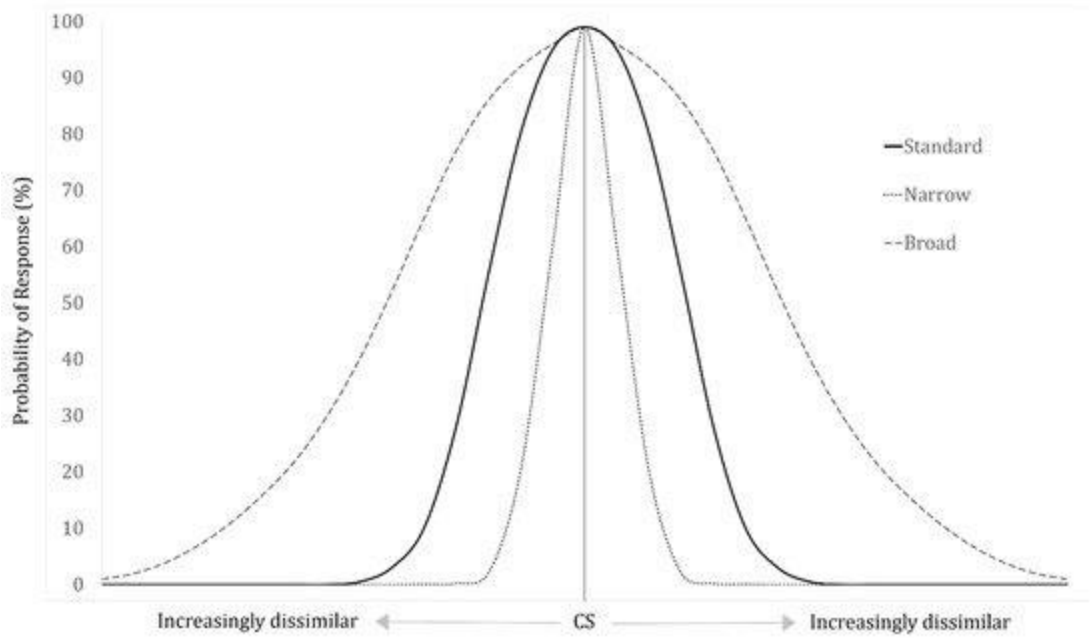


Figure 38. Theoretical generalization gradients varying along one spectrum, showing the probability of responding to the conditioned stimulus (CS). A narrower gradient represents less generalization (more discrimination) while a broader gradient represents more generalization [151].

Similarly, with marijuana and hemp, it is expected that levels of generalization will occur as both plants are *Cannabis* with similar odor profiles. As generalization gradients can also be affected by other factors such as the amount of training received as well as overall olfactory perception, variation in responses to hemp amongst dogs is also expected.

4.2 Trial 1: Investigating the Response of Dogs to Marijuana and Hemp.

4.2.1 Trial Design and Materials.

Marijuana samples were provided by licensed law enforcement canine officers who participated in the study. All hemp samples were purchased from reputable licensed companies that publicly displays third-party lab testing analysis for all of their samples. This was to ensure that the purchased samples were in fact hemp (<0.3% Δ9-THC). A total of eight different hemp samples were used and will be referred to as hemp 1, hemp 2 etc. The online listed "strain" names for these products will not be referenced as they may not provide much information since the actual contents in a said strain can vary widely from one company to another. The corresponding strain names however can be found in Appendix A. It is important to note that the hemp samples under investigation were buds from hemp plants and not products derived from processed hemp (e.g. hemp twine, hemp gummies, hemp oils etc.). It was previously determined that dogs do not alert to processed hemp products and as a result, these products are not a cause for concern. Hemp sample 8 was not a pure hemp bud, but a cigarette blend of hemp buds along with other additives. It was included due to reports of some dogs alerting to them.

For this trial, metal cans were used to place odors in for searching. The cans weighed 16oz and were 2 ½ inches in diameter and 1 ¾ inches in height. To allow for odor delivery, five holes were punctured in the middle of the lids as shown below in Figure 39.

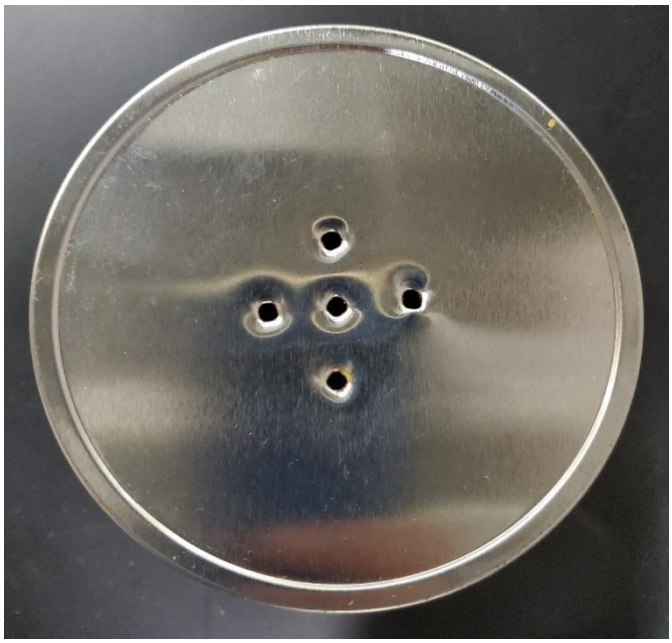


Figure 39. Holes placed in the middle of metal cans to allow for sufficient odor delivery during testing.

A total of 24 certified law enforcement dogs participated this trial. The trial was blind to dog-handler teams and divided into two sessions with each session consisting of four separate search lineups which were all randomized. In each lineup there were five metal cans (Figure 40); one can contained approximately one gram of a particular hemp sample, two cans contained additional "distracting" odors and two cans were blank. Distractors included orange peels, banana peels, cigarettes (non-hemp), dog treats, cigarette/hemp rolling paper, cat food, hemp gummies, hemp seeds, CBD oil and thyme (Appendix A). Cans with odor samples were prepared approximately 30 minutes prior to each search session. Cans were placed two feet apart in each lineup and the order was randomized to ensure that there was no learnt odor pattern by either the dog or the handler. Prior to the start of the trial, each dog-handler team was required to complete a blind marijuana odor

recognition test (ORT). The ORT also consisted of a five can lineup containing two blanks and two distracting odors and served to ensure that the dog was in fact working up to par and able to recognize *Cannabis* odor.

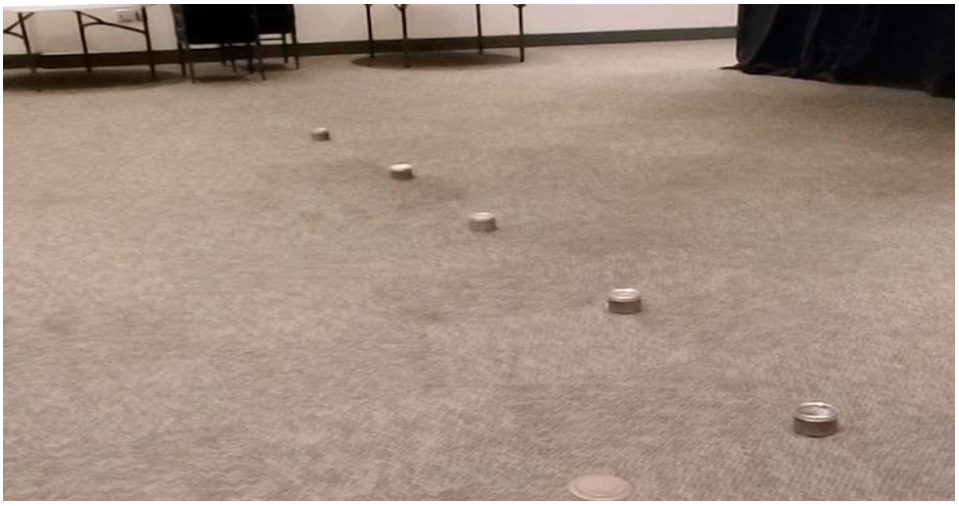


Figure 40. Trial 1 search lineup consisting of five metal cans, two feet apart.

Handlers were advised to allow their dogs to conduct the search in a manner consistent with the dog's prior training. For alerts to the marijuana sample, handlers were asked to positively reinforce their dog i.e. toy or praise (Figure 41) . For alerts to hemp however, handlers were advised to gently remove their dog from the search and continue to the next lineup. All dogs were trained using a variable reward system so concerns regarding decrease in drive and motivation due to not being rewarded were negated. Furthermore, at the end of the first session, teams were allowed to retake the ORT to allow the dog to end the session on a "positive" note to increase drive. Negative reinforcement was not allowed for alerts to hemp as the goal of this trial was not to prevent the dogs from alerting to hemp but instead elicit a genuine response from the dog to the hemp samples.

Figure 41. A dog being positively reinforced for correctly identifying (alerting) to a can containing a marijuana sample.

4.2.2 Trial 1 Results

Figure 42 shows the response of dogs (n=24) to marijuana and each of the 8 hemp samples. There was a 100% alert rate to the marijuana ORT. Dogs also alerted to the various hemp samples with alert rates varying from 25% for hemp 8 to 75% for hemp 3. One dog (ID#6) did not alert to any of the hemp samples. The lowest response to hemp 8 can possibly be explained by the fact that hemp cigarettes contain other additives which would result in more variation in its odor profile when compared to pure hemp. There were a total of three alerts to cigarette/hemp rolling paper (6.25%), one alert to dog treats (2%), one alert to cat food (2%) and two alerts to blank cans (0.5%). There were no alerts to the hemp gummies, hemp seeds or hemp derived CBD oil. The individual results for each dog can be found in Appendix B.

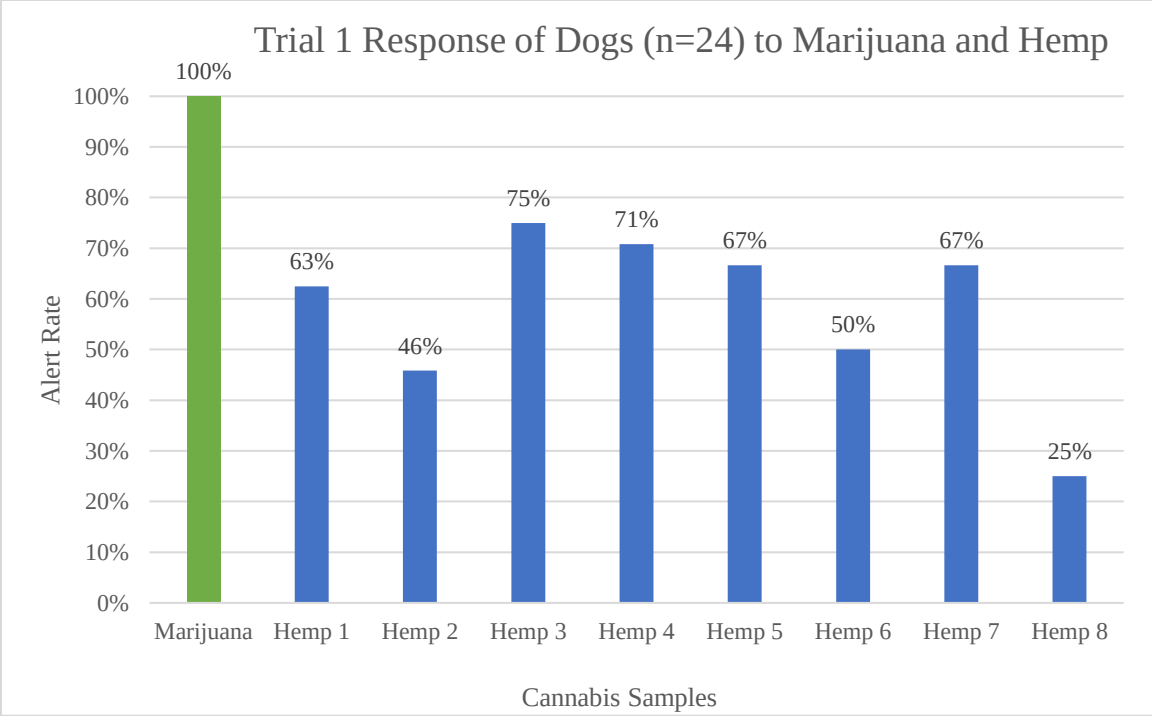


Figure 42. The response of dogs (n=24) to a marijuana sample and 8 different hemp samples

4.3 The Process of Proofing Dogs off Hemp

One process that can impact the generalization gradient discussed previously in Figure 38, is training off non-target stimuli (i.e. extinction of responses) also commonly referred to as "proofing". Proofing, which can be accomplished by negative reinforcement, results in narrowing of the generalization gradient allowing for more discrimination between the conditioned stimuli and non-target stimuli [152]. An example of this phenomenon was observed by Wright et al. studying the generalization of bees to different mixtures of 1-hexanol and 2-octanone [153]. In Wright's study, an additional group of bees were negatively reinforced for responding to one mixture while positively reinforced for responding to another. The result was a narrowing of the generalization gradient as bees showed decreased response to nontarget odors.

Building upon this concept, a training protocol was designed to proof dogs off hemp odor while simultaneously positively reinforcing the odor of marijuana. Hemp samples 1 through 8 from trial 1 were used for proofing. All dogs were subjected to varying levels of negative reinforcement (e.g., slight tug on collar) determined by the trainer, in order to extinguish undesirable responses to hemp. Training sessions were conducted with search lineups using a patented electronic Canine Odor Recognition Training (CORT) System boxes that allows for dogs to remotely receive an instantaneous reward for a correct alert. Lineups contained samples of marijuana, hemp, distracting odors (e.g. dog food, cat food, toys) and blank boxes. The order of the boxes were randomized during each training session to ensure no pattern recognition by dogs. Dogs were rewarded for alerts to marijuana and negatively reinforced for alerts to hemp. Each dog was required to complete a minimum of 10 lineups per session. Training sessions were held twice per week and lasted for approximately 8 weeks.

4.4 Trial 2: Response of Dogs to Marijuana and Hemp after being Proofed Off Hemp.

4.4.1 Trial Setup

This trial consisted of 10 dog teams, 5 of which did not participate in trial 1 but still completed the proofing process. These 5 dogs, however, did have documented alerts to hemp prior to proofing. Results from all 10 dogs will be presented to demonstrate the overall efficacy of the proofing process. For the dogs that competed in both trials, a comparison of hemp alerts before and after proofing will also be presented.

In addition to hemp samples 1-8, four new hemp samples (hemp 9 - 12) that the dogs had not been previously exposed to, were introduced in this trial. The purpose of these new samples was to determine the extent of carryover from the proofing process since ideally, after being proofed off hemp, dogs should learn to ignore additional hemp products and not only those to which they were trained not to alert to.

This trial was blind to dog-handler teams and consisted of 4 sessions, each with a randomized 18-box fence lineup (Figure 43). Each lineup contained 1 marijuana sample, all 12 hemp samples, three distractors and two blank boxes. All lineups contained the same products but in a different sequence to prevent any pattern recognition with the dog or handler. Distractors included dog treats, cat/dog food and toys. Since toys also contain odor, a toy was placed in the reward chamber of the CORT boxes for hemp 5 and hemp 9 to ensure that alerts to marijuana was not simply due to the presence of *Cannabis* odor paired with a toy. As with the first trial, if the dogs alerted to marijuana, they received a positive reinforcement in the form of praise or a toy. For alerts to hemp, handlers were once again instructed to gently pull the dogs off with no reward. All marijuana and hemp samples used in the trials weighed approximately 1-2 grams.

Figure 43. Trial 2 search lineup consisting of 18 fence boxes.

4.4.2 Trial 2 Results and PPV of Dog's Alert Rate to Marijuana

The results presented in Table 10 shows a 100% trial alert rate for marijuana with one alert (2.5%) to hemp 9 and no responses to the remaining hemp samples. There were three alerts (7.5%) to toys and no additional alerts to remaining distractors. The complete trial 2 results for each dog can be found in Appendix C.

Table 10. Trial 2 dog alert rate (n=10) for marijuana and hemp samples 1 through 12.

Sample	Alert Rate (n=10)
Marijuana	100%
Hemp 1	0%
Hemp 2	0%
Hemp 3	0%
Hemp 4	0%
Hemp 5	0%
Hemp 6	0%
Hemp 7	0%
Hemp 8	0%
Hemp 9	2.5%
Hemp 10	0%
Hemp 11	0%
Hemp 12	0%

Using alerts to marijuana as true positives and alerts to hemp as false positives, PPVs were calculated for marijuana alerts in each lineup. Table 11 shows canine PPVs for lineups 1-4 along with combined PPVs for the trial. All dogs achieved trial PPVs of 100% with the exception of 1 dog with a PPV of 87.5%. Overall, these results demonstrated the high probability of canine alerts being due to the presence of marijuana and not hemp.

Table 11. Trial 2 PPVs for alerts to marijuana.

PPVs for Alerts to Marijuana in Trial 2					
Dog ID#	**Lineup 1**	**Lineup 2**	**Lineup 3**	**Lineup 4**	**Combined**
3	100%	100%	100%	100%	**100%**
4	100%	100%	100%	100%	**100%**
5	100%	100%	100%	100%	**100%**
6	100%	100%	100%	100%	**100%**
16	100%	50%	100%	100%	**87.5%**
25	100%	100%	100%	100%	**100%**
26	100%	100%	100%	100%	**100%**
27	100%	100%	100%	100%	**100%**
28	100%	100%	50%	100%	**100%**
29	100%	100%	100%	100%	**100%**

As previously mentioned, only 5 dogs from trial 2 participated in trial 1 prior to the proofing phase. Of these 5 dogs, one (ID #6) did not have any alerts to hemp in trial 1. Table 12 compares the alert rates of the remaining 4 dogs for hemp samples 1 through 8 for both trials. Trial 2 results showed no alerts by all 4 dogs to any of these samples.

Table 12. Comparison of the alert rates to hemp samples 1 through 8 by the same dogs (n=4) used in trial 1 and trial 2

Sample	Trial 1 Alert Rate (n=4)	Trial 2 Alert Rate (n=4)
Marijuana	100%	100%
Hemp 1	50%	0%
Hemp 2	25%	0%
Hemp 3	75%	0%
Hemp 4	25%	0%
Hemp 5	25%	0%
Hemp 6	50%	0%
Hemp 7	75%	0%
Hemp 8	25%	0%

These results showed an increase in the PPV of the canine alerts to marijuana from 27% in trial 1 to 100% in trial 2 (Table 13) indicating a higher probability of detecting marijuana while now being able to ignore the hemp samples to which they had previously alerted.

Table 13. Trial 1 vs Trial 2 PPVs for alerts to marijuana.

PPV for Alerts to Marijuana in Trial 1 vs Trial 2		
Dog ID #	**Trial 1**	**Trial 2**
3	50%	100%
4	17%	100%
5	20%	100%
16	20%	100%
Combined PPV	**27%**	**100%**

4.4.3 Operational Training

As it is important to acclimatize dogs to the environments in which they are expected to encounter target odors, the canine teams have now transitioned into operational training for discrimination of hemp and marijuana. shows the response of two dogs to a vehicle containing both hemp and marijuana during a recent training session. Hemp was hidden in both the gas cap and rear bumper with marijuana in the front right quarter panel. Both dogs performed a complete vehicle search beginning at the left side then continuing to the rear and right side of the vehicle. There were alerts to only marijuana with no interest in either of the hemp hides.

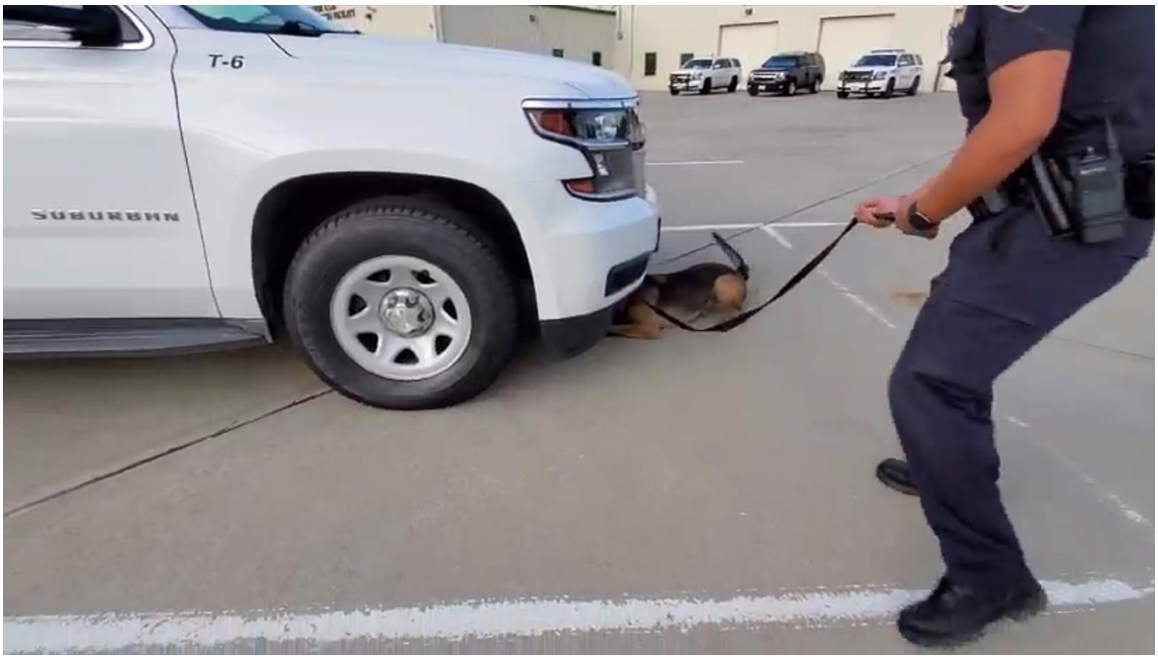


Figure 44. Dog 1 alerting to the marijuana hide in the front right quarter panel of a vehicle.

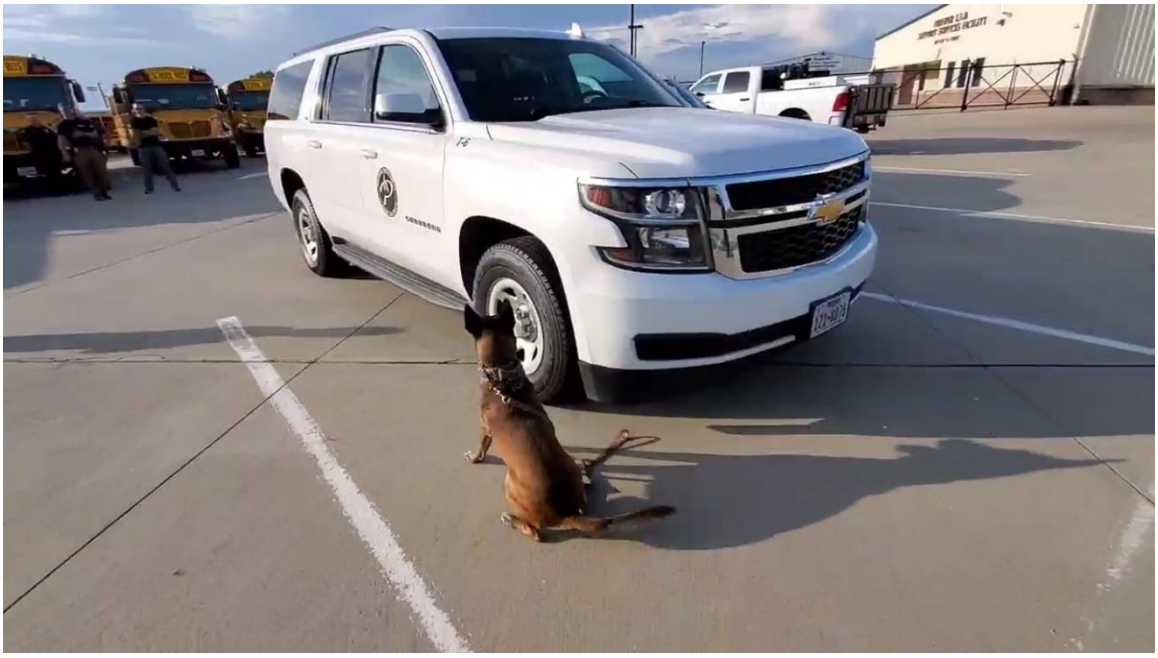


Figure 45. Dog 2 alerting to the marijuana hide in the front right quarter panel of a vehicle.

It is important to note based on the results in this study, that dogs can discriminate between hemp and marijuana despite both substances containing THC. There is a common misconception within the canine community that the presence of THC would prevent discrimination of the two. However, THC is an essentially non-volatile compound having a very low vapor pressure. It has been observed that dogs tend to respond to the more volatile compounds in a substance as these compounds are readily available in the vapor phase under ambient temperature and pressure [90], [154], [89] . In the case of *Cannabis*, dogs would instead be imprinted on the more volatile terpenes and respond to these VOCs [155] . Consequently, differences in these more volatile compounds can allow for discrimination between hemp and marijuana.

4.5 Efficacy of Current Marijuana Canine Training Aid Mimics and its Effects on the Response of Dogs to both Hemp and Marijuana

Illicit drugs are not always readily available for canine teams to train and maintain proficiency. Depending on the agency, only a head trainer within the agency or a certified outside trainer may possess the license to handle these drugs. As a result, training sessions are very limited. The use of commercial training aid mimics or "pseudos" have often been used to circumvent this issue. Pseudo training aids essentially mimics the odor of the substances. This is most often achieved by first determining the headspace VOCs then obtaining those chemical compounds and mixing them in an absorbent material. Other methods employ trapping the VOCs directly from the substance onto a material that will later release the VOCs to the dog for training. These pseudos are available not only for illicit drugs but also for explosives as well.

The legalization of hemp has also raised the question about the specificity of current marijuana training aid mimics. These aids can now potentially function as a dual training aids for both substances. To investigate this, two commercial marijuana training aids were first purchased, one from Scentlogix and the other from Sigma Aldrich. The VOC profile of both training aids were analyzed and the Scentlogix aid was chosen for canine imprinting since it's VOCs showed more consistency with known marijuana VOCs [156][157] . Figure 46 and Figure 47 shows the chromatograms of Sigma and Scentlogix training aids along with confirmed VOCS in Table 14 and Table 15. The method used for HS-GCMS analysis was based on the method development for hemp and marijuana products in the next section 4.6.

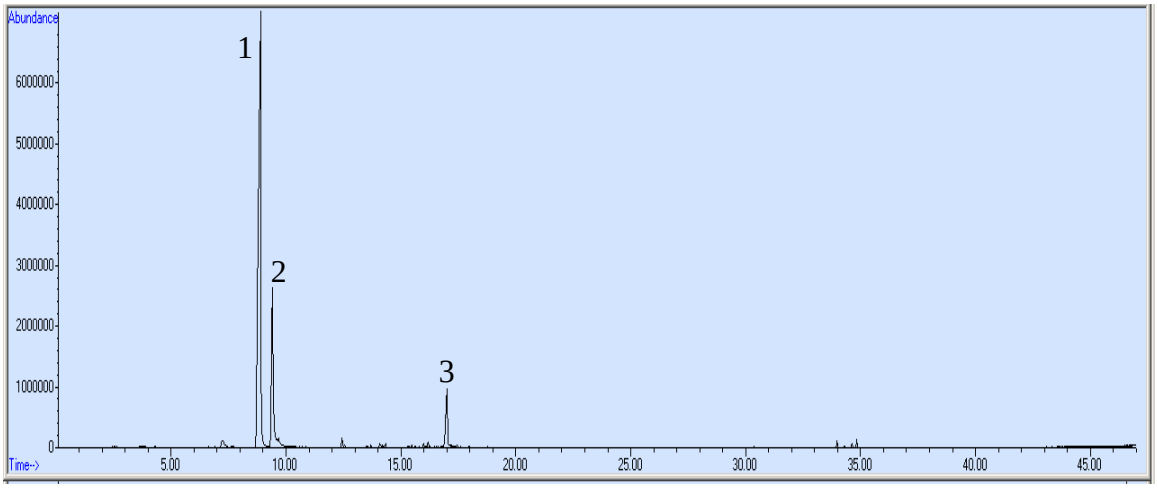


Figure 46. Chromatogram of Sigma Marijuana canine training aid mimic.

*Table 14. VOCs associated with Sigma Marijuana canine training aid mimic. * Indicates VOCs confirmed by both the NIST 2017 mass spectral library and an analytical standard (Appendix E).*

Peak number	VOCs
1	gamma-terpinene*
2	para-Cymene
3	2,3-Butanediol

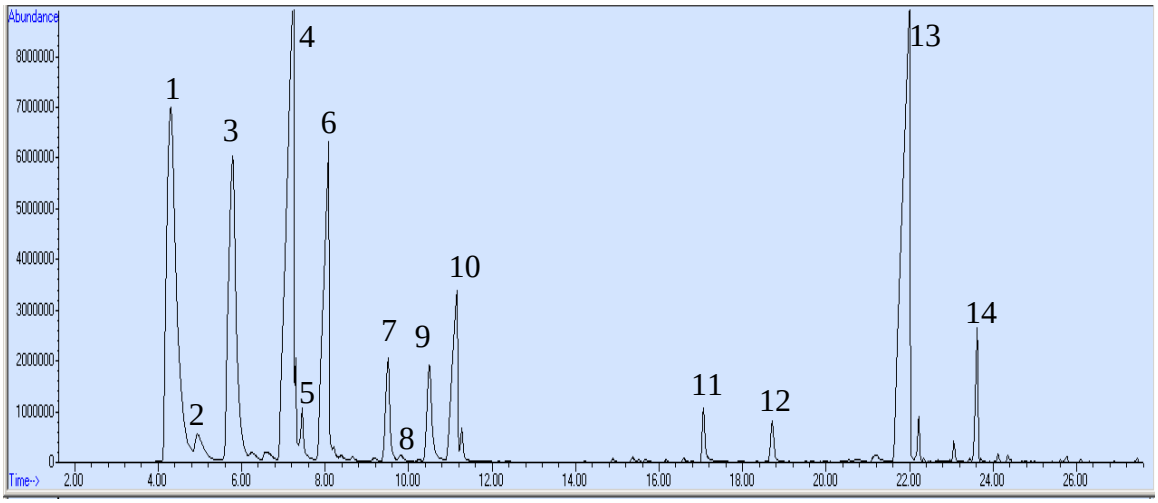


Figure 47. Zoomed in chromatogram of the Scentlogix marijuana canine training aid mimic.

*Table 15. VOCs detected in the Scentlogix marijuana training aid mimic. * Indicates VOCs confirmed by both the NIST 2017 mass spectral library and an analytical standard (Appendix E).*

Peak number	VOC
1	alpha-Pinene*
2	Camphene*
3	beta-Pinene*
4	beta-Myrcene*
5	alpha-Terpinene*
6	D-Limonene*
7	gamma-Terpinene*
8	beta-Ocimene*
9	para-Cymene*
10	alpha-Terpinolene*
11	alpha-Copaene
12	para-Cymenene
13	beta-Caryophyllene*
14	alpha-Humulene*

4.5.1 Trial Setup and Results

For this trial a "green" dog that had never been used for any form of odor detection was selected and trained. Training was conducted by a certified law enforcement canine trainer. The dog was first imprinted on the Scentlogix training aid after which maintenance training was conducted 2-3 times per week for 6 weeks. During the six-week period it was ensured that the dog did not come into contact with any form of *Cannabis* odor. After the 6-week period the dog was deemed proficient by the trainer for the trial stage.

The trial was blind to the dog-handler team and consisted of an odor recognition test (Scentlogix pseudo) and four lineups. Two of the four lineups contained marijuana and the other two contained hemp. Each lineup consisted of one *Cannabis* substance (marijuana or hemp), two blanks and two additional distracting odors. Distracting odors included orange peels, banana peels, cigarettes, dog treats, hemp rolling paper, cat food, hemp gummies, hemp seeds, CBD oil and thyme (Appendix A). All substances were placed in metal cans (identical to those used for the hemp trial in section 4.2) with perforated holes approximately 30 minutes prior to the trial. Table 16 shows the complete trial setup along with the results. Results showed that the dog alerted to both hemp and marijuana products with no responses to either blanks or additional distracting odors. As hypothesized the training aid did in fact function as a dual training aid enabling the dog to detect both marijuana and hemp.

Figure 48. Dog alerting to hemp product 6 in lineup #2.

Table 16. Setup and results of the Scentlogix marijuana training aid mimic dog trial. Unchecked boxes indicates no response.

	ORT				
	A1	A2	Blank	Blank	MJ Mimic
Response					Alert
	Lineup #1				
	A3	Marijuana	A4	Blank	Blank
Response		Alert			
	Lineup #2				
	Blank	A5	Hemp 6	Blank	A6
Response			Alert		
	Lineup #3				
	A7	Marijuana	Blank	A8	Blank
Response		Alert			
	Lineup #4				
	Blank	A9	A10	Blank	Hemp 2
Response					Alert

4.6 HS-SPME-GC-MS Analysis of Marijuana and Hemp

4.6.1 Materials and Method Development

The first part of the method development involved the development of a reliable GC-MS method for the detection of both marijuana and hemp VOCs. An Agilent 6890 Gas chromatograph fitted with a polar Polyethylene Glycol (PEG) Solgel Wax 0.25mm ID x 30m column coupled to a 5973N Mass Selective Detector was the instrument of choice. Table 17 shows the initial GC oven parameters used for analysis. The oven was set to 40 ˚C then ramped at 5˚C/min until a final temperature of 250 ˚C was reached. The final oven temperature was determined by the maximum operating temperature of this column which is around 270 ˚C The sample inlet port was set to 270˚C (maximum operating temperature for DVB/CAR/PDMS fibers described below) with the GC-MS transfer line set at 280 ˚C. The MS was run in positive ion ESI mode with a scan range of 40-500 m/z.

Table 17. The initial GC oven parameters for analysis of Cannabis samples.

GC Oven Parameters			
Temp	˚C/min	Next ˚C	Hold (min)
Initial Temp		40	
Ramp 1	5.00	250	

For sampling, 1-gram of hemp sample number 1 was used. Since hemp is legal and easily available, hemp was used in the method development for the detection of both hemp and marijuana. Divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) 50/30µm SPME fibers were used as this fiber allows for the extraction of the widest molecular weight range of VOCs. Figure 49 shows the general extraction setup. Samples were placed and tightly sealed in 8oz mason jars with lids containing silicone rubber septa and allowed to equilibrate for 24 hours. Fibers supported by the ring stand and clamp were then inserted via the rubber septa for a 24-hour period. After VOC extraction, SPME fibers were removed and inserted into the GC inlet port for 3 minutes to allow sufficient time for compounds to desorb off of the fiber and into the GC column for separation.

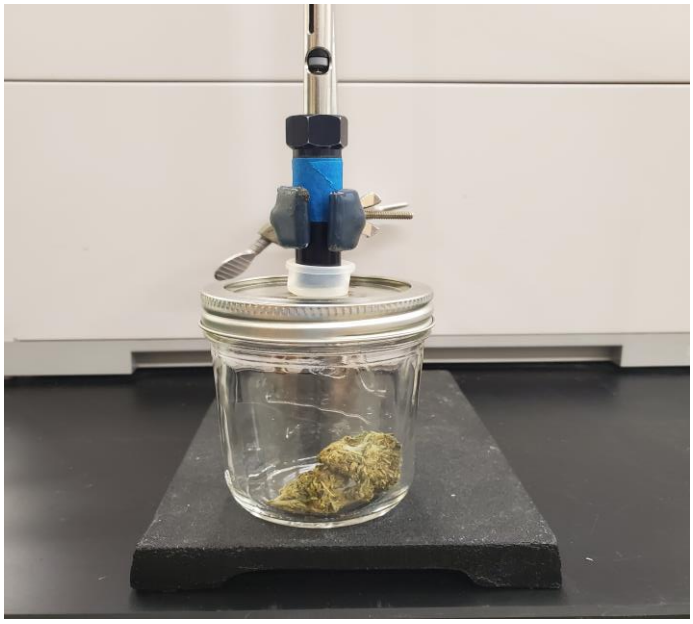


Figure 49. HS-SPME sampling process for hemp and marijuana.

Figure 50 (a) shows the chromatogram that was obtained with a high concentration of peaks between retention times 16-22. As a result of insufficient peak resolution in this region

(Figure 50 (b)), a 5-minute isothermal hold was added at 120 ˚C for subsequent analysis. Part (c) shows the results of this isothermal hold which allowed for better peak separation. Table 18 shows the final GC oven parameters for the analysis of *Cannabis* samples.

Table 18. The final GC oven parameters for analysis of Cannabis samples.

GC Oven Parameters			
Temp	˚C/min	Next ˚C	Hold (min)
Initial Temp		40	
Ramp 1	5.00	120	5
Ramp 2	5.00	250	

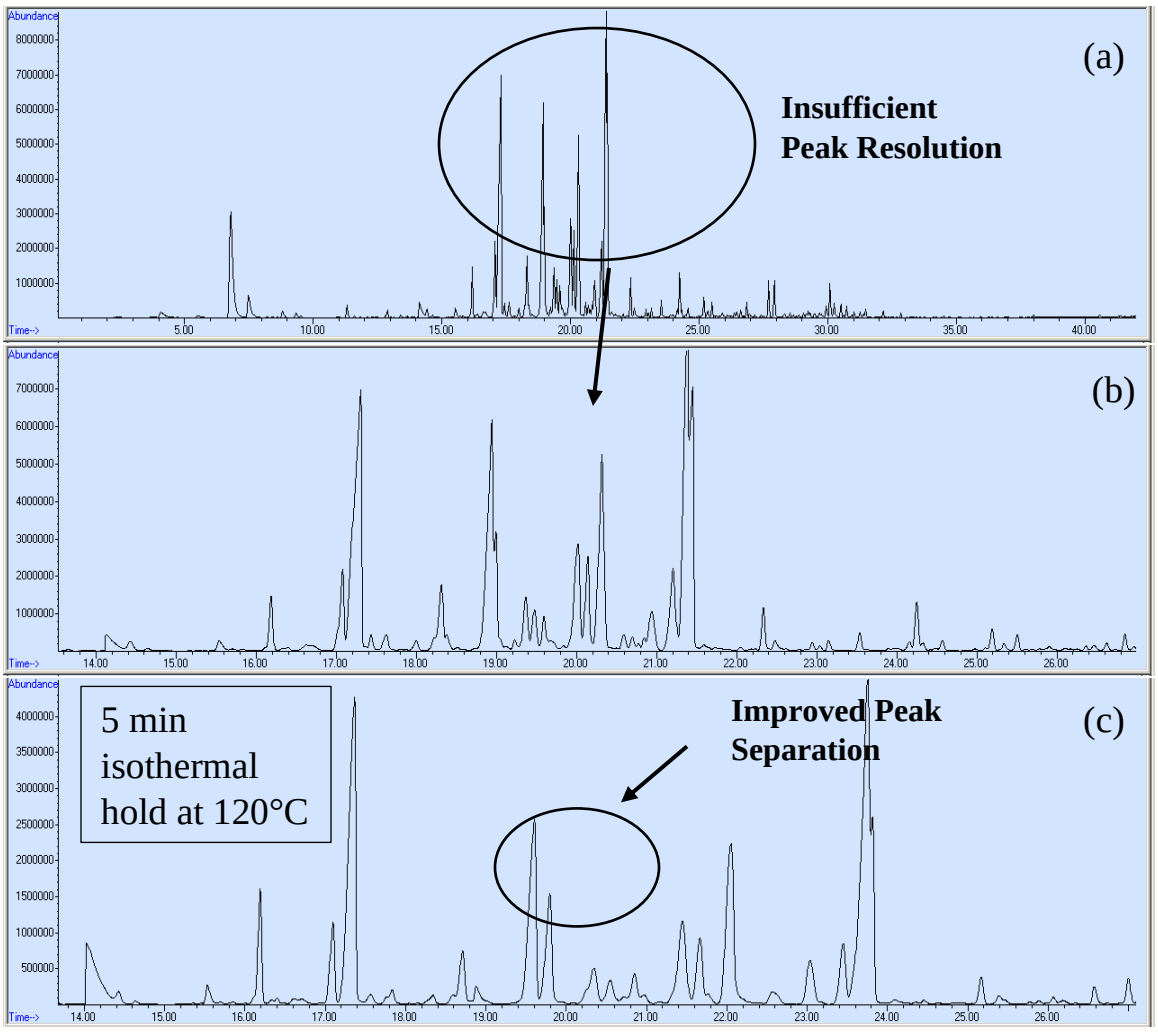


Figure 50. Chromatograph obtained from the initial GC method (a) showing insufficient peak resolution (b) between retention time 16-22minutes. The addition of a 5-minute isothermal hold at 120°C (c) resulted in overall improved peak separation.

The next phase of method development involved determining the optimum HS-SPME extraction time (Figure 51). A range of shorter extraction times, 5 minutes, 30 minutes and 1 hour were performed and compared. These shorter times did not allow for extraction of a wide range of compounds, particularly those that were less volatile, with no compounds being observed after a retention time of 24 minutes. As a result, the 24-hour extraction was selected for further analysis of all samples to be analyzed. Additionally, the longer extraction time still allowed for lower molecular weight compounds to be detected which is important as competition for fiber can occur overtime with the lower molecular weight compounds being displaced due to the limited extraction capacity of a SPME fiber. Therefore, depending on the application, optimum extraction times should provide a balance between extracting both high and low molecular weight compounds. It is also possible to utilize several extraction times for a particular sample in order to overcome this limitation.

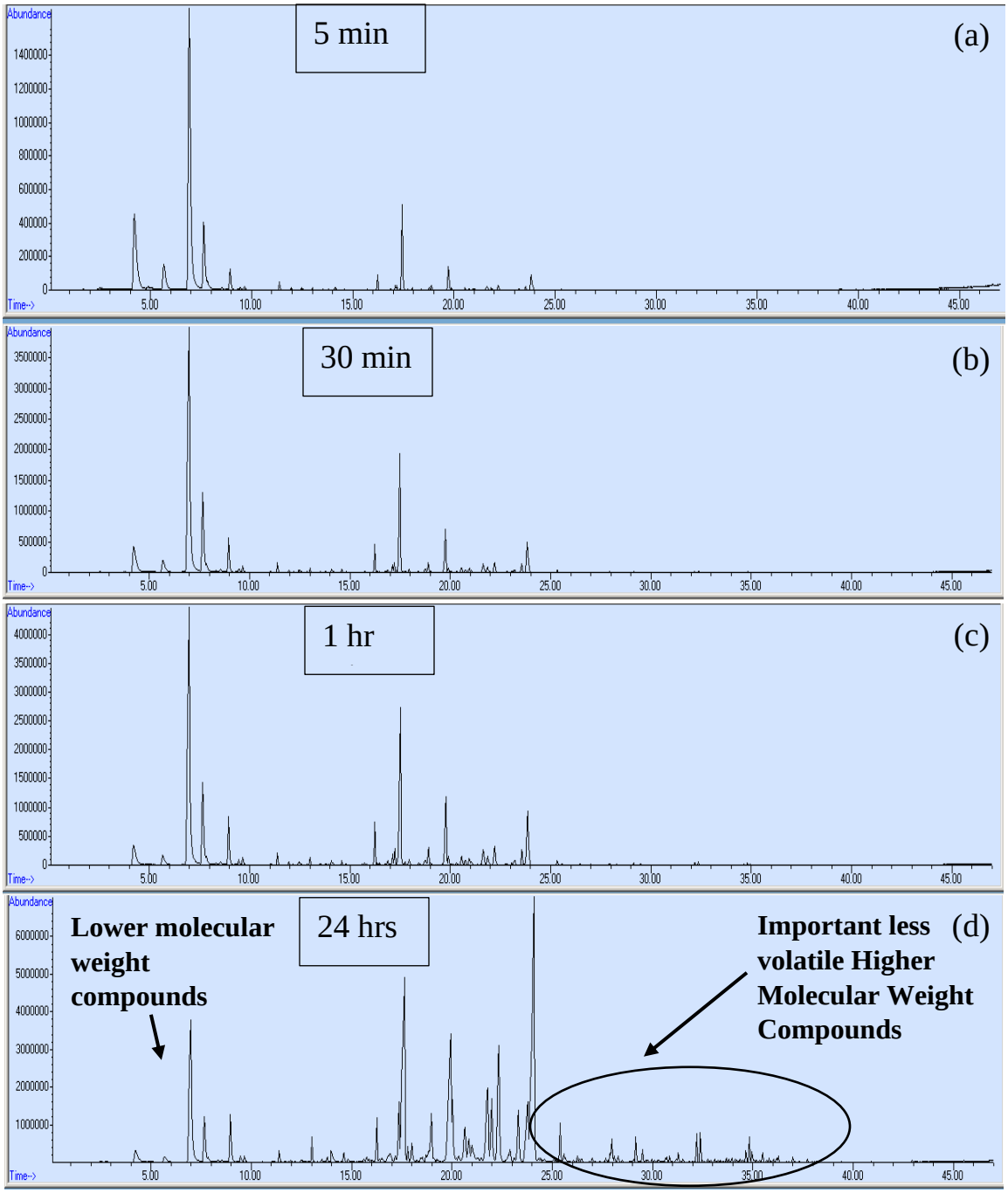


Figure 51. Chromatograms showing the comparison of HS-SPME extraction times; (a) 5 minutes, (b) 30 minutes, (c) 1 hour and (d) 24 hours for hemp samples.

A total of 12 samples were analyzed which included four marijuana samples and hemp samples 1-8. All samples were subjected to the same parameters as discussed above from the method development. Samples of marijuana were sampled offsite while all hemp samples were sampled in the laboratory at Florida International University. Blank controls were analyzed for each sample in order to rule out accidentally confirming any exogenous compounds. The identity of all VOCs were confirmed by comparison to a NIST 2017 mass spectral library with some VOCs additionally confirmed using commercially available analytical standards (Appendix E).

4.6.2 Results and Analysis

Table 19 shows the list of confirmed VOCs for both hemp (H1-H8) and marijuana (MJ1-MJ4) samples and the respective samples in which they were detected. The identity of all VOCs were confirmed by comparison to a NIST 2017 mass spectral library with some VOCs additionally confirmed using commercially available analytical standards (Appendix E).

The results shows that hemp and marijuana do in fact share similar VOCs which would allow for similarities in their overall odor profiles. There are a couple important observations to note from the VOC table below with respect to Trial 1 in Section 4.2 and the marijuana pseudo trial in Section 4.5. Hemp product number 8 had the least number of VOCs in common with hemp and marijuana which might provide an explanation the lowest combined alert rate (25%) by dogs in Trial 1. The VOCs present in the Scentlogox marijuana pseudo (alpha pinene, beta pinene, beta myrcene, d-limonene, beta-ocimene, alpha-terpinolene, para-cymenene, alpha-copaene, beta-caryophyllene and alpha-

humulene) were also found in hemp samples and as such would explain why a dog imprinted on these VOCs can elicit a response to hemp.

There were no unique VOCs that could be attributed to marijuana. Eight compounds: cosmene, alpha-gurjunene, guaiol, epi-gamma-eudesmol, gamma-eudesmol, agarospirol, alpha-eudesmol and beta-selinenol were present in the hemp samples that but not present in marijuana. With the exception of cosmene, these VOCs have however been reported in other studies analyzing marijuana and therefore cannot be attributed to only hemp [156], [158], [159]. As many strains of *Cannabis* exist (experts estimate over 700), VOC variations among studies is expected [160], [161], [162]. A total of 17 compounds (beta-pinene, beta-myrcene, d-limonene, benzaldehyde, linalool, fenchol, alpha-bergamotene, beta-Caryophyllene, alpha-humulene, cis-beta-farnesene, selina-3,7(11)-diene, 3,5,11-eudesmatriene, 4,5,9,10-dehydro- isolongifolene, caryophyllene oxide, humulene oxide II, humulenol-II and isoaromadendrene epoxide) were found to be consistent in all hemp and marijuana samples (hemp sample 8 was excluded as it is not pure hemp). Using the peak areas of these 17 compounds, PCA was used to assess the relationship between hemp and marijuana. Figure 52 shows the results of a PCA scores plot where complete separation of marijuana and hemp was not observed concluding that there were no differences between both group of samples.

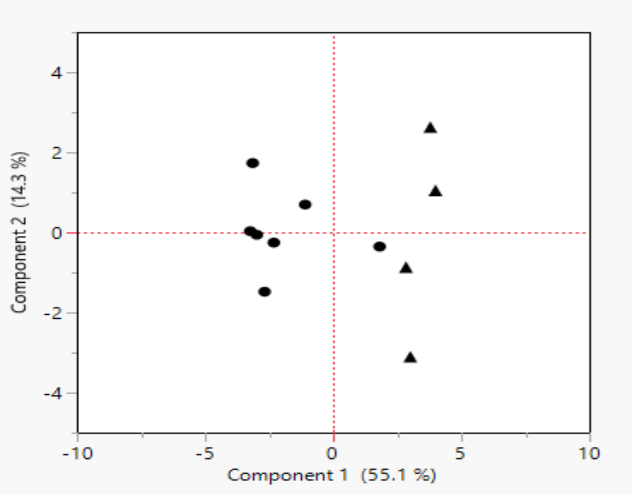


Figure 52. PCA scores plot for marijuana (▲) and hemp (●).

There were two main limitations with the samples used in this study. The first limitation was the small sample size (particularly for marijuana). Since many strains of *Cannabis* exist, a more extensive sample set with hemp and marijuana products must be evaluated in order to determine if any significant differences exist at the VOC level. Additionally, the use of complementary extraction methods (e.g., SPME fiber with different chemistry) to extract additional VOCs can be utilized as studies to date have in fact assessed over 200 VOCs associated with *Cannabis* [156]. The second limitation was the difference in age of both sample sets. Fresh hemp samples were purchased while the marijuana samples which were accessible for sampling were older (estimated to be 1-1.5 years old). As *Cannabis* samples age, the levels of the more volatile compounds can decrease which can result in lower limits of detection [163]. This might potentially explain why alpha-pinene which is a known marijuana VOC was only detected in 1 of the 4 marijuana samples .

*Table 19. Detected VOCs from HS-SPME GC-MS analysis of marijuana (MJ1-MJ4) and hemp (H1-H8). *Indicates VOCs confirmed by both a NIST 2017 mass spectral library and an analytical standard (Appendix E).*

Compounds	MJ1	MJ2	MJ3	MJ4	H1	H2	H3	H4	H5	H6	H7	H8
alpha-Pinene*				X	X	X	X	X	X	X	X	
beta-Pinene*	X	X	X	X	X	X	X	X	X	X	X	
beta-Myrcene*	X	X	X	X	X	X	X	X	X	X	X	X
D-Limonene*	X	X	X	X	X	X	X	X	X	X	X	X
trans-beta ocimene		X				X	X	X	X	X		
beta-Ocimene*	X	X			X	X	X	X	X	X	X	
alpha-Terpinolene*		X			X	X					X	
Sulcatone	X	X	X	X			X	X	X	X	X	X
Neo-allo-ocimene		X			X	X	X	X	X	X		
para-cymenene	X	X		X	X	X	X	X	X	X	X	
Cosmene					X	X	X	X	X	X		
Ylangene	X	X		X	X	X		X	X	X	X	X
Copaene		X		X	X	X		X	X		X	
Benzaldehyde	X	X	X	X	X	X	X	X	X	X	X	X
alpha-Gurjunene					X		X		X			
Linalool*	X	X	X	X	X	X	X	X	X	X	X	X
Selina-5,11-diene	X	X	X						X		X	
cis-alpha-Bergamotene				X	X	X	X	X	X	X	X	X
Fenchol	X	X	X	X	X	X	X	X	X	X	X	X
alpha-bergamotene	X	X	X	X	X	X	X	X	X	X	X	
beta-Caryophyllene*	X	X	X	X	X	X	X	X	X	X	X	X
Guaia-6,9-diene	X	X	X	X	X	X		X		X	X	
alpha-humulene*	X	X	X	X	X	X	X	X	X	X	X	
cis-beta-farnesene	X	X	X	X	X	X	X	X	X	X	X	
4a,8-dimethyl-2-(prop-1-en-2-yl)-1,2,3,4,4a,5,6,7-octahydrohaphthalene			X	X	X	X			X	X	X	

alpha-terpineol	X	X	X	X		X	X	X	X	X	X	
beta-Selinene	X	X	X			X		X				X
alpha-selinene	X	X	X	X	X	X	X	X	X	X		X
alpha-himachalene				X	X	X		X	X	X	X	X
gamma-muurolene	X	X		X	X	X		X	X		X	X
Selina-3,7(11)-diene	X	X	X	X	X	X	X	X	X	X	X	X
beta-Maaliene	X	X	X	X	X	X		X	X	X	X	
Calamenene	X	X	X	X				X	X	X	X	
3,5,11-Eudesmatriene	X	X	X	X	X	X	X	X	X	X	X	X
alpha-Patchoulene	X	X			X	X	X		X	X	X	
alpha-calacorene	X	X	X	X	X	X		X	X		X	
Isolongifolene, 4,5,9,10-dehydro-	X	X	X	X	X	X	X	X	X	X	X	
Cadina-1(10),6,8-triene	X		X			X			X	X	X	
Caryophyllene oxide*	X	X	X	X	X	X	X	X	X	X	X	X
Humulene oxide II	X	X	X	X	X	X	X	X	X	X	X	X
E-Nerolidol*	X	X	X	X	X	X	X	X	X	X		X
alpha-Corocalene	X	X	X	X	X	X		X	X	X	X	
Guaiol*					X	X	X	X	X	X	X	X
epi-gamma-Eudesmol					X	X	X	X	X	X	X	X
Selin-6-en-4α-ol	X			X	X	X		X	X			
gamma-Eudesmol					X	X	X	X	X	X		
Agarospirol					X	X		X	X	X		X
beta-Guaiene			X		X	X	X		X			
alpha-Bisabolol*	X	X		X							X	
alpha-Eudesmol					X	X	X	X	X	X		
beta-Eudesmol					X	X	X	X	X			
3,5,11-eudesmatriene	X	X	X	X	X	X		X	X	X	X	
β-Guaiene	X	X	X	X		X	X					
Humulenol-II	X	X	X	X	X	X	X	X	X	X	X	X
Isoaromadendrene epoxide	X	X	X	X	X	X	X	X	X	X	X	

4.7 Conclusions and Recommendations for Future Work

This study demonstrated that dogs that are previously trained to detect marijuana, can also alert to hemp as shown from the results of trial 1. However, dogs that are trained on marijuana can be further trained to accurately differentiate between the two substances providing that the correct training methodologies are applied as shown from the results of trial 2. Documentation of this training can provide legal assistance for canine teams currently trained to detect marijuana as this can demonstrate the dog's reliability in alerting only to an illicit substance, hence preserving probable cause for a search.

With regards to the use of current commercially available marijuana canine training aids mimics, caution should be exercised with their use as analysis revealed similar VOC profiles of these aids and hemp. Training on these marijuana pseudo aids may result in the dog also alerting to hemp due to lack of specificity. Further analytical research is needed with larger sample sets in order to determine if there are any significant VOC markers that can be used to create a mimic that is specific to marijuana to aid in further enhancing a dog's ability to differentiate between marijuana and hemp.

5. INVESTIGATION OF THE VOCS ASSOCIATED WITH TRIACETONE TRIPEROXIDE (TATP) USING HS-SPME-GC-MS AND THE EFFICACY OF TRAINING AID MIMICS

5.1 Introduction

With many traditional explosives, detection via vapor sampling is not possible due to very low vapor pressures. Consequently, as discussed earlier in Table 5, volatile byproducts and taggants are used as target chemicals for their detection. Investigating the VOC profile of explosives have therefore been a key area of research for vapor detection in not only instruments but also detector dogs. Previous research has demonstrated that dogs can in fact be trained on these volatile compounds to successfully locate explosives [164] [92]. VOCs of explosives have been the basis for many training aid mimics that are used for maintenance training of detector dog teams. Some of these mimics can utilize a single VOC (e.g., taggant) or a combination of VOCs to increase the dog's acuity to the explosive. It is important that these aids are similar with respect to odor availability and in the case of multiple VOCs, be in the correct ratios as these factors can affect overall canine odor perception. Scientific validation of these aids is therefore paramount This task explored the VOCs associated with TATP as well as analyzed commercial training aid mimics with the goal of offering recommendations for optimum training methods for dogs.

5.2 HS-SPME-GC-MS analysis of TATP

5.2.1 Method Development

The first task was the development of a reliable GC-MS method for the detection of TATP. An Agilent 6890 Gas chromatograph fitted with a non-polar DB-5ms (5%-phenyl-methylpolysiloxane) 0.32mm ID x 30m column was used which was coupled to a 5973N Mass Selective Detector was the instrument of choice. A 100 parts per million (ppm) standard of TATP in an acetonitrile solvent was first prepared. Part of the sample was then transferred to a 2mil vial and placed into the GC autosampler. The GC inlet was set at 270 ˚C and was run in split mode with a 10:1 split ratio of sample to solvent and with an injection volume of 1µl. The mass spectrometer transfer line was set at 300 ˚C and the MS was run in positive ion EI mode with a scan range of 40-500 m/z and a 5-minute solvent delay. Table 20 shows the GC oven parameters that was used for the analysis. Although the TATP standard was dissolved in acetonitrile, the GC oven was not set to start at a temperature higher than the boiling point of acetonitrile (82 ˚C) which is normally done for liquid standards to avoid solvent peaks in the chromatogram. This was because a comparable method was needed for both liquid samples and headspace samples. Since solid TATP samples were expected to contain highly volatile small MW compounds such acetone, an overall low starting temperature was needed for the method. As a result a 5-minute solvent delay was used. The oven was first set to 40 ˚C then ramped to 100 ˚C at 20˚C/min then held for 2 minutes after which it was ramped to 300 ˚C at 20˚C/min. Figure 53 shows the chromatogram results with TATP being detected at a retention time of approximately 6.2 minutes.

Table 20. GC oven parameters for the detection of TATP.

GC Oven Parameters			
Temp	˚C/min	Next ˚C	Hold (min)
Initial Temp		40	
Ramp 1	20.00	100	2
Ramp 2	20.00	300	

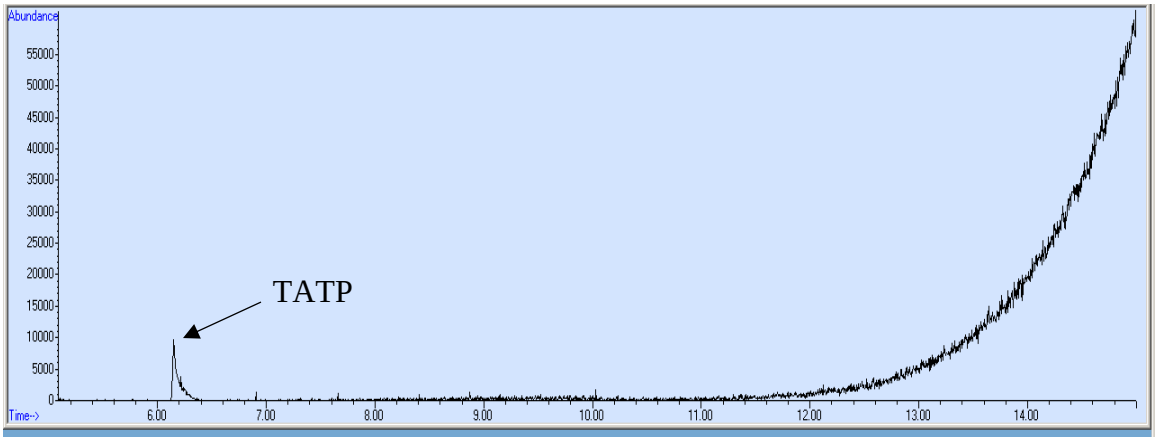


Figure 53. Chromatogram showing GC-MS detection of a 100ppm standard of TATP in acetonitrile with a retention time of approximately 6.2.

5.2.2 Analysis and Results of Solid TATP

Headspace analysis of TATP was conducted offsite at the Office of Naval Research in Washington DC. For sampling, approximately 800mg of TATP was placed into an explosive headspace sampling chamber (Figure 54). The sample was allowed to equilibrate for 1 hour after which the headspace was sampled in triplicate for 30 minutes using

DVB/CAR/PDMS fibers. Blank controls were also sampled in the same manner. It is important to note that the equilibrium and extraction times were estimated as determining optimum extraction parameters was not possible since sampling was done off site.

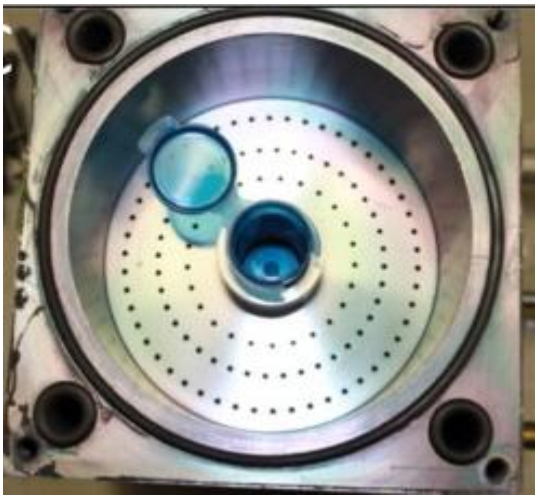


Figure 54. Opening of the explosive sampling chamber with an antistatic vial for sample placement [165].

After sampling was completed, SPME fibers were stored and shipped on ice to the laboratory at Florida International University. The ice served to ensure that there was no significant loss in VOCs during transport. Samples were then analyzed on the GC-MS using the method described in Table 20 with the only difference being the removal of the solvent delay and the split mode. Figure 55 shows the chromatogram results with two compounds being confirmed: TATP at a retention time of 6.2 minutes and acetone at a retention time of 1.6 minutes. It is worth noting that compared to traditional explosives which are essentially non-volatile, TATP has an appreciable vapor pressure at room temperature, allowing it to be the predominant VOC in the headspace. This results in

further challenges for the development of mimics as there are no non-explosive VOCs in the headspace. The use of precursors such as acetone or peroxide may not be feasible as this can result in unwanted and costly false alerts.

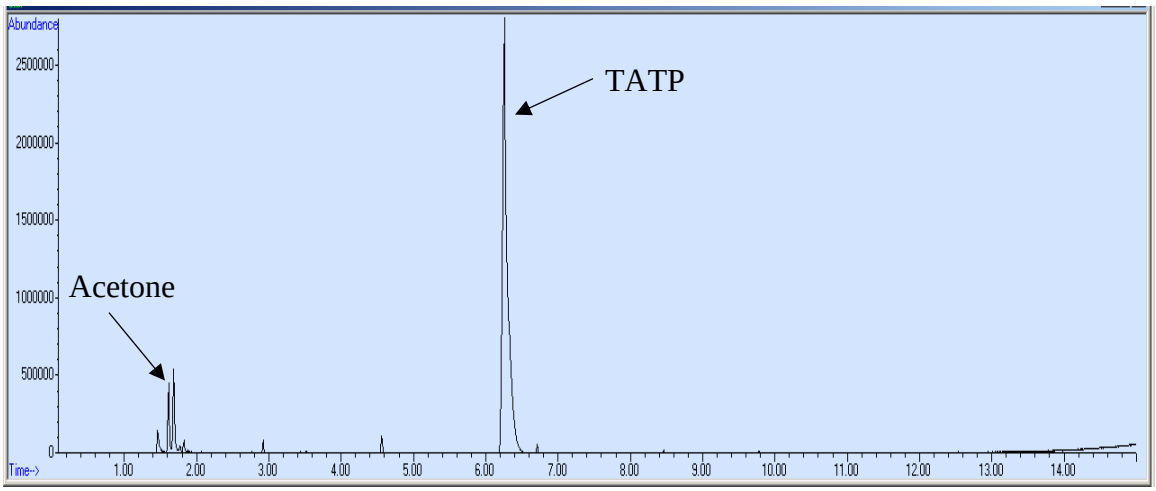


Figure 55. Chromatogram showing the HS-SPME-GC-MS Analysis of TATP.

5.3 Analysis of commercial TATP training aid mimics

Two commercial training aid mimics, one from Scentlogix and the other from Signature Science were obtained (Figure 56). Weights were approximately 1.6 grams and 52 grams respectively for Signature Science and Scentlogix.

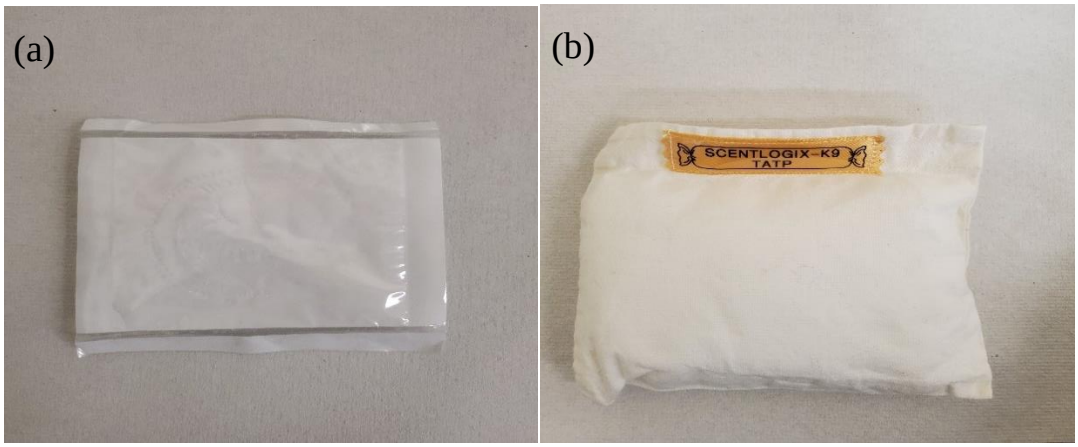


Figure 56. (a) Signature Science TATP pseudo and (b) Scentlogix TATP pseudo

Each training aid was placed in a sealed 8oz mason jar and allowed 1 hour for equilibration. A 30-minute HS-SPME extraction was then performed using DVB/CAR/PDMS SPME fibers.

5.3.1 HS-SPME-GC-MS Results

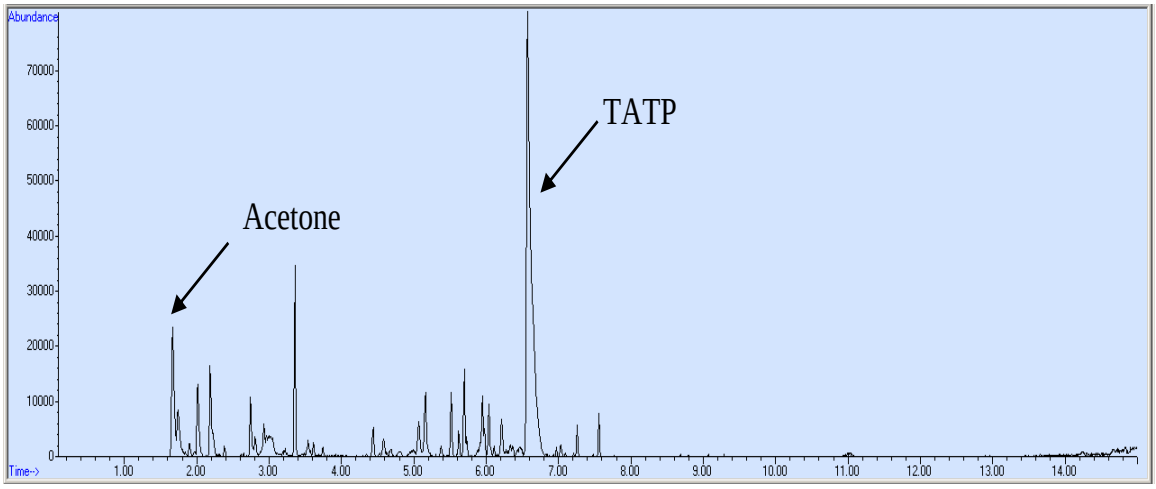


Figure 57. Chromatogram of Signature Science TATP training aid mimic

Table 21. The VOCs associated with the Signature Science TATP training aid mimic.

Peak number	VOC
1	Acetone
2	Tetrahydrofuran
3	Dimethylsilanediol
4	Toluene
5	Trimethylamine
6	Neohexane
7	Decane
8	2,2,4,6,6-pentamethylheptane
9	Hexadecane
10	2,2,3,4 trimethylpentane
11	TATP
12	3, methylundecane

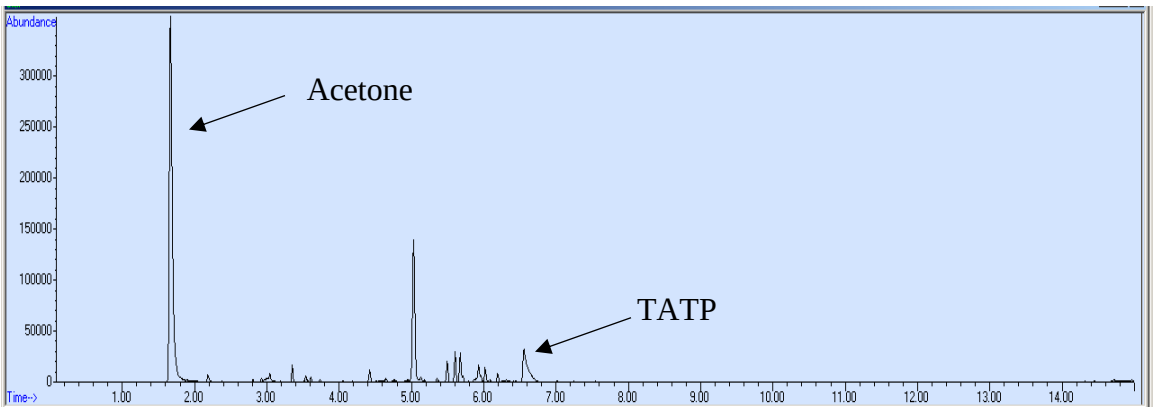


Figure 58. Chromatogram of Scentlogix TATP training aid mimic.

Table 22. VOCs associated with the Scentlogix TATP training aid mimic.

Peak number	VOC
1	Acetone
2	Diacetone alcohol
3	2,2,4,6,6-pentamethylheptane
4	TATP

Results for both training aids showed the presence of TATP and acetone in addition to other compounds with the Signature Science aid showing more confirmed compounds compared Scentlogix. Based on a literature search, these additional compounds in the signature science aid were most likely exogenous VOCs from the packaging materials and not part of the actual training aid. Tetrahydrofuran, toluene and neohexene for example are used in plastics and adhesives. The Scentlogix training aid showed less exogenous compounds in comparison to signature science, however the abundance of TATP in comparison to acetone was significantly lower with acetone being the most abundant compound in the headspace. This is in contrast to the signature science aid where TATP was the most abundant. Figure 59 shows a comparison of the average (n=3) ratio of acetone and TATP in the headspace of an actual TATP sample compared to both training aids.

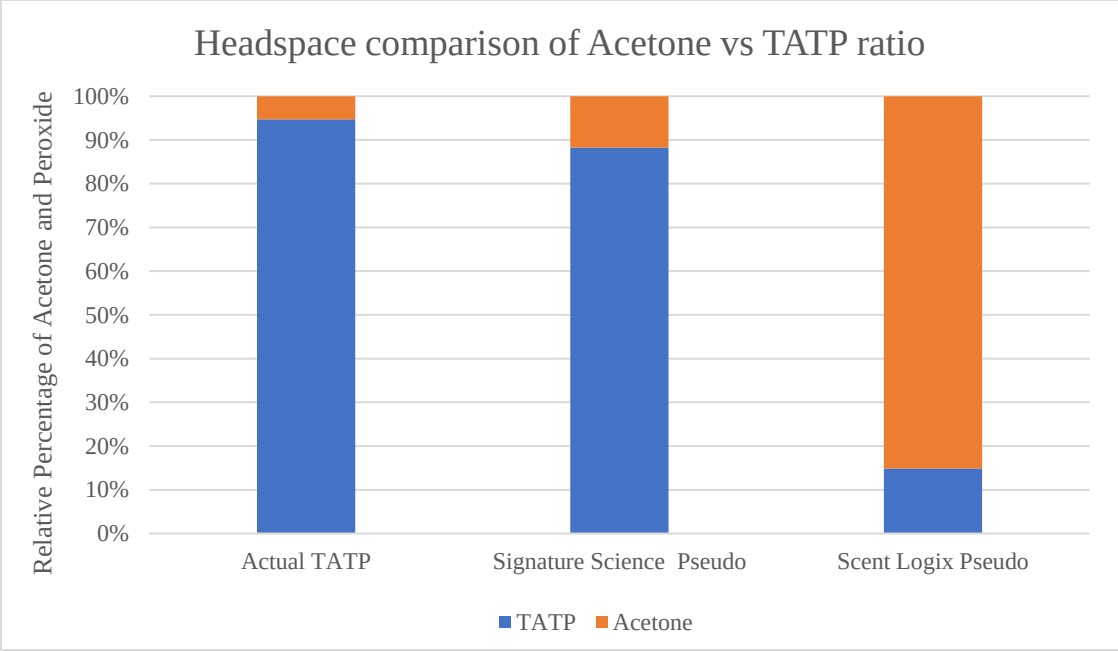


Figure 59. Comparison of the ratio of acetone and peroxide in an actual sample of TATP compared to Signature Science TATP mimic and Scentlogix TATP mimic.

It was observed that the Signature Science aid bore more much more similarity to TATP in terms of the ratio of acetone to peroxide in the sample. Using the Scentlogix training aid for imprinting or maintenance training may prove problematic as it known that dogs often respond to the more volatile VOC(s) of a sample that they are trained to detect [89]. This may result in unwanted and costly false alerts as the dog's olfactory system will become more sensitive to acetone over time. Full details regarding the actual manufacturing process of both training aids are unknown. However, Signature Science does make mention of an inert material in its blank (all of the components except the odor). It is surmisable that as with other explosive training aids, that aid consists of the actual explosive mixed with an inert material to render it non-explosive, hence the reason for its similarity to actual TATP.

5.3.2 Response of Dogs to Commercial TATP Training Aids, Acetone and Peroxide

This goals of this task was twofold. The first goal was to determine how explosive detection dogs who had been trained on TATP would respond to the commercial training aids. The second goal was to observe how these dogs would respond to samples of acetone and peroxide as they are both precursor materials to TATP which are more volatile and are also present in the headspace (peroxides are not detectable by GC-MS unless it is derivatized). Despite TATP being more abundant, dogs might be imprinted on these compounds as their volatility might allow for it to be more readily available in the headspace, hence overshadowing TATP.

Two law enforcement dogs that were previously imprinted on TATP were used for this trial. The trial consisted of four metal can lineups. Lineups consisted of two blanks, two distractors and either the signature science TATP training aid, Scentlogix TATP training aid, acetone (99%) or hydrogen peroxide (30%). Acetone and peroxide samples were prepared by spiking 100µl of the compound on a gauze pad. Distractors used were alpha pinene, limonene, benzaldehyde and methyl benzoate. All lineups were conducted in a blind fashion and the position of blanks and odors randomized. Odor recognition tests prior to the start of the trial were not possible due to actual TATP not being available.

Dog 1 alerted to both training aids, acetone and hydrogen peroxide with one false alert to a distractor in the peroxide lineup. Dog 2 alerted to both training aids with no alerts to acetone and hydrogen peroxide and one false alert to a distractor in the Scentlogix mimic lineup. Assuming both training aids, acetone and hydrogen peroxide as true positives for

dogs who alerted, Table 23 below provides the positive predictive values for alerts of both dogs. Appendix G contains the complete trial setup and results.

Table 23. PPV of alerts to Scentlogix TATP mimic, Signature Science TATP mimic, acetone and peroxide.

	PPV	
	Dog #1	Dog #2
Scentlogix TATP	100%	50%
Signature Science TATP	100%	100%
Acetone	100%	-
Hydrogen Peroxide	50%	-

The differences in response of dogs to both acetone and peroxide may have been due to the overshadowing effect as previously mentioned. Also, it is known that mixtures can be perceived configurally (as an entire unit) or elementally (individual odors) depending on the chemistry of the compounds in question and can vary between subjects [166][167]. Dog 2 for example may have perceived the mixture of TATP, acetone and peroxide as an entire unit and might be less prone to alert to the individual components while dog 1 the opposite.

5.4 Conclusions and Recommendations for Future Work

As with all canine training aid mimics, mimics of TATP should ideally contain the correct VOCs in ratios that are reflective of the actual explosive in order to ensure accuracy and reliability of the dog. Failure to do achieve this may result in unwanted false positives or false negatives during canine testing or deployment. For dogs imprinted on TATP, overshadowing by the more volatile components may occur. It might also be hypothesized that proofing the dogs off of these individual components while reinforcing TATP might assist in decreasing unwanted false alerts to either substance. With regards to canine results from this study, further testing of a larger number of canines should be done in order to make any significant generalizations. It is also worth noting that the dogs used in this study had not undergone regular maintenance training on TATP since being imprinted. The last time both dogs had received training on TATP was approximately 8 months prior to this trial.

6. DETERMINATION OF THE VOCS ASSOCIATED WITH MASS STORAGE DEVICES USING HS-SPME-GC-MS AND THE RELIABILITY OF CURRENT DETECTOR DOG TRAINING METHODS

6.1 Introduction

The method of training dogs to detect mass storage devices (MSDs) varies greatly, with limited scientific work done to validate the practice or determine the mechanism by which these dogs detect these devices. As a result, theories as to the target material to be used for training are numerous, from training on entire devices for detection (e.g., cellular phone) to training on only portions of devices (e.g., lithium battery), creating even further variability and reliability in the detection capabilities of the canine.

The VOCs that dogs are alerting to in MSDs remain to be scientifically determined. In addition, devices may produce different VOCs depending on the model, make etc. This study analyzed the VOCs associated with a wide variety of mass storage devices including cellular telephones, hard drives, thumb drives, SD cards, SIM cards, CDs/DVDs as well as other controls. Additionally, the existence of two chemical compounds, hydroxycyclohexylphenyl ketone (HPK) and triphenylphospine oxide (TPPO) were investigated. Based on anecdotal accounts, HPK and TPPO are currently two signature chemicals for detector dog training of mass storage devices. These accounts however are filled with inconsistencies as trainers often have varying rationale for its use as well as the types of storage devices it can effectively be used to train for. Reports have speculated that TPPO is found in all circuit boards of electronic devices to prevent them from overheating while HPK can be found in removable media devices such as CDs, DVDs and floppy disks [168] [169].

6.2 HS-SPME-GC-MS Analysis of Mass Storage Devices

6.2.1 Materials and Method Development

The first part of this task involved the development of a reliable GC method for detection of VOCs. An Agilent 6890 Gas chromatograph fitted with a Polar Solgel Wax 0.25mm ID Column coupled to a 5973N Mass Selective Detector was the instrument of choice. Table 24 shows the initial GC oven parameters used for analysis. The oven was set to 40 ˚C then ramped at 6˚C/min until a final temperature of 250 ˚C was reached. The sample inlet port was set to 270˚C (maximum operating temperature for fibers described below) with the mass spectrometer transfer line set at 280 ˚C. The MS was run in positive ion EI mode with a scan range of 40-500 m/z.

Table 24. The GC oven parameters for the analysis of mass storage devices.

GC Oven Parameters			
Temp	˚C/min	Next ˚C	Hold (min)
Initial Temp		40	
Ramp 1	6.00	250	

For HS-SPME extraction, a TCL LX 4G LTE smartphone was utilized. Although several types of mass storage devices were used in this study, method development was based on cellular phones since this type of device was expected to have the most volatile compounds and overall number of VOCs based on its components. The cellular phone was placed in a

32oz mason jar, sealed and left for 24 hours to allow for equilibration between the sample and the headspace. The equilibration was then followed by a 24-hour SPME extraction using (DVB/CAR/PDMS) fibers. After extraction, the SPME fibers were removed and inserted into the GC inlet port for 5 minutes to allow sufficient time for compounds to desorb off the fiber and into the GC column for separation. Figure 60 shows the obtained chromatogram from this analysis. Due to sufficient peak resolution of extracted compounds, the GC method was deemed reliable and selected as the final method for analysis of all storage devices.

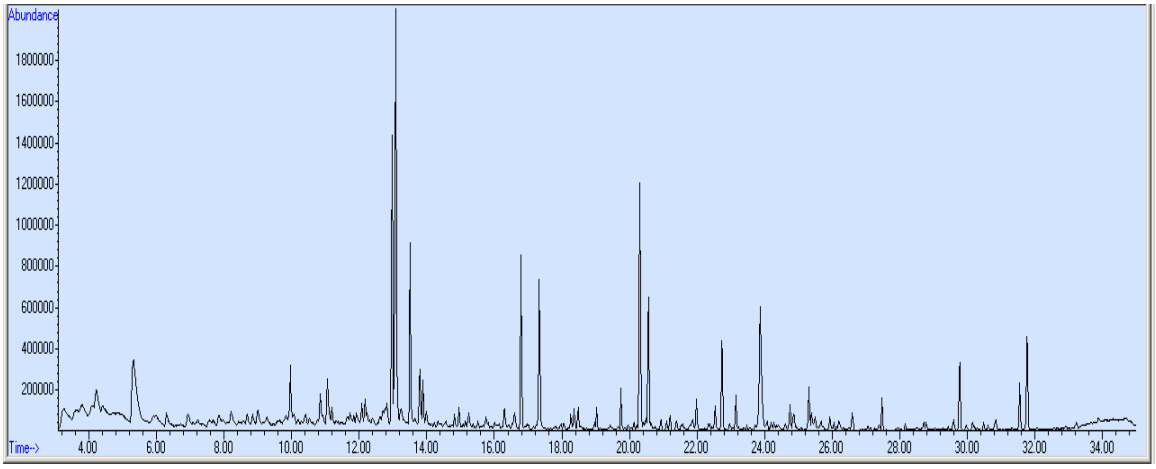


Figure 60. HS-SPME GC-MS chromatogram of a TCL LX 4G LTE smartphone.

The second part of the method development involved determining an optimal HS-SPME extraction time comparing short and long extraction times of 1 hour, 4 hours, 24 hours and 72 hours (Figure 61). As expected, these shorter times did not allow for sufficient extraction of a wide range of compounds. For example, 1-hydroxycyclohexyl phenyl ketone that will be discussed later in this section was not extracted with these shorter times.

Accordingly, a 24-hour extraction time was retained for all further analysis. Longer extraction times (72 hours) did not show any improvement in compound detection.

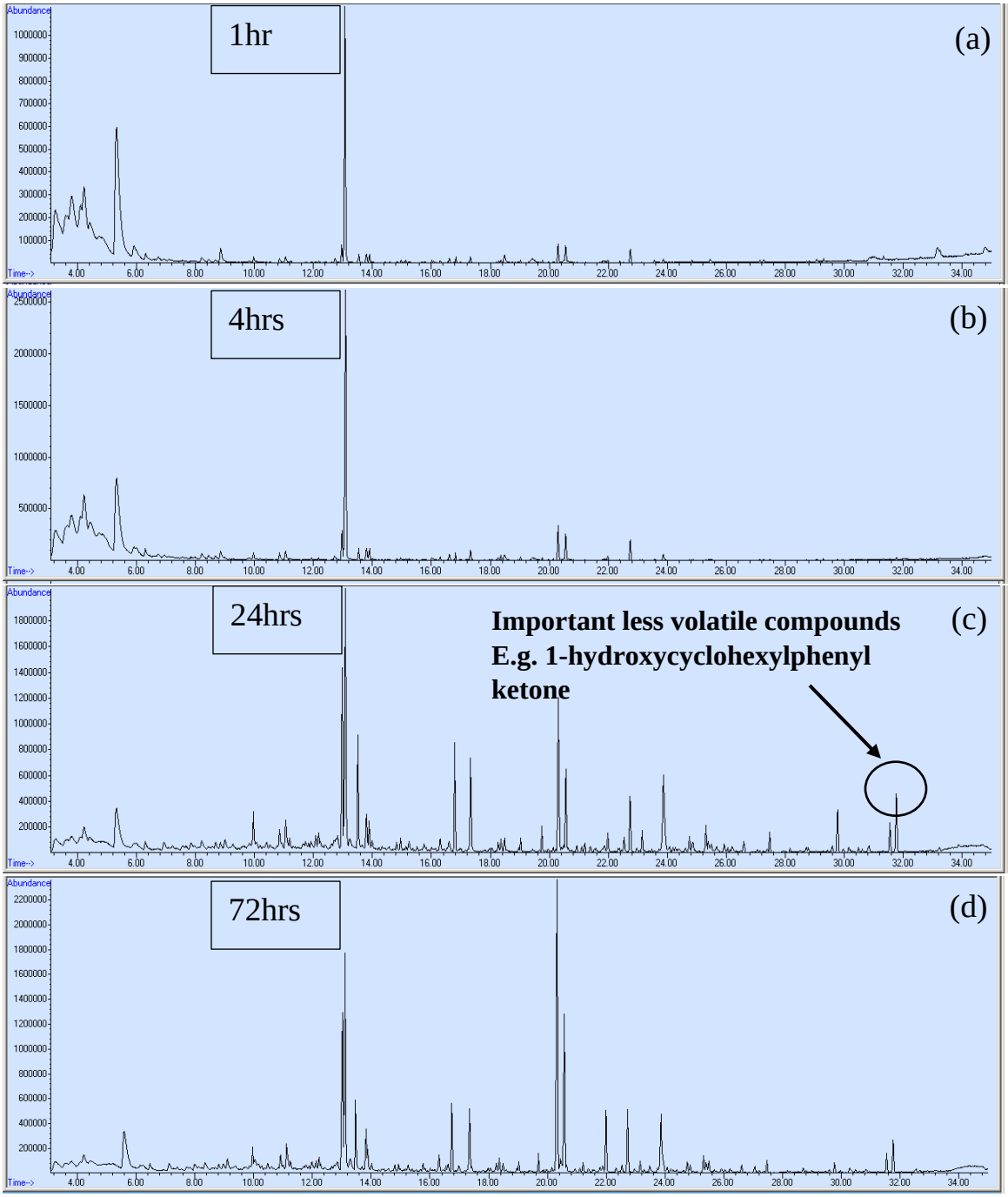


Figure 61. HS-SPME GC-MS chromatograms showing the comparison of extraction times: (a) 1hour, (b) 4 hours, (c) 24 hours and 72 hours.

Sampling containers varied depending on the storage device in question. This was selected based on the size of the device in order to allow for faster equilibration between the sample and headspace. Table 25 below provides a list of the sampling containers used for each type of device. All containers were cleaned by oven baking for at least 12 hours at 250 ˚C.

Table 25. Sampling containers for respective mass storage devices.

Device	**Sampling container**
Handheld devices	32oz Mason Jar
Sim/SD Cards	40ml glass vial
Thumb drives	8oz Mason Jar
CDs	1-gallon paint can
Hard drives	1-gallon paint can

The full list of mass storage devices analyzed in this study is listed in Table 26. Cellular phones and hard drives were obtained used, while thumb drives, SIM cards, CDs/DVDs and controls were new. All devices were first thoroughly cleaned with 91% isopropyl alcohol as this would have allowed for the removal of any background human imparted VOCs [170], [171]

Table 26. List and brands of mass storage devices for VOC analysis.

Cellular Phones	**Hard drives**	**Thumb drives**	**CDs/DVDs**	**SIM Cards**	**Controls**
Blackberry	Crucial (laptop)	No brand (#1)	TDK	Verizon	TV Remote
Nokia	Seagate (laptop)	No brand (#2)	Verbatin	At&t Go	MP3 player
Motorola	Samsung (laptop)	No brand (#3)	Memorex	T-mobile	Bluetooth car adapter
ZTE burner phone	Toshiba 1 (laptop)	No brand (#4)	Phillips	At&t	Mouse
Plum burner phone	Toshiba 2 (laptop)	No brand (#5)	Maxell	Tracfone	Charging hub
LG burner phone	Seagate 1 (desktop)				
LG escape smartphone	Samsung 2 (desktop)				
TCL smartphone					
I-phone-6s smartphone					
Samsung galaxy S6 smartphone					

6.2.2 Results and Analysis

Figure 62 to Figure 71 shows the relevant VOCs associated with cellular phones, hard drives, CDs, thumb drives and SIM cards along with VOCs deemed significant within each group. A VOC was considered relevant if it was detected in more than one sample for sample for sample sets n=5, and more than twice for sample sets n=7 and n=10. Table 28 lists the possible rationale for these compounds being present in mass storage devices based

on literature search. The identity of all VOCs were confirmed by comparison to a NIST 2017 mass spectral library with some VOCs additionally confirmed using commercially available analytical standards (Appendix F).

The most predominant compounds detected for each type of device included diethyl carbonate, benzyl alcohol, 2-phenoxyethanol and 1-hydroxycyclohexylphenyl ketone (HPK) for cellular phones; 1,3-dichlorobenzene, benzaldehyde, benzyl alcohol and 2-phenoxyethanol for hard drives; benzaldehyde, acetophenone, 2-hydroxy-iso-butyrophenone, 2-phenoxyethanol, benzophenone and 1-hydroxycyclohexylphenyl ketone for CDs; 3,5-ditert-butyl-4-hydroxybenzaldehyde, 4-hydroxy-4-methyl-2-pentanone and diethylene glycol hexyl ether for thumb drives; diethyl carbiol, dibutylformamide, diethyl pthalate and 2-phenoxyethanol for SIM cards. Some of these compounds such as HPK are consistent with those found in DeGreeff et al [172]. A few compounds such as 2-ethyl 1-hexanol, acetic acid and nonanal (also detected by DeGreeff et al.) that was originally believed to be associated with some of these devices were detected in blank samples and as a result were removed from the list of relevant compounds.

The results presented here indicates that mass storage devices, despite sharing some common VOCs, do appear to have characteristic combination of compounds that can allow for successful detection by trained dogs while also allowing for discrimination between other devices. Knowledge of these compounds can be the first step in possibly creating reliable mimics to increase a dog's specificity to a desired class of device.

Of the compounds detected, 1-hydroxycyclohexylphenyl ketone was of particular interest due to its increasing prevalence amongst dog trainers. As mentioned earlier, according to

reports, HPK can be used for the detection of CDs and other removable disks [169]. The analysis here did find that HPK is present in CDs and cellular phones but also in other controls such as MP3 players. Therefore, the use of this compound as a training device for mass storage devices should be treated with caution depending on the overall goal of the mission. If specificity is the goal, then using HPK can result in unwanted false alerts. However, if the goal is to detect a wide range of electronic devices, then using this compound for training might suffice. As seen in Table 27, not only HPK, but some of the other common VOCs detected in mass storage devices are also present in controls as well.

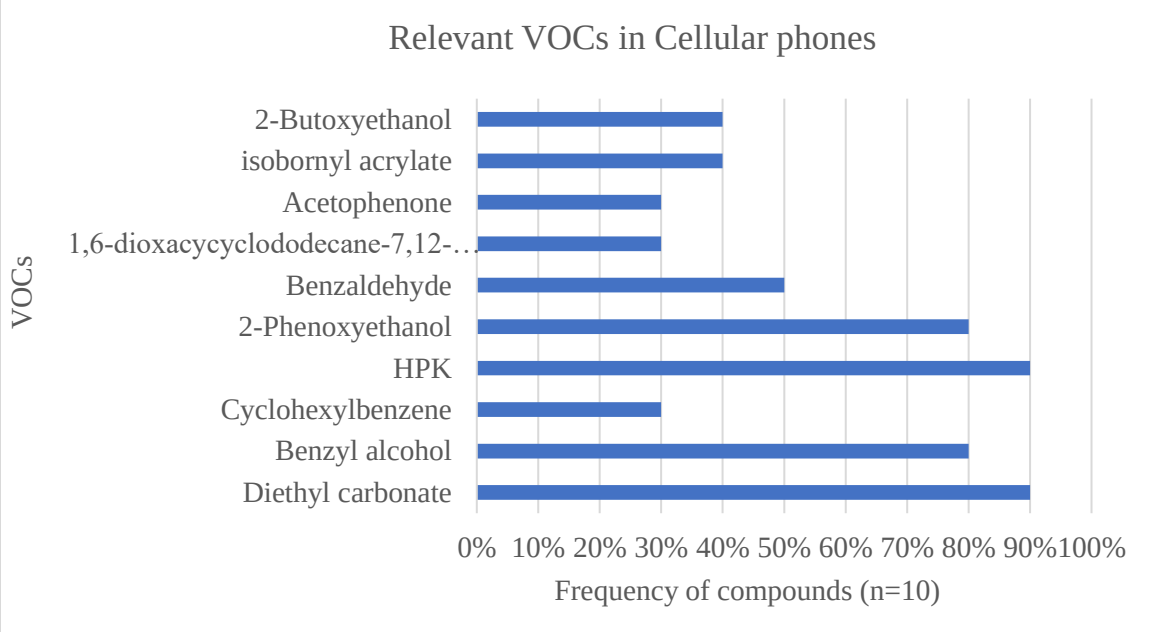


Figure 62. Relevant VOCs associated with cellular phones and their frequency (n=10).

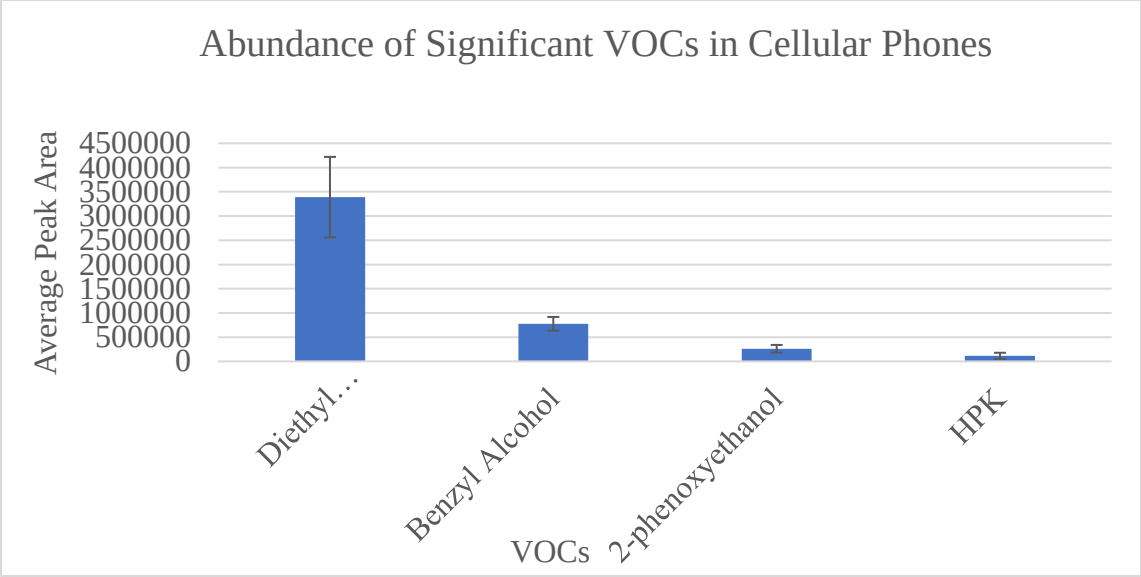


Figure 63. Abundance of Significant VOCs in Cellular Phones.

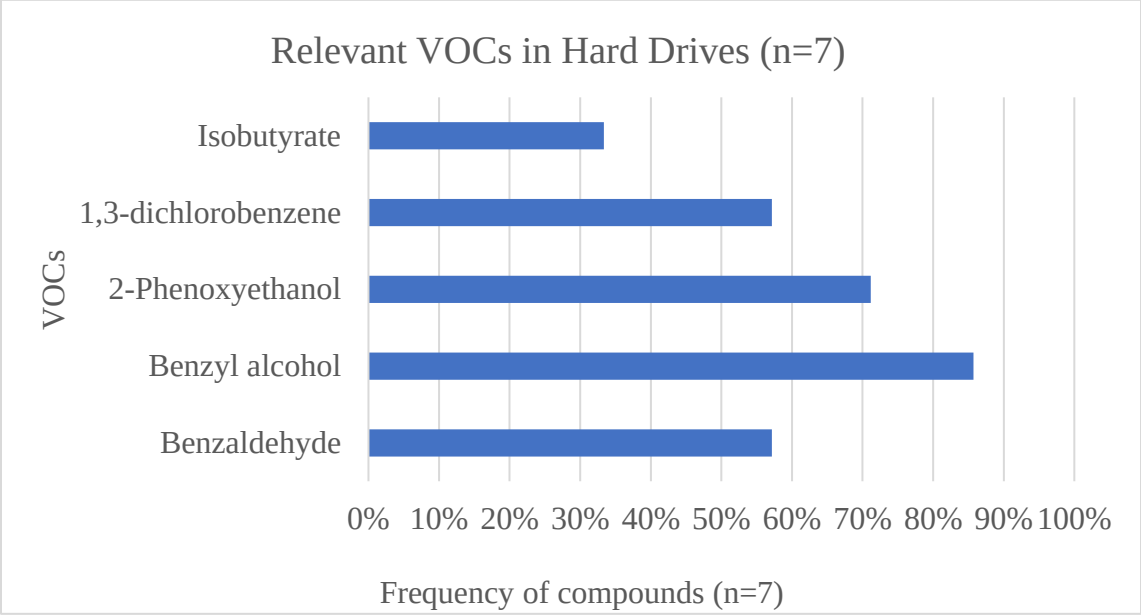


Figure 64. Relevant VOCs associated with hard drives and their frequency (n=7).

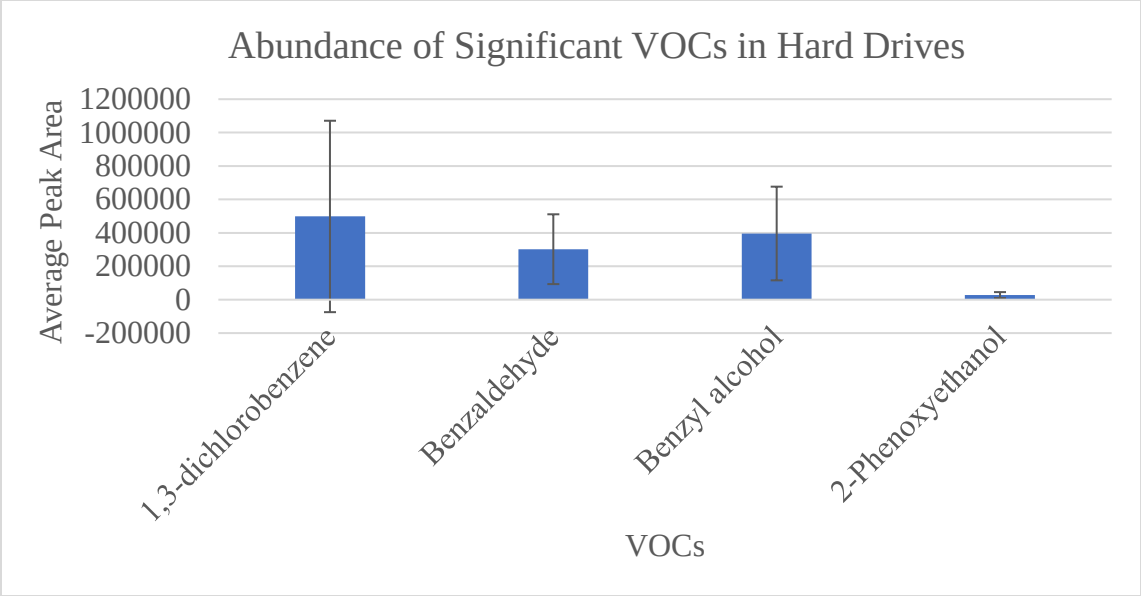


Figure 65. Abundance of Significant VOCs in Hard Drives.

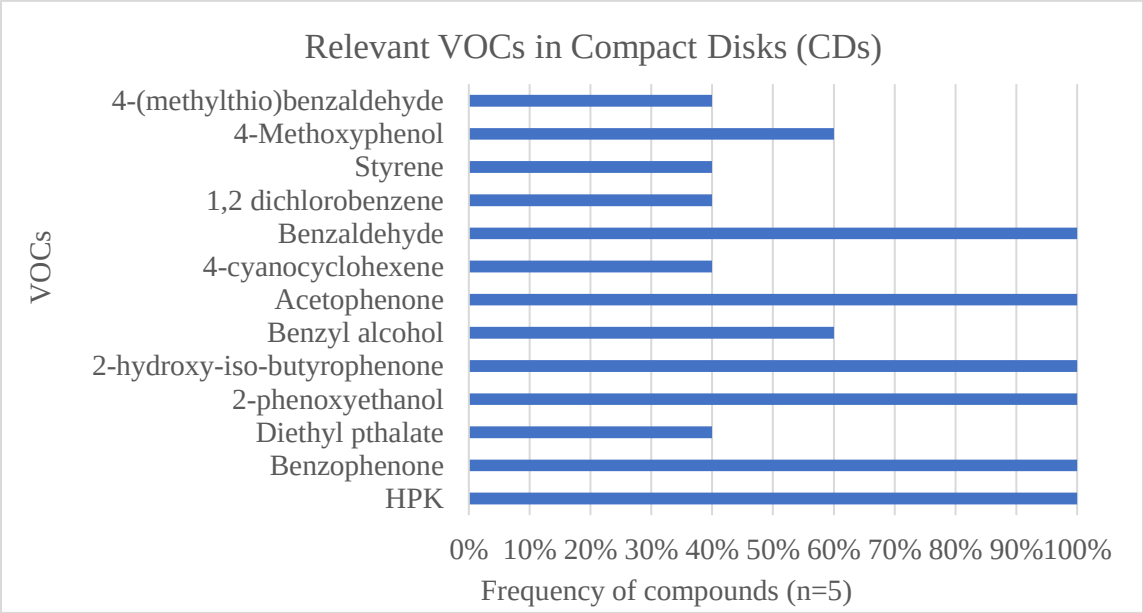


Figure 66. Relevant VOCs associated with CDs and their frequency n=5.

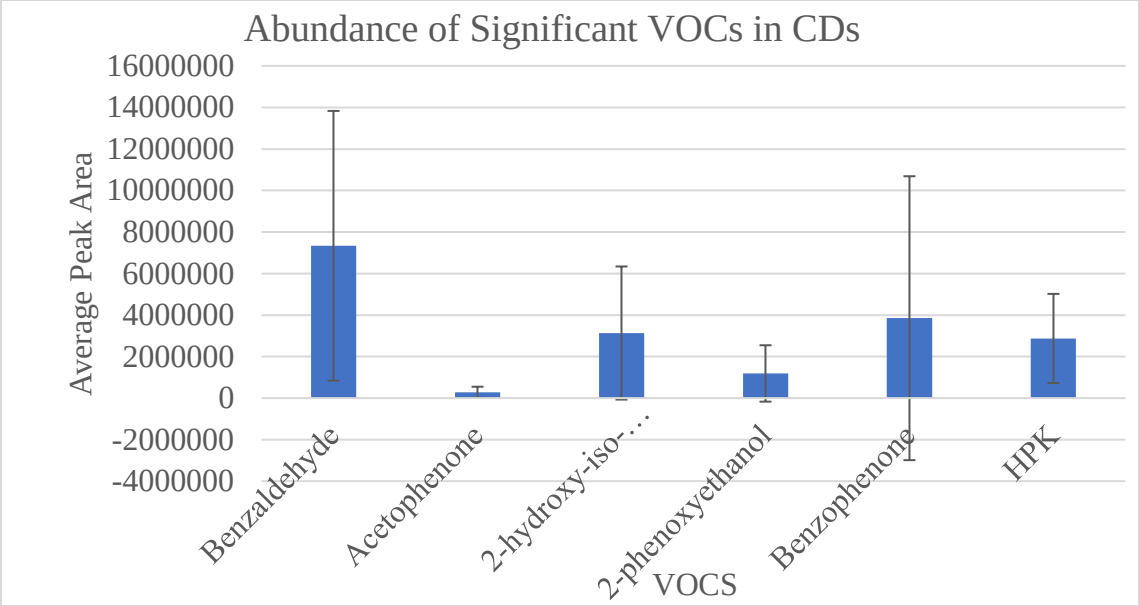


Figure 67. Abundance of Significant VOCs in CDs.

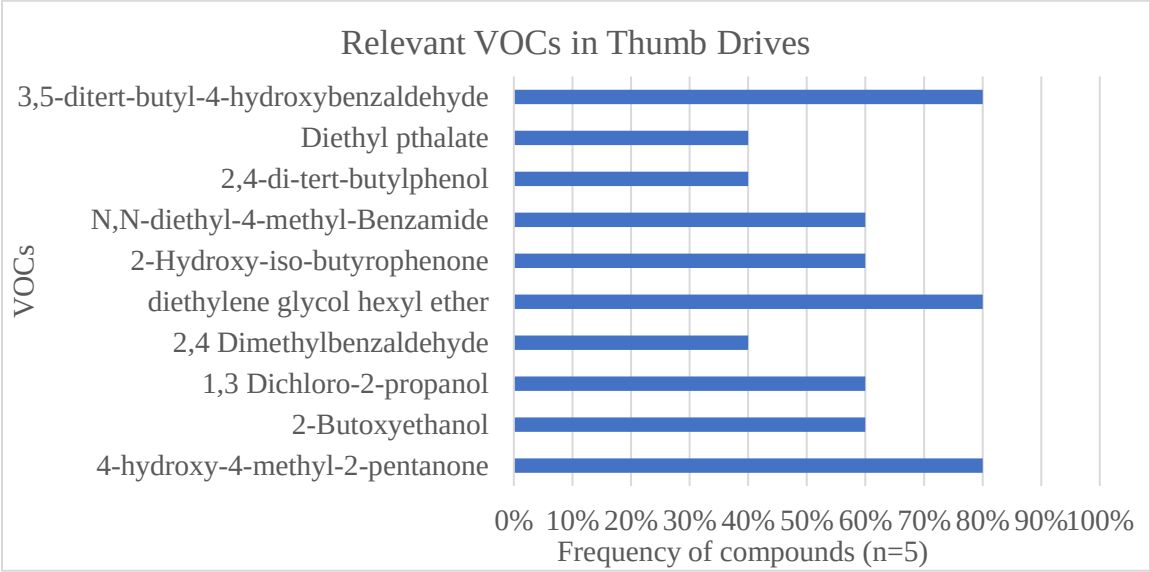


Figure 68. Relevant VOCs associated with Thumb Drives and their frequency (n=5).

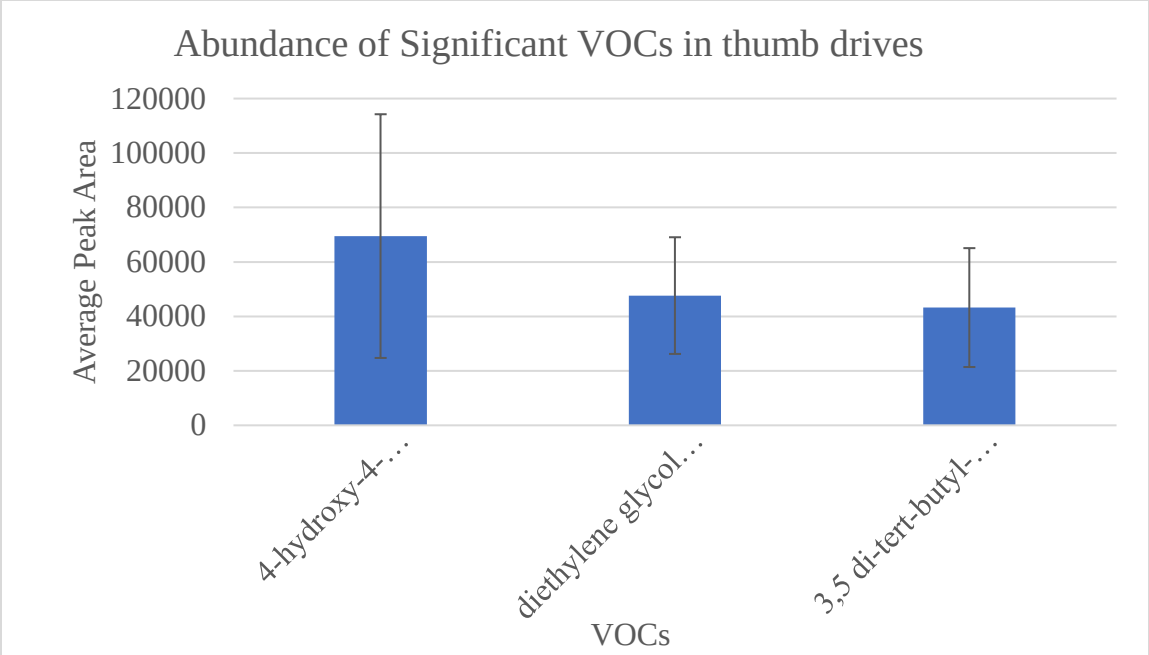


Figure 69. Abundance of Significant VOCs in Thumb Drives.

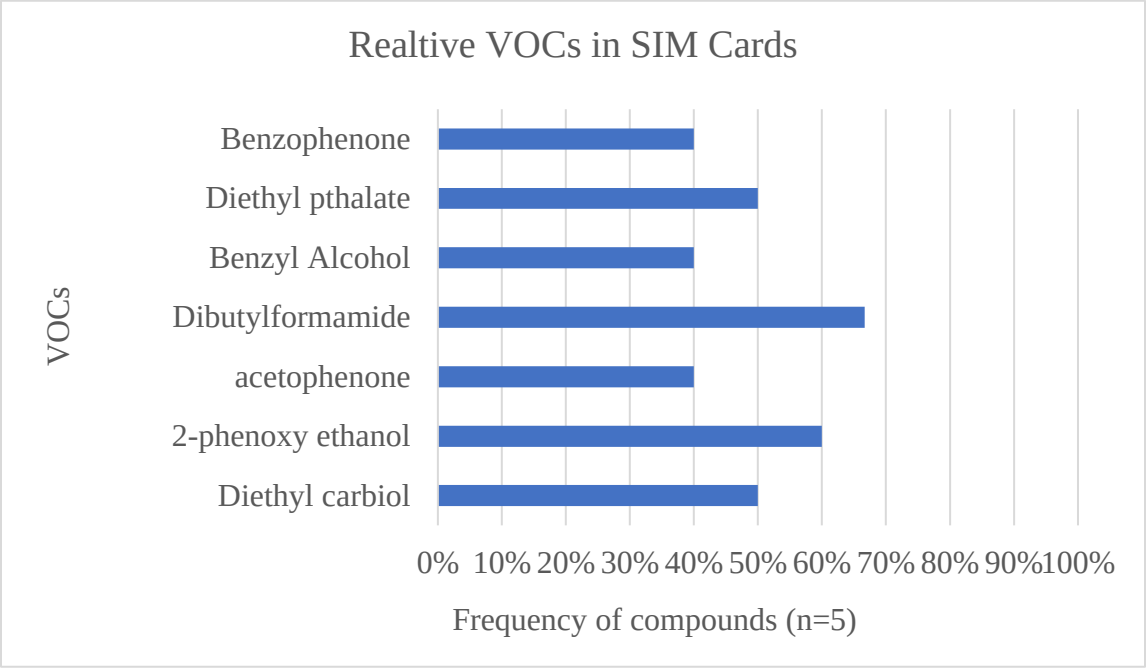


Figure 70. Relevant VOCs associated with Thumb Drives and their frequency (n=5).

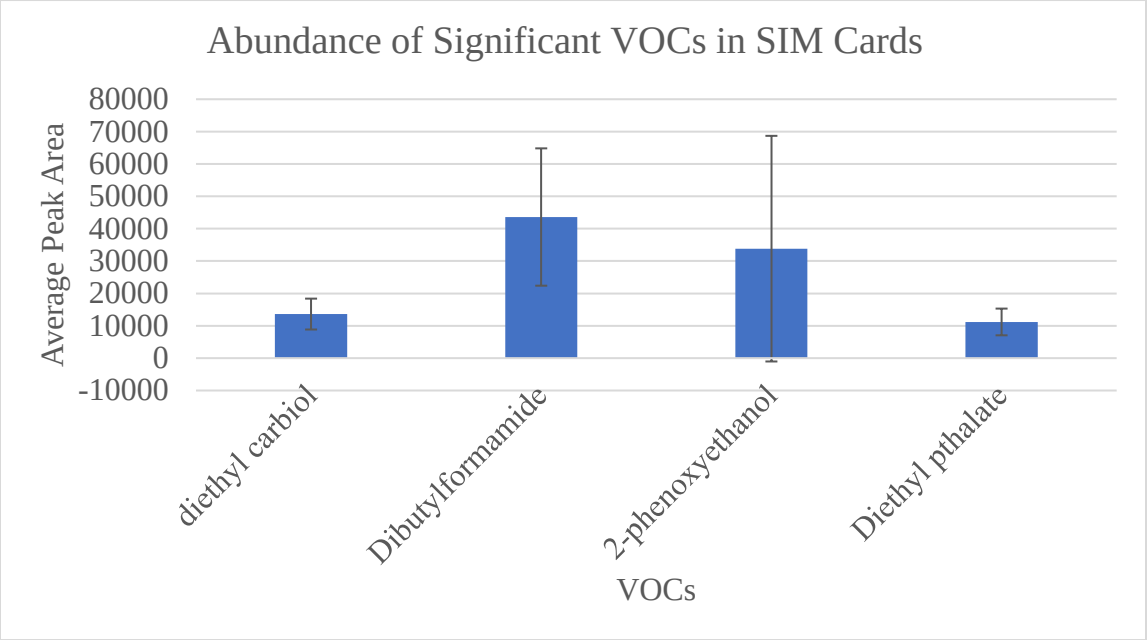


Figure 71. Abundance of Significant VOCs in SIM Cards

Table 27. VOCs detected in electronic controls that were also present in MSD samples.

Controls	VOCs detected
Computer mouse	Styrene, 4-hydroxy-4-methyl 2 pentanone, 2-butoxyethanol, 1,4 dichlorobenzene, benzaldehyde, 4-cyanocyclohexene, 2-phenoxyethanol
TV remote	Styrene
MP3 Player	Diethyl carbonate, styrene, 2-butoxyethanol, benzaldehyde, 1-hydroxycyclohexylphenyl ketone
Bluetooth car adapter	Diethyl carbonate
USB charging adapter	Benzyl alcohol

Table 28. Relevance of the VOCs found to be present in mass storage devices based in literature search. (NA=No relevance found) [173]. **Indicates VOCs confirmed by both a NIST 2017 mass spectral library and an analytical standard (Appendix F).*

#	Compound	Uses
1	Diethyl carbonate	Plasticizer/Permittivity component of electrolytes in lithium batteries
2	Benzyl alcohol*	Adhesives
3	Cyclohexylbenzene	N/A
4	2-Phenoxyethanol*	Adhesives
5	Diethyl Pthalate	Plasticizer
6	Acetophenone*	Adhesive
7	2-Butoxyethanol	Adhesive and Abrasive
8	Isobornyl acrylate	Adhesive/sealing
9	Benzophenone*	Adhesives/binding agents
10	Benzaldehyde*	UV resistance
11	1-hydroxycyclohexylphenyl ketone (HPK)*	Inks, dyes, pigments
12	1,6-dioxacycyclododecane-7,12-dione	N/A
13	Isobutyrate	N/A
14	1,3-dichlorobenzene	N/A
15	4-(methylthio)benzaldehyde	N/A
16	4-Methoxyphenol	Adhesives/pigments
17	Styrene*	Plastics and Resins
18	1,2-dichlorobenzene	Solvent for resins, rubbers etc.
19	4-cyanocyclohexene	Inks, dyes, pigments
20	2-hydroxy-isobutyrophenone	Adhesives/pigments
21	3,5-ditert-butyl-4-hydroxybenzaldehyde	N/A

22	2,4-di-tert-butylphenol*	Plastics
23	N,N-diethyl-4-methyl-Benzamide	N/A
24	diethylene glycol hexyl ether	Electrical Insulation
25	2,4 Dimethylbenzaldehyde	N/A
26	1,3 Dichloro-2-propanol	Adhesive
27	4-hydroxy-4-methyl-2-pentanone	Adhesive/pigments
28	Dibutylformamide	Surface treatment
29	Diethyl carbinol	Solvent

6.3 HS-SPME-GC-MS Detection of Triphenylphosphine Oxide in Mass Storage Device Components

Analysis of MSD VOCs in section 6.2 did not show any indication of TPPO in the headspace of these devices. This was however expected since TPPO is a high molecular weight compound with a very low vapor pressure of 2.60 e^{-09} mmHg TPPO and a boiling point of 360˚ C (Figure 72). This means that it is not readily available in the headspace for analysis. To overcome this, TPPO can be heated in order to increase its overall vapor pressure.

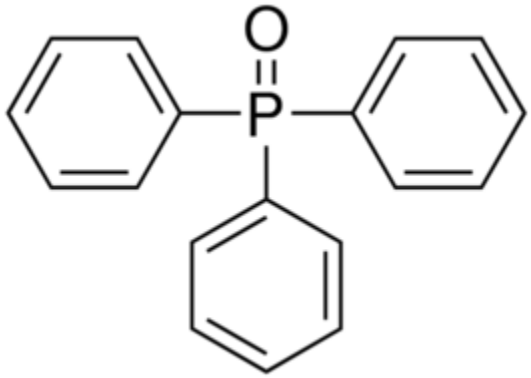


Figure 72. Chemical structure of triphenylphosphine oxide (TPPO). MW 278 g/mol and vapor pressure 2.60 e^{-09} mmHg [174]

6.3.1 Materials and Method Development

A non-polar DB-5ms (5%-phenyl-methylpolysiloxane) 0.32mm ID x 30m column was used for the detection of TPPO. This was due to the high maximum operating temperature (350˚C) of this column. Due to the high boiling point of TPPO, a high oven temperature

was necessary. This instrument also used a 6890 Gas chromatograph coupled to a 5973N Mass Selective Detector.

A 100 parts per million (ppm) standard of TPPO in a methylene chloride solvent was first prepared. A portion of the sample was then transferred to a 2mil vial and placed into the GC autosampler. The GC inlet was set at 270 ˚C and was run in split mode with a 10:1 split ratio of sample to solvent and with an injection volume of 1µl. The mass spectrometer transfer line was set at 300 ˚C and the MS was run in positive ion EI mode with a scan range of 40-500 m/z and a 3-minute solvent delay. Table 29 shows the GC oven parameters for the analysis. The oven began with an initial oven temperature of 100 ˚C then ramped to 200 ˚C at 15 ˚C/min followed by a 10 ˚C/min ramp to a final oven temperature of 300 ˚C where the temperature was held for 3 minutes. A hold at the maximum operating temperature is often used to allow compounds with higher boiling points to eventually elute.

Table 29. GC oven parameters for the analysis of TPPO.

GC Oven Parameters			
Temp	˚C/min	Next ˚C	Hold (min)
Initial Temp		100	
Ramp 1	15.00	200	
Ramp 2	10.00	300	3.00

Figure 73 (a) shows the chromatographic results with TPPO being detected at an approximate retention time of 14.4 minutes. Figure 73 (b) shows the mass spectrum with the abundance of several fragments including the M-1 peak 277 m/z and the molecular ion peak (M) 278 m/z. The spectrum was matched to TPPO using the NIST 2017 Mass Spectral Library database

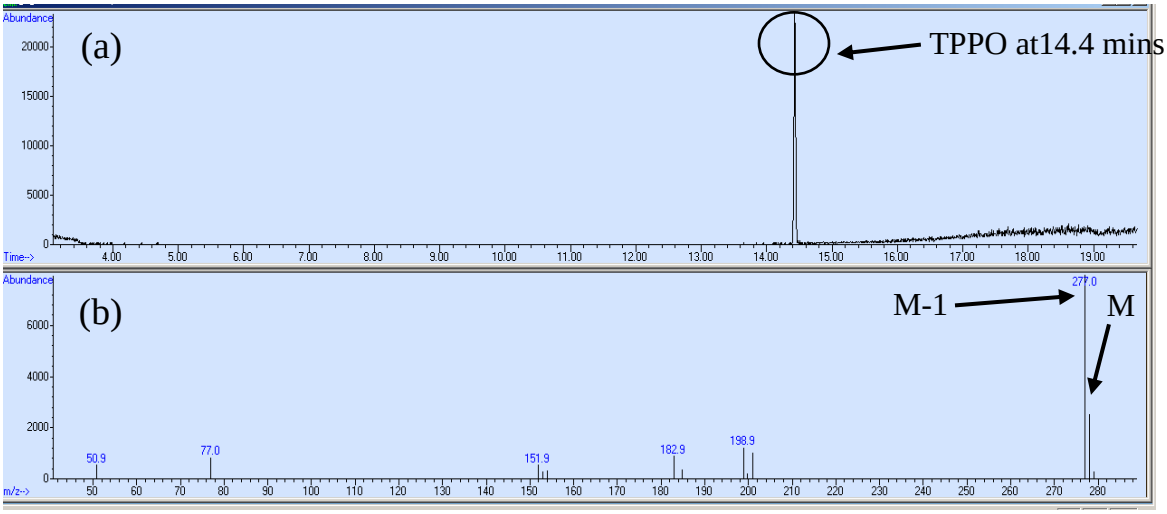


Figure 73. (a) GC Chromatogram of a 100ppm TPPO sample with an approximate retention time of 14.4 minutes. (b) The mass fragments of TPPO with M-1 peak at 277 m/z and molecular ion peak (M) at 278m/z

An additional set of TPPO liquid standards were then prepared in order to construct a calibration curve. Concentrations of standards were 1ppm, 5ppm, 10ppm, 25ppm, 50ppm, 75ppm, 100ppm, 125ppm and 150ppm. Figure 74 displays the obtained calibration curve. The concentrations below 10ppm showed no instrument response indicating a limit of detection in this region.

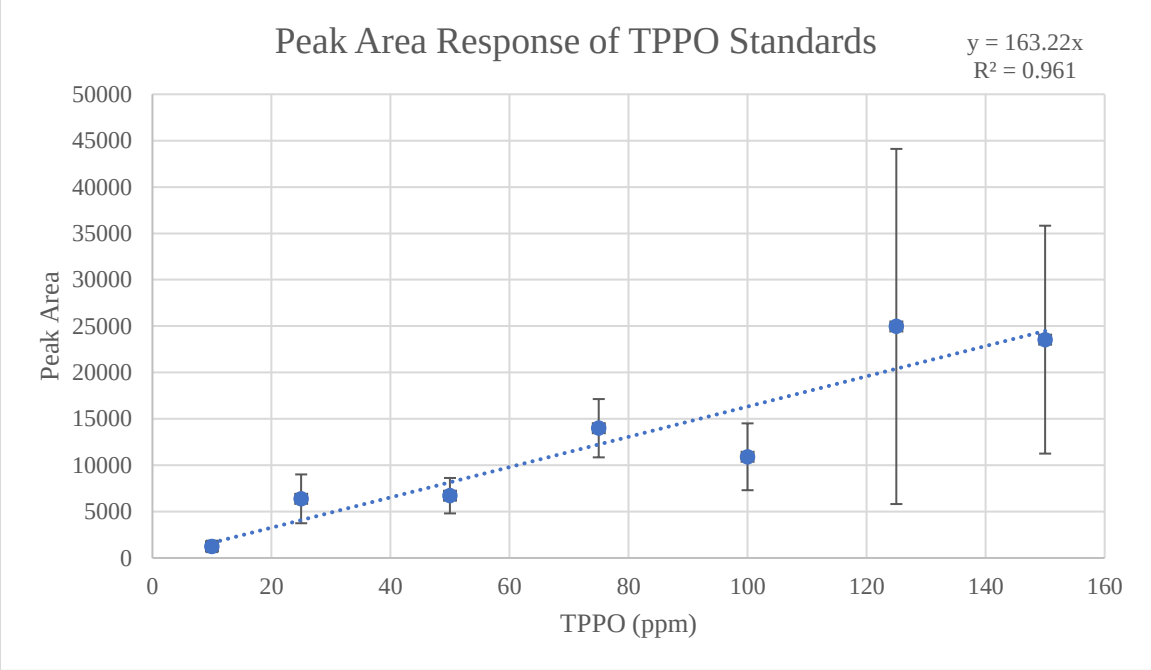


Figure 74. Calibration curve showing the average peak area response of TPPO standards.

The next step involved the development of a method for HS-SPME detection of TPPO. This was done using an incremental thermal study using solid TPPO samples. First, an approximately 0.25gram sample of solid analytical grade TPPO was weighed and placed in a 40ml glass vial containing a PFTE/Silicone rubber septa. The sample was then placed in a heating block at 50˚C for 1 hour which was followed by a 30-minute HS-SPME extraction. For GC-MS analysis, the method described above in Table 29 was used with the only difference being the removal of the 3-minute solvent delay and the split mode. This entire procedure was then repeated by increasing the temperature of the heating block by increments of 10 ˚C. New samples were weighed and used for each increment. Figure 75 shows the extraction setup using the heating block.

Figure 75. TPPO extraction setup using a heating block.

It was concluded that using the selected sampling parameters (1-hour sample heating time and 30-minute SPME extraction time), a minimum temperature of 80˚C was needed to allow for TPPO to be detected in the headspace. Figure 76 below shows the full results of the thermal study using temperatures that ranged from 50˚C to 100 ˚C. Based on these findings, a heating temperature of 100 ˚C was selected for the analysis of MSD components.

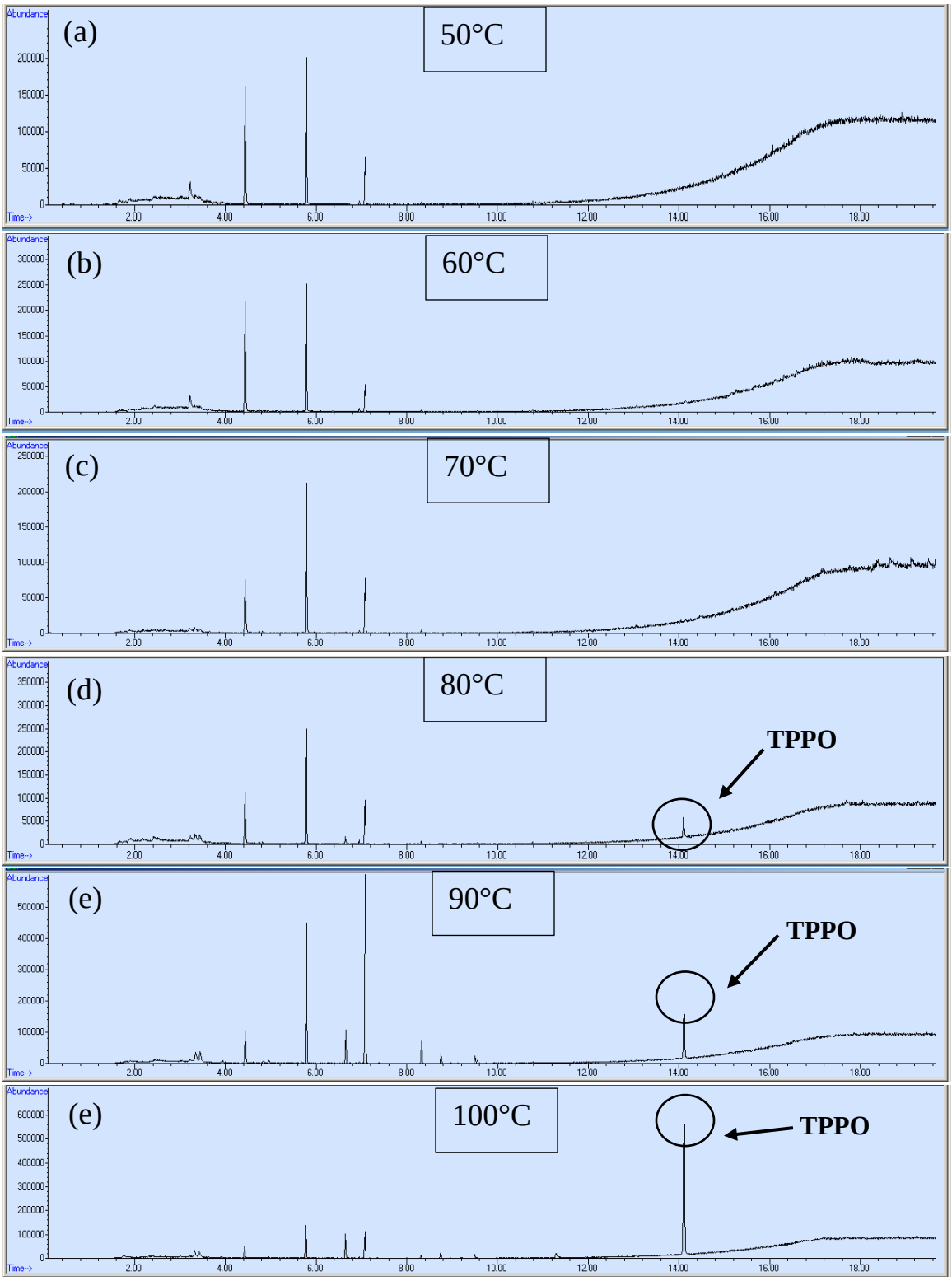


Figure 76. HS-SPME-GC-MS detection of solid TPPO at 10°C heating increments.

The MSD components used for the investigation of TPPO were three separate circuit boards. The first circuit board (circuit board #1) was obtained from an unknown manufacturer, the second (circuit board #2) and third (circuit board #3) came from hard drive number #4 and the TCL smartphone respectively (Table 26), both which were analyzed in section 6.2. A 1-inch x .5-inch sample of each circuit board was cut and placed inside the 40ml vial after which it was placed in the heating block at 100 °C for 1 hour prior to HS-SPME extraction. For the HS-SPME extraction, increasing extraction times were used: 30 minutes, 4 hours and 24 hours. Although the TPPO was extracted for 30 minutes during the method development phase, no other compounds were present as this was a pure analytical grade sample. Therefore this parameter did not cater for fiber competition and the preference of lower molecular weight, more volatile compounds with short extraction times. As seen earlier in Figure 51, longer extraction times are needed for extraction of less volatile compounds. Consequently, longer extraction times were applied.

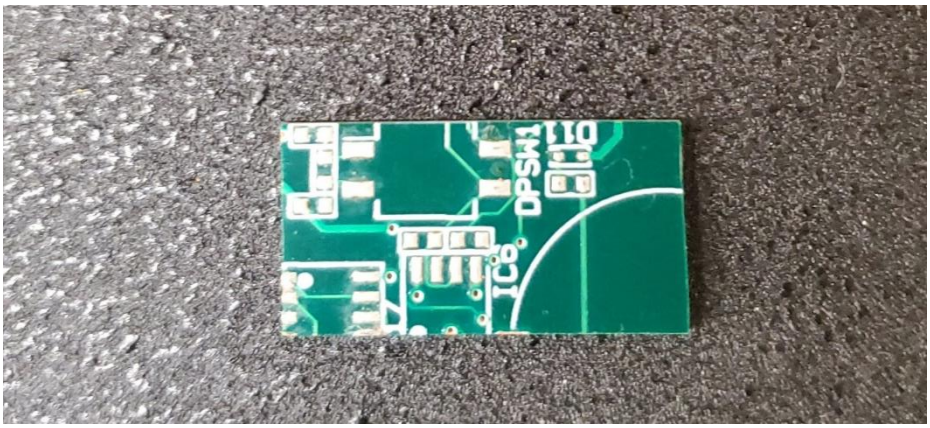


Figure 77. Example of the circuit board used for HS-SPME analysis.

6.3.2 Results

Figure 78 to Figure 80 shows the results of the 30-minute, 4-hour and 24-hour HS-SPME extractions for all three circuit boards. TPPO was not detected in any of the samples. Chromatographic peaks that appeared close to the retention time of TPPO (e.g. Figure 80 c) were analyzed with none being confirmed as TPPO.

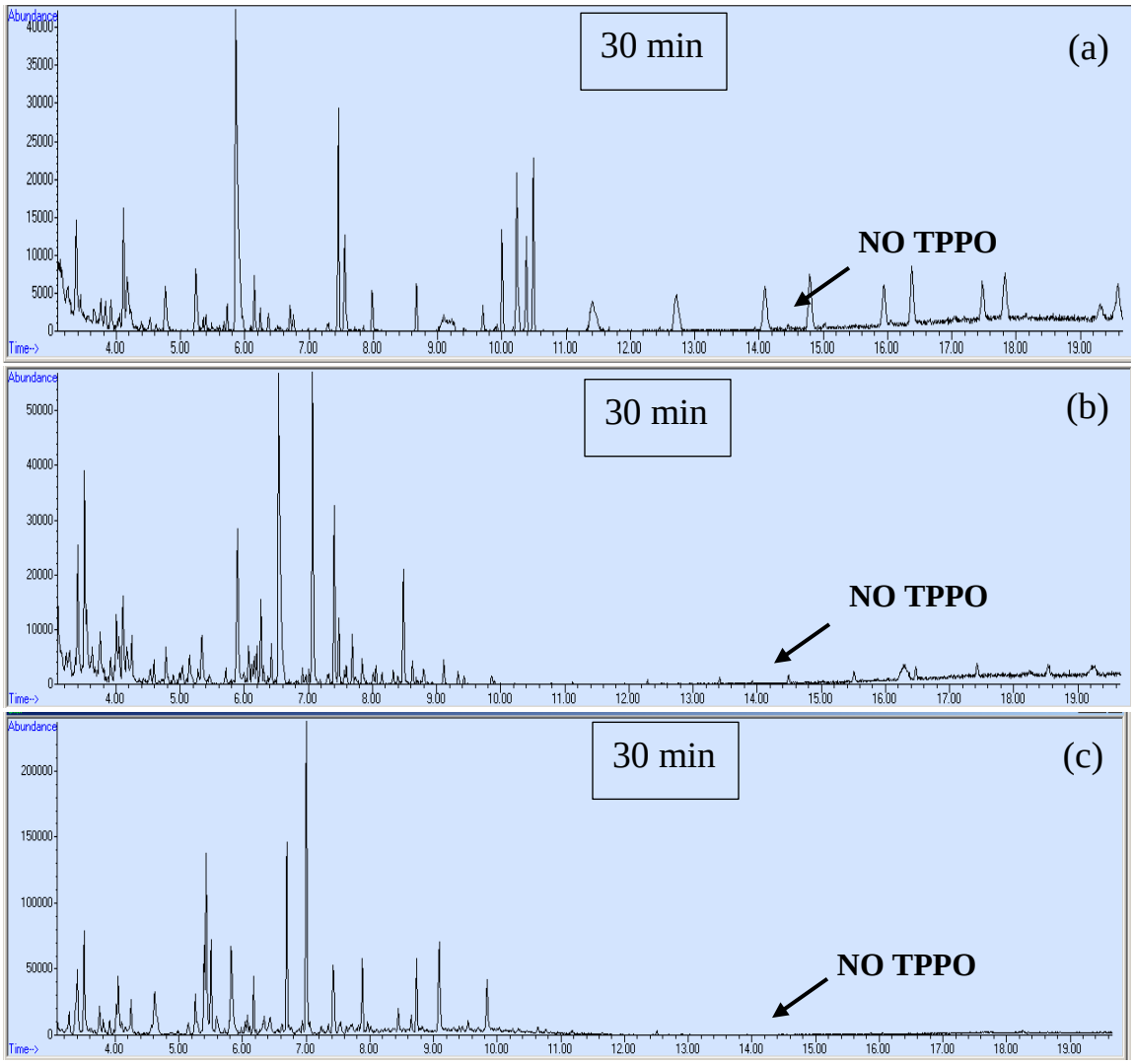


Figure 78. 30-minute HS-SPME extraction time for (a) circuit board #1, (b) circuit board #2 and (c) circuit board #3.

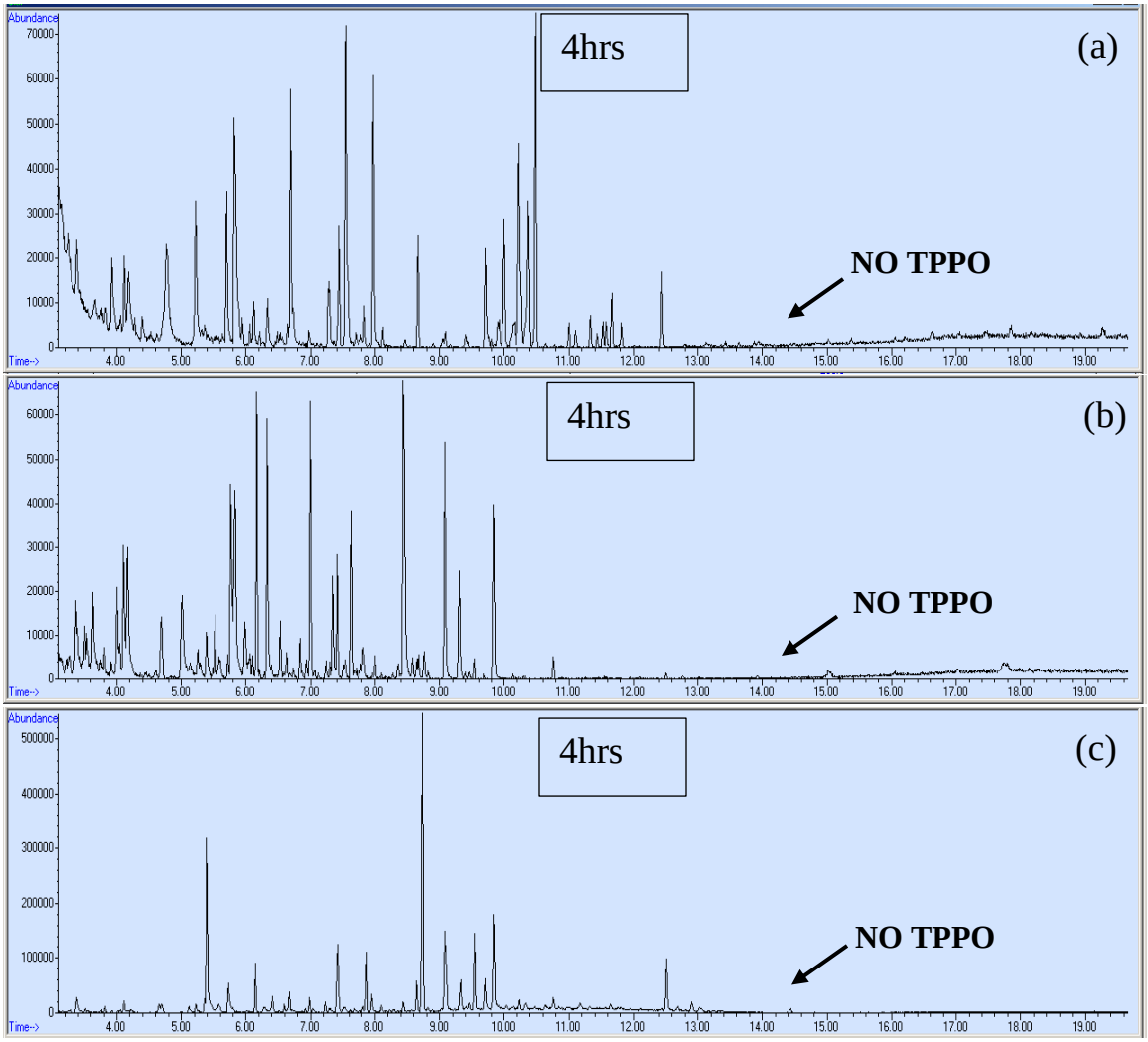


Figure 79. 4-hour HS-SPME extraction time for (a) circuit board #1, (b) circuit board #2 and (c) circuit board #3.

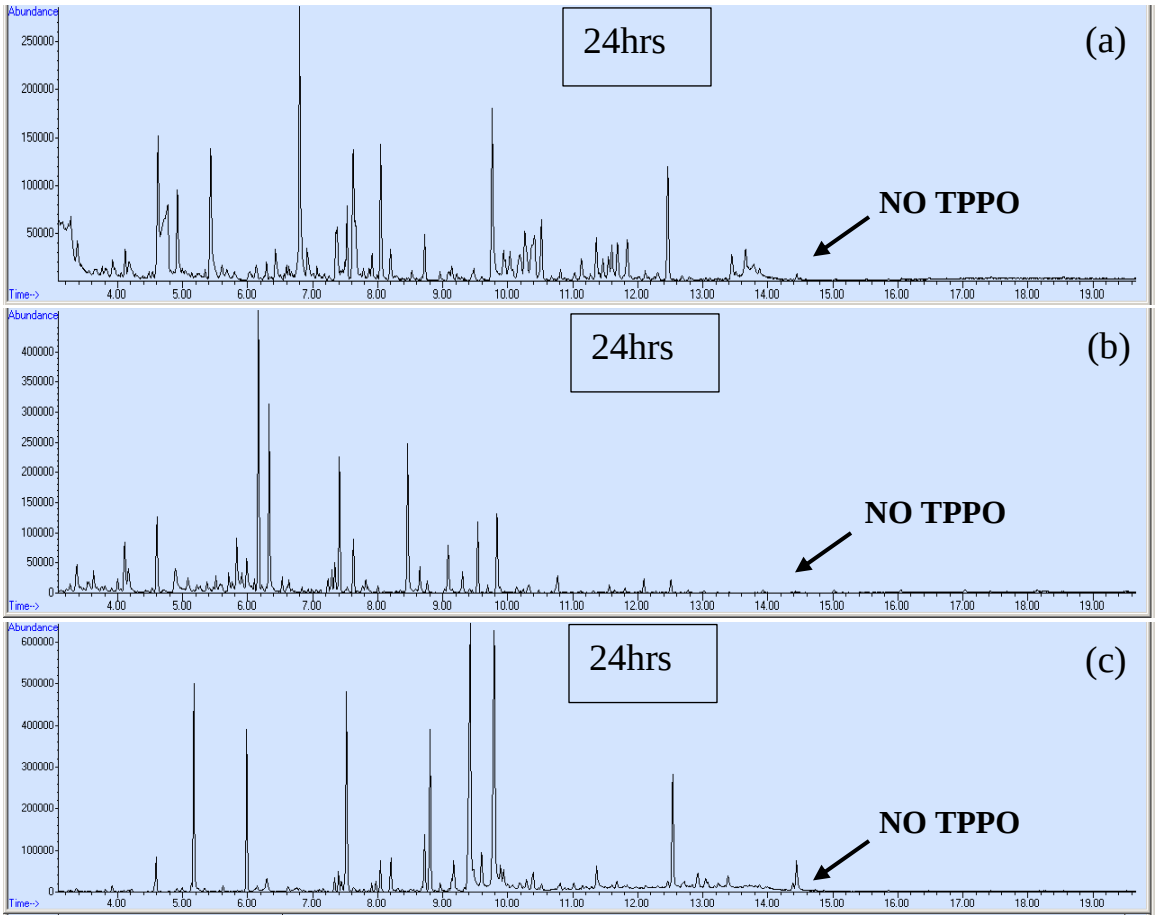


Figure 80. 24-hour HS-SPME extraction time for (a) circuit board #1, (b) circuit board #2 and (c) circuit board #3.

6.4 Conclusions and Recommendations for Future Work

As the use of dogs for the detection of storage devices increases, it is necessary that science-based training methods are utilized for optimum performance. This study in part helped to lay the scientific foundation for this field. Results showed that these devices do in fact have characteristic odors that can aid in successful detection. The existence of 1-hydroxycylohexylphenyl ketone in storage devices was confirmed. However it was also

found in controls and its reliability as a training aid will depend on the mission of the dog. If the aim is detecting any type of electronic device as is the case in some prisons, then HPK can potentially be an option. HPK however still needs to be validated using field trials by first imprinting green dogs on HPK then observing their response to electronics. With regards to the use of TPPO, it was not found to be in the headspace of three circuit boards that was analyzed. Currently, two dogs are being imprinted on TPPO with the overall goal being to observe the dog's response to a series of devices after imprinting

7. FURTHER DEVELOPMENT OF A UNIVERSAL DETECTOR CALIBRANT UTILIZING A CONTROLLED ODOR MIMIC PERMEATION SYSTEM

As mentioned earlier, the Universal Detector Calibrant utilizes a patented controlled odor mimic permeation system (COMPS). Using COMPS, the target odor 1-Bromooctane (1-BO) is housed in a permeable polymer such as low-density polyethylene (LDPE) where it can be released at a controlled and measurable rate. This allows the manipulation of COMPS to achieve desirable permeation rates. Currently, the UDC is used as a tool for training green dogs on basic tasks such as searching and locating odors prior to the beginning of their careers in respective fields. It is also used as maintenance training for dogs engaged in non-traditional forms of odor detection such as detecting invasive species or diseased trees. In these non-traditional forms of odor detection, consistent training on target odors is not feasible. As a result, the UDC provides the necessary day to day training to keep the dogs working up to par.

With detector dogs, it is essential that they can respond to varying levels of a target odor with some requiring very low limits of detection (e.g., human tracking) . For this reason, it is essential to have a tool that can effectively gauge the dog's day to day olfactory capabilities such as a calibrant. This task describes how COMPS can be applied to manipulate the odor levels for the UDC hence allowing for varying calibration standards.

7.1 Manufacturing the Universal Detector Calibrant

A desired amount of the target odor. (i.e., 1-Bromooctane) is spiked onto cellulose powder that is housed inside of the LDPE bag and serves to absorb the compound . After the compound is spiked, the bag is then tripled sealed. The LDPE bag can then be used as is, or for further reduction in odor availability, it can be housed in an Aluminum bag containing a hole. Figure 81 shows displays a LDPE bag along with a perforated Aluminum bag.

To know the rate at which the odor is permeating through the COMPS, it is measured by the process of gravimetric analysis. After being manufactured, the COMPS are placed on an analytical balance and its initial weight recorded. This is done in triplicate measurement along with a blank. The blank serves to correct any change in weight of the COMPS that is not due to the permeation of the target odor. After being weighed, the COMPS along with the blank are then suspended Over time, the weight of the COMPS along with the blank are recorded and the decrease in mass of the bag indicates the average rate of permeation for the odor. Section 7.2 below shows the gravimetric data a series of COMPS with varying parameters for manufacturing.

Figure 81. Low density polyethylene (LDPE) bag (top) alongside a perforated Aluminum bag.

7.2 Gravimetric Analysis and Rates of Permeation

Figure 82 to Figure 84 shows the permeation data for 3 different UDCS made by varying the thickness of the LDPE polymer: 4MIL, 6MIL and 8MIL. As the thickness of the bags increased, the rate of permeation decreased. Permeation rates of 5075 ng/sec, 3488 ng/sec and 1865ng/sec respectively were achieved. Note that all rates are converted to ng/sec as this provides a better representation as to the amount of odor the dog is receiving in real time.

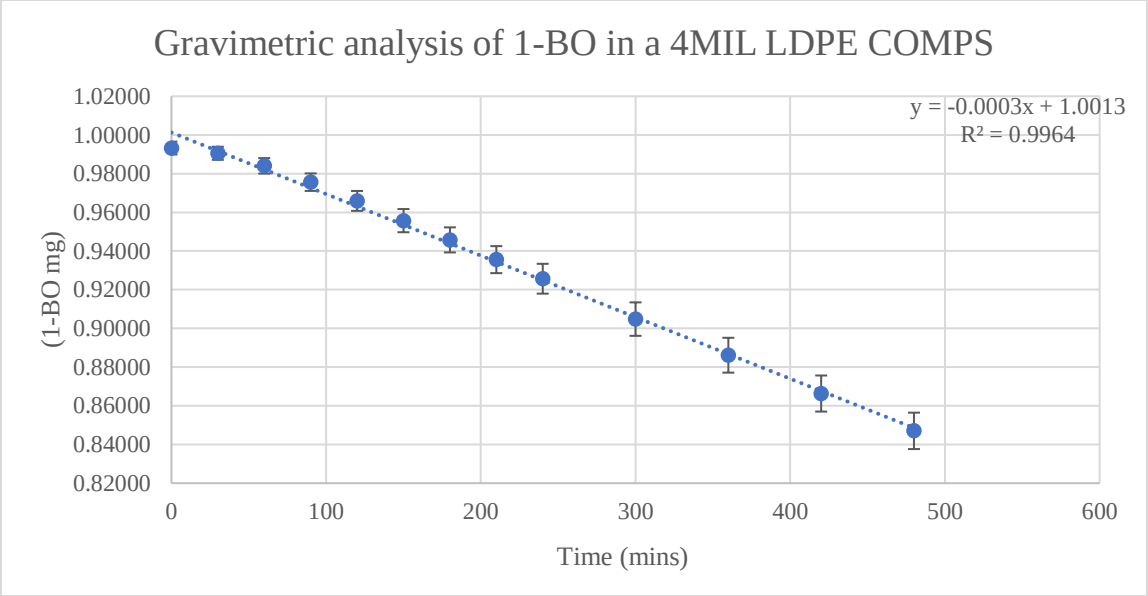


Figure 82. 1-Bromooctane housed in a 3" x 5" 4MIL COMPS with a measured permeation rate of 5075ng/sec

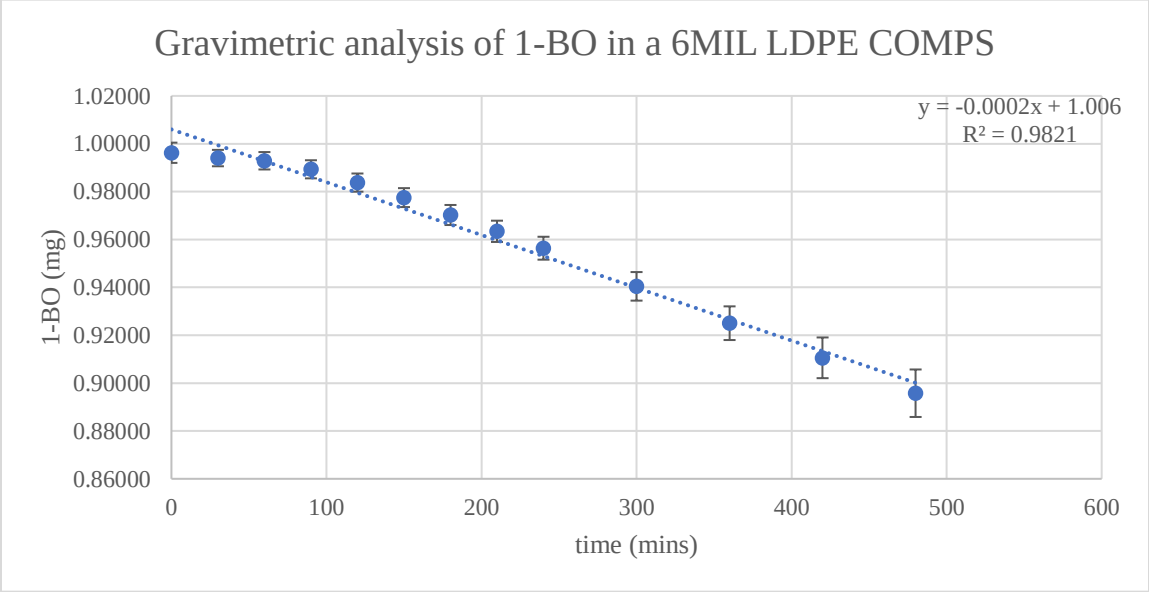


Figure 83. 1-Bromooctane housed in a 3" x 5" 6MIL COMPS with a measured permeation rate of 3488ng/sec

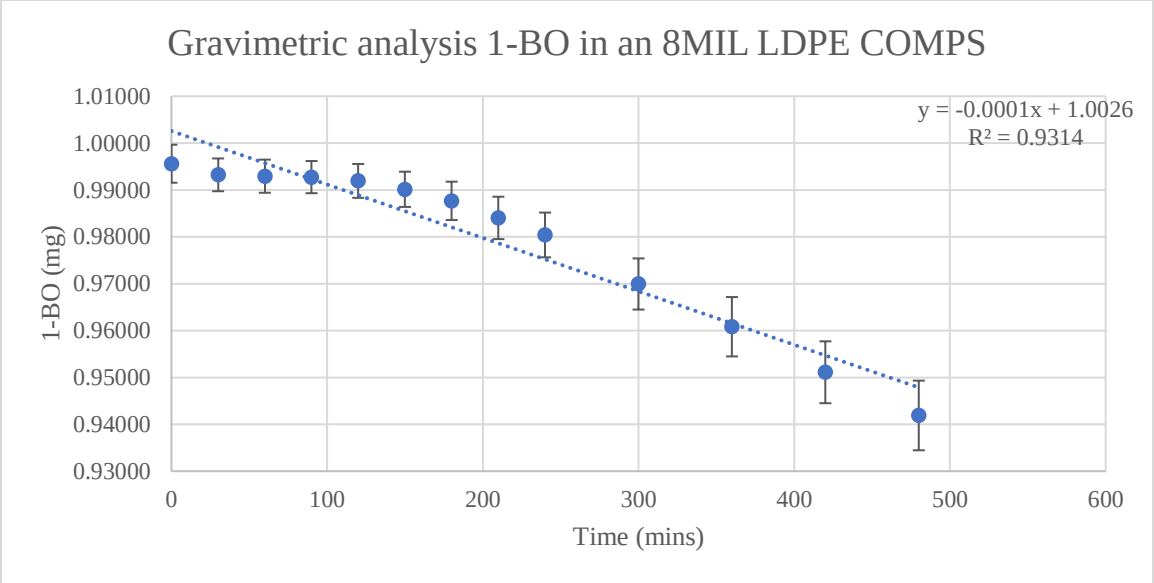


Figure 84. 1-Bromooctane housed in a 3" x 5" 8MIL COMPS with a measured permeation rate of 1865ng/sec.

For decreased rates of permeation, COMPS are further manipulated by housing the polymer bags inside of the Aluminum bags. Gravimetric analysis for three of these type UDCs are shown in Figure 85 to Figure 87 where LDPE bags were placed in Aluminum bags with hole sizes of 31.8mm^2, 7.92mm^2 and 1.024mm^2

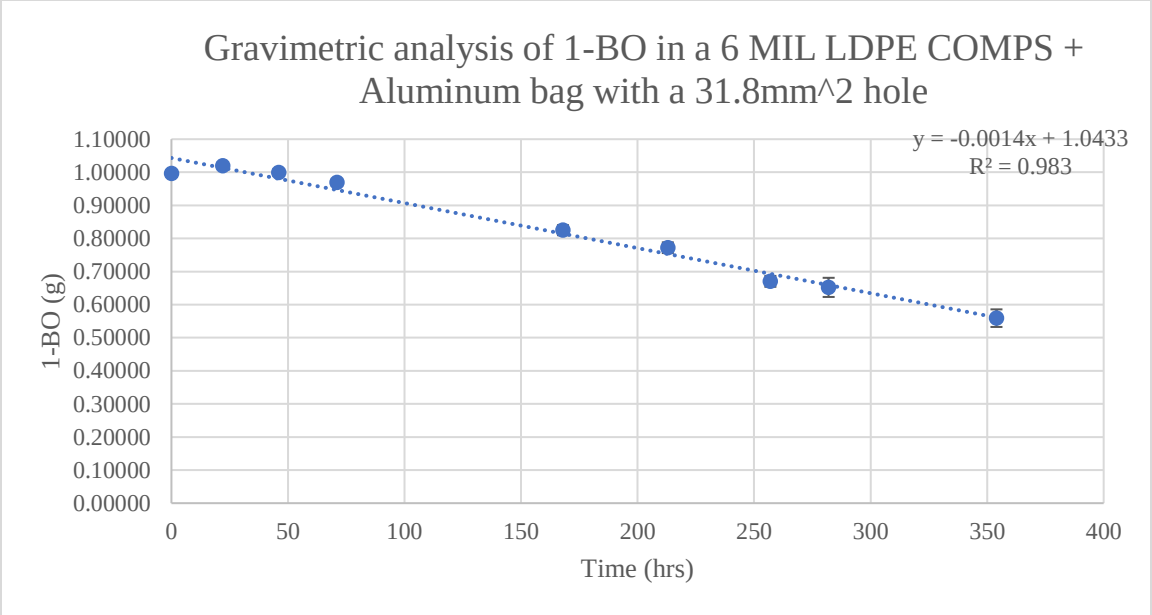


Figure 85.1-Bromooctane in a 6MIL LDPE COMPS housed in an Aluminum bag with a 31.8mm^2 hole and measured rate of permeation of 378ng/sec.

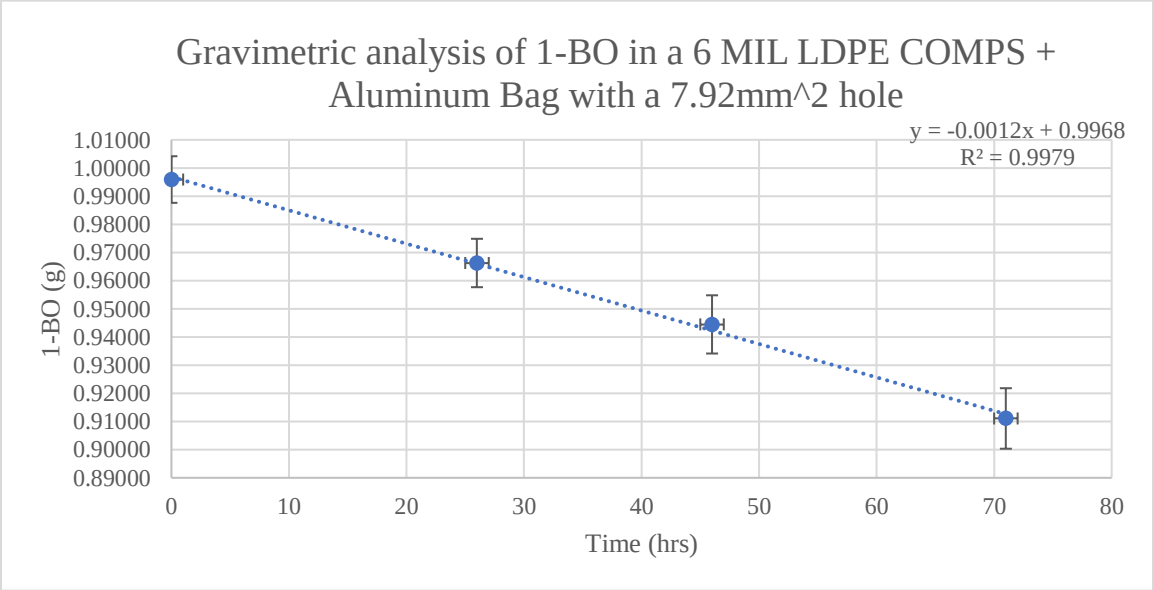


Figure 86. 1-Bromooctane in a 6MIL LDPE COMPS housed in an Aluminum bag with a 31.8mm^2 hole and measured rate of permeation of 327ng/sec.

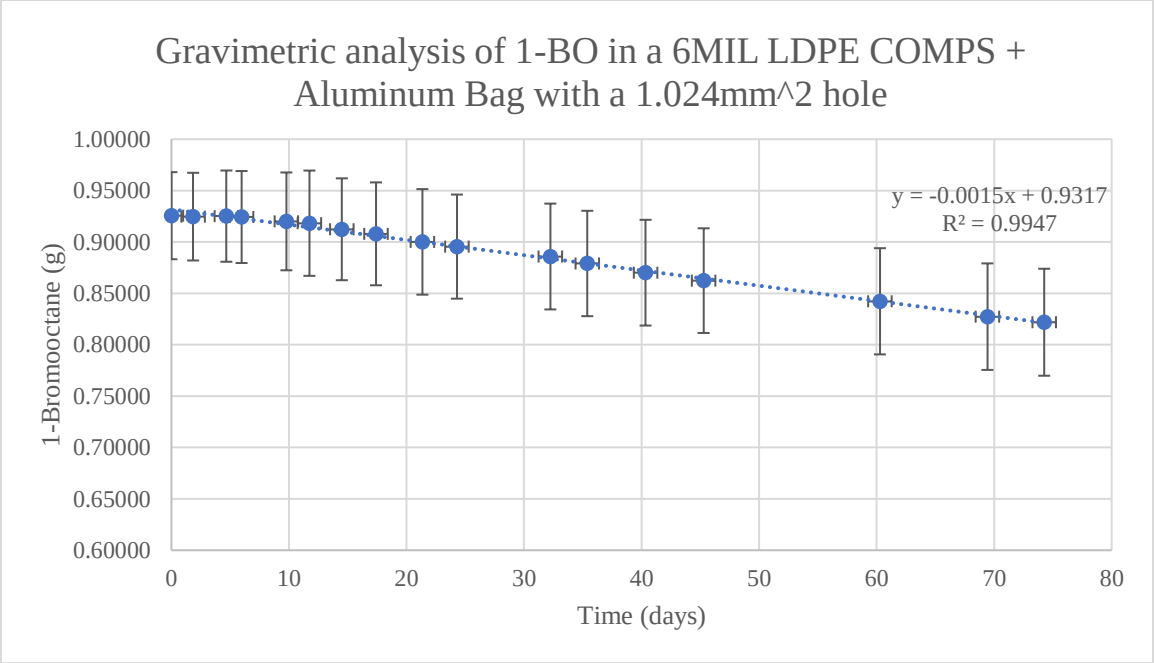


Figure 87. 1-Bromooctane in a 6MIL LDPE COMPS housed in an Aluminum bag with a 1.024mm^2 hole and measured rate of permeation of 17 ng/sec.

Table 30. below provides the comparison of the permeation rates achieved for the UDC calibrants discussed so far ranging from a "high" odor delivery of 5075ng/sec to a "low" odor delivery of 17.2 ng/sec, almost 300 times. This demonstrates that COMPS is a reliable method for achieving desired rates of odor delivery for tools such as the UDC.

Table 30. UDC with manipulated COMPS parameters showing varying rates of target odor permeation.

UDC Parameters	Rate of Permeation (ng/sec)
4MIL LDPE Bag	5075ng/sec
6MIL LDPE Bag	3488ng/sec
8MIL LDPE Bag	1865/sec
6MIL LDPE Bag + Aluminum bag with a 31.8mm^2 hole	378ng/sec
6MIL LDPE Bag + Aluminum bag with a 7.92mm^2 hole	327ng/sec
6MIL LDPE Bag + Aluminum bag with a 1.024mm^2 hole	17ng/sec

8. OVERALL CONCLUSIONS

Through the use of analytical chemistry alongside reliable field testing, this project was able to provide several important recommendations to the detector dog community for optimum science-based training practices in several odor detection disciplines.

Dogs that are currently trained to detect marijuana may generalize to hemp as they do share many common and VOCs. However, these same dogs can be successfully trained to ignore hemp products while at the same time positively identifying marijuana. This strategy can now be adopted by various law enforcement agencies who are concerned about the possible liabilities of having their dogs alerting to a legal substance. Meanwhile, the use of any current marijuana training aid mimics should be discontinued as this will most likely result in dogs alerting to both substances due to the lack of specificity that the training aid provides.

Despite the TATP molecule being the most abundant VOC in its headspace, precursors acetone and peroxide, due to their higher volatilities, might allow for dogs to be imprinted on them. It is therefore necessary to also train dogs to ignore to these substances to ensure minimal false alerts. Also, the manufacture of TATP training aid mimics must ensure similarities in the overall headspace compared to the actual explosive. It was noted herein that some commercial mimics may not contain TATP in significant amounts compared to precursors, which is not ideal.

Mass storage devices do have characteristic combination of VOCs that can allow for their successful detection by dogs with specificity. The methods used for training should depend on the overall goal of the agency. For example, the use of compounds such as HPK as a

training aid might be viable as it was found in almost every cellular phone and CD that was analyzed. It was however, also found in controls such as mp3 players and can therefore result in false alerts. The rationale for the use of TPPO still remains questionable as it was not detected in any of the circuit boards analyzed. Future studies involving imprinting dogs on TPPO and observing their response to MSDs should be conducted to further investigate the efficacy of this compound.

To continue improving the day-to-day reliability of detector dogs, tools such as the Universal Detector Calibrant can be implemented. Using COMPS, this device can provide varying levels of the target odor 1-Bromooctane, allowing handlers to gauge the dog's olfactory capabilities prior to beginning a workday.

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APPENDICES

Appendix A: Complete list of Hemp products and Distractors used for Trial 1 and Trial 2

Table 31. List of hemp products 1-12 used in Trial 1 and Trial 2, their purchasing strain name and company information.

	Purchasing Name	**Company**
Hemp 1	Lifter	Fields of Hemp
Hemp 2	Hawaiian Haze	
Hemp 3	Suver Haze	
Hemp 4	AC/DC	
Hemp 5	Elektra	
Hemp 6	Cherry Wine	
Hemp 7	Bubba Kush	
Hemp 8	Hempettes (Hemp cigarettes)	Wild Hemp
Hemp 9	Hemp Midwest	Tweedle Farms
Hemp 10	Hemp White CBG	
Hemp 11	Hemp Special Sauce	Mr. Hemp Flower
Hemp 12	Hemp Remedy	

Table 32. Key for list of distractors used for Hemp vs Marijuana Trial 1

List of Distractors Used	
D1	Orange Peel
D2	Banana Peel
D3	Cigarettes (any brand)
D4	Dog Treats
D5	Hemp/Cigarette rolling paper
D6	Cat Food
D7	Hemp Gummies
D8	Hemp Seeds
D9	CBD Oil
D10	Thyme

Table 33. Key for list of distractors used for Hemp vs Marijuana Trial 2

List of Hemp Products Used	
D1	Dog Treats
D2	Cat/Dog Food Mix
D3	Toys (Ball, Rope etc.)

Appendix B: Individual Results for Hemp vs Marijuana Trial 1.

ID#: 1 K9: Ajax Breed: Malinois Age:4yrs Time in service: 3yrs

	ORT				
	D1	D2	MJ	B	B
Response			Alert		

	Lineup #1				
	D3	H1	D4	B	B
Response					

	Lineup #2				
	B	D5	H2	B	D6
Response			Alert		

	Lineup #3				
	D7	H3	B	D8	B
Response					

	Lineup #4				
	B	D9	D10	B	H4
Response					

	Lineup #5				
	H5	B	B	D3	D4
Response	Alert				

	Lineup #6				
	D5	B	D6	H6	B
Response					

	Lineup #7				
	D7	B	H7	B	D8
Response			Alert		

	Lineup #8				
	B	H8	D9	D10	B
Response		Alert			

ID#: 2 K9: Ador Breed: Belgian Malinois Age: 5yrs Time in service: 3yrs

	ORT				
	D1	D2	MJ	B	B
Response			Alert		

	Lineup #1				
	D3	H1	D4	B	B
Response		Alert			

	Lineup #2				
	B	D5	H2	B	D6
Response					

	Lineup #3				
	D7	H3	B	D8	B
Response		Alert			

	Lineup #4				
	B	D9	D10	B	H4
Response					Alert

	Lineup #5				
	H5	B	B	D3	D4
Response	Alert				

	Lineup #6				
	D5	B	D6	H6	B
Response					

	Lineup #7				
	D7	B	H7	B	D8
Response					

	Lineup #8				
	B	H8	D9	D10	B
Response					

ID#: 3 K9: Paco Breed: Shepherd/Malinois Age: 2.5yrs Time in service: 1.5yrs

	ORT				
	D1	D2	MJ	B	B
Response			Alert		

	Lineup #1				
	D3	H1	D4	B	B
Response					

	Lineup #2				
	B	D5	H2	B	D6
Response					

	Lineup #3				
	D7	H3	B	D8	B
Response					

	Lineup #4				
	B	D9	D10	B	H4
Response					

	Lineup #5				
	H5	B	B	D3	D4
Response					

	Lineup #6				
	D5	B	D6	H6	B
Response					

	Lineup #7				
	D7	B	H7	B	D8
Response			Alert		

	Lineup #8				
	B	H8	D9	D10	B
Response					

ID#: 4 K9:Cino Breed: German Shepherd Age:4.5yrs Time in service: 3.5yrs

	ORT				
	D1	D2	MJ	B	B
Response			Alert		

	Lineup #1				
	D3	H1	D4	B	B
Response		Alert			

	Lineup #2				
	B	D5	H2	B	D6
Response					

	Lineup #3				
	D7	H3	B	D8	B
Response		Alert			

	Lineup #4				
	B	D9	D10	B	H4
Response					

	Lineup #5				
	H5	B	B	D3	D4
Response					

	Lineup #6				
	D5	B	D6	H6	B
Response				Alert	

	Lineup #7				
	D7	B	H7	B	D8
Response			Alert		

	Lineup #8				
	B	H8	D9	D10	B
Response		Alert			

ID#: 5 K9: Kimbo Breed: Shepherd Age: 2.5yrs Time in service: 1yr

	ORT				
	D1	D2	MJ	B	B
Response			Alert		

	Lineup #1				
	D3	H1	D4	B	B
Response					

	Lineup #2				
	B	D5	H2	B	D6
Response			Alert		

	Lineup #3				
	D7	H3	B	D8	B
Response		Alert			

	Lineup #4				
	B	D9	D10	B	H4
Response					Alert

	Lineup #5				
	H5	B	B	D3	D4
Response	Alert				

	Lineup #6				
	D5	B	D6	H6	B
Response					

	Lineup #7				
	D7	B	H7	B	D8
Response					

	Lineup #8				
	B	H8	D9	D10	B
Response					

ID#: 6 K9: Amor Breed: Shepherd/Malinois Age:4.5yrs Time in service: 2.5yrs

	ORT				
	D1	D2	MJ	B	B
Response			Alert		

	Lineup #1				
	D3	H1	D4	B	B
Response					

	Lineup #2				
	B	D5	H2	B	D6
Response					

	Lineup #3				
	D7	H3	B	D8	B
Response					

	Lineup #4				
	B	D9	D10	B	H4
Response					

	Lineup #5				
	H5	B	B	D3	D4
Response					

	Lineup #6				
	D5	B	D6	H6	B
Response					

	Lineup #7				
	D7	B	H7	B	D8
Response					

	Lineup #8				
	B	H8	D9	D10	B
Response					

ID#: 7 K9: Kaz Breed: Malinois Age: 5yrs Time in service: 3yrs

	ORT				
	D1	D2	MJ	B	B
Response			Alert		

	Lineup #1				
	D3	H1	D4	B	B
Response					

	Lineup #2				
	B	D5	H2	B	D6
Response					

	Lineup #3				
	D7	H3	B	D8	B
Response		Alert			

	Lineup #4				
	B	D9	D10	B	H4
Response					Alert

	Lineup #5				
	H5	B	B	D3	D4
Response					

	Lineup #6				
	D5	B	D6	H6	B
Response					

	Lineup #7				
	D7	B	H7	B	D8
Response					

	Lineup #8				
	B	H8	D9	D10	B
Response					

ID#: 8 K9: Astor Breed: German Pointer Age:6yrs Time in service: 5yrs

	ORT				
	D1	D2	MJ	B	B
Response			Alert		

	Lineup #1				
	D3	H1	D4	B	B
Response		Alert			

	Lineup #2				
	B	D5	H2	B	D6
Response			Alert		

	Lineup #3				
	D7	H3	B	D8	B
Response		Alert			

	Lineup #4				
	B	D9	D10	B	H4
Response					Alert

	Lineup #5				
	H5	B	B	D3	D4
Response	Alert				

	Lineup #6				
	D5	B	D6	H6	B
Response					

	Lineup #7				
	D7	B	H7	B	D8
Response			Alert		

	Lineup #8				
	B	H8	D9	D10	B
Response					

ID#: 9 K9: Bloo Breed: Belgian Malinois Age:3yrs Time in service: 2yrs

	ORT				
	D1	D2	MJ	B	B
Response			Alert		

	Lineup #1				
	D3	H1	D4	B	B
Response					

	Lineup #2				
	B	D5	H2	B	D6
Response					

	Lineup #3				
	D7	H3	B	D8	B
Response					

	Lineup #4				
	B	D9	D10	B	H4
Response					

	Lineup #5				
	H5	B	B	D3	D4
Response	Alert				

	Lineup #6				
	D5	B	D6	H6	B
Response					

	Lineup #7				
	D7	B	H7	B	D8
Response			Alert		

	Lineup #8				
	B	H8	D9	D10	B
Response					

ID#: 10 K9: Rex Breed: German Shepherd Age:5yrs Time in service:2yrs

	ORT				
	D1	D2	MJ	B	B
Response			Alert		

	Lineup #1				
	D3	H1	D4	B	B
Response		Alert			

	Lineup #2				
	B	D5	H2	B	D6
Response			Alert		

	Lineup #3				
	D7	H3	B	D8	B
Response		Alert			

	Lineup #4				
	B	D9	D10	B	H4
Response					Alert

	Lineup #5				
	H5	B	B	D3	D4
Response	Alert				

	Lineup #6				
	D5	B	D6	H6	B
Response					

	Lineup #7				
	D7	B	H7	B	D8
Response			Alert		

	Lineup #8				
	B	H8	D9	D10	B
Response					

ID#: 11 K9: Kazan Breed: German Shepherd Age:2yrs Time in service: 1yr

	ORT				
	D1	D2	MJ	B	B
Response			Alert		

	Lineup #1				
	D3	H1	D4	B	B
Response		Alert			

	Lineup #2				
	B	D5	H2	B	D6
Response			Alert		

	Lineup #3				
	D7	H3	B	D8	B
Response		Alert			

	Lineup #4				
	B	D9	D10	B	H4
Response					Alert

	Lineup #5				
	H5	B	B	D3	D4
Response	Alert				

	Lineup #6				
	D5	B	D6	H6	B
Response				Alert	

	Lineup #7				
	D7	B	H7	B	D8
Response			Alert		

	Lineup #8				
	B	H8	D9	D10	B
Response					

ID#: 12 K9:Klaus Breed: Czech Shepherd Age:4yrs Time in service: 2 weeks

	ORT				
	D1	D2	MJ	B	B
Response			Alert		

	Lineup #1				
	D3	H1	D4	B	B
Response		Alert			

	Lineup #2				
	B	D5	H2	B	D6
Response					

	Lineup #3				
	D7	H3	B	D8	B
Response		Alert			

	Lineup #4				
	B	D9	D10	B	H4
Response					Alert

	Lineup #5				
	H5	B	B	D3	D4
Response	Alert				

	Lineup #6				
	D5	B	D6	H6	B
Response				Alert	

	Lineup #7				
	D7	B	H7	B	D8
Response			Alert		

	Lineup #8				
	B	H8	D9	D10	B
Response		Alert			

ID#: 13 K9: Milan Breed: Shepherd Age:3yrs Time in service:2yrs

	ORT				
	D1	D2	MJ	B	B
Response			Alert		

	Lineup #1				
	D3	H1	D4	B	B
Response		Alert			

	Lineup #2				
	B	D5	H2	B	D6
Response			Alert		

	Lineup #3				
	D7	H3	B	D8	B
Response		Alert			

	Lineup #4				
	B	D9	D10	B	H4
Response					Alert

	Lineup #5				
	H5	B	B	D3	D4
Response					

	Lineup #6				
	D5	B	D6	H6	B
Response					

	Lineup #7				
	D7	B	H7	B	D8
Response					

	Lineup #8				
	B	H8	D9	D10	B
Response					

ID#: 14 K9: Bane Breed: Malinois Age: 5yrs Time in service: 4yrs

	ORT				
	D1	D2	MJ	B	B
Response			Alert		

	Lineup #1				
	D3	H1	D4	B	B
Response		SI			

	Lineup #2				
	B	D5	H2	B	D6
Response			I		

	Lineup #3				
	D7	H3	B	D8	B
Response					

	Lineup #4				
	B	D9	D10	B	H4
Response					I

	Lineup #5				
	H5	B	B	D3	D4
Response					

	Lineup #6				
	D5	B	D6	H6	B
Response					

	Lineup #7				
	D7	B	H7	B	D8
Response					

	Lineup #8				
	B	H8	D9	D10	B
Response		Alert			

ID#: 15 K9: Knox Breed: German Shepherd Age: 2.5yrs Time in service: 1yr

	ORT				
	D1	D2	MJ	B	B
Response			Alert		

	Lineup #1				
	D3	H1	D4	B	B
Response		Alert			

	Lineup #2				
	B	D5	H2	B	D6
Response			Alert		

	Lineup #3				
	D7	H3	B	D8	B
Response		Alert			

	Lineup #4				
	B	D9	D10	B	H4
Response					Alert

	Lineup #5				
	H5	B	B	D3	D4
Response	Alert				

	Lineup #6				
	D5	B	D6	H6	B
Response				Alert	

	Lineup #7				
	D7	B	H7	B	D8
Response			Alert		

	Lineup #8				
	B	H8	D9	D10	B
Response		Alert			

ID#: 16 K9: Lolli Breed: Labrador Age: 4yrs Time in service: 2yrs

	ORT				
	D1	D2	MJ	B	B
Response			Alert		

	Lineup #1				
	D3	H1	D4	B	B
Response		Alert			

	Lineup #2				
	B	D5	H2	B	D6
Response		Alert			Alert

	Lineup #3				
	D7	H3	B	D8	B
Response		Alert			

	Lineup #4				
	B	D9	D10	B	H4
Response					

	Lineup #5				
	H5	B	B	D3	D4
Response					

	Lineup #6				
	D5	B	D6	H6	B
Response				Alert	

	Lineup #7				
	D7	B	H7	B	D8
Response			Alert		

	Lineup #8				
	B	H8	D9	D10	B
Response					

ID#: 17 K9:Truus Breed: Dutch Shepherd Age: 5yrs Time in service: 3yrs

	ORT				
	D1	D2	MJ	B	B
Response			Alert		

	Lineup #1				
	D3	H1	D4	B	B
Response		Alert			

	Lineup #2				
	B	D5	H2	B	D6
Response			Alert		

	Lineup #3				
	D7	H3	B	D8	B
Response		Alert			

	Lineup #4				
	B	D9	D10	B	H4
Response					Alert

	Lineup #5				
	H5	B	B	D3	D4
Response					

	Lineup #6				
	D5	B	D6	H6	B
Response				Alert	

	Lineup #7				
	D7	B	H7	B	D8
Response					

	Lineup #8				
	B	H8	D9	D10	B
Response					

ID#: 18 K9:Edge Breed: Malinois Age:6yrs Time in service:4.5yrs

	ORT				
	D1	D2	MJ	B	B
Response			Alert		

	Lineup #1				
	D3	H1	D4	B	B
Response					

	Lineup #2				
	B	D5	H2	B	D6
Response		Alert			

	Lineup #3				
	D7	H3	B	D8	B
Response		Alert			

	Lineup #4				
	B	D9	D10	B	H4
Response					Alert

	Lineup #5				
	H5	B	B	D3	D4
Response	Alert				

	Lineup #6				
	D5	B	D6	H6	B
Response				Alert	

	Lineup #7				
	D7	B	H7	B	D8
Response					

	Lineup #8				
	B	H8	D9	D10	B
Response					

ID#: 19 K9: Frankie Breed: Mixed Shepherd Age: 2.5yrs Time in service: 1yr

	ORT				
	D1	D2	MJ	B	B
Response			Alert		

	Lineup #1				
	D3	H1	D4	B	B
Response					

	Lineup #2				
	B	D5	H2	B	D6
Response					

	Lineup #3				
	D7	H3	B	D8	B
Response					

	Lineup #4				
	B	D9	D10	B	H4
Response					Alert

	Lineup #5				
	H5	B	B	D3	D4
Response	Alert				

	Lineup #6				
	D5	B	D6	H6	B
Response				Alert	

	Lineup #7				
	D7	B	H7	B	D8
Response			Alert		

	Lineup #8				
	B	H8	D9	D10	B
Response					

ID#: 20 K9: Renno Breed: Belgian Shepherd Age: 2yrs Time in service: 1yr

	ORT				
	D1	D2	MJ	B	B
Response			Alert		

	Lineup #1				
	D3	H1	D4	B	B
Response		Alert			

	Lineup #2				
	B	D5	H2	B	D6
Response		Alert			

	Lineup #3				
	D7	H3	B	D8	B
Response		Alert			

	Lineup #4				
	B	D9	D10	B	H4
Response					Alert

	Lineup #5				
	H5	B	B	D3	D4
Response	Alert				

	Lineup #6				
	D5	B	D6	H6	B
Response				Alert	

	Lineup #7				
	D7	B	H7	B	D8
Response			Alert		

	Lineup #8				
	B	H8	D9	D10	B
Response		Alert			

ID#: 21 K9: Brix Breed: Malinois Age: 7yrs Time in service: 5yrs

	ORT				
	D1	D2	MJ	B	B
Response			Alert		

	Lineup #1				
	D3	H1	D4	B	B
Response		Alert	Alert		

	Lineup #2				
	B	D5	H2	B	D6
Response			Alert		

	Lineup #3				
	D7	H3	B	D8	B
Response		Alert			

	Lineup #4				
	B	D9	D10	B	H4
Response					Alert

	Lineup #5				
	H5	B	B	D3	D4
Response	Alert				

	Lineup #6				
	D5	B	D6	H6	B
Response					Alert

	Lineup #7				
	D7	B	H7	B	D8
Response			Alert		

	Lineup #8				
	B	H8	D9	D10	B
Response	Alert				Alert

ID#: 22 K9: Peper Breed: Malinois Age: 3yrs Time in service: 1yr

	ORT				
	D1	D2	MJ	B	B
Response			Alert		

	Lineup #1				
	D3	H1	D4	B	B
Response		Alert			

	Lineup #2				
	B	D5	H2	B	D6
Response			Alert		

	Lineup #3				
	D7	H3	B	D8	B
Response		Alert			

	Lineup #4				
	B	D9	D10	B	H4
Response					Alert

	Lineup #5				
	H5	B	B	D3	D4
Response	Alert				

	Lineup #6				
	D5	B	D6	H6	B
Response				Alert	

	Lineup #7				
	D7	B	H7	B	D8
Response			Alert		

	Lineup #8				
	B	H8	D9	D10	B
Response					

ID#: 23 K9:Zane Breed: Malinois/Shepherd Age: 7yrs Time in service: 6yrs

	ORT				
	D1	D2	MJ	B	B
Response			Alert		

	Lineup #1				
	D3	H1	D4	B	B
Response		Alert			

	Lineup #2				
	B	D5	H2	B	D6
Response			Alert		

	Lineup #3				
	D7	H3	B	D8	B
Response		Alert			

	Lineup #4				
	B	D9	D10	B	H4
Response					Alert

	Lineup #5				
	H5	B	B	D3	D4
Response	Alert				

	Lineup #6				
	D5	B	D6	H6	B
Response				Alert	

	Lineup #7				
	D7	B	H7	B	D8
Response			Alert		

	Lineup #8				
	B	H8	D9	D10	B
Response					

ID#: 24 K9: Jakel Breed: Malinois Age: 4yrs Time in service: 2yrs

	ORT				
	D1	D2	MJ	B	B
Response			Alert		

	Lineup #1				
	D3	H1	D4	B	B
Response		Alert			

	Lineup #2				
	B	D5	H2	B	D6
Response					

	Lineup #3				
	D7	H3	B	D8	B
Response					

	Lineup #4				
	B	D9	D10	B	H4
Response					Alert

	Lineup #5				
	H5	B	B	D3	D4
Response	Alert				

	Lineup #6				
	D5	B	D6	H6	B
Response				Alert	

	Lineup #7				
	D7	B	H7	B	D8
Response			Alert		

	Lineup #8				
	B	H8	D9	D10	B
Response					

Appendix C: Individual results and PPV for Hemp vs Marijuana Trial 2. A=Alert

ID#: 3 **K9: Paco** **Breed: Shepherd/Malinois** **Age: 3yrs** **Time in service: 3yrs**

	Lineup #1																	
	H2	H11	H6	H1	D1	H5	H10	B	MJ	D2	H3	H9	D3	H7	H4	H8	H12	B
Response									A									

	Lineup #2																	
	H2	H11	H6	H1	D1	MJ	H10	B	H5	D2	H3	H9	D3	H7	H4	H8	H12	B
Response						A												

	Lineup #3																	
	H2	MJ	H6	H1	D1	H11	H10	B	H5	D2	H3	H9	D3	H7	H4	H8	H12	B
Response		A																

	Lineup #4																	
	H2	H8	H6	H1	D1	H11	H10	B	H5	D2	H3	H9	D3	H7	H4	MJ	H12	B
Response																A		

ID#: 4 **K9: Cino** **Breed: German Shepherd** **Age: 5yrs** **Time in service: 4yrs**

	Lineup #1																	
	H2	H11	H6	H1	D1	H5	H10	B	MJ	D2	H3	H9	D3	H7	H4	H8	H12	B
Response									A									

	Lineup #2																	
	H2	H11	H6	H1	D1	MJ	H10	B	H5	D2	H3	H9	D3	H7	H4	H8	H12	B
Response						A												

	Lineup #3																	
	H2	MJ	H6	H1	D1	H11	H10	B	H5	D2	H3	H9	D3	H7	H4	H8	H12	B
Response		A																

	Lineup #4																	
	H2	H8	H6	H1	D1	H11	H10	B	H5	D2	H3	H9	D3	H7	H4	MJ	H12	B
Response																A		

ID#:5 **K9: Kimbo** **Breed:Shepherd** **Age: 3yrs** **Time in service: 1.5yrs**

	Lineup #1																	
	H2	H11	H6	H1	D1	H5	H10	B	MJ	D2	H3	H9	D3	H7	H4	H8	H12	B
Response									A									

	Lineup #2																	
	H2	H11	H6	H1	D1	MJ	H10	B	H5	D2	H3	H9	D3	H7	H4	H8	H12	B
Response						A												

	Lineup #3																	
	H2	MJ	H6	H1	D1	H11	H10	B	H5	D2	H3	H9	D3	H7	H4	H8	H12	B
Response		A											A					

	Lineup #4																	
	H2	H8	H6	H1	D1	H11	H10	B	H5	D2	H3	H9	D3	H7	H4	MJ	H12	B
Response																A		

ID#: 6 **K9: Amor** **Breed: Shepherd/Malinois** **Age: 5yrs** **Time in service: 3yrs**

	Lineup #1																	
	H2	H11	H6	H1	D1	H5	H10	B	MJ	D2	H3	H9	D3	H7	H4	H8	H12	B
Response									A									

	Lineup #2																	
	H2	H11	H6	H1	D1	MJ	H10	B	H5	D2	H3	H9	D3	H7	H4	H8	H12	B
Response						A												

	Lineup #3																	
	H2	MJ	H6	H1	D1	H11	H10	B	H5	D22	H3	H9	D3	H7	H4	H8	H12	B
Response		A																

	Lineup #4																	
	H2	H8	H6	H1	D1	H11	H10	B	H5	D2	H3	H9	D3	H7	H4	MJ	H12	B
Response																A		

ID#:16 **K9: Lolli** **Breed:Labrador** **Age: 2.5yrs** **Time in service: 4.5ys**

	Lineup #1																	
	H2	H11	H6	H1	D1	H5	H10	B	MJ	D2	H3	H9	D3	H7	H4	H8	H12	B
Response									A									

	Lineup #2																	
	H2	H11	H6	H1	D1	MJ	H10	B	H5	D2	H3	H9	D3	H7	H4	H8	H12	B
Response						A						A	A					

	Lineup #3																	
	H2	MJ	H6	H1	D1	H11	H10	B	H5	D2	H3	H9	D3	H7	H4	H8	H12	B
Response		A																

	Lineup #4																	
	H2	H8	H6	H1	D1	H11	H10	B	H5	D2	H3	H9	D3	H7	H4	MJ	H12	B
Response																A		

ID#:25 **K9: Kora** **Breed: Shepherd** **Age: 3yrs** **Time in service: 1yr**

	Lineup #1																	
	H2	H11	H6	H1	D11	H5	H10	B	MJ	D2	H3	H9	D3	H7	H4	H8	H12	B
Response									A									

	Lineup #2																	
	H2	H11	H6	H1	D1	MJ	H10	B	H5	D2	H3	H9	D3	H7	H4	H8	H12	B
Response						A												

	Lineup #3																	
	H2	MJ	H6	H1	D1	H11	H10	B	H5	D2	H3	H9	D3	H7	H4	H8	H12	B
Response		A																

	Lineup #4																	
	H2	H8	H6	H1	D1	H11	H10	B	H5	D2	H3	H9	D3	H7	H4	MJ	H12	B
Response																A		

ID#: 26 **K9: Dante** **Breed: Malinois** **Age:6yrs** **Time in service: 4yrs**

	Lineup #1																	
	H2	H11	H6	H1	D1	H5	H10	B	MJ	D2	H3	H9	D3	H7	H4	H8	H12	B
Response									Alert									

	Lineup #2																	
	H2	H11	H6	H1	D1	MJ	H10	B	H5	D2	H3	H9	D3	H7	H4	H8	H12	B
Response						Alert												

	Lineup #3																	
	H2	MJ	H6	H1	D1	H11	H10	B	H5	D2	H3	H9	D3	H7	H4	H8	H12	B
Response		Alert																

	Lineup #4																	
	H2	H8	H6	H1	D1	H11	H10	B	H5	D2	H3	H9	D3	H7	H4	MJ	H12	B
Response																Alert		

ID#: 28 **K9: Dejavu** **Breed: Malinois** **Age: 6yrs** **Time in service: 4yrs**

	Lineup #1																	
	H2	H11	H6	H1	D1	H5	H10	B	MJ	D2	H3	H9	D3	H7	H4	H8	H12	B
Response									A									

	Lineup #2																	
	H2	H11	H6	H1	D1	MJ	H10	B	H5	D2	H3	H9	D3	H7	H4	H8	H12	B
Response						A												

	Lineup #3																	
	H2	MJ	H6	H1	D1	H11	H10	B	H5	D2	H3	H9	D3	H7	H4	H8	H12	B
Response		A																

	Lineup #4																	
	H2	H8	H6	H1	D1	H11	H10	B	H5	D2	H3	H9	D3	H7	H4	MJ	H12	B
Response																A		

ID#: 29 **K9: Kane** **Breed: Malinois** **Age: 7yrs** **Time in service: 5yrs**

	Lineup #1																	
	H2	H11	H6	H1	D1	H5	H10	B	MJ	D2	H3	H9	D3	H7	H4	H8	H12	B
Response									A									

	Lineup #2																	
	H2	H11	H6	H1	D1	MJ	H10	B	H5	D2	H3	H9	D3	H7	H4	H8	H12	B
Response						A												

	Lineup #3																	
	H2	MJ	H6	H1	D1	H11	H10	B	H5	D2	H3	H9	D3	H7	H4	H8	H12	B
Response		A											A					

	Lineup #4																	
	H2	H8	H6	H1	D1	H11	H10	B	H5	D2	H3	H9	D3	H7	H4	MJ	H12	B
Response																A		

Officer ID#: 30 **K9: Daisy** **Breed: Dutch Shepherd** **Age: 8yrs** **Time in service:1yr**

	Lineup #1																	
	H2	H11	H6	H1	D1	H5	H10	B	MJ	D2	H3	H9	D3	H7	H4	H8	H12	B
Response									A									

	Lineup #2																	
	H2	H11	H6	H1	D1	MJ	H10	B	H5	D2	H3	H9	D3	H7	H4	H8	H12	B
Response						A												

	Lineup #3																	
	H2	MJ	H6	H1	D1	H11	H10	B	H5	D2	H3	H9	D3	H7	H4	H8	H12	B
Response		A																

	Lineup #4																	
	H2	H8	H6	H1	D1	H11	H10	B	H5	D2	H3	H9	D3	H7	H4	MJ	H12	B
Response																A		

Appendix E: *Cannabis* VOCs confirmed using liquid reference standard terpene mixes purchased from AccuStandard.

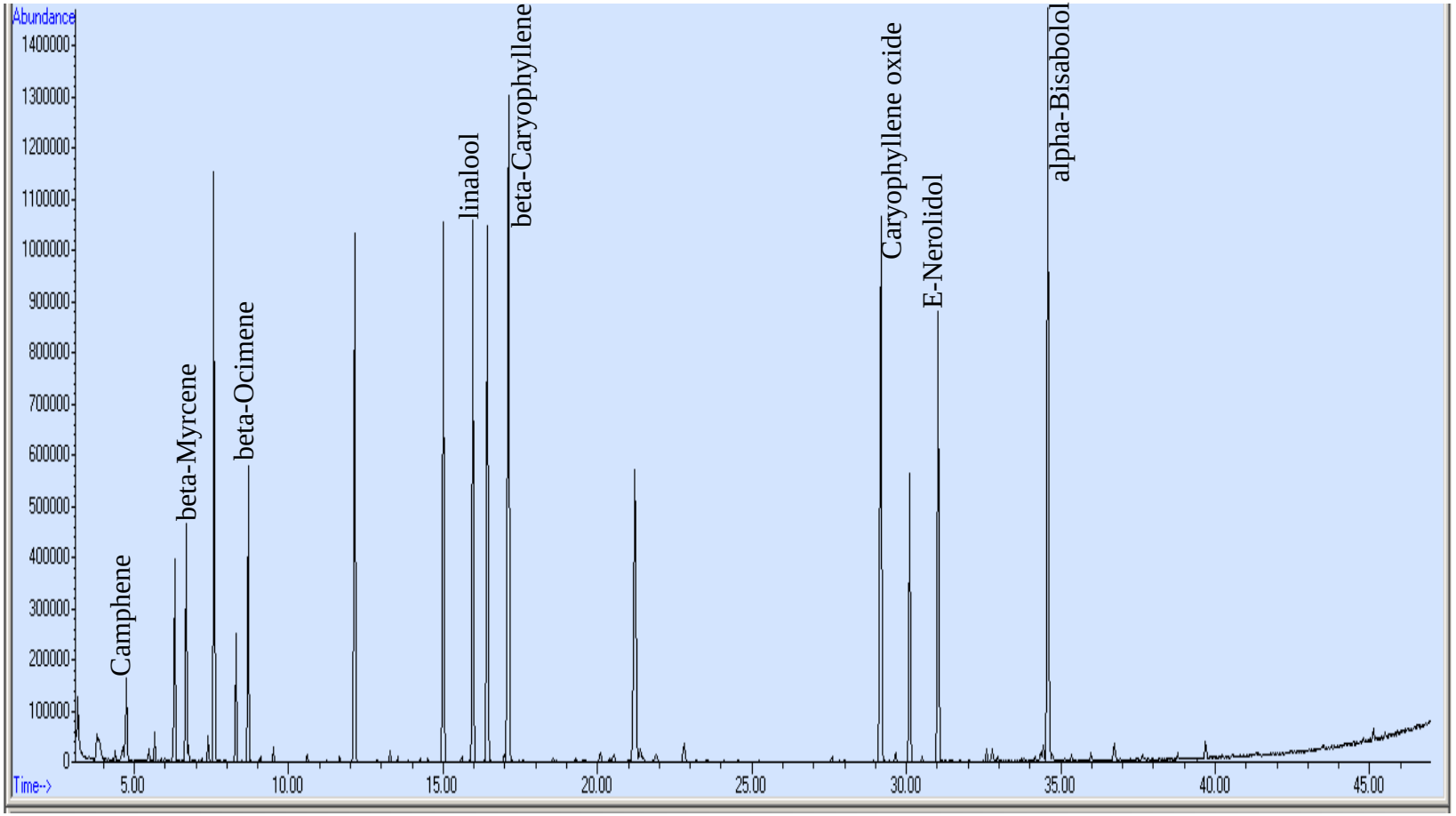

Figure 88. Chromatogram of terpene mix #1 (100ppm in methanol) with labeled peaks representing the respective compounds used to additionally confirm Cannabis VOCs based on similar retention times. Unlabeled peaks represent terpene compounds present in the mix that were not detected in this study.

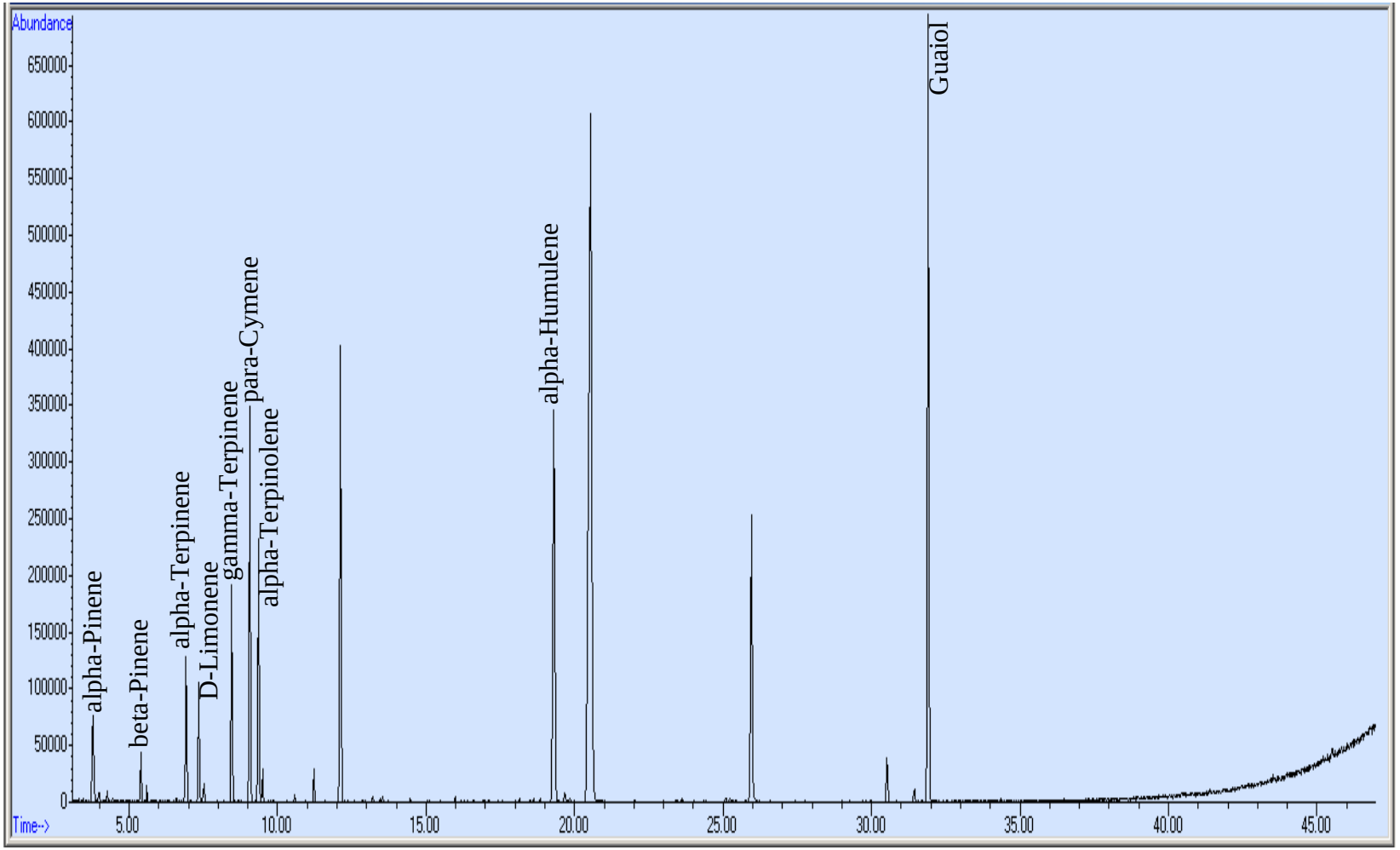

Figure 89. Chromatogram of terpene mix #2 (100ppm in methanol) with labeled peaks representing the respective compounds used to additionally confirm Cannabis VOCs based on similar retention times. Unlabeled peaks represent terpene compounds present in the mix that were not detected in this study.

Appendix F: Mass Storage Devices VOCs confirmed using a 100ppm mix of eight compounds in methylene chloride.

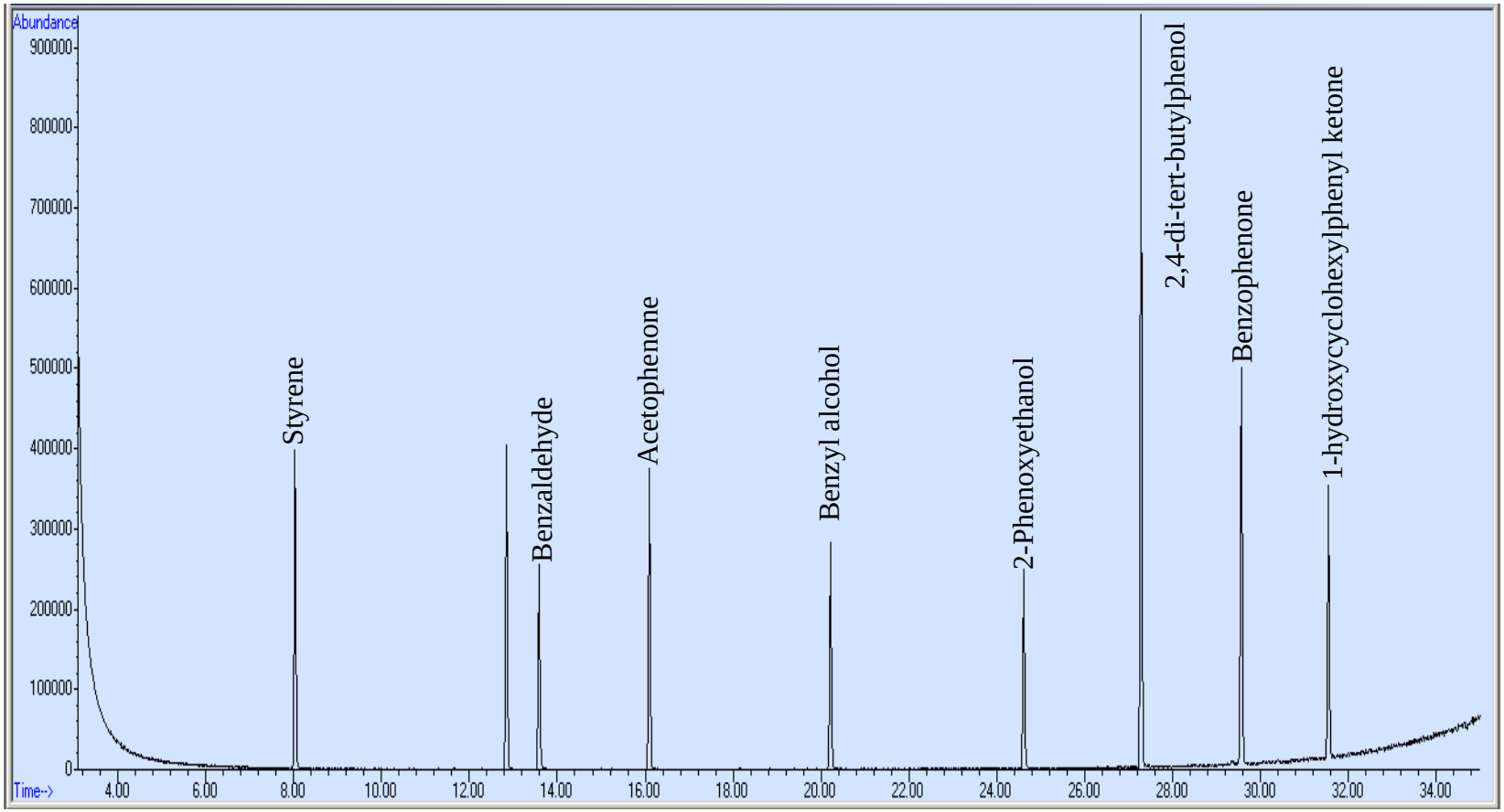

Figure 90. Chromatogram of a 100ppm in methylene chloride mix of eight compounds used to confirm mass storage devices VOCs based on similar retention times.

Appendix G: Setup and Results of the TATP Pseudo dog Trial

Table 34. List of targets and distractors used for the TATP Pseudo dog trial.

List of Targets and Distractors	
Pseudo 1	Scent Logix TATP
Pseudo 2	Signature Science TATP
D1	Alpha-pinene
D2	Limonene
D3	Benzaldehyde
D4	Methyl Benzoate

ID#: 1 K9: Fritz Breed: Malinois Age: 5yrs Time in service:

	Lineup #1				
	D1	B	Pseudo1	B	D2
Response			Alert		

	Lineup #2				
	Pseudo2	B	B	D4	D3
Response	Alert				

	Lineup #3				
	B	D1	D2	Acetone	B
Response				Alert	

	Lineup #4				
	D3	H.Peroxide	D4	D8	B
Response		Alert		Alert	

ID#: 2 K9: Sam Breed: Shepherd Age: 8yrs Time in service:

	Lineup #1				
	D1	B	Pseudo1	B	D2
Response			Alert		Alert

	Lineup #2				
	Pseudo2	B	B	D4	D3
Response	Alert				

	Lineup #3				
	B	D1	D2	Acetone	B
Response					

	Lineup #4				
	D3	H.Peroxide	D4	D8	B
Response					

VITA

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PUBLICATIONS AND PRESENTATIONS

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