

ELECTRONICS AUTHENTICITY TESTING USING COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY

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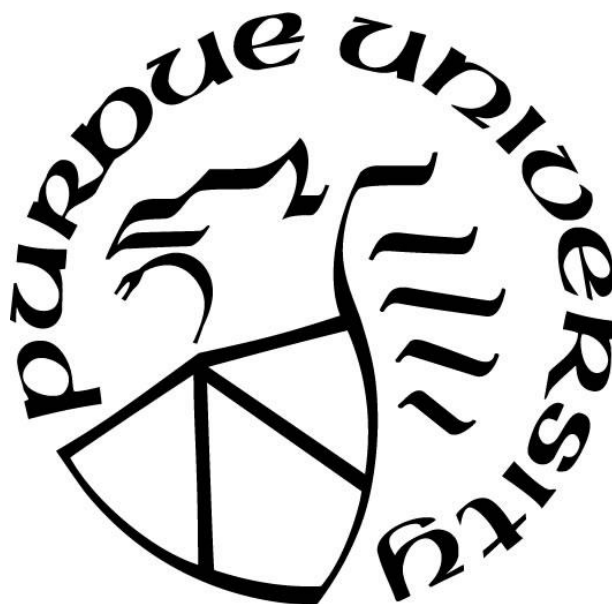
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LIST OF ABBREVIATIONS

DoD	United States Department of Defense
ESD	Electronic Scent Detection
GC×GC	Comprehensive Two-Dimensional Gas Chromatography
GC×GC-FID	Comprehensive Two-Dimensional Gas Chromatography with Flame Ionization Detector
GC×GC-TOF/MS	Comprehensive Two-Dimensional Gas Chromatography with Time-of-Flight Mass Spectrometry
MSD	Mass Storage Device
SPME	Solid-Phase Microextraction
TPPO	Triphenylphosphine Oxide
VOC	Volatile Organic Compound (See Volatile Chemical)

DEFINITIONS

This document uses project-specific terms. This definition list defines specific terms used within the scope of this project.

- Comprehensive Two-Dimensional Gas Chromatography (GC×GC): “A means of increasing the separation capability of a chromatographic system for complex samples” (Jan Beens, Hans Boelens, 1997, p. 47).
- Electronic Device: “Electronic devices are components for controlling the flow of electrical currents for the purpose of information processing and system control ... Electronic devices are usually small and can be grouped together into packages called integrated circuits” (Nature, n.d.). Referred to coequally in this thesis as “electronic component,” “device,” or “component.”
- Headspace: “The term “headspace” in gas chromatography denotes the vapor phase within a sealed container also containing a liquid or solid.” (Sithersingh & Snow, 2012, p. 221).
- Solid-Phase Microextraction (SPME): A method for “sampling a wide range of analytes from gases, liquids and solids with various ... compositions ... It can be used indirectly for analysing the composition of liquid and solid samples by extracting the analytes from the headspace above them.” (Spietelun, Pilarczyk, Kloskowski, & Namieśnik, 2010).
- Volatile Chemicals: Chemicals which are “readily vaporizable at a relatively low temperature” (Merriam-Webster, n.d.). Also referred to as Volatile Organic Compounds (VOCs) in this thesis.
- United States Department of Defense (DoD): “The Department of Defense provides the military forces needed to deter war and ensure our nation [The United States]’s security.” (U.S. Government, n.d.).

ABSTRACT

Technology has become increasingly more prevalent in all aspects of society since the age of the computer. The United States Military has successfully integrated the powerful processing capabilities of computers to increase the proficiency and lethality of its Soldiers, Sailors, Marines, and Airmen. However, this increased lethality comes at risk due to the inherent vulnerabilities of computer systems to spyware, malware, and counterfeit components. Inspired by the ability of canines to seek out and find electronic devices, this research sought methods to characterize components by their “scent” using precise analytical tools. Using these tools, this thesis sought to develop and utilize non-invasive methods to show proof-of-concept for electronic device classification by volatile compounds unique to different types of components. The findings of this research proved that electronic components that vary by age, origin, type, or manufacturer emit different volatile compounds available for detection using modern two-dimensional gas chromatography and solid-phase microextraction technologies. If developed further, the methods used in this research have the potential for application in the United States Department of Defense to ensure that all electronic components installed in their systems are authentic, come from a trusted source, and can be relied upon in even the most stressful operating conditions.

CHAPTER 1. INTRODUCTION

1.1 Introduction to the Problem

Electronic components are prevalent throughout the vast majority of warfare systems utilized by the United States Armed Services. In radios, complex onboard airplane flight computers in airplanes, guidance computers used in intercontinental ballistic missiles, AN/SPY-1 Aegis defense radars, nuclear reactors, and many more systems, electronic components provide the processing power and computation functionality required to run all these systems. Ensuring that each of these systems reliably functions at all times is mission-critical to the Army, Air Force, Navy, and the Marine Corps (Petel, 2014, p. 2). Failures of these systems to support the warfighters that use them can introduce risk into operations that can endanger equipment, mission success, and lives. At best, system failures may result in slightly limited situational awareness. However, at worst, critical system failures can cause loss of essential functionalities that can cause catastrophic loss of assets that claim the lives of service members as well as cost the taxpayers up to billions of dollars.

Thus, there is an incentive for the United States Department of Defense (DoD) to ensure that the components and electronic devices used in complex electronic systems function correctly in the most adverse and strenuous environments imaginable. The United States military in the past 75 years has operated in significantly varying climates. In jungles, tundra, deserts, and temperate climates, electronic equipment has assisted the Army, Navy, Air Force, and Marine Corps to fight and win against adversaries. Hot, cold and wet environments are significant challenges to the functionality of electronic devices. An inability for the Nation's military forces to operate and communicate with, as well as support each other in these challenging environments presents a heightened risk to mission completion and the lives of Soldiers, Sailors,

Airmen, and Marines. Counterfeit or otherwise compromised electronic components that find their way into the DoD procurement network present a dire risk to the functionality of these systems under strenuous operating conditions.

Failure of electronic components can be caused by many variables, including the installation of counterfeit components. Currently, there is no way to verify the authenticity of electronic components prior to installing them in systems. Accordingly, the discovery of counterfeit parts usually does not occur until there is a rise in system failures. Further investigations of these failures can uncover multiple counterfeit components and even incorrectly assign cause (Stradley & Karraker, 2006, p. 703). The amount of counterfeit electronic devices that have found their way into the DoD supply chain has increased in recent years (Livingston, 2010, p. 1). In a period of four years, reported counterfeit electronic devices more than doubled from 3,868 in 2005 to 9,356 in 2008 (U.S. Department of Commerce, 2010, p. 169). This trend has undoubtedly continued as the use of DoD systems is extended past the systems' respective end-of-service dates.

Counterfeit components, for the purposes of this thesis, include all components which do not originate from a known, trusted source. Developing an alternative method for assessing the authenticity and performance potential of unknown and unproven components may decrease the risk of unfortunate equipment malfunctions and system failures within the DoD.

1.2 Statement of the Problem

The DoD purchases electronic components that must withstand the demands of modern military electronic systems. Ensuring new and capable electronic components, rather than repurposed or counterfeit components, are used in these systems is essential to the functionality of these systems and maintaining a decisive edge over peer rivals. Currently, it is difficult to

determine the authenticity and true source of an electronic component unless it can be traced directly from the manufacturer to the user.

The purpose of this study was to analyze the chemical signatures of electronic components as they vary with age, origin, type, and manufacturer to generate a method to predict the source of an unknown component. Comprehensive two-dimensional gas chromatography (GC×GC) partnered with solid-phase microextraction (SPME) methods were used to detect any volatile compounds which may be emitted from components. Results from sampled components were analyzed with regard to type and source of component. This research sought to develop methods for detecting chemical indicators that might be useful for the DoD to determine, with accuracy, if the electronic components they receive for systems are genuine new products from reliable sources and not disguised, repurposed counterfeits.

1.3 Research Question

What volatile chemical species can be detected from electronic components using GC×GC and SPME methods?

1. Are volatile compounds present and measurable in microcontrollers and MSDs?
2. Does the chemical signature of electronic components vary with origin and type of the components?

1.4 Significance

Identifying the authenticity of components used in high-end electronic devices is essential to ensure that those components can withstand the operating conditions required by the DoD. Currently, it is difficult to determine the authenticity of an electronic component unless it can be traced directly from the manufacturer to the user. This issue is specifically important to the DoD,

as it seeks to maintain its edge over peer rivals. Electronic devices are becoming more prevalent on the battlefield. Thus, the use of electronic devices in war has exponentially increased the United States' ability to dominate in both kinetic and electronic warfare (Berkowitz, 1995).

Securing cyberspace is one of the 14 grand challenges to engineering as published by the National Academy for Engineers in 2015. This thesis addresses this challenge by demonstrating proof-of-concept for an evaluation method that might mitigate the risks posed by the continued proliferation of counterfeit electronic components in the DoD supply chain.

1.5 Scope

For this research, GC×GC and SPME was utilized to analyze volatile compounds taken from the headspace surrounding electronic devices. This research was limited to the analysis of volatile compounds potentially found in electronic equipment which can be detected with current GC×GC and SPME technology. Further, this research sought to identify variations, if any, in the volatile organic compound (VOC) profiles between electronic components and mass storage devices (MSDs) originating from various manufacturers and types.

1.6 Assumptions

In order for this research to be conducted within the scope outlined previously, it is important to note a few key assumptions that must be accepted. These assumptions are to be considered as true, indisputable facts for the scope of this research. However, the results of this research may clarify, confirm, or refute some of these assumptions.

The assumptions for this research project are as follows:

1. Certain volatile compounds are found commonly and uniquely across all types of electronic devices in varying quantities.

2. These volatile compounds are available in the headspace surrounding electronic components and MSDs for sampling using SPME.
3. Electronic components are characterized by different chemical vapor profiles, the make-up of which is dictated by the type, age, manufacturer, and origin of the component.
4. Canines have the ability to detect volatile compounds in low concentrations via their olfactory sensory organs.

1.7 Limitations

The intent of this research was to develop a repeatable method by which the DoD can verify MSD and electronic component authenticity despite the occurrence of the following limitations:

1. The sensitivity of GC×GC: Gas chromatographs may not have the sensitivity to detect the low levels of volatile compounds that are being detected by canines in similar situations. Depending on the compound, GC×GC has varying limits of detection for analyzing compounds at low concentrations.
2. Canine Training Procedures: Aids used by handlers to train canines for electronic scent detection (ESD) may not represent the true range of compounds that are being emitted by electronic devices.
3. Selection of GC×GC Methodology: Despite the capabilities of GC×GC to detect individual compounds in a sample, it is important to select the best GC×GC method to increase the separation of compounds. An incorrect method can cause co-elution of VOCs, which results in compounds being confused with others.

1.8 Delimitations

Some delimitations may have affected the research due to the path which was chosen in an effort to complete this research.

The delimitations of the research are as follows:

1. Selection of a general method for GC×GC analysis using SPME: GC×GC methods which are not optimized run the risk of misinterpreting VOCs or missing some VOCs entirely.

A general method for VOC detection was selected to capture the largest amounts of characteristic VOCs. The selection of certain method parameters can cause significant VOCs of interest to not be detected.

2. Independent variables: Component type, age, and manufacture origin are selected as the independent variables to investigate effects on volatile compound concentrations. Other independent variables that have not been anticipated may manipulate the concentrations of volatile compounds in unexpected ways.

CHAPTER 2. REVIEW OF LITERATURE

2.1 Electronic Device Counterfeiting and the Department of Defense

Computers and electronic devices have been successfully integrated into the warfare systems of every one of the service branches within the DoD. Electronics aid Soldiers, Sailors, Airmen, and Marines to globally navigate ships, aircraft, and ground units with GPS, communicate with networks supported by satellites, track and target adversaries with radar systems, deliver precision strikes with laser-guided smart-bombs, deter nuclear proliferation with ballistic missiles, and run nuclear power plants both underwater in submarines as well as aircraft carriers. These systems allow the United States of America to successfully support all mission areas across the globe, from waging and winning wars to delivering humanitarian aid. Without electronic devices, it would be extremely difficult to operate at the same operational skill and tempo. Protecting these systems from failure is essential to the national security interests of the United States and the protection of DoD personnel and property. One significant threat to these systems is counterfeit electronic devices which introduce the risk of system failure at crucial moments.

The introduction and proliferation of counterfeit electronic devices in DoD systems is attributed to two primary causes. Many systems within the DoD are used far beyond their expected end-of-service dates and the development of the globally integrated economy prevents logistically sourcing products produced solely within the United States (Gansler, Lucyshyn, & Rigilano, 2014, p. iv). These factors have made it easier for counterfeit products to find their way into the DoD logistics supply chain. It is estimated that in 2006, the DoD purchased between 15 and 21 million dollars in counterfeit semiconductors alone (Stradley & Karraker, 2006, p. 703). The source of these counterfeits is largely from electronics brokers.

Figure 2.1 details a sample supply flow chart for electronic components that are used in DoD systems (U.S. Department of Commerce, 2009). Sources for electronic components can come from four primary sources: the original manufacturer, the original manufacturer's authorized distributors, independent distributors or brokers, or aftermarket manufacturers (Sullivan & Wilson, 2017, p. 318). As a pre-emptive measure, the DoD first seeks to purchase components from a trusted source which is a source known to produce genuine electronic components. This trusted source is typically the original manufacturer. However, because some systems have been extended far past their end-of-service dates, components may have to be purchased from sources other than the original manufacturer because they may no longer manufacture the component (Livingston, 2010, p. 2). Thus, the DoD may be forced to purchase from the original manufacturer's authorized distributors or even independent brokers who may not be as completely vetted. This less-than-desirable situation creates an opportunity for counterfeit electronic components to find their way into DoD systems, creating a weakness in the Nation's security as components may not be constructed to required specifications or components could be manufactured with a vulnerability to malicious malware via backdoor applications (Petel, 2014, p. 2).

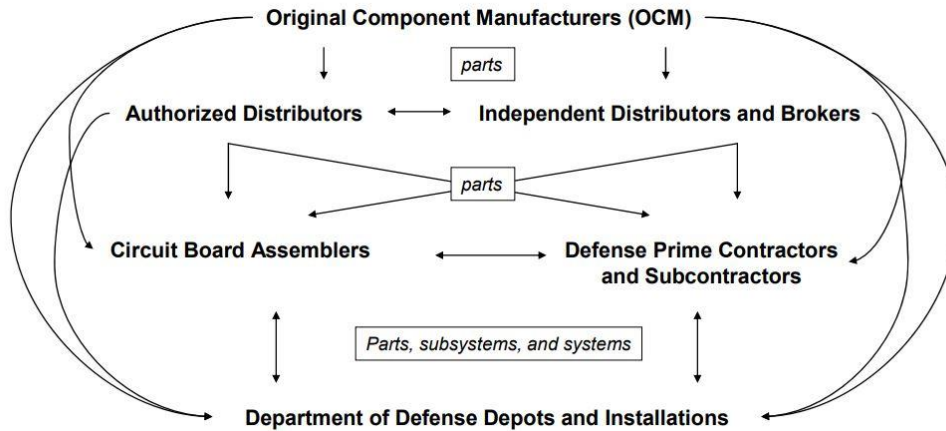


Figure 2.1 DoD Logistics Supply Map for Electronic Components

These concerns have existed since the first large-scale integrations of computers into DoD systems. In his article regarding the recent integration of computers with modern military equipment in the mid-1990s, Bruce Berkowitz wrote about the risks of relying on computers to run integral parts of warfare systems. Specifically, Berkowitz references the fact that the majority of the electronic components that the DoD installs in its systems are purchased from commercial retailers. Unfortunately, even then, many of these retailers were located in foreign countries (Berkowitz, 1995, p. 60). The obvious threat presented by Berkowitz is that when you rely on foreign entities to produce vital parts of weapons systems, someone could tamper with electronic components that are sent to the DoD. Then, when these compromised components are installed in systems, they would cause the weapons to fail at the most critical moments (Berkowitz, 1995, p. 60). Since the DoD cannot produce these components within the organization, it is important to ensure that even domestically produced components are fit for installation in weapons systems.

There are some methods in use by the United States Government or other organizations in industry for the purpose of verifying the integrity and functionality of authentic trusted source

parts. However, these tests are not necessarily designed to detect counterfeits, but rather the performance of the components (Livingston, 2010, p. 2). These methods include visual inspection, x-ray analysis, scanning electron microscopy, solderability, and decapsulation (Hillman, 2011, p. 13). Some of these, such as solderability tests and decapsulation, are invasive tests and result in the destruction of the components. The other tests require 100% testing for full confidence and are time-consuming (Hillman, 2011, p. 13).

Additionally, testing using these time-consuming methods usually does not occur prior to installation in systems. There exists no current method for comprehensively determining the authenticity of electronic components used in electronic devices prior to installing them in systems. This process is reactive and the DoD typically only detects counterfeits after an unexplained rise in system failures necessitates a thorough examination (U.S. Department of Commerce, 2010, p. 160). When it comes to high functionality systems such as those used in the DoD, there is no efficient way to evaluate the authenticity of the sheer numbers of components used in the thousands of electronic systems in the Army, Navy, Air Force, and Marine Corps. However, there is an identified need for ensuring that electronics that are sourced domestically and imported from manufacturers located in other countries are authentic. Developing a non-invasive method for evaluating the authenticity and quality of these critical components prior to installation might increase confidence in the systems and eliminate the risks outlined in the literature.

The first step in developing a method to test for the quality of electronic equipment is identifying unique aspects of electronic components that can be tested and measured to differentiate between a variety of variables such as age, manufacturer, country of origin, or performance. Suggestions for differentiating characteristics originate from existing knowledge

about canine scent detection. Canines have been proven to be successful in locating electronic devices using olfactory detection. The use of canines has been famously used in high profile law enforcement cases where canines successfully located small electronic devices that contained incriminating information stored on them (Kim, 2015). Todd Jordan, the owner of Jordan Detection K-9, is a professional whose business trains search dogs to specifically locate electronic devices. They are known as ESD canines. By using the organic compound Triphenylphosphine Oxide (TPPO), Mr. Jordan has been able to train multiple dogs to alert to these electronic devices. TPPO has been reported to be an additive used in coatings on electronic storage devices in order to facilitate heat transfer (Rayome, n.d.). Understanding how ESD canines detect TPPO and other volatile compounds aids significantly in developing methods for detecting chemical indicators that may be present in electronic components and MSDs.

2.2 Canine Scent Detection

Canines have been historically used to detect a variety of scents from explosives, drugs, cadavers, blood, cancer, and more recently, electronic devices. The unique application of canines in scent detection is due to their superior olfactory system, which is orders of magnitudes more sensitive than a human's. In Jehuda Yinon's article (2003) in *Analytical Chemistry*, Yinon described the specific reason why canines have been bred and are so adept at identifying odors. Their superior olfactory system is dominated by their large epithelium membrane. This membrane in long-snouted dogs such as German Shepherds is up to 30 times as large as a humans' (100 cm^2 compared to 3 cm^2 respectively). Receptors on this membrane are individually connected to the olfactory bulb, where scents are processed into signals that are then sent to the canine's brain. Yinon states that "good" scent detection canines can differentiate and alert to up to 14 different scents. Their advanced olfactory systems and versatility allow them to detect very

minute traces of many compounds or odors which they have been trained to detect or acknowledge (Yinon, 2003, p. 100).

For thousands of years, canines have been used as a tool because of their enhanced scent-detecting capabilities. But, how do they compare to other similar animals like wolves or even other domesticated canine breeds in studies? A research group in Hungary sought to develop a standardized method for comparing different breeds of canines and the sensitivity of those breeds when tasked to alert to samples containing decreasing scent thresholds (Polgár, Kinnunen, Újváry, Miklósi, & Gácsi, 2016). Researchers divided 41 adult domesticated canines into three groups: scent dogs, non-scent dogs, and short nose dogs. The different groups of dogs were exposed to rounds of samples which were increasingly more difficult to detect. In the most difficult round, scent dogs were the only group that detected positive samples at a rate higher than chance. This study concluded that canine breeds which were historically bred for scent-intensive functions like hunting or tracking prey were more sensitive to identifying scents repeatedly over a period when compared to other domestic canines not necessarily breed for scent work. In addition, canines traditionally used for hunting and tracking performed comparably to wolves in the same test (Polgár et al., 2016). Canines are a useful tool for scent detection and certain breeds have been developed for that exact task.

Understanding the olfactory sensitivity and limitations of canines is essential to establish a baseline for electronics detection by using alternative methods. Potential limitations on the ability of canines to detect certain scents may lie in biological factors as well as temperament. When interviewed about the evidence collected in the famous Jared Fogle (former Subway Spokesman) investigation, Todd Jordan explained the different factors that may limit the abilities of canines. He said that canines like Labrador Retrievers, which have long snouts and wide

muzzles, are more effective in picking up faint scents. In addition, due to the increased appetite characteristic of their breed, they are more enthusiastic to perform and successfully locate the electronic devices when a successful alert to a device is followed by a treat because they are “food motivated” (Jordan, 2019). Canines that also have a temperament to be more resourceful are more desirable for training in ESD because of their increased interest in searching for devices in hard-to-reach or well-hidden locations (Ng, 2018).

However, there is a significant disadvantage to using canines in some cases. External stimuli can affect the performance of canines. In a study conducted to assess the capabilities and limitations of canines to identify specific scents, researchers in Berlin tested seven dogs of varying breeds to detect samples of tea when placed on a training board (Johnen, Heuwieser, & Fischer-Tenhagen, 2013). The results of the study indicated that there is a plausible influence of trainers in both the overall effectiveness of canines to detect scent. This influence can be attributed to different quality training as well as bias during the experiments. If a canine trainer is more experienced in training for scent detection, they might be more effective in training their dogs to detect even unfamiliar scents in a relatively short period. In the experiment itself, trainers aware of the experiment layout and even trainers who are blind to the positive samples can influence the performance of canines. Canines often are sent on searches by verbal commands and the prior knowledge of positive samples may allow for trainers to unintentionally influence the performance of the canines. In addition, this publication also compiled 14 different studies comparing the success rates of canines to detect other types of scents. The success rates of these 14 studies varied widely, and the researchers speculated that the differences may be accounted for by the influences of trainers (Johnen et al., 2013).

During this same experiment, the researchers tested the limitations of canines to detect different concentrations of samples. The sample scent concentrations were decreased with each successive round. It was determined that the canines bred for scent detection were the only canines able to properly alert to the least concentrated samples of tea. This indicates that there is a lower limit for the capability of scent-trained dogs to detect odors (Johnen et al., 2013). Noting that there is definitely a lower limit of canines to smell the chemical indicators found in electronic components demonstrates the need for more sophisticated, reliable methods to be developed which might be able to outperform canines in both detection and authenticity determination without the bias and assistance of trainers and handlers.

Canines currently hold an important role in law enforcement and other areas where they are used specifically for their scent detection capabilities. For instance, many canines in law enforcement and the military are reliably used to detect hydrocarbons and combustible materials for bomb detection (Browne, Stafford, & Fordham, 2014). Many of the chemicals found in electronic devices are hydrocarbon-based, so canines offer a viable detection method. In addition, a review of quantitative literature shows that canines have a superior ability over other animals to discriminate unique scents ranging from biological to artificial chemicals. One study proved canines to be very effective in identifying common scents with low numbers of errors (Johnen et al., 2013). In this study, seven canines were each evaluated over an 1120 sample test. They correctly alerted 92.1% of positive samples and correctly did not alert on 97.1% of negative samples. The individual dogs had little effect on the test result, indicating that they all performed within a narrow range of the mean (Johnen et al., 2013). In addition, canines have been proven to be able to identify some unique biological indicators for cancer, epilepsy, diabetes, and other dangerous medical conditions. Sometimes, the canines can even detect these

conditions before they can be diagnosed using modern medicine and equipment (Browne et al., 2014). On the other hand, in another evaluation, canines did not perform as well when screening for lung cancer. Researchers presented canines with true positive and negative breath samples for adults who had been diagnosed with lung cancer. Canines correctly identified only 78.6% of positive samples (Hackner et al., 2016).

The results of these studies show that although there is some variation within canines regarding their capability to detect different types of scents, they can be used to correctly identify a variety of compounds with degrees of accuracy. Therefore, canines could be used to detect electronic devices but their accuracy in doing so remains a question for future research.

2.3 Triphenylphosphine Oxide

One of the requirements for electrical components used in the systems employed by the DoD is that they must withstand the maximum operating temperatures found in those systems. Although these temperatures are typically classified, it can be assumed that they would operate at around the same temperatures as high-performance computers. In electronic devices, one of the significant concerns is heat transfer from the components and the effects of that heat on the processors. Many different chemicals are used in the manufacturing process of electronic components. According to Mr. Todd Jordan, ESD canines are trained to detect TPPO, which allegedly is found in all electronic devices as a heat-resistant coating on some components (Jordan, 2019). One study from the Medical College of Wisconsin states that TPPO and similar phosphorous compounds are used as flame retardant additives to polymeric materials (Suebsaeng, Wilkie, & Brown, 1988, p. 2705). This study introduces three compounds that are known to inhibit flammability in polymers (listed in terms of least to most efficient): triphenylphosphine, TPPO, and triphenylphosphate. (Suebsaeng et al., 1988, p. 2706). TPPO and

triphenylphosphate are produced as a product of reaction with triphenylphosphine and polymers at high temperatures (Suebsaeng et al., 1988, p. 2706).

These compounds have also been found on laptop computers. In their article on the recyclability of laptop components, David Meyer and John Katz analyzed the environmental impacts of the different components of electronics and their potential impact on the environment. They specifically identified triphenylphosphate as a chemical used in the flame-retardant coatings used on electrical components in generic laptops (Meyer & Katz, 2016, p. 371). More significantly, they speculated that due to the high temperatures found during use, it is possible that emission of the flame-retardant compounds, especially triphenylphosphate, could occur. Although, there is no data available to characterize the emission of this and other similar compounds (Meyer & Katz, 2016, p. 373). This is a gap in the current knowledge regarding the emissions of electronic devices which can be exploited by this and future research.

As stated previously, the canines that Mr. Todd Jordan trains to detect electronic devices are taught to alert to the presence of TPPO (Jordan, 2019). Since this training aid and similar phosphorous flame retardants are proven to be found in electronic components, the next challenge is to develop a way to detect this and other compounds that may allow for the future non-invasive characterization of electronic component authenticity and performance. TPPO is a volatile chemical that has a boiling point of 360 degrees C. It is inexpensive and easily obtained through chemical supply companies such as Sigma-Aldrich (Sigma-Aldrich, 2018). Thus, if it is found in electronic devices used in this research, it is a good candidate for the quantitative characterization of components.

2.4 Comprehensive Two-Dimensional Gas Chromatography (GC×GC)

One method for analyzing the composition of an unknown sample is GC×GC. GC×GC is a powerful tool used by chemists to determine the exact chemical make-up of a liquid or gas sample. GC×GC is an upgrade to one-dimensional gas chromatography, where a sample is heated through a column in order to separate the individual volatile compounds (Górecki, Panić, & Oldridge, 2006, p. 1077). Traditional gas chromatography is an ideal tool that aids in the determination of sample composition, but some samples are simply too complex and contain too many different compounds to be fully eluted separated in one column of a gas chromatograph. Therefore, it is necessary to connect a second column in series to further elute compounds that fall out of the mixture at similar temperatures in the first column. The result of this new method is a two-dimensional composition assessment, where thousands of different individual compounds can be identified. This form of composition assessment is especially useful when dealing with complex mixtures such as those found in petroleum products, forensics, and the health and medical industries (Górecki et al., 2006, p. 1078). GC×GC was developed to meet the shortcomings of one-dimensional gas chromatography, specifically the restricted specificity and limits in peak capacity. At the end of the first separation process, the sample is placed into a temperature-controlled modulator, which is also serially connected to the second separation column. This two-step process deconflicts co-eluting compounds and provides an added layer of definition that cannot be seen by one-dimensional chromatography (Brasseur, Dekeirsschieter, Schotsmans, Koning, Wilson, Haubruge, & Focant, 2012). GC×GC analysis is the ideal tool for the identification of chemical indicators found in electronic components because it is available at Purdue University and has the highest chance to produce an accurate composition assessment of unknown samples. Gas chromatography is selected over other types of liquid chromatography because it does not require samples to be dissolved in a solvent prior to sampling, therefore

preserving the integrity and functionality of the electronic device. There are two types of GC×GC instruments potentially available to this research, GC×GC with Flame Ionization Detection (GC×GC-FID) and GC×GC Time of Flight Mass Spectrometry (GC×GC-TOF/MS).

GC×GC analysis can be performed on both vapor and liquid samples. Since the canines trained to detect electronic devices can do simply by sniffing them, it should be fitting to analyze the electronic component compositions using gas samples that are taken from the headspace around the electronic components and MSDs themselves. The methods used for sampling vapors can vary, and it is most important to take samples as close as possible to the item of interest. There has been research and developments conducted which shed some light on some ways to collect vapor samples. For example, researchers in Tel Aviv developed the “SnifProbe” to collect and transfer gas samples from a source to GC×GC as efficiently as possible (Gordin & Amirav, 2000, p. 155). Using two pieces of 15 mm capillary tubular columns to take samples from a source that may not be located near the GC×GC itself, samples were collected and then transferred for analysis. This method is significant because it allowed for the capture of a gas sample without the need for the item of interest to be in close proximity to the GC×GC (Gordin & Amirav, 2000 p. 156). One of the essential takeaways from this development was to develop sampling and containment chambers out of non-porous and non-absorbent materials which might interfere with the sample. The use of this method to sample the headspace of beer, wine, coffee, breath, explosives, and drugs was effective (Gordin & Amirav, 2000, p. 166). Glass headspace vials are commonly used for sampling gas samples. By using a similar method and sample preparation process as outlined in literature, it should be possible to sample many of the same substances that canines are trained to detect, especially electronic devices.

2.5 Solid-Phase Microextraction (SPME)

This research uses SPME to isolate and sample compounds of interest from the headspace of microcontrollers and MSDs. SPME is a method that has previously been used to measure the compounds in the headspace of electronic devices. The key inspiration and precursor to this project is DeGreeff, Cerreta, and Rispoli's (2017) research on the feasibility of canines to detect MSDs (DeGreeff, Cerreta, & Rispoli, 2017). In this publication, the researchers laid out a comprehensive method for using SPME to detect volatile compounds from MSDs. They utilized a variety of electronic devices and MSDs for testing: SIM cards, SD cards, USB drives, and cell phones were compared to controls such as batteries, cables, and circuit boards. The MSDs and controls were placed in either 1 pint or 1 liter metal evidence cans, which were previously cleaned with isopropyl alcohol and baked for four hours at 85°C to remove any contaminants. The MSDs were also baked for 2 hours at 60°C to remove any human odors. The cans were left to equilibrate for 18 hours before sampling. Following the equilibrium period, a divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) SPME fiber was inserted for another 18 hours at room temperature. The DVB/CAR/PDMS fibers were chosen for their ability to "extract the widest range of analyte polarities" (DeGreeff et al., 2017, p. 2). All of the samples were sampled in duplicate.

The SPME fibers were desorbed at 260°C into a 6890 Agilent gas chromatograph with a 5975 mass spectrometer and a 30 m Rtx-5MS column. The flow rate of the column was 2 ml/min with a split ratio of 10:1. The gas chromatograph oven was programmed to 50°C for 30 seconds, followed by an increase to 100°C at a rate of 40°C/min and then an increase to 260°C at a rate of 20°C/min. The results of the tests were significant to this research. Six volatile compounds were determined as characteristic of the odor profile of MSDs. The research concluded with a suggestion for more research to be conducted to expand the types of MSDs tested and correlated

with the performance of ESD canines (DeGreeff et al., 2017, p. 3). This research sought to expand this study's list of identified compounds that make up the odor profile of MSDs. This was accomplished by the advanced separation capability of GC×GC over one-dimensional gas chromatography and the enhanced ability of qualitative compound identification provided by GC×GC-TOF/MS instrument available at Purdue University.

The process that SPME utilizes to isolate analytes is called adsorption, where VOCs are collected in pores on the surface of the SPME fibers. The VOCs remain adsorbed to the SPME pores until heat energy is applied to release them. For applications to GC×GC, SPME fibers should be exposed to VOCs for at least 30 minutes to extract compounds with low-volatility. However, highly volatile compounds can be extracted in far less time. Desorption of VOCs occurs in a much faster time frame; most of the extracted VOCs are desorbed in 60 seconds in the high temperature inlet of a GC×GC. Selection of sufficiently long adsorption and desorption times is essential for generating a reliable, repeatable method for electronic component analysis (Agarwal & Daneshkhah, 2019).

The next topic of interest is the effectiveness of GC×GC when compared to canine abilities to detect varying concentrations of compounds.

2.6 Comparing GC×GC Capabilities to Canines

Other than the study described above which utilized one-dimensional gas chromatography, there have been no applications of gas chromatography in electronic device detection to date. The most obvious reason for this is that electronic device detection using purely canines is still a fairly new practice that is just coming to the forefront of forensic news due to high profile arrests made with evidence collected from devices found by canines. There has simply not been enough time for researchers to fully investigate the full range and

effectiveness of GC×GC applications in this field. Research applying GC×GC and SPME to develop reliable, non-invasive methods to authenticate and measure the performance capabilities of electronic components relies on the successful implementation of lessons learned from previous studies designed to correlate the capability of ESD canines with those of GC×GC.

For example, researchers from Canada and Belgium analyzed the challenges and capabilities of using a GC×GC to analyze the chemical makeup of synthetic canine training aids (Stadler, Stefanuto, Byer, Brokl, Forbes, & Focant, 2012, p. 202). They stated that the most difficult aspect of determining the chemical composition of an unknown sample is to identify individual compounds. This is a challenge because some compounds may elute from the columns at close intervals and it could be difficult to separate GC×GC peaks which may be close together without optimized methods (Stadler et al., 2012). The study stated that synthetic training aids are most likely only composed of a few compounds due to their nature of being laboratory-produced. As such, and despite the challenges of analyzing an unknown substance, the researchers were able to identify two compounds from the first formulation, two more from the second and a handful of other less abundant compounds from the unknown mixture (Stadler et al., 2012, p. 204). This study is a useful guide for developing a method for determining the composition of a simple mixture of a few compounds. However, the Volatile Organic Compound (VOC) makeup of electronic components may be far more complex than canine training aids. This complicates method development as optimization of methods is a time-consuming process.

Finally, this study also compared the GC×GC analysis of synthetic training aids with the known chemical composition of the actual scent. They found that synthetic training aids were not accurate to the true chemical composition of the scents they intended to mimic, which in this case was the scent of a decaying corpse. However, canines which were trained on synthetic aids

have been known to correctly alert to cadavers, which seemed to indicate that at least some if not all of the synthetic compounds are also found in the cadavers themselves (Stadler et al., 2012, p. 205). If synthetic aids of any variety are compared to the true samples, GC×GC composition analysis offers the potential to assist in the improvement of synthetic training aids by helping developers to better reflect the true range of compounds canines should expect when they are searching for their real-life objectives. This opens a potential follow-on research project which may seek to improve canine electronic device detection by helping to develop training aids that are more representative of the true chemical profiles of electronic devices.

In a similar band of research, a group sought to identify and characterize the volatile organic compounds that are present in decaying corpses which canines have been able to detect (Brasseur et al., 2012). To be clear, this research did not investigate the effectivity of canines to detect cadavers, but rather, was intended to determine the true chemical composition of decaying bodies using a GC×GC (Brasseur et al., 2012). In the performance of the experiment, pig carcasses were buried in the soil in shallow graves dug by hand. Six months later, they were exhumed, and soil samples were taken from the graves at regular intervals above and below the carcass. Samples were also taken from a control pit which did not contain a carcass. Gas samples were collected from the testing area using a “closed volatile collection device” filled by pulling air at a rate of .5 L/min for 1 to 2 hours after 15 min of equilibrium time (Brasseur et al., 2012). The results of this study indicated that there are 20 specific compounds that were found below the carcass (Brasseur et al., 2012, p. 166). They opted to not utilize SPME but rather a similar volatile collection trap, on which the volatile compounds bind to the solid fibers before desorption in the GC×GC inlet. Once again, the methods used in this study aided the determination of the appropriate sampling method for the electronic device gas samples which

was collected in this research project. In addition, research done on the exact chemical composition of the carcasses shows that it might be possible to detect unknown chemicals in the electronic device samples which may be a better indicator for age or origin and would be more useful to professionals, like Mr. Todd Jordan, who are employed to train these canines. In addition, this study aided in the development of a methodology for sampling. When performing experiments, it is important to sample a control group. With a defined control group and statistically significant sample sizes, it is easier to determine which chemical compounds found in the GC×GC analysis are actually a result of the presence of electronic devices and which ones are not.

Comparing the limits of canines' abilities to detect specific compounds to the absolute lowest concentration observable with GC×GC would be useful to determine if GC×GC is a feasible alternative for canine scent detection of electronic devices and whether it might be useful in the future to characterize electronic components based on date and place of manufacture. In a study using both canines and GC×GC, a research group in Australia sought to find the lower threshold for canine detection (Chilcote, Rust, Nizio, & Forbes, 2018). The stated goal for this study was to provide information which would be valuable to improving canine training aids for law enforcement and other applications (Chilcote et al., 2018, p. 99). After applying blood samples to wood and concrete, the researchers ran canine scent detection trials to determine the time period after which the dogs would no longer alert to biological samples. They tested multiple dogs which had varying experience, age, genders, and were either trained to detect cadavers or blood. This report claims that previous research had concluded that canines could reliably alert to biological samples for longer periods than GC×GC. However, the results of this study disproved that assumption. The experimental limit found for canines to detect blood

on both concrete and wood was one month, while the GC×GC could still identify key compounds up to 59 days after the initial application (Chilcote et al., 2018, p. 108). If this is true, then GC×GC may have the potential to surpass both the accuracy and lower concentration threshold for canines. If key chemical indicators that may aid in the characterization of age or performance prove to be only present in low concentrations, then GC×GC is the best option for this research.

Like all sensors, a GC×GC has a limit to which it can detect different compounds of interest. Depending on the nature and composition of the sample, the detection threshold may differ depending on the volatility of the compounds contained in the samples. Highly volatile compounds elute more effectively than others. Conversely, compounds with high boiling points are more difficult to detect unless they are exposed to high temperatures. For example, TPPO has a boiling point of 360 degrees C, which is outside of the upper-temperature limit of some GC×GC instruments (Sigma-Aldrich, 2018). Because of this, it is essential to develop methods for detection using GC×GC which heats the samples to a high enough temperature so that compounds with lower volatility have the opportunity to elute, which better characterizes the scent profile of samples.

2.7 Summary of Literature

There is an identified need within the DoD to develop a way to verify the authenticity and processing capability of electronic components which are found in many of the systems used by the United States' Army, Navy, Air Force, and Marine Corps. Because the DoD cannot produce all the essential electronic components and devices organically, there is a gap that may be exploited by corporations or nations which may seek to sabotage mission-critical infrastructure and capabilities used by the United States Armed Forces. Currently, there is no way to reliably

evaluate the status of every electronic component or device before installing them in these systems.

One of the most promising potential methods of mitigating this risk may originate from the use of ESD canines which have recently gained notoriety in forensic science where they discovered key incriminating information which led to the conviction of high-profile sex criminals. The expert in this field, Mr. Todd Jordan, owner of Jordan Detection K-9, has proven canines' abilities to detect electronic equipment in challenging environments (Jordan, 2019). The training compound that he uses to accomplish this is called TPPO, an organic compound which literature has shown to be found on every electronic component. TPPO acts as a flame-retardant material that protects vital memory and computing capabilities of electronic components. TPPO and other volatile compounds yet to be observed may prove to be the most effective indicators of electronic component age or manufacturer origin, as they may diffuse over time and manufacturers may use different processes to construct components. Currently, there is no prior research using GC×GC to measure volatile compound emission as a result of the normal use of MSDs and electronic components.

In order to understand the need for a non-invasive authentication method for electronic components, it is essential to first understand the full capabilities and limitations of canines to detect VOCs found on those components. Prior research exists which analyze the effectiveness and capabilities of canines to detect a multitude of different chemicals, conditions, and substances. Canines are uniquely adapted due to their advanced olfactory systems.

Research suggests strongly that canines can detect low concentrations of compounds, but there is little concrete evidence of the exact quantitative limit to a dog's ability to detect a compound at low concentrations. Even when comparing canine performance to GC×GC, the

research was more involved with the maximum detection time threshold rather than the lowest concentrations. Evaluating the lowest detection for canines to detect TPPO may assist future research to determine at which concentrations TPPO and other compounds in electronics can be observed using other methods like GC×GC.

When determining an alternative method for the detection of volatile compounds in MSDs, research suggests that GC×GC-TOF/MS analysis using headspace sampling with SPME is the most effective method for measuring odor characterization. When analyzing canines' ability to detect other compounds found in blood, cancer and other scents, GC×GC was a useful tool. GC×GC has a unique ability to separate extremely complex mixtures and can precisely identify the composition by mass of individual compounds. However, the most important aspect of using GC×GC to detect the chemical indicators found in electronics is developing effective GC×GC methods to properly isolate the individual compounds that may be present in gas samples taken from the headspace around electronic equipment. GC×GC analysis of some of the samples from the literature yielded promising results for this research project in that unexpected compounds were identified. If the same were to occur within this research project, then perhaps a more effective chemical indicator might be identified which can more easily predict the authenticity of electronic components.

This research ultimately built on previous research on the composition of electronic components' odor signatures. This was accomplished via the advanced capabilities of GC×GC-TOF/MS available to the project.

CHAPTER 3. RESEARCH METHODOLOGY

3.1 Research Framework and Inspiration

There have been many studies that correlate the performance of canines to GC×GC in many areas of scientific and forensic detection of various materials. These studies focus mainly on the detection reliability and the maximum time threshold for detecting compounds by canines when compared to the performance of GC×GC to detect the same compounds sampled in similar conditions. Many of these studies have concluded that GC×GC has superior ability to detect compounds of interest in these conditions, even when using multiple different canine breeds and varying experience of both canines as well as trainers (Sampat, Lopatka, Sjerps, Vivo-Truyols, Schoenmakers, and van Asten, 2016).

There currently is a need within the DoD to ensure the quality of electronic components which are used in their electronic systems in order to maintain its competitive edge over near-peer nation-state rivals (Berkowitz, 1995). Many electronic components used in military equipment are sourced from private corporations, many of which have manufacturing facilities located in foreign nations. The potential danger with utilizing these components is that there is no current way to positively ensure the authenticity of all components, should they be compromised by foreign actors.

This research is designed to investigate the applications of GC×GC capabilities to detect the presence of key chemical indicators in electronic components and MSDs. Through analysis of components of varying age and manufacture, the primary goal of this research is to determine a method to characterize different sample groups of components based on the concentrations of volatile compounds as analyzed using GC×GC.

3.2 Research Type

This research was a non-targeted experimental quantitative research study. This study collected empirical data regarding the presence of any volatile compounds found in electronic components with the goal of developing a non-invasive testing method for determining the authenticity of an MSD with applications to the DoD. Ultimately, this study determined which VOCs may be reliable markers for electronic devices differing in type, age, and origin of manufacture.

3.3 Research Design

This research sought to identify VOCs using a non-targeted analysis of three groups of electronic components. A non-targeted analysis was selected because of the lack of prior knowledge for characteristic VOCs found in components. Three sample groups were assessed to determine qualitatively which VOCs were present in the components. Confirmation of these VOCs was conducted using retention time analysis. Reliable compounds were selected for quantitative comparison using peak areas.

In order to confirm or disprove the hypotheses regarding the use of GC×GC to characterize the authenticity of electronic components, it was essential to confirm that volatile compounds can be detected in significant concentrations using GC×GC detection capabilities coupled with SPME. Successfully analyzing the chemical profiles of components which differed in type, age, and origin is the first step to developing a method for the DoD to assess the authenticity of unknown electronic components.

The composition of samples selected for this study and the methods by which they were analyzed are outlined below.

3.4 Sample Composition

For this study, three types of electronic devices were selected for testing. Three sample populations, each with sample size $n=30$, were purchased to represent a variety of electronic component type and country of origin/manufacturer. Two sample populations of 14-pin 16-bit microcontrollers were purchased with equivalent specifications and were produced by Microchip Technology and Texas Instruments. In addition, one sample population of 16 GB microSD cards produced by SanDisk was purchased. To the best of ability, the newest components were sought for each sample population. However, due to the limitations on product stock at the distributor, there was an age difference between all sample populations. Components were produced in or after October 2015 and were produced in either Thailand, Malaysia, or China. The sample compositions are outlined in Table 3.1. Data for the sample groups was determined using component datasheets (Microchip Technology Incorporated, 2009; SanDisk, n.d.; Texas Instruments Incorporated, 2019).

Table 3.1 Sample Composition

Sample	<i>Microchip Technology</i>	<i>Texas Instruments</i>	<i>SanDisk</i>
Description	14-pin 16-bit Microcontroller	14-pin 16-bit Microcontroller	16 GB MicroSD
Country of Origin	Thailand	Malaysia	China
Date of Manufacturer	October 2015	May 2017	2019
Component Mass (g)	0.0580	0.0614	0.2434
Surface Area (mm ²)	62.8	62.8	380.2
Device Classification	Integrated Circuit	Integrated Circuit	Circuit Board
Sample Size	$n=30$	$n=30$	$n=30$

3.5 Control Composition

In addition, a control group was devised to illustrate a comprehensive range of VOCs which may exist in the ambient environment as well as originate from the SPME fibers or GC×GC-TOF/MS columns. In total, 16 controls were sampled. The control compositions are

outlined in Table 3.2. Compounds that are found in more than half of the control group samples were automatically excluded from consideration for possible VOCs of significance.

Table 3.2 Control Compositions

Control Type	<i>Column Only</i>	<i>SPME and Column Only</i>	<i>SPME Exposed to Empty Vial</i>
Number Performed	1	2	13

3.6 Sampling Method

1. Prior to testing, 20 mL headspace sampling vials were baked in an oven at 100°C for a period longer than 6 hours to remove any volatile compounds which may have resulted from sample vial manufacturing or human interaction during manufacturing and shipping.
2. MSDs of known origin and age were placed in the glass headspace sampling vials. These vials were purged with inert gas (N₂) for at least ten seconds to remove any ambient volatiles that may have resulted from the environment.
3. Sample vials were submerged in a 70°C water bath and the DVB/CAR/PDMS SPME fibers were exposed to the samples for 50 min. The water bath is intended to force more volatile compounds to bind to the SPME fibers because volatile compounds are available in the headspace at higher temperatures. 70°C was selected as it is within the range of operating temperatures for electronic devices.
4. The SPME fibers were manually injected into the inlet of the GC×GC-TOF/MS. The inlet temperature is set at 240°C for compound desorption from the SPME fibers.
5. The GC×GC-TOF/MS primary oven was increased in temperature following the temperature ramp rate provided below:
 - a. Held at 40°C for two minutes

- b. Increased by 8°C per minute to 280°C
- c. Held at 280°C for one minute

This method was developed with the assistance of Dr. Agrawal and Dr. Daneshkhah at Indiana University-Purdue University Indiana, who are collaborating on this research which is funded by the Indiana Innovation Institute (IN3) (Agarwal & Daneshkhah, 2019).

The sample group experiments were completed alongside control samples and repeated multiple times in order to ensure replicability, robustness, and integrity of the experiment. Once a sufficient population ($n = 30$) was sampled from each sample group, their chemical signatures were compared to the volatile compounds identified in the controls to determine the common and unique VOCs for of each group.

3.7 Sample Analysis

For this study, GC×GC-TOF/MS was used to determine VOCs from populations of electronic devices sampled using 24-gauge DVB/CAR/PDMS SPME fibers. Pegasus GC-HRT 4D (EI) High-Resolution TOF/MS (LECO Corporation, Saint Joseph, MI) with an Agilent 7890B gas chromatograph, a non-moving quad-jet dual stage thermal modulator cooled with liquid nitrogen was used for qualitative analysis of the samples. Chromatographic conditions for GC×GC-TOF/MS are shown in Table 3.3. The ion source temperature was set to 250°C, and the electron energy was 70 eV. ChromaTOF (Version 1.90.60.043266) software was utilized for data collection (with an m/z of 50-1000), processing, and analysis. Signal to noise was set to 15. Identification of the compounds was achieved by matching the measured mass spectra (similarity value > 600) with Wiley (2011) and NIST (2011) mass spectral databases.

Table 3.3 Data Processing Parameters and Descriptions

Parameter	Value	Description
Ion Source Temperature	250°C	The temperature of the ion source
Electron Energy	70 eV	The energy imparted on ions for fragmentation
Mass Range	50-1000	Mass/charge ratio
Signal to Noise	>15	Strength of instrument readings above the noise level required to identify VOCs
Similarity Score	>600	A score assigned based on the similarity of VOCs to library standards

3.8 Unit of Measurement

The concentrations of indicating compounds was within the lower sensitivity bounds of GC×GC detection capability. The GC×GC-TOF/MS used in this experiment has been tested in previous research studies to have a sensitivity of around 1 parts-per-million (ppm).

3.9 Variables

There are two principle independent variables in this study: the type and origin of the electronic components. The dependent variable is the combination of VOCs found in the sample. Components specifically vary by age, type and manufacturer to determine the effects on the dependent variable, their respective VOC composition.

3.10 Experimental Instruments

This research performed two-dimensional gas chromatography with a GC×GC-TOF/MS produced by Agilent Technologies to detect the minute concentrations of compounds of interest (Agilent Technologies, n.d.). This resource is located in the H. C. Brown Laboratory of Chemistry at Purdue University. Sample VOCs were adsorbed manually via 24 gauge DVB/CAR/PDMS SPME fiber assemblies for desorption in the inlet of the GC×GC-TOF/MS.

The fibers are produced by Supelco and were purchased from MilliporeSigma Chemical Supply Company. These fibers were selected because they offer the widest range of VOC adsorption over the range of temperatures utilized in the GC×GC-TOF/MS method outlined previously.

3.11 Research Question

The research question for this study is as follows:

1. What volatile chemical species can be detected from electronic components using GC×GC and SPME methods?
 - a. Are volatile compounds present and measurable in microcontrollers and MSDs?
 - b. Does the chemical signature of electronic components vary with origin and type of the components?

3.12 Hypotheses

The hypotheses for this project are as follows:

1. H₀: Volatile compounds can be measured in significant concentrations from electronic components within the bounds of GC×GC detection capability.

H_a: Volatile compound emissions from electronic components are outside the bounds of GC×GC detection capability.
2. H₀: VOC emissions for electronic components vary by component type, age, or origin.

H_a: VOC emissions for electronic components do not vary by component type, age, or origin.

3.13 Data Analysis

Quantitative data was collected and stored in the appropriate hard drives located in the H. C. Brown Laboratory of Chemistry at Purdue University. Once data collection was finished, a comprehensive comparative analysis was conducted to determine the relationship between the independent variables (age and origin) and the dependent variable (the combination of identified VOCs). VOCs were not be considered for significance unless they are present in at least 25 samples of each respective sample size and were present in less than half of the control samples. The primary tool for data analysis was Excel. The analysis process was multistep, including sorting the data for duplicate identified peaks and comparing the results of samples to the list of control VOCs. VOCs of significance were further quantitatively analyzed by retention times and peak areas.

3.14 Conclusion

With this methodology, the research project produced results with the aim of providing answers to the research questions and hypotheses laid out in this thesis. This data was used to determine whether it is feasible to characterize electronic components via GC×GC analysis of VOCs discovered in the process of the research. With the successful characterization of electronic component age or origin, this project has the potential to serve as the first stepping stone to develop a dependable and non-invasive method for ensuring that the electronic components installed in DoD systems can be relied upon by the warfighters that use them.

CHAPTER 4. RESULTS

4.1 GC×GC-TOF/MS Output

Over the course of this research, 106 total samples were collected between the three populations of electronic components – 30 for each type and 16 controls. Tables 4.1 through 4.4 illustrate the general trend of the raw data output for each type. The sampling order is outlined in Table 4.5. Identified peaks include all VOCs which were detected by the instrument. Compounds named include all VOCs from the identified peaks which were successfully identified using the mass spectral libraries. Unique compounds include all named VOCs excluding duplicate peaks identified by the mass spectral libraries as the same compound

Table 4.1 Microchip Technology Raw Data Output

<i>Sample</i>	<i>Number of Peaks Identified</i>	<i>Number of Compounds Named</i>	<i>Number of Unique Compounds</i>
1	344	302	225
2	358	299	216
3	407	350	272
4	407	346	268
5	349	299	228
6	432	336	262
7	355	305	232
8	399	326	246
9	418	360	280
10	420	347	250
11	421	348	260
12	377	314	243
13	429	374	259
14	402	339	236
15	844	710	406
16	755	635	389
17	788	661	375
18	768	664	384
19	788	675	376
20	800	676	371

Table 4.1 Microchip Technology Raw Data Output (continued)

21	890	738	360
22	868	714	421
23	845	714	388
24	825	706	399
25	840	720	377
26	710	634	357
27	745	644	354
28	730	641	351
29	757	668	386
30	794	688	394
\bar{x}	609	518	319
s	209	179	70

Table 4.2 Texas Instruments Raw Data Output

Sample	<i>Number of Peaks Identified</i>	<i>Number of Compounds Named</i>	<i>Number of Unique Compounds</i>
1	741	643	358
2	795	688	390
3	833	732	388
4	874	736	398
5	801	688	399
6	811	730	408
7	811	737	422
8	825	726	402
9	777	656	389
10	738	639	358
11	822	712	416
12	785	679	390
13	784	688	404
14	716	626	390
15	678	588	372
16	776	680	392
17	709	621	348
18	725	635	385
19	771	668	381
20	769	669	394
21	726	634	364
22	664	591	360
23	647	586	353

Table 4.2 Texas Instruments Raw Data Output (continued)

24	635	557	363
25	618	543	349
26	655	556	328
27	699	611	372
28	658	577	357
29	674	590	368
30	600	527	334
\bar{x}	737	644	378
s	72	62	24

Table 4.3 SanDisk MicroSD Raw Data Output

Sample	<i>Number of Peaks Identified</i>	<i>Number of Compounds Named</i>	<i>Number of Unique Compounds</i>
1	675	580	392
2	663	556	364
3	704	597	406
4	675	576	389
5	658	537	362
6	685	576	402
7	739	606	416
8	740	619	440
9	692	586	391
10	731	625	413
11	723	598	410
12	753	637	408
13	764	629	402
14	806	661	421
15	760	638	405
16	807	662	433
17	759	636	427
18	752	616	427
19	760	643	408
20	764	639	423
21	813	652	439
22	752	607	417
23	704	586	393
24	734	615	415
25	674	577	385
26	681	565	376

Table 4.3 SanDisk MicroSD Raw Data Output (continued)

27	685	579	376
28	718	589	409
29	735	616	413
30	709	590	396
\bar{x}	727	606	405
s	43	32	20

Table 4.4 Controls Raw Data Output

Control	<i>Number of Peaks Identified</i>	<i>Number of Compounds Named</i>	<i>Number of Unique Compounds</i>
1	60	55	14
2	445	335	219
3	440	344	262
4	402	359	257
5	728	593	357
6	768	642	364
7	848	686	372
8	805	695	345
9	770	586	325
10	756	634	364
11	813	659	370
12	696	566	347
13	647	555	340
14	739	606	396
15	733	599	373
16	815	622	386
\bar{x}	654	534	318
s	212	173	95

Table 4.5 Sampling Order

Sample Source	Description
Microchip Technology Microcontroller	Sample 1
Microchip Technology Microcontroller	Sample 2
Control (Column Only)	Control 1
Microchip Technology Microcontroller	Sample 3
Microchip Technology Microcontroller	Sample 4
Microchip Technology Microcontroller	Sample 5
Microchip Technology Microcontroller	Sample 6

Table 4.5 Sampling Order (continued)

Microchip Technology Microcontroller	Sample 7
Control (SPME and Column Only)	Control 2
Control (SPME Exposed to Empty Vial)	Control 3
Microchip Technology Microcontroller	Sample 8
Microchip Technology Microcontroller	Sample 9
Microchip Technology Microcontroller	Sample 10
Microchip Technology Microcontroller	Sample 11
Microchip Technology Microcontroller	Sample 12
Control (SPME Exposed to Empty Vial)	Control 4
Microchip Technology Microcontroller	Sample 13
Microchip Technology Microcontroller	Sample 14
Control (SPME Exposed to Empty Vial)	Control 5
Control (SPME Exposed to Empty Vial)	Control 6
Microchip Technology Microcontroller	Sample 15
Microchip Technology Microcontroller	Sample 16
Microchip Technology Microcontroller	Sample 17
Microchip Technology Microcontroller	Sample 18
Microchip Technology Microcontroller	Sample 19
Microchip Technology Microcontroller	Sample 20
Control (SPME Exposed to Empty Vial)	Control 7
Microchip Technology Microcontroller	Sample 21
Control (SPME and Column Only)	Control 8
Microchip Technology Microcontroller	Sample 22
Microchip Technology Microcontroller	Sample 23
Microchip Technology Microcontroller	Sample 24
Microchip Technology Microcontroller	Sample 25
Control (SPME Exposed to Empty Vial)	Control 9
Microchip Technology Microcontroller	Sample 26
Microchip Technology Microcontroller	Sample 27
Microchip Technology Microcontroller	Sample 28
Microchip Technology Microcontroller	Sample 29
Microchip Technology Microcontroller	Sample 30
Control (SPME Exposed to Empty Vial)	Control 10
Texas Instruments Microcontroller	Sample 1
Texas Instruments Microcontroller	Sample 2
Texas Instruments Microcontroller	Sample 3
Texas Instruments Microcontroller	Sample 4
Texas Instruments Microcontroller	Sample 5
Texas Instruments Microcontroller	Sample 6
Texas Instruments Microcontroller	Sample 7

Table 4.5 Sampling Order (continued)

Texas Instruments Microcontroller	Sample 8
Control (SPME Exposed to Empty Vial)	Control 11
Texas Instruments Microcontroller	Sample 9
Texas Instruments Microcontroller	Sample 10
Texas Instruments Microcontroller	Sample 11
Texas Instruments Microcontroller	Sample 12
Texas Instruments Microcontroller	Sample 13
Control (SPME Exposed to Empty Vial)	Control 12
Texas Instruments Microcontroller	Sample 14
Texas Instruments Microcontroller	Sample 15
Texas Instruments Microcontroller	Sample 16
Texas Instruments Microcontroller	Sample 17
Texas Instruments Microcontroller	Sample 18
Texas Instruments Microcontroller	Sample 19
Texas Instruments Microcontroller	Sample 20
Texas Instruments Microcontroller	Sample 21
Texas Instruments Microcontroller	Sample 22
Texas Instruments Microcontroller	Sample 23
Control (SPME Exposed to Empty Vial)	Control 13
Texas Instruments Microcontroller	Sample 24
Texas Instruments Microcontroller	Sample 25
Texas Instruments Microcontroller	Sample 26
Texas Instruments Microcontroller	Sample 27
Texas Instruments Microcontroller	Sample 28
Texas Instruments Microcontroller	Sample 29
Texas Instruments Microcontroller	Sample 30
SanDisk MicroSD	Sample 1
SanDisk MicroSD	Sample 2
SanDisk MicroSD	Sample 3
SanDisk MicroSD	Sample 4
Control (SPME Exposed to Empty Vial)	Control 14
SanDisk MicroSD	Sample 5
SanDisk MicroSD	Sample 6
SanDisk MicroSD	Sample 7
SanDisk MicroSD	Sample 8
SanDisk MicroSD	Sample 9
SanDisk MicroSD	Sample 10
SanDisk MicroSD	Sample 11
SanDisk MicroSD	Sample 12
SanDisk MicroSD	Sample 13

Table 4.5 Sampling Order (continued)

SanDisk MicroSD	Sample 14
SanDisk MicroSD	Sample 15
SanDisk MicroSD	Sample 16
Control (SPME Exposed to Empty Vial)	Control 15
SanDisk MicroSD	Sample 17
SanDisk MicroSD	Sample 18
SanDisk MicroSD	Sample 19
SanDisk MicroSD	Sample 20
SanDisk MicroSD	Sample 21
SanDisk MicroSD	Sample 22
Control (SPME Exposed to Empty Vial)	Control 16
SanDisk MicroSD	Sample 23
SanDisk MicroSD	Sample 24
SanDisk MicroSD	Sample 25
SanDisk MicroSD	Sample 26
SanDisk MicroSD	Sample 27
SanDisk MicroSD	Sample 28
SanDisk MicroSD	Sample 29
SanDisk MicroSD	Sample 30

4.2 Data Sorting

The data produced by the instrument was collected and stored on hard drives in the H. C. Brown Laboratory of Chemistry at Purdue University. Peak tables generated by the instrument were migrated to Excel for data sorting and comparison. Each sample was treated individually using the same method. First, duplicate peaks identified by the instrument were excluded from the analysis. In addition, unidentified peaks that were not named in the data processing stage of the experiment were excluded. These peaks did not meet the minimum threshold for consideration due to low signal to noise ratio and/or insufficiently high similarity scores to compounds in the mass spectral databases.

4.3 Common VOCs in Controls

Table 4.6 details the most common VOCs found in the 16 samples of controls. These VOCs were found in at least half of the controls. VOCs listed in this table are considered part of the ambient environmental VOC composition and are thought to originate from the air, SPME fibers, or columns within the instrument.

Table 4.6 Common VOCs in Controls

VOC Name	<i>Number of Occurrences in Control Samples (Out of 16 Samples)</i>
Perfluorobutylsulfonyl azide	16
Cyanoacetaldehyde	16
1-Prenyloxy-1-(tert-butyldimethylsilyloxy)cyclopropane	16
3-Bromo-2,2-dimethyl-5-phenyltetrahydrofuran	16
(2R,6R)-2,6-Dimethyl-1,3-dioxane-4-one	16
1-(per-Fluorohexyl)-1-(acetoxy)-2-fluoroethylene	16
Octasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl-	15
Cyclopentasiloxane, decamethyl-	15
Cyclohexasiloxane, dodecamethyl-	15
Cyclotetrasiloxane, octamethyl-	15
Cyclotrisiloxane, hexamethyl-	15
4-Methyl-2,4-bis(p-hydroxyphenyl)pent-1-ene, 2TMS derivative	15
(2Z,6E)-3-Chloromethyl-1-chloroocta-2,6-dien-8-al	15
[1R-(1 α ,4 β ,5 β)]-[5-(5-Chloro-4,7,7-trimethyl-6-oxabicyclo[3.2.1]oct-4-yl)-1-pentynyl]trimethylsilane	15
Tetracosamethyl-cyclododecasiloxane	14
Ethyl (1S,3R,4R)-2-Methyl-2-azabicyclo[2.2.1]heptane-3-carboxylate	14
Heptasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13-tetradecamethyl-	14
Cyclononasiloxane, octadecamethyl-	14
Cyclooctasiloxane, hexadecamethyl-	14
3-Acetyl-2-methyl-9b-(1-naphthyl)-3aH-benzo[e]cyclohexa[1,2-b]furan	14
(3E)-3-Chloromethyl-1,1-dimethoxy-7-methylocta-2,6-diene	14
1-Butanamine, 1,1,2,2,3,3,4,4,4-nonafluoro-N,N-bis(nonafluorobutyl)-	14
Heptanal	13
Trimethyl(trimethylsilyl)silane	13

Table 4.6 Common VOCs in Controls (continued)

TRIVINYL-S-TRIAZINE-2,4,6-(1H,3H,5H)-TRIONE	13
Arsenous acid, tris(trimethylsilyl) ester	13
4,4-Dimethyl-3-phenyl-1-pentyn-3-ol	13
1-Ethynylcyclopentanol	13
Silanediol, dimethyl-	12
Heptacosafuoro-tributylamine	12
N-(tert-Butoxycarbonyl)-2-(4-methoxyphenyl)allylamine	12
Perfluoro-[(1-Isopropoxy)cyclopropane]	12
α -Fluoro-(p-methyl)chalcone	12
Vanillin, TBDMS derivative	12
Benzoic acid, 2,4-bis(trimethylsiloxy)-, trimethylsilyl ester	12
Benzene, ethenyl-	12
2-Propen-1-one, 1,3-diphenyl-	12
2-(2',4',4',6',6',8',8'-Heptamethyltetrasiloxan-2'-yloxy)- 2,4,4,6,6,8,8,10,10-nonamethylcyclopentasiloxane	12
3-Hexadecyloxycarbonyl-5-(2-hydroxyethyl)-4- methylimidazolium ion	12
2-[(2-Benzoyloxyimino-3-selenobornyl)methyl]-2,3- dihydrobenzofuran	12
(5-Methyl-1,3-dioxo-1,3,3a,4,8a,8b-hexahydroindeno[4,5- c]furan-6-ylidene)acetic acid ethyl ester	12
Oxime-, methoxy-phenyl-	11
Octadecanoic acid	11
Benzothiazole	11
Cycloheptasiloxane, tetradecamethyl-	11
Benzeneacetic acid, α ,3,4-tris[(trimethylsilyl)oxy]-, trimethylsilyl ester	11
Ethanol, 2-(2-ethoxyethoxy)-	11
Benzeneacetic acid, α ,4-bis[(trimethylsilyl)oxy]-, trimethylsilyl ester	11
3-acetyl-4-ethenyl-4-(4-hydroxy-3-methoxyphenyl)butan-2-one	11
2 - methoxy - 2,5 - dihydro - furan	11
2,2,4,4,6,6,8,8,10,10,12,12,14,14,16,16,18,18,20,20- ICOSAMETHYLCYCLODECASILOXANE	11
2-Propenal, 3-phenyl-	11
2-[(Trimethylsilyl)oxy]-2-{4- [(trimethylsilyl)oxy]phenyl}ethanamine	11
2-Naphthalene-sulfonic acid	11
1,1,1,3,5,5,5-Heptamethyltrisiloxane	11
1,3-Dioxolane	11
(2RS,3SR)-3-Hydroxy-2-[(RS)- α -trimethylsilylbenzyl]butanoic acid	11

Table 4.6 Common VOCs in Controls (continued)

1H-Indene, 2,3-dihydro-1,1,3-trimethyl-3-phenyl-	11
Hexasiloxane, tetradecamethyl-	10
Heptasiloxane, hexadecamethyl-	10
Nonanal	10
Benzene, 1,3,5-trimethyl-	10
Cyclododecasiloxane, tetracosamethyl-	10
2-(Trimethylsilyl)ethyl 1-oxo-2-azaspiro[5.5]undec-8-ene-2-carboxylate	10
3,3,6,6,7,7-Hexamethyl-2-oxobicyclo[3.2.0]heptane-1-carbonitrile	10
3-Dodecanol, 3,7,11-trimethyl-	10
2-Phenyl-4,7-dihydro-4,7-methano-2H-isoindole	10
3,5-Dibutoxy-1,1,1,7,7,7-hexamethyl-3,5-bis(trimethylsiloxy)tetrasiloxane	10
2,8-bis(trimethylsiloxy)-2,7-dimethyloct-6-en-3-one	10
2-Methoxy-6-phenyl-6,6a,7,8-tetrahydro-9aH-furo[3,2-c]quinoline isomer	10
Tetradecane, 1-chloro-	9
Silane, (phenyloxiranylidene)bis[trimethyl-	9
Octadecane, 1-chloro-	9
Decanal	9
7,7-Bis(methylthio)-6-methyl-1-(2-thienyl)-2,4,6-heptatrien-1-one	9
Dodecanedioic acid, bis[(1,1-dimethylethyl)dimethylsilyl]ester	9
7-tert-Butyldimethylsilyloxy-3-hydroxy-1-trimethylsilylhept-1-yne	9
Benzeneethanamine, N-[(pentafluorophenyl)methylene]-β,4-bis[(trimethylsilyl)oxy]-	9
2-Butanol, 3-methyl-	9
2,3,4,5-Tetrahydro-7,8-dimethoxy-N-(trifluoroacetyl)-[(Z)-2-(trimethylsilyl) ethylidene]-1H-3-benzazepine	9
4-Cyanocyclohexene	9
1-Propyl-2,2-dimethoxyethylamine Hydrochloride	9
1,1,1,5,7,7,7-Heptamethyl-3,3-bis(trimethylsiloxy)tetrasiloxane	9
1-Hexanol, 2-ethyl-	9

4.4 Common VOCs in Microchip Technology Microcontrollers

Table 4.7 details the most common VOCs found in the 30 samples of Microchip Technology 14-pin 16-bit microcontrollers. These VOCs were found in at least 25 of the samples as well as less than half of the controls. VOCs listed in this table are considered candidates for electronic VOC markers for this component type and source.

Table 4.7 Common VOCs Found in Microchip Technology Microcontroller Samples

VOC Name	<i>Number of Occurrences in Samples (Out of 30 Samples)</i>
Silicate Anion Tetramer	26
Benzene, 1,3-dimethyl-	26
1,3,5-Cycloheptatriene	25

4.5 Common VOCs in Texas Instruments Microcontrollers

Table 4.8 details the most common VOCs found in the 30 samples of Texas Instruments 14-pin 16-bit microcontrollers. These VOCs were found in at least 25 of the samples as well as less than half of the controls. VOCs listed in this table are considered candidates for electronic VOC markers for this component type and source.

Table 4.8 Common VOCs Found in Texas Instruments Microcontroller Samples

VOC Name	Number of Occurrences in Samples (Out of 30 Samples)
Phenol	29
Benzene, 1,1'-(1,2-cyclobutanediyl)bis-, trans-	29
Benzaldehyde	27
2-Hexen-1-ol, 2-ethyl-	27
2-Undecanethiol, 2-methyl-	27
tert-Dodecanethiol	26
Pentanoic acid, 2,2,4-trimethyl-3-hydroxy-, isobutyl ester	26
Hexanal	26
Benzene, 1,3-dimethyl-	26
2H-Pyran-6-methanol, 2-ethoxy-3,4-dihydro-4-methyl-	26
1,3,5-Cycloheptatriene	26
(R)-Ethyl 2-(2-methoxymethoxy-3,3-dimethylbutyl)prop-2-enoate	26

4.6 Common VOCs in SanDisk MicroSDs

Table 4.9 details the most common VOCs found in the 30 samples of SanDisk 16GB MicroSDs. These VOCs were found in at least 25 of the samples as well as less than half of the controls. VOCs listed in this table are considered candidates for electronic VOC markers for this component type and source.

Table 4.9 Common VOCs found in SanDisk MicroSD Samples

VOC Name	Number of Occurrences in Samples (Out of 30 Samples)
Hexamethylene diacrylate	30
Morpholine, 4-acetyl-	30
Hi-oleic safflower oil	30
FURAN, 2,3-DIHYDRO-5-METHYL-	30
2-Pentanone, 5-hydroxy-	30
1,3,5-Triazine-2,4-diamine, 6-chloro-N-ethyl-	30
1,6-Hexanediol	30
Pentanoic acid, 2,2,4-trimethyl-3-hydroxy-, isobutyl ester	29
Heptanoic acid	29
1,3,5-CYCLOHEPTATRIENE	29

Table 4.9 Common VOCs found in SanDisk MicroSD Samples (continued)

Propanoic acid, 2-methyl-, 1-(1,1-dimethylethyl)-2-methyl-1,3-propanediyl ester	28
9-Octadecenoic acid (Z)-	28
2,4-Di-tert-butylphenol	28
(R)-Ethyl 2-(2-methoxymethoxy-3,3-dimethylbutyl)prop-2-enoate	28
Phenol	27
Benzaldehyde, 4-(methylthio)-	27
4,4-Dimethyl-3-phenyl-1-pentyn-3-ol	27
butyl dodecanoate	26
2-Piperidinone, N-[4-bromo-n-butyl]-	26
1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	26
1b,5,5,6a-Tetramethyl-octahydro-1-oxa-cyclopropa[a]inden-6-one	26
1,2,3,5-Tetramethylbenzene, 2-oxime-	26
Tetrahydropyrrolo[2,1-c][1,4]oxazin-4-one	25
Tetracosamethyl-cyclododecasiloxane	25
N,N,N-TRIETHYLAMINE	25
Benzoic acid, 2,4,6-trimethyl-	25
Benzophenone, 2,4,6-trimethyl-	25
9H-Thioxanthen-9-one, 2-(1-methylethyl)-	25
Benzene, (2-decyldodecyl)-	25
5,7-Dodecadiyn-1,12-diol	25
Benzene, 1,2,3-trimethyl-	25
3-Acetyl-2-methyl-9b-(1-naphthyl)-3aH-benzo[e]cyclohexa[1,2-b]furan	25

4.7 Significant VOCs Unique to Sources

Silicon Anion Tetramer was identified as the only VOC which met the selection criteria and was unique to only the sample size of the Microchip Technology microcontrollers.

Tables 4.10 and 4.11 detail the significant VOCs for each of the sample sizes of the Texas Instruments microcontrollers and the SanDisk microSDs. These VOCs were found in at least 25 samples of each source and less than 8 of the control samples and are considered unique to their respective sample populations because they were not common to either of the two other sources. There were 7, and 25 VOCs identified that were unique to the Texas Instruments

microcontrollers and the SanDisk microSDs, respectively. These compounds are the best candidates for differentiating each component by source.

Table 4.10 Significant VOCs Unique to Texas Instruments Microcontrollers

VOC Name	<i>Number of Occurrences in Samples (Out of 30 Samples)</i>
Benzene, 1,1'-(1,2-cyclobutanediyl)bis-, trans-	29
Benzaldehyde	27
2-Hexen-1-ol, 2-ethyl-	27
2-Undecanethiol, 2-methyl-	27
tert-Dodecanethiol	26
Hexanal	26
2H-Pyran-6-methanol, 2-ethoxy-3,4-dihydro-4-methyl-	26

Table 4.11 Significant VOCs Unique to SanDisk MicroSDs

VOC Name	<i>Number of Occurrences in Samples (Out of 30 Samples)</i>
Hexamethylene diacrylate	30
Morpholine, 4-acetyl-	30
Hi-oleic safflower oil	30
FURAN, 2,3-DIHYDRO-5-METHYL-	30
2-Pentanone, 5-hydroxy-	30
1,3,5-Triazine-2,4-diamine, 6-chloro-N-ethyl-	30
1,6-Hexanediol	30
Heptanoic acid	29
Propanoic acid, 2-methyl-, 1-(1,1-dimethylethyl)-2-methyl-1,3-propanediyl ester	28
9-Octadecenoic acid (Z)-	28
2,4-Di-tert-butylphenol	28
Benzaldehyde, 4-(methylthio)-	27
4,4-Dimethyl-3-phenyl-1-pentyn-3-ol	27
butyl dodecanoate	26
2-Piperidinone, N-[4-bromo-n-butyl]-	26
1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	26
1b,5,5,6a-Tetramethyl-octahydro-1-oxa-cyclopropa[a]inden-6-one	26
1,2,3,5-Tetramethylbenzene, 2-oxime-	26
Tetrahydropyrrolo[2,1-c][1,4]oxazin-4-one	25

Table 4.11 Significant VOCs Unique to SanDisk MicroSDs (continued)

Tetracosamethyl-cyclododecasiloxane	25
N,N,N-TRIETHYLAMINE	25
Benzoic acid, 2,4,6-trimethyl-	25
Benzophenone, 2,4,6-trimethyl-	25
9H-Thioxanthen-9-one, 2-(1-methylethyl)-	25
Benzene, (2-decyldodecyl)-	25
5,7-Dodecadiyn-1,12-diol	25
Benzene, 1,2,3-trimethyl-	25
3-Acetyl-2-methyl-9b-(1-naphthyl)-3aH-benzo[e]cyclohexa[1,2-b]furan	25

4.8 VOCs Unique to Microcontrollers and MicroSDs with Regard to Type

There was one VOC, Benzene 1,3-dimethyl-, identified as characteristic of both types of microcontrollers and was not identified as a significant marker in the microSD samples. This VOC was identified in 26 of 30 samples in both the Microchip Technology and Texas Instruments samples. The 25 VOCs listed Table 4.10 make up the list of VOCs that were unique to only the sample size of SanDisk microSDs. Notably, there were 7 VOCs present in all 30 samples and one VOC found in 29 samples.

4.9 Common VOC Across All Sample Populations

One VOC, 1,3,5 Cycloheptatriene, met the selection criteria for all three of the sample populations. This VOC was found in 25, 26, and 29 samples of the Microchip Technology microcontrollers, Texas Instrument microcontrollers, and the SanDisk microSDs, respectively. This VOC was found in 6 of the controls. This VOC is a possible indicator of electronic components in general, regardless of source.

4.10 Confirmation of VOCs using Retention Time Analysis

After narrowing the list of identified VOCs to those unique to each component type or VOCs common across all samples, it was necessary to determine if those compounds were reliably identified by the instrument. Retention time analysis was used to determine the accuracy of the instrument to identify the same compound across all the samples. Retention times are typically unique to individual compounds because all compounds have specific volatility and polarity. Because every sample was performed using the same methods and temperature ramp rate, consistent VOCs should leave the column at the same time across the samples. Thus, retention times for compounds that were correctly named should fall in a narrow range, although some variation is permissible due to instrument drift. In this analysis, retention times were recorded manually from peak tables or all instances of identified peaks for each VOC, including duplicate peaks in single samples. In addition, peak area, a crude indicator of the concentration of a VOC in a sample, was also recorded to quantify the concentrations of each candidate compound relative to each other. Sample standard deviations were calculated to measure the reliability of VOC peak areas.

In order to be selected as a viable VOC for electronic component detection or characterization, VOC candidates must have had consistency in first column retention times and minimal duplicate peaks across all samples tested in one component source. Table 4.12 details the compounds with notable consistency with respect to first column retention times and their respective average peak area and peak area standard deviation.

The peak area of each of these VOCs was further analyzed to determine concentration differences between individual VOCs as they appeared within each component type. A box plot of peak areas for all significant VOCs (Figure A.1) is located in the Appendix. Notably, the typical peak area of the SanDisk microSD samples was orders of magnitudes larger than any of

the VOCs discovered in either of the Microchip Technology or Texas Instruments 14-pin 16-bit microcontrollers. Figures 4.1 and 4.2 display the peak area variations between the VOCs named in Table 4.12 for each component type. To demonstrate the large difference in VOC peak area between the microcontrollers and microSDs, common VOCs found in both types are compared in Figures 4.3 and 4.4.

Table 4.12 Significant VOCs Having Consistent Retention Times

VOC	Sample Group	Retention Time Range (sec)	Average Peak Area (\bar{x})	Peak Area Standard Deviation (s)	Sample Consistency
	Microchip				
Benzene, 1,3-dimethyl-	Technology	626-632	370578.458	199390.037	24/26
	Microchip				
1,3,5-Cycloheptatriene	Technology	496-522	527743.500	521233.663	24/25
	Texas				
Phenol	Instruments	836-840	772719.276	238526.623	29/29
Benzene, 1,1'-(1,2-cyclobutanediyl)bis-, trans-	Texas				
	Instruments	1682-1686	288299.414	75769.013	29/29
	Texas				
Benzaldehyde	Instruments	846-850	308734.370	108914.620	27/27
	Texas				
Hexanal	Instruments	546-550	114482.885	46920.295	26/26
	Texas				
Benzene, 1,3-dimethyl-	Instruments	628-632	241562.538	90126.303	26/26
	Texas				
1,3,5-Cycloheptatriene	Instruments	498-502	559748.192	235300.000	26/26
Hexamethylene diacrylate	SanDisk	1492-1496	7880933.167	2234515.536	30/30
Morpholine, 4-acetyl-	SanDisk	1180-1184	1269914.767	439377.378	30/30
FURAN, 2,3-DIHYDRO-5-METHYL-	SanDisk	370-376	6506794.276	2874736.945	29/30

Table 4.12 Significant VOCs Having Consistent Retention Times (continued)

1,6-Hexanediol	SanDisk	1062-1068	6530446.167	1870261.839	30/30
Pentanoic acid, 2,2,4-trimethyl-3-hydroxy-, isobutyl ester	SanDisk	1228-1232	5468829.034	929500.545	29/29
1,3,5-CYCLOHEPTATRIENE	SanDisk	496-514	2893777.759	1442400.532	29/29
Propanoic acid, 2-methyl-, 1-(1,1-dimethylethyl)-2-methyl-1,3-propanediyl ester	SanDisk	1430-1432	6562101.071	1975497.739	28/28
2,4-Di-tert-butylphenol	SanDisk	1390-1394	2614759.929	1086890.502	28/28
Phenol	SanDisk	838-842	6476379.519	3969005.689	27/27
Benzaldehyde, 4-(methylthio)-butyl dodecanoate	SanDisk	1678-1682	755241.833	460783.098	24/27
1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	SanDisk	1732-1736	2492935.038	1530628.695	26/26
1,2,3,5-Tetramethylbenzene, 2-oxime-Tetrahydropyrrolo[2,1-c][1,4]oxazin-4-one	SanDisk	1426-1430	1031586.115	420548.734	26/26
	SanDisk	1392-1396	2358846.880	757767.221	25/25
Tetracosamethyl-cyclododecasiloxane	SanDisk	1952-1956	203291.957	67934.533	23/25
N,N,N-TRIETHYLAMINE	SanDisk	354-368	2507838.080	1609380.431	25/25
Benzoic acid, 2,4,6-trimethyl-	SanDisk	1356-1362	4241861.080	2929835.510	25/25
Benzophenone, 2,4,6-trimethyl-	SanDisk	1736-1740	97187.960	50312.396	25/25

Table 4.12 Significant VOCs Having Consistent Retention Times (continued)

9H-Thioxanthen-9-one, 2-(1-methylethyl)-	SanDisk	1970-1978	4844492.160	3748763.626	25/25
Benzene, (2-decyldodecyl)-	SanDisk	1460-1472	242678.500	116493.138	18/25
Benzene, 1,2,3-trimethyl-	SanDisk	812-814	807414.364	146285.086	22/25

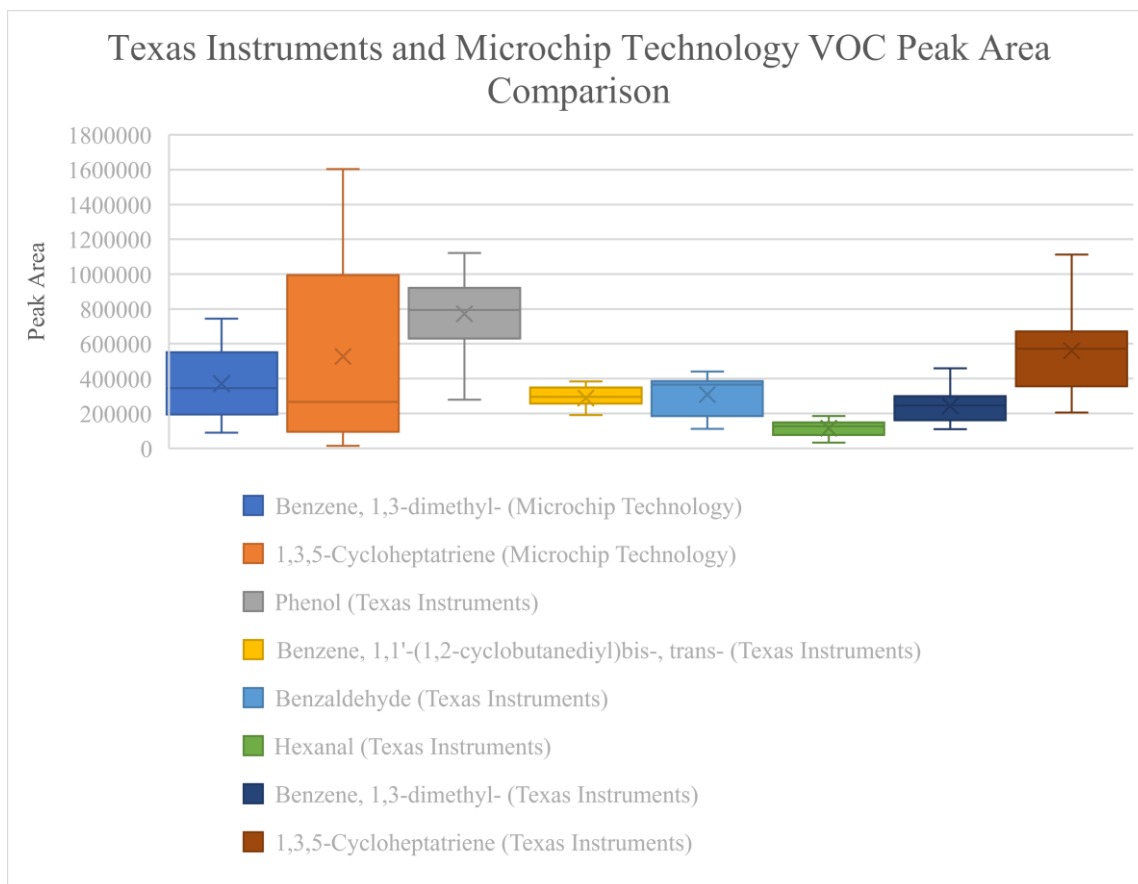


Figure 4.1 Microcontroller VOC Peak Area Comparison

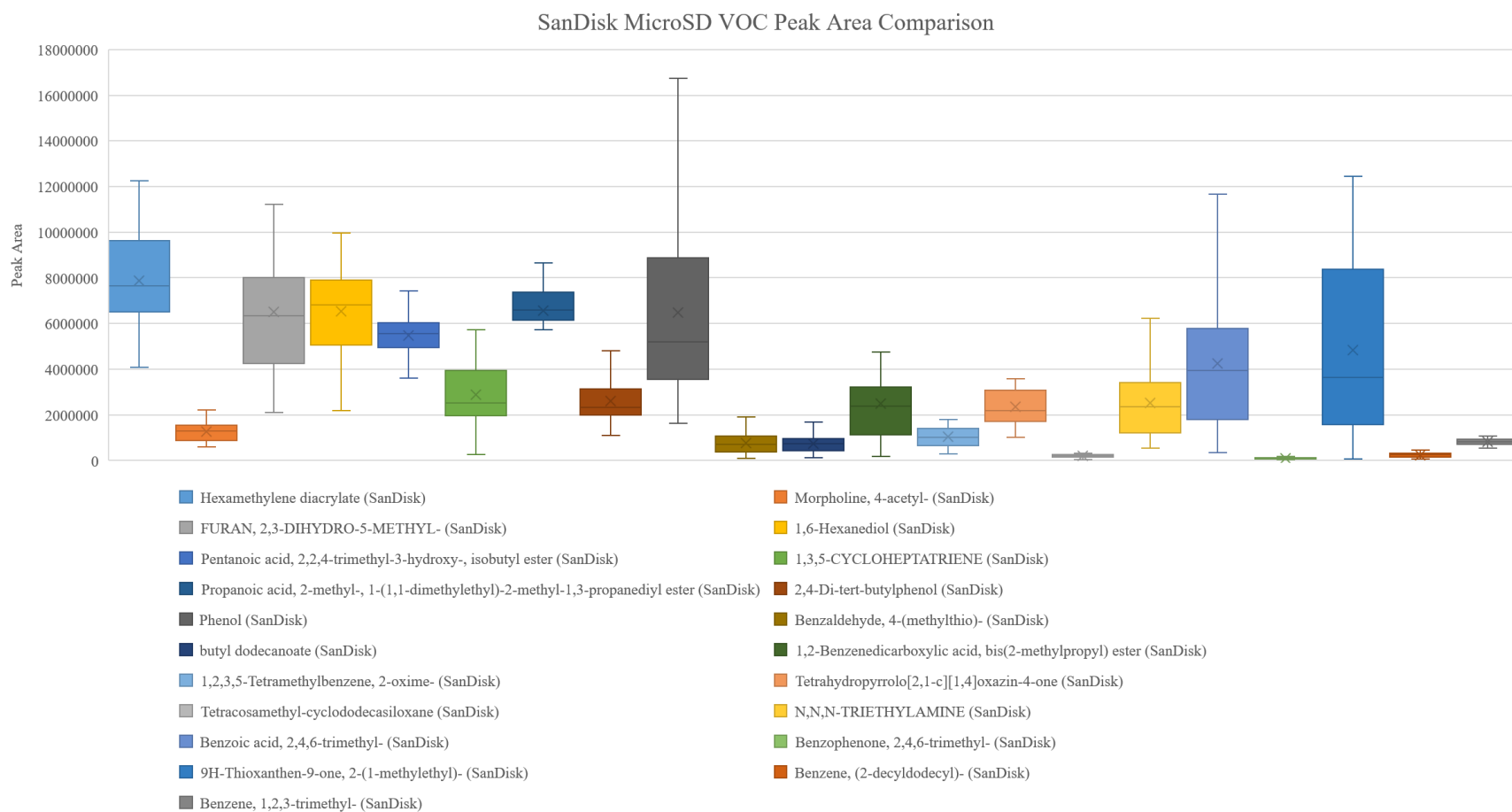


Figure 4.2 MicroSD VOC Peak Area Comparison

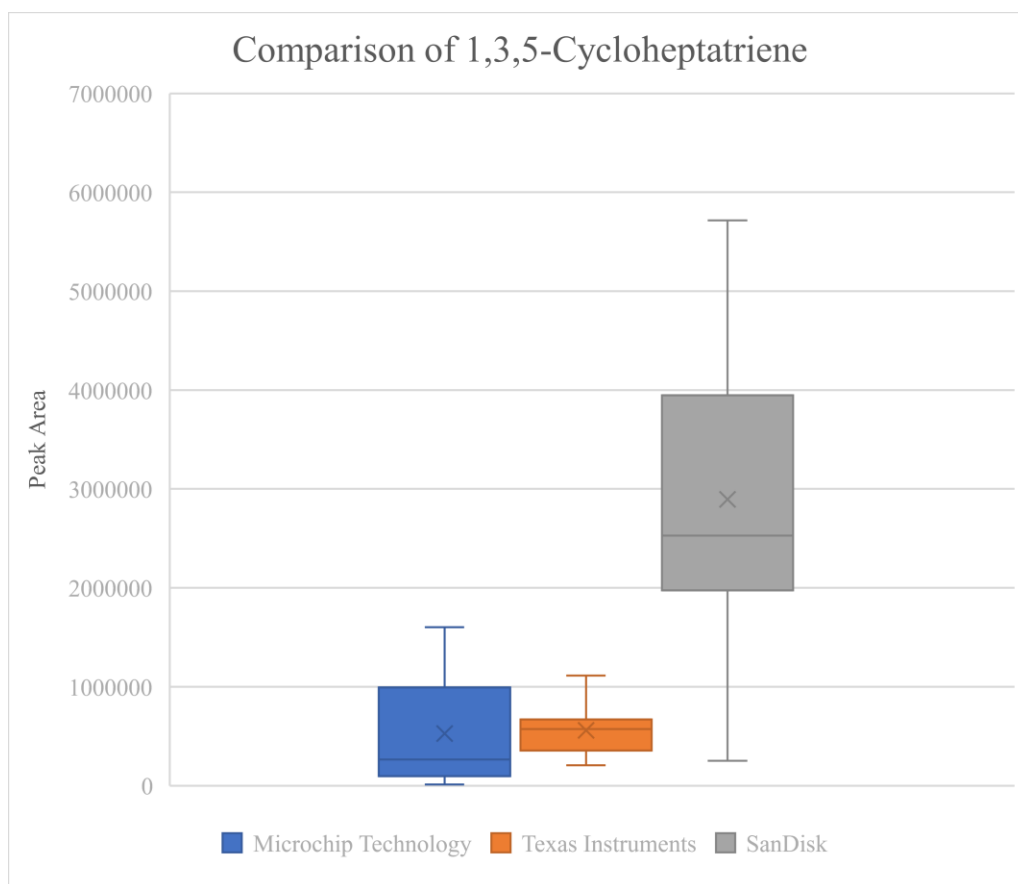


Figure 4.3 Comparison of Component Types Using 1,3,5-Cycloheptatriene

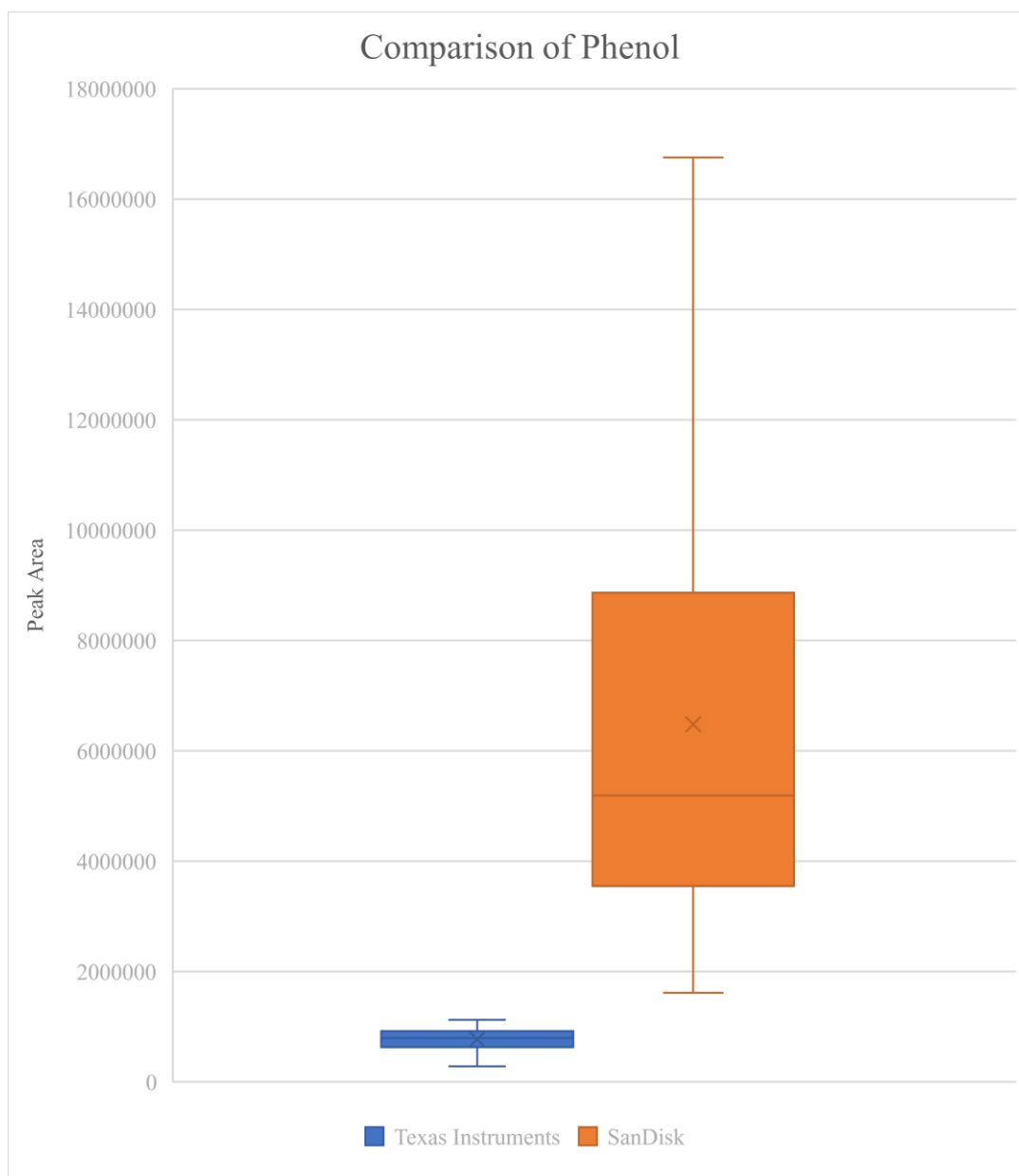


Figure 4.4 Comparison of Component Types Using Phenol

CHAPTER 5. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

5.1 Summary

The thesis outlined the need for a solution to address the proliferation of counterfeit electronic components within the DoD supply chain. This necessity is exasperated by the increasingly globalized economy and the fact that the United States Armed Services continue to utilize warfare systems and components well past their initial end-of-service dates. Without a solution to the counterfeit electronics issue, the operational competence, tempo, and safety of Soldiers, Sailors, Airmen, and Marines continues to be at risk.

Inspired by the success of ESD canines to locate electronic devices and other items of interest using their advanced olfactory abilities, GC×GC and SPME technology was identified as a likely avenue for developing a non-invasive method to determine the authenticity of electronic components. This thesis outlined a general method for evaluating the proof-of-concept for the application of these technologies to bridge the difficulties created by counterfeit electronic components. The research conducted identified multiple likely unique VOC markers for individual types of electronic components as well as common VOCs for electronic components in general. This research leaves multiple avenues of approach for improvement of the methods used as well as additional follow-on research projects regarding this topic. This project successfully demonstrated the proof-of-concept for a general method for VOC detection in electronic components using GC×GC and SPME technology, which is the first step to fielding a non-invasive comprehensive electronic device authentication process for use in the DoD.

5.2 Conclusions

The hypotheses of this study were that VOCs could be detected from electronic components using GC×GC and SPME technology in significant concentrations and that VOC signatures would vary due to component type, age, or origin. Tables 4.1, 4.2, and 4.3 demonstrate that VOCs of significant concentrations were identified in all three sample types. These VOCs met the signal/noise and similarity score thresholds necessary to be identified by the instrument using the data processing methods outlined in Chapter 3. Tables 4.7, 4.8, and 4.9 list VOCs that were identified in at least 25 out of 30 samples in each respective type and less than half of the control samples. These VOCs were selected as candidate characteristic markers for each sample group.

These VOCs, qualitatively determined to be present in the sample groups, were then analyzed by retention times to assess the reliability of the compounds. Consistent retention times for a candidate VOC, across all samples in which it was identified, would indicate that the instrument correctly named the VOC in question. Large variations in retention times, as well as multiple identified peaks across multiple samples, decreases the likelihood that the VOC was correctly identified. Of the three candidate VOCs for the Microchip Technology microcontrollers (Table 4.7), two were found to have reliable retention times. Of the twelve candidate VOCs for the Texas Instruments microcontrollers (Table 4.8), six were found to have reliable retention times. Finally, of the 32 VOC candidates for the SanDisk microSDs, 21 were found to have reliable retention times. Notably, there was one common VOC found across all three sample groups with reliable retention times: 1,3,5-Cycloheptatriene. The remaining VOCs that had reliable retention times (Table 4.12) indicate that there is a significant variation in the numbers of unique, reliable VOCs discovered between the sample groups. Feasibly, the component type can be eliminated as an explanation for this difference due to the large disparity between

microcontroller samples. It is therefore likely that the difference in numbers of VOCs can be attributed to the age of the components. This conclusion is further supported by the fact that the number of reliable, unique VOCs varies between the microcontroller groups, which differ in age by nearly two years. Further, the microSD samples, which also differ in age by two years from the Texas Instruments microcontrollers, had even more reliable, unique VOCs identified.

These remaining VOCs, found to be reliably identified by the instrument, were compared by peak area. VOCs found in both microcontroller sample groups had comparable peak areas (Figure 4.1). However, the majority of the VOCs in microSDs were found to be around one order of magnitude greater than the VOCs found in either of the microcontroller sample groups (Figure A.1). This disproportion is further demonstrated in Figures 4.3 and 4.4, where peak areas of 1,3,5-Cycloheptatriene and Phenol were shown to vary across different component types.

The peak area difference between component types, microcontroller or microSDs, was significant and unexpected. During the study, three microcontrollers or one microSD were placed in sampling vials. Although the mass of microSD samples was slightly larger than the total mass of microcontrollers (~33% more), the disparity is probably not caused solely by total mass of the samples because the trend in peak area differences was more than one order of magnitude for compounds found in both microcontrollers and microSDs (Figure 4.3 and 4.4). The total surface area of the electronic devices sampled may also help explain this disparity. The total surface area of components, listed in Table 3.1, shows that the surface area of the sampled microSDs (380.2 mm²) was slightly more than twice as large as the total surface area of the sampled microcontrollers (188.4 mm²). Both these factors may affect the diffusion rates of VOCs into the headspace for sampling. Besides these two factors, it is possible that the differences between functionality of microcontrollers and microSDs may further explain this difference due to

memory size or another similar characteristic which varies greatly between the two device types, which would cause VOCs to exist on devices in varying quantities based on type.

When examining the differences in peak areas along the common VOCs as analyzed in the box plots in Figures 4.3 and 4.4, the large disparity of the SanDisk microSDs appears to follow an exponential decay based on age. However, more sample groups would have to be examined to confidently prove or refute this conclusion.

Initially, TPPO was thought to be a prospective characteristic VOC for electronic component identification, as it is a compound utilized by trainers to train ESD canines. However, TPPO was not found in any sample tested during this study. Through the methods utilized in this project, TPPO was not identified in any sample of the three electronic components. There can be multiple explanations for this. First, the chromatographic methods utilized in this study may not be optimized to detect TPPO. Due to the non-targeted analysis nature of this study, methods were chosen to detect a broad range of VOCs from electronic components. TPPO, with its exceptionally high boiling point, may not be volatile enough to elute from the columns within the allotted heating profile. TPPO may, in fact, be present, but not visible in this method. Second, it is possible that TPPO may be used in electronic components as a flame-retardant additive on larger circuit boards, and not individual components or smaller boards such as the samples tested in this research. Finally, another explanation for the absence of TPPO in these results may be that although TPPO is used to initially train the ESD canines, it may not be the scent that the canines are actually detecting or acknowledging. Some aspects of their complex training regimen may cause the canines to gradually train on the true scent of electronic devices as they are transitioned from the training aids to actual components. However, consultations and testing with canine

trainers to confirm or deny the plausibility of this final explanation was not possible due to the proprietary nature of their training processes.

5.3 Recommendations

Outlined below are multiple recommendations for follow-on research to be conducted regarding the subject matter addressed in this thesis. As stated above, there are five principle unanswered questions remaining after the conclusion of this study:

1. Is it possible to validate the identity of the VOCs detected in this study?
2. What is the cause of the variation in the numbers of VOCs identified in the three sample groups as well as the large disparity in VOC peak areas between microcontrollers and microSDs?
3. Is TPPO actually present in electronic components?
4. Are VOCs identified in this study better training aids for ESD canines?
5. Would the results of this study be affected by sampling powered electronic components?

To address question one, it is possible to analytically confirm the VOCs using standards. It is recommended that follow-on research purchase pure standards of the compounds in question and analyze them with the same methods detailed in this study to confirm or refute the retention times of the instrument identified VOCs. This requires large amounts of pure compounds to be purchased, a task which was not feasible due to the financial and time constraints on this study.

To address question two, follow-on research should be conducted to address the differences in numbers of reliable VOCs and their peak areas found between the sample groups in this study. This can be evaluated by analyzing multiple types of electronic components sourced from different manufacturers of the same age. In addition, it would be beneficial to test

components of many types. The result of this analysis may ultimately determine the true cause of variations, whether it be age, origin, or component type. This study was not able to source components of the same age due to the composition of stock at electronic supply companies. In addition, the number of samples that could be performed was limited due to the method used, requiring the manual injection of samples on the column. Thus, follow-on research attempting to address this question would benefit from the use of an autosampler for use with SPME, which can greatly accelerate sampling. This device was not available to this study.

To address question three, follow-on research should be conducted to optimize a method for GC×GC detection of TPPO using SPME. Optimizing a method for detecting a certain compound was outside the scope of this study, as the primary effort of this research was to demonstrate proof-of-concept for the use of GC×GC to identify VOCs for electronic components. Once such a method is optimized, it is recommended that electronic components be analyzed to determine definitively if TPPO is contained in electronic components. In addition, evaluation of other types of components, as well as complete circuit boards using an optimized method for TPPO, may provide further insights that would confirm or positively refute the presence of TPPO due to the large differences in construction between components. It is possible that TPPO may be present on some types of complex components and circuit boards while it may not be found on others.

To address question four, follow-on research should be conducted to determine if any of the VOCs detected in this study are better training aids for ESD canines. To answer this question, pure compounds should be purchased for testing with two groups of ESD canines. One group of canines, trained with current methods, should be exposed to these compounds to determine if they detect the pure compounds. Positive alerts to these compounds may indicate that canines are

more attuned to the true scent of electronic devices, rather than their training aid, TPPO. Another group of canines should also be trained to specifically alert to VOCs identified in this study.

Successful and more consistent alerts to electronic devices from these canines would indicate the superiority of another training compound over TPPO. Investigating this course of action would be extremely difficult due to the proprietary nature of the ESD canine trainers' processes.

To address question five, follow-on research should be conducted to investigate the characteristic VOCs from electronic components that are powered during the SPME VOC adsorption process. This research, by nature of its design, did not investigate powered components due to the complexity of variables. However, VOCs may differ due to the increased temperatures generated by components in operation. In order to investigate this, components of the same age, origin, type, and manufacturer should be selected for testing. One sample group of devices should be analyzed unpowered, while one group should be actively powered or otherwise running during the VOC adsorption process. Results from this future research may point to VOCs which not only characterize the devices themselves but also may identify VOCs which characterize certain operating conditions. Further, causing devices to fail and investigating their VOCs before and after may show proof-of-concept for identifying predictive VOCs for device failure.

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APPENDIX VOC PEAK AREA COMPARISON

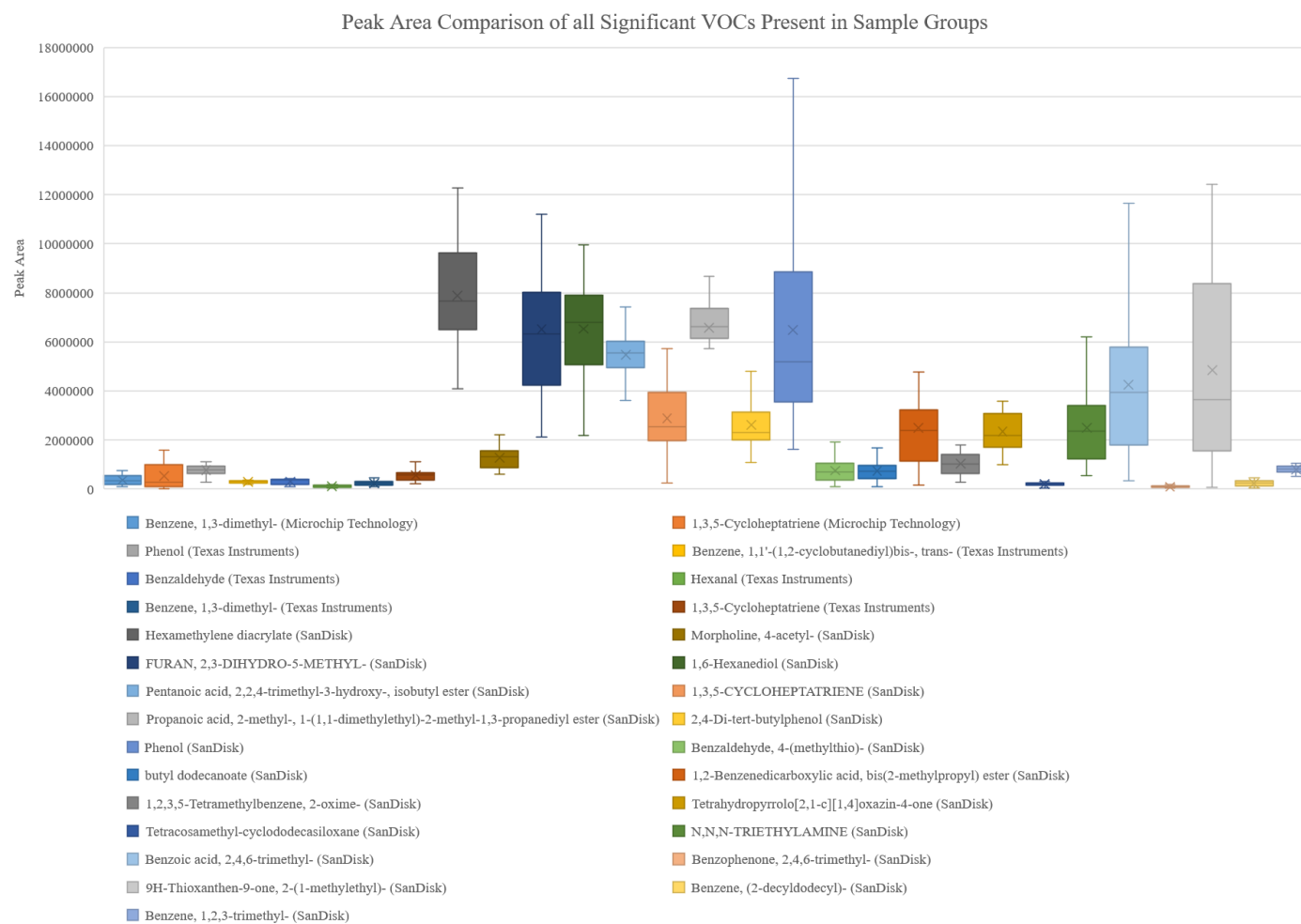


Figure A.1 VOC Peak Area Comparison for All Significant VOCs