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Evaluation of commercial products as possible sources of oxygenates in fire debris samples

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EVALUATION OF COMMERCIAL PRODUCTS AS POSSIBLE SOURCES OF
OXYGENATES IN FIRE DEBRIS SAMPLES

by

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DEDICATION

This thesis is dedicated to my family, for their continued support and belief in me, and for inspiring my passion for knowledge.
ACKNOWLEDGMENTS

I could not complete this remarkable journey without the help of many. First, I would like to most sincerely thank my thesis advisor, Dr. Adam Hall, for this opportunity. His guidance and patience throughout was instrumental to the success of this project. I also want to express my gratitude toward Ms. Emily Ross, for her insightful feedback, which I am truly grateful for. I would also like to extend my thanks to Ms. Corissa Rodgers, for her encouragement and the foundation that her own work had laid for me. A thank you to the faculty, staff and students of the Biomedical Forensic Sciences program, for their support and enthusiasm the past two years. Lastly, a thank you to my family and friends for their love and inspiration at times of hardship.
EVALUATION OF COMMERCIAL PRODUCTS AS POSSIBLE SOURCES OF OXYGENATES IN FIRE DEBRIS SAMPLES

WAI POK VERNON CHAN

ABSTRACT

In fire debris analysis, substrate contribution refers to compounds present within the material collected that can interfere with the instrumental detection of ignitable liquids or contribute petroleum or alcohol-based compounds, which may complicate the interpretation. The concept of substrate contribution was brought to light by “The petroleum-laced background” by Lentini et al. focusing on commercial products (e.g. tennis shoes, magazines, etc.), the publication successfully illustrated that these products can produce chromatograms similar to those generated by the presence of petroleum-based ignitable liquids (ILs). As a result, Lentini et al. demonstrated that fire debris analysts can identify the presence of ignitable liquids without realizing the compounds in question might be the result of the manufacturing processes, and are inherent to the substrate in question. Therefore, the findings may or may not be probative.

Gasoline is easily accessible and is frequently used by arsonists. As such, fire debris analysis focuses primarily on petroleum-based compounds. However, oxygenated solvents, which encompass all oxygen-containing compounds as defined by the American Society for Testing and Materials (ASTM) classification scheme, can also be used in an arson event. Despite the potential to be used as ILs, little is known regarding the recovery of these compounds. Previous thesis projects from the Biomedical Forensic Sciences program at Boston University School of Medicine explored and optimized the use of

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zeolites in recovering low molecular weight oxygenated ignitable liquids. An isothermal gas chromatography/mass spectrometry (GC/MS) method was also developed to detect these oxygenated ILs. The results from these projects show that zeolites have the potential to be used in forensic casework.

Inspired by previous publications and thesis research, the goal of this project was to first develop a reference library on substrate contribution from oxygenates (e.g. ethanol, isopropanol and acetone) present in commercial products using the isothermal GC/MS methods. The development of this reference library included a specific interest in wood treatment products, considering wood is one of the most commonly submitted fire debris materials. The second stage involved an attempt at evaluating extraction efficiencies of activated charcoal strip and zeolites.

The results of this project suggested that automotive and food products examined contained only acetone and ethanol respectively, while the variety of oxygenates found in household and personal care products indicated further analysis of additional products in these categories would be beneficial. Moreover, the results also reaffirmed zeolites’ role in recovering oxygenated ILs in a controlled testing environment using KimWipes as a non-contributing substrate. However, the instrumental method required some modifications, as there was partial separation between ethanol and acetone.

The results from applying products onto wooden blocks suggested that activated charcoal strips recovered more oxygenates than zeolites. This unexpected result prompted an investigation into the existing extraction parameters. The investigation suggested that
the wooden blocks themselves were responsible for the unexpected recovery results, and future studies would be needed to understand if this recovery was substrate-specific.
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LIST OF ABBREVIATIONS

% Percent

13X Specific type of zeolite

Å Angstrom

ACS Activated charcoal strip

ACS/CS$_2$ Activated charcoal strip with carbon disulfide as the desorption solvent

ACS/MeOH Activated charcoal strip with methanol as the desorption solvent

a.k.a. Also known as

Al Aluminum

AlO$_2$ Aluminum oxide

ASTM American Society for Testing and Materials

°C Degree Celsius

C Carbon

Ca$^{2+}$ Calcium ion

cm$^3$ Cubic centimeter

CS$_2$ Carbon disulfide

CSB Chemical Safety and Hazard Investigation Board

CSV Comma-separated values

e.g. exempli gratia

EIP Extracted ion profile

et al. et alia

etc. et cetera

EtOH Ethanol
°F  Degree Fahrenheit
FEMA  Federal Emergency Management Agency
GC  Gas chromatography
GC/MS  Gas chromatography/Mass Spectrometry
GHS  Globally Harmonized System of Classification and Labeling of Chemicals
gmol⁻¹  grams per mole
H₂O  Water
HCS  Hazard Communication Standard
hrs  Hours
i.e.  id est
in  Inch(es)
IL(s)  Ignitable liquid(s)
IPA  Isopropanol
LOD  Limit of detection
LOQ  Limit of quantitation
m/z  Mass-to-charge ratio
M⁺  Metal ion
MEK  Methyl ethyl ketone, butanone
MeOH  Methanol
mg  Milligram(s)
mins  Minutes
mL/min  Milliliter per minute
MS  Mass Spectrometry
MSDS(s)  Material safety data sheet(s)
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na&lt;sup&gt;+&lt;/sup&gt;</td>
<td>Sodium ion</td>
</tr>
<tr>
<td>NFPA</td>
<td>National Fire Protection Association</td>
</tr>
<tr>
<td>NIJ</td>
<td>National Institute of Justice</td>
</tr>
<tr>
<td>o-, p-, m-</td>
<td>Ortho-, para-, meta-; Refers to the specific locations of attachment around a ring</td>
</tr>
<tr>
<td>OSHA</td>
<td>Occupational Safety and Health Administration</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>psi</td>
<td>Pounds per square inch</td>
</tr>
<tr>
<td>SDS</td>
<td>Safety Data Sheet</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Silicon dioxide</td>
</tr>
<tr>
<td>TIC</td>
<td>Total ion chromatogram</td>
</tr>
<tr>
<td>U.S.</td>
<td>United States</td>
</tr>
<tr>
<td>U.S.A.</td>
<td>United States of America</td>
</tr>
<tr>
<td>µL</td>
<td>Microliter(s)</td>
</tr>
<tr>
<td>µm</td>
<td>Micrometer</td>
</tr>
<tr>
<td>X</td>
<td>Synthetic faujasite, a type of zeolite</td>
</tr>
<tr>
<td>Z</td>
<td>Zeolite</td>
</tr>
<tr>
<td>Z/MeOH</td>
<td>Zeolite as adsorbent with methanol as the desorption solvent</td>
</tr>
</tbody>
</table>
1. INTRODUCTION

1.1 Fire

1.1.1 Chemistry of fire

The National Fire Protection Association (NFPA) defines fire as a process of rapid oxidation, accompanied by the presence of light and heat.¹ This exothermic reaction requires the interaction of three components: a fuel, an oxidizer and a heat source, which together form the fire triangle (Figure 1). Any combustible materials, regardless of phase, can be used as fuel. The oxidizer provides the oxygen, and the heat source provides the activation energy needed to start the reaction. Some consider the uninhibited chain reaction as a fourth component, thus forming a fire tetrahedron. A deficiency in any one of the components will either prevent a fire from being started or extinguish an existing fire.

![Fire triangle/Fire tetrahedron](image)

Figure 1: Fire triangle/Fire tetrahedron
1.1.2 Fire in the United States

According to data collected by the Federal Emergency Management Agency (FEMA), on average, there were 1.6 million fires and over 3500 deaths per year between 2003 and 2007 in the United States (U.S.).\(^2\) The financial loss during the same time period was an estimated average of $12 billion dollars a year (inflation adjusted), while the total cost for fire protection was over $182 billion dollars per year. Despite these astonishing numbers presented in the FEMA report, the decreasing numbers of injuries and deaths justified the spending on fire protection. The same trend was also observed globally. However, compared to other industrial nations, the U.S. still lagged behind in preventing fire deaths. From a regional standpoint, New England states (Maine, New Hampshire, Vermont, Massachusetts and Rhode Island) have had a lower fire death rate per one million population than the national average between 2003 and 2007.\(^2,3\) The District of Columbia and several southern states (e.g. Mississippi and West Virginia) consistently have a comparatively higher death rate. The report did not provide any explanation for such observations, but high population density (for the District of Columbia) and lack of fire safety readiness could explain the high death rates.
1.1.3 Arson and the criminal justice system

The cause of a fire can generally be divided into two categories: natural or artificial. In artificially caused fires, the presence of intent determines whether it can be ruled as arson or not. Arson is defined by the NFPA as “the crime of maliciously and intentionally, or recklessly, starting a fire or causing an explosion”. FEMA suggests that, for fires in non-residential buildings, arson accounted for 12% of the fires (the second highest cause), 27% of civilian deaths (the highest cause of death) and 13% of money loss (the highest cause). Therefore, the severity of this crime should not be understated.

Arson is considered a felony in the state of Massachusetts, and an arsonist can be sentenced to imprisonment of up to 20 years, a fine of not more than $10,000, or both. Most arson cases are under the jurisdiction of the state, except cases that take place within “special maritime and territorial jurisdiction”. These cases fall under the jurisdiction of the federal government, as defined by the U.S. Code Title 18, Section 81. Despite the use of harsh sentencing as a deterrent, early crime statistics from the Federal Bureau of Investigation indicated an increase in arson-related crime in the first six months of 2012, with only the southern states showing an opposing trend. In addition, the National Institute of Justice (NIJ) reported the backlog of forensic cases as one of the biggest concerns to an efficient judicial system. The NIJ defines “backlog” as any casework that has not been analyzed within 30 days of being received.
1.2 Current practice in fire debris analysis

1.2.1 ASTM guidelines

Currently, the analysis of evidence collected from arson scenes follows the American Society for Testing and Materials (ASTM) International guidelines. These guidelines provide forensic scientists with established and consistent procedures to analyze and classify ignitable liquids (ILs) which may be present within fire debris collected at a crime scene. Nevertheless, the proper collection of fire debris is equally important to the success of the analysis.

Due to the volatile nature of the compounds within accelerants involved in arson, a quick and secure collection method is crucial to the success of recovering ILs. There are several containers that fire debris analysts can use. However, metal paint cans remain the container of choice within the U.S. Compared to other containers, such as plastic bags, plastic jars or glass jars, metal paint cans have better structural integrity and maintain a tight seal, providing better protection and containment of the volatile samples collected. Analysts should, however, beware of rust formation when using metal paint cans.

In addition to choosing the appropriate containers, special consideration should be made when collecting samples. Since the objective is to recover ILs, materials that are porous and highly absorbent (e.g. cardboard, soil, etc.) are desired. Charred substrates are less likely to retain any IL. The exception to this is charred wood, because the fire-damaged wood will have a layer of charcoal on the surface, which can be used as an adsorbent for ILs. Moreover, under the high temperatures generated by the fire in an
anaerobic environment, materials may undergo pyrolysis, the thermal breakdown of materials into smaller compounds. The presence of these pyrolysis products can potentially complicate the analysis, since these products are similar to the ones identified in petroleum products. Therefore, a fire debris analyst should look for debris that has no visible fire damage from a less superficial source that comprises of a highly adsorbent material.

Currently, there are five ASTM documents detailing the extraction of IL from debris and the subsequent analysis of ILs. E1386 describes the procedure required for solvent extraction. Solvent extraction refers to the idea that, in the presence of two immiscible solvents, compounds can be separated based on their relative solubility in the solvents. This extraction, albeit sensitive, is destructive and can potentially extract contaminants. Because of these factors, solvent extraction is not commonly used in fire debris analysis. E1388 provides a standard practice of extraction using the headspace of the container. It is closely related to E1412 and E1413, which describe passive and dynamic headspace extractions, respectively. Passive headspace extraction uses an activated charcoal strip (ACS) as an adsorbent for the ILs. Utilizing the same metal paint can used to collect the debris, an ACS is suspended within the headspace using a paperclip and unwaxed dental floss. The whole setup is heated in an oven at 50°C-80°C for two to 24 hours. At an elevated temperature, the compounds have more kinetic energy to leave the debris, enter the headspace within the container, and subsequently adsorb onto the ACS. In addition to an adsorbent (e.g. ACS), dynamic headspace extraction also
requires the flow of an inert gas. The types of volatiles adhering to the adsorbent can be manipulated by adjusting the flow of gas and/or temperature of the system.

Regardless of which headspace sampling method is used, the adsorbent will then be immersed into a solvent for 15 minutes. This allows the compounds to be extracted from the adsorbent and enter the solution. Afterwards, the solution will undergo separation and analysis using gas chromatography/mass spectrometry (GC/MS), which is detailed in E1618. The separation process begins in the capillary column. After volatizing the compounds in the gas chromatograph oven, the carrier gas, acting as the mobile phase, will transport the compounds through the column, which is the stationary phase. This transport of compounds will be inhibited due to various factors, such as adsorption to the column or size. As a result, different compounds will exit the column at different times. After being separated in the column, compounds will undergo fragmentation and detection in the mass spectrometer. This is a popular analytical technique for many reasons. As a sensitive technique, the instrument is capable of detecting microliter volume ILs from the debris. In addition, the versatility of the GC/MS allows a variety of samples to be analyzed, making it a valuable instrument to have in the laboratory. In addition to the analysis of fire debris evidence, it can also be used to analyze samples from other forensic fields (e.g. poisons in toxicology, paint chips in trace evidence, etc.). Together with heated passive headspace and dynamic headspace extractions, it is one of the integral components in fire debris analysis.
1.2.2 Classification of ignitable liquids

The ASTM classification scheme categorizes ILs into eight classes based on chemical composition and boiling point range.\textsuperscript{13} The classes include gasoline, petroleum distillates, isoparaffinic products, aromatic products, naphthenic-paraffinic products, normal-alkane products, oxygenated solvents and miscellaneous products. Each class can further be divided into three subclasses based on the number of carbon atoms: light (C\textsubscript{4}-C\textsubscript{9}), medium (C\textsubscript{8}-C\textsubscript{13}) and heavy (C\textsubscript{8}-C\textsubscript{20+}). Currently, the identification of ILs from chromatograms generated using GC/MS is based on the principle of pattern recognition.\textsuperscript{17} The interpretation of the raw chromatograms, or total ion chromatogram (TIC), starts with analyzing the overall pattern, followed by comparing the relative abundances generated by each of the extracted ion profile (EIP). Compared to the TIC, the EIP is a processed version of the former. It represents a selection of results based on selected mass-to-charge ratios (m/z). Therefore, by inputting a series of m/z values, analysts can obtain information on abundances regarding a general group of organic compounds (e.g. isoparaffin, aromatics, etc.). From the EIP, the relative abundance of each group can then be compared to make a proper determination regarding the class of IL. After a complete interpretation, the IL will have both class (e.g. oxygenated solvents, normal alkane products, etc.) and subclass (e.g. light, medium or heavy) information associated with it. However, it should be noted that ILs often span different weight classes. In this case, ILs can be classified as “light to medium” or “medium to heavy,” depending on its weight range.
1.3 The increasing use of oxygenated solvents

The present ASTM guidelines define oxygenated solvents as mixtures that has any oxygen-containing species (e.g. alcohol, ketone, etc.).\textsuperscript{13} The broad definition means that oxygenated solvents are not as well defined as other classes of ILs, with the exception of miscellaneous products. Given that petroleum-based compounds (e.g. gasoline) are a popular choice among arsonists, analysts have a better understanding in recovering petroleum-based ILs based on more research versus oxygenated solvents.\textsuperscript{17} Nonetheless, oxygenated solvents can be found in many commercial products, including, but not limited to, personal care (e.g. nail polish remover), cleaning (e.g. disinfecting wipes), automotive (e.g. brake part cleaners) and household products (e.g. lacquer thinners).\textsuperscript{18–22}

Moreover, the rise of environmentalism in recent decades has also triggered the move from petroleum-based to oxygenated products, which are more environmental friendly. Perhaps no other oxygenated solvents have received more attention than alternate fuel sources, specifically biodiesel and ethanol (EtOH). The amendment to the Energy Policy Act of 1992 popularizes the use of biodiesel by providing financial incentives for logistics companies.\textsuperscript{23} It allows logistics companies to comply with the U.S. Environmental Protection Agency’s (EPA) Alternative Fuel Vehicle acquisition requirements by using biodiesel, rather than purchasing new vehicles to replace the aging fleet. As for EtOH, its blending with gasoline is popularized by the partial waivers granted to fuel or fuel additive manufacturers by the EPA.\textsuperscript{24} In addition to the developments in the energy industry, a research group has recently invented a sucrose
ester-based paint. Various manufacturing companies are marketing their products as “green” to indicate the use of more environmentally friendly components. When comparing lacquer thinners produced by the company Klean-Strip, the green product has more oxygenated components and less petroleum-based components than the “normal” lacquer thinner (Table 1).

Table 1: Comparison between different lacquer thinners by the same manufacturer

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Lacquer Thinner</th>
<th>Green Lacquer Thinner</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>5.0-20.0%</td>
<td>3.0-35.0%</td>
</tr>
<tr>
<td>2-Butanone</td>
<td>5.0-10.0%</td>
<td>20.0-35.5%</td>
</tr>
<tr>
<td>Ethylene glycol n-butyl ether</td>
<td>1.0-5.0%</td>
<td>&lt;10.0%</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>5.0-15.0%</td>
<td>15.0-25.0%</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Absent</td>
<td>20.0-30.0%</td>
</tr>
<tr>
<td>Methanol</td>
<td>20.0-25.0%</td>
<td>&lt;2.0%</td>
</tr>
<tr>
<td>Light aliphatic naptha hexane</td>
<td>30.0-50.0%</td>
<td>Absent</td>
</tr>
</tbody>
</table>

While the increasing use of green products is good for the environment, some of the compounds used in the manufacturing process are highly flammable. In Table 2, fire safety information of four of the most common oxygenated solvents are listed. Auto-ignition temperature refers to the lowest temperature at which the compound will spontaneously ignite without an ignition source. Flash point refers to the lowest temperature at which the compound will form an ignitable mixture with air. The flammable limits define the range of fuel concentrations for the fuel-air mixture to burn. The low flash points exhibited by all four oxygenated solvents suggest an ignitable mixture will inevitably be present at room temperature, which creates a high risk for fire. Analysts should be concerned given that all four compounds can be found in everyday
products, and they can be used as fuel in fire setting. With the increasing addition of green products to the market, it is important for forensic scientists to optimize the recovery of these oxygenated ILs.

Table 2: Properties of oxygenates of interest

<table>
<thead>
<tr>
<th></th>
<th>Methanol\textsuperscript{26-28}</th>
<th>Ethanol\textsuperscript{27,29}</th>
<th>Acetone\textsuperscript{20,30,31}</th>
<th>Isopropanol\textsuperscript{32,33}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td><img src="image" alt="Methanol structure" /></td>
<td><img src="image" alt="Ethanol structure" /></td>
<td><img src="image" alt="Acetone structure" /></td>
<td><img src="image" alt="Isopropanol structure" /></td>
</tr>
<tr>
<td>Molecular weight</td>
<td>32.04gmol\textsuperscript{-1}</td>
<td>46.07gmol\textsuperscript{-1}</td>
<td>58.08gmol\textsuperscript{-1}</td>
<td>60.1gmol\textsuperscript{-1}</td>
</tr>
<tr>
<td>Molecular diameter</td>
<td>3.8Å</td>
<td>4.5Å</td>
<td>6.2Å</td>
<td>4.3Å</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>64.5°C (148.1°F)</td>
<td>78.5°C (173.3°F)</td>
<td>56.2°C (133.2°F)</td>
<td>82.5°C (180.5°F)</td>
</tr>
<tr>
<td>Auto-ignition Temperature</td>
<td>464°C (867.2°F)</td>
<td>363°C (685.4°F)</td>
<td>465°C (869°F)</td>
<td>399°C (750.2°F)</td>
</tr>
<tr>
<td>Flash Point</td>
<td>12°C (53.6°F)</td>
<td>13°C (55°F)</td>
<td>-20°C (-4°F)</td>
<td>12°C (53°F)</td>
</tr>
<tr>
<td>Flammable limits</td>
<td>36.5% 6%</td>
<td>19% 3.3%</td>
<td>12.8% 2.6%</td>
<td>12.7% 2%</td>
</tr>
<tr>
<td></td>
<td>Upper</td>
<td>Lower</td>
<td></td>
<td></td>
</tr>
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</table>
1.4 Zeolites

1.4.1 The basis for recovering oxygenated solvents using zeolites

The literature suggests that hydrophilic zeolites can be good adsorbents for oxygenates of low molecular weight (e.g. acetone, EtOH, IPA). With a microcrystalline structure, zeolites (Z) are mostly composed of aluminum (Al) and silicon (Si) dioxides. Together with oxygen atoms, the three elements form a tetrahedral framework, which serves as a functional unit. This functional unit has a general formula of $\text{M}^+\times(\text{AlO}_2)_x(\text{SiO}_2)_y$, where $\text{M}^+$ refers to the monovalent metal ion. Ever since the discovery of zeolites, they have become an important component in various processes (e.g. manufacturing of laundry detergent, etc.). Based on ion-exchange principles, hard water ions (e.g. Ca$^{2+}$) are replaced by Na$^+$ in the production of laundry detergents using zeolites. In addition to ion exchange, scientists also explored the shape selectivity nature of zeolites. It was reported that the diffusion coefficients of positional isomers (i.e. o-, m-, p-xylene) were different, with p-xylene diffusing ten times faster out of zeolites than the other two positional isomers, showcasing zeolites’ filtering ability. As a catalyst, zeolites also play a role in several organic transformation, including the ring-opening of epoxides.

Understanding the general principles of zeolites is crucial to identifying the role that they play in the extraction of oxygenated ILs for subsequent analysis. The metallic aluminum and silicon each coordinate to four oxygen atoms of an oxygen-containing species to form coordinated anionic complexes, which results in an unbalanced electrical charge within the structure. The presence of this electrical charge on the aluminum
is pivotal to zeolite interaction with polar molecules. By adjusting the Al to Si ratio, the amount of charges on the aluminosilicate framework can be altered. Coulomb’s Law dictates that the electrostatic force is proportional to the amount of charges. Therefore, an increase in the ratio (and consequently a greater charge) will result in an increase in electrostatic force, which in turn will improve zeolites’ interaction with polar compounds. Therefore, depending on the level of interaction needed between zeolites and polar molecules, scientists can select an appropriate type of zeolite. Moreover, rings within the structure create apertures that limit the size of compounds that can pass through. Together with the small and uniform pores, zeolites are able to function as molecular sieves.

1.4.2 Developing an oxygenated IL extraction technique using zeolites

Previous thesis projects from the Biomedical Forensic Sciences program at Boston University School of Medicine have been dedicated to developing an extraction technique to recover oxygenated ILs using zeolites.\textsuperscript{40–42} St. Pierre first proposed the use of zeolites in recovering oxygenated ILs. This feasibility study looked into the use of different kinds of zeolites to recover acetone.\textsuperscript{40} Gugliotta continued with comparing recovery using ACS and zeolite packets with additional oxygenates, whereas Rodgers optimized the zeolite extraction parameters and evaluated a dual-mode extraction technique utilizing both ACS and zeolite packets.\textsuperscript{41,42}

A zeolite packet consists of approximately 64 (approximately 510mg) 13X zeolite beads as an adsorbent in a porous teabag.\textsuperscript{40} 13X zeolite (formula: M\textsubscript{86}(AlO\textsubscript{2})\textsubscript{86}(SiO\textsubscript{2})\textsubscript{106}•264H\textsubscript{2}O) is a kind of zeolite X, or synthetic faujasites, with a pore
The sodium-containing 13X zeolite is currently employed in commercial gas drying, air purification or sweetening of petroleum products (i.e. removal of sulfur-containing compounds). Similar to the ACS extraction setup, the zeolite packet is suspended within the headspace of the paint can with a paperclip and unwaxed dental floss.

After sealing the can, it will go through an incubation period in the oven. With regards to the oven parameters, the results of the studies suggest the temperature should be set at 80°C. However, the incubation time depends on the identity of the oxygenates to be recovered. Therefore, a minimum of two hours heating in the oven is recommended. It should be noted that a longer incubation time (8-12 hours) can potentially improve recovery. Given analysts typically have no information on the identity of compounds present in casework samples, it would be best to incubate samples for approximately four hours. This ensures oxygenate recovery without favoring one compound over another.

Similar to ACS, the zeolites undergo a desorption period after an incubation period. MeOH was proved to be a better desorption solvent for oxygenates than carbon disulfide (CS₂). Overall, using zeolites with MeOH as the desorption solvent (Z/MeOH) recovers more oxygenates than using ACS with carbon disulfide (ACS/CS₂). In addition to being more efficient in recovering oxygenated ILs, zeolites are also the more financially responsible option as well. Compared to approximately $2.75 per half ACS, the same sample can be analyzed for approximately $0.007 using zeolites. Therefore, zeolites are considered an attractive alternative for recovering oxygenated ILs.
1.5 Substrate contribution and issues with ignitable liquid analysis

The publication “The petroleum-laced background” by Lentini et al. states that the substrate can interfere with the chromatogram generated. This interference can come from one of two sources: substrates containing the ILs and pyrolysis products formed as a result of the fire events. To this date, various pyrolysis mechanisms have been proposed in peer-reviewed journals. These mechanisms include products ranging from fire debris to carbohydrates. Lentini et al. argues that analysts should develop an understanding on substrate contributions, which refers to the concept that commercial products can contain ILs. As a result, analysts will not be able to conclude whether the ILs are from the substrate or from the arson event without comparison samples or substrate controls.

Several publications following the Lentini et al. article also looked into substrate contribution. Lentini later published an article that looked into the persistence of
floor coating solvents.\textsuperscript{47} His results suggested that the medium petroleum distillates present in wood floor solvents would remain with the wood substrate after the evaporation of solvents. His results also suggested, with the exception of terpenes, the concentrations of alkanes and aromatics would remain stable over the two-year study period. He noted the necessity of having a precautionary statement in forensic reports when encountering this type of product. A similar study was performed by Hetzel et al. in 2005.\textsuperscript{48} Instead of studying the persistence of ILs indoors, like in the Lentini et al. studies, Hetzel et al. exposed their sealed wood samples, sealed by floor coating solvents, to the outdoor environment. The results suggested medium petroleum distillates would diminish over time and the alkanes would be overshadowed by the aldehydes present. The group suggested the use of additional extraction methods (e.g. solvent extraction) to avoid heavy volatile compounds from displacing the lighter compounds from the adsorbent when extracting using passive heated headspace. Cavanagh et al. investigated how daily activities (e.g. using the vehicle or filling up the gas tank) interfered with the amount of gasoline residues in automobile carpets.\textsuperscript{49} The group first studied the relationship between the amount of substrate contribution and time, and concluded that there was a negative correlation between the two. Based on these findings, they claimed that, after a prolonged period of time, the low level presence of substrate contribution from auto carpets should allow the analysts to differentiate between the background interference and the presence of ILs. They also concluded that IL residues found in carpets could result from being exposed in normal daily activities. Therefore, analysts should take into account the person’s living or working environment and other possible
routes of exposure. Despite these findings, they reaffirmed the need for substrate controls. Research by Coulson et al. focused on the level of gasoline present after certain activities (e.g. mowing lawn, working, etc.) and concluded that it was ‘extremely unlikely’ that an individual would have traces of gasoline remaining on their clothing and shoes from the activities they performed.\textsuperscript{50} However, using a gasoline-powered lawn mower could lead to the detection of gasoline. Although this was a small pilot study, it suggested how individuals could come across detectable levels of ILs through daily activities. Overall, the literature indicated that more experiments would be needed to achieve the confidence level when associating an individual with an arson event.

1.6 Objective of this thesis

Inspired by previous publications, the first stage (Section 3.1) of this research was to develop a reference library on substrate contribution from oxygenates present in common consumer products using the GC/MS methods developed by previous thesis research. The development of this reference library included a specific interest in wood treatment products (Section 3.2). The second stage involved an attempt at evaluating extraction efficiencies of two adsorbents: ACS and Z (Section 3.3).
1.7 Properties of wood

Given how often wood is submitted as fire debris evidence and the importance of addressing substrate contribution, there is an interest in understanding the chromatographic effects of applying wood treatment products onto wooden blocks (Section 3.2). Out of the four wood species used in this project, maple, oak (white) and pine are considered commonly used wood species in flooring, while cypress is considered a limited wood sample. Maple and oak are classified as angiosperms, or hardwood, whereas pine and cypress are classified as gymnosperms, or softwood. This distinction is made based on botanical considerations. Hardwood refers to wood species that have their seeds enclosed in the ovaries of the flowers, while softwood refers to their seeds enclosed in cones. Although there can be intra-genus differences, they cannot be accounted for because lumber suppliers tend not to differentiate species of the same genus.

A literature search was performed to acquire information on different wood properties (Table 3). The Janka hardness rating measures the wood’s ability to resist indentation. It is measured by the amount of force necessary to embed half of a 0.444 inch steel ball. The numerical value corresponds to the hardness of the wood. The dimensional change coefficient can be used to estimate shrinkage or swelling. A small dimensional change coefficient indicates that the wood is more resistant to dimensional change. Both the Janka hardness rating and the dimensional change coefficient can be used to attest to the stability of wood species. Based on the similarities between the two
types of hardwood, it was expected that maple and oak would produce comparable results in terms of recovering oxygenated ILs.\textsuperscript{51–53}

Density and porosity are other important factors to consider with wood samples, since both can affect the retention capability of ILs.\textsuperscript{52} It has been established that low density and/or high porosity wood samples are more favorable for ILs to penetrate.

Table 3: Summary of wooden blocks used

<table>
<thead>
<tr>
<th>Type\textsuperscript{51–53}</th>
<th>Maple</th>
<th>Oak (white)</th>
<th>Pine</th>
<th>Cypress</th>
</tr>
</thead>
<tbody>
<tr>
<td>Janka hardness rating\textsuperscript{51}</td>
<td>Hardwood</td>
<td>Hardwood</td>
<td>Softwood</td>
<td>Softwood</td>
</tr>
<tr>
<td>Dimensional change coefficient\textsuperscript{51}</td>
<td>1450</td>
<td>1360</td>
<td>690-870</td>
<td>1375</td>
</tr>
<tr>
<td>(Average)</td>
<td>0.00353</td>
<td>0.00365</td>
<td>0.00265 (Above average)</td>
<td>0.00162 (Excellent)</td>
</tr>
<tr>
<td>Relative availability\textsuperscript{51}</td>
<td>Common</td>
<td>Common</td>
<td>Common</td>
<td>Limited</td>
</tr>
<tr>
<td>Density (g/cm\textsuperscript{-3})\textsuperscript{53}</td>
<td>0.727</td>
<td>0.720</td>
<td>0.412</td>
<td>0.528</td>
</tr>
</tbody>
</table>
2. EXPERIMENTAL

2.1 Materials

Thirty-eight commercial products collected were either donated from individuals or purchased from local Home Depot stores. Of the 38 products collected, 17 contained EtOH, seven contained isopropanol (IPA), 13 contained acetone, and the last six did not contain any of the three oxygenates studied (Figure 3, Appendix 1). After the initial characterization effort, those that did not contain any oxygenates took no further part in the project. Of the remaining 32 items analyzed, they could be divided into four categories based on usage (Figure 3). There were six automotive products (e.g. brake cleaners), nine household products (e.g. disinfectant spray), 14 personal care products (e.g. cologne) and three food products (e.g. beer). All samples were aliquoted using transfer pipettes and stored in black top vials in drawers at room temperature. The wood was obtained from Anderson & McQuaid Co, Inc. (Cambridge, Massachusetts, U.S.A.), and was cut into blocks measuring approximately one cubic inches.
ACS were obtained from Albrayco Technologies, Inc. (Cromwell, Connecticut, U.S.A.), while zeolite 13X was obtained from ZeoChem L.L.C. (Louisville, Kentucky, U.S.A.). A generic brand of unwaxed dental floss and #1 paper clips were purchased from local CVS Pharmacy and Office Depot, respectively. Solvents used were obtained from Fisher Scientific (part of Thermo Fisher, Pittsburgh, Pennsylvania, U.S.A.), Acros Organics (part of Thermo Fisher, Waltham, Massachusetts, U.S.A.) and Pharmaco-AAPER (part of Greenfield Ethanol, Brookfield, Connecticut, U.S.A.). Optima grade solvents were used, with the exception of ethanol provided by Pharmaco-AAPER, whose purity information was not verified by the manufacturer’s Certificate of Analysis (Table 4). The porous teabags used to prepare the zeolite packets were obtained from local Teavana stores.
The gas chromatograph (GC; Agilent Technologies 7890A) was coupled with a mass spectrometer (MS; 5975C inert XL EI/CI MSD) detector. The GC had a column of 5% phenyl methyl siloxane, with a dimension of 30m x 250µm x 0.25µm, produced by HP. The analysis of the results was completed using MSD ChemStation® software (version G1701EA E.02.00.493) that was developed by Agilent Technologies, Inc. (Santa Clara, California, U.S.A.). All GC vials, caps and liners were obtained from Fisher Scientific.

Table 4: Source and purity of solvents used

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Purity</th>
<th>Lot Number</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopropanol</td>
<td>99.9</td>
<td>070259</td>
<td>Fisher-Scientific</td>
</tr>
<tr>
<td>Methanol</td>
<td>99.9</td>
<td>130057</td>
<td>Fisher-Scientific</td>
</tr>
<tr>
<td>Acetone</td>
<td>99.5</td>
<td>B0523059</td>
<td>Acros Organics</td>
</tr>
<tr>
<td>Ethanol</td>
<td>99.9</td>
<td>W1128</td>
<td>Pharmco-AAPER</td>
</tr>
</tbody>
</table>

2.1.1 Summary of the wood treatment products

While the first goal of this project was to generate enough information for the reference library, a particular interest was in the chromatographic effects resulting from applying wood treatment products onto wooden surfaces. Special attention was paid to wood treatment products because wood was one of the more common fire debris materials submitted to laboratories during arson investigations. Eleven commercial products were purchased from Home Depot, including five that did not contain any oxygenates. As a result, three products, namely Howard Restor-A-Finish, Minwax® Clear Aerosol Lacquer Clear Satin and Zinsser Bulls Eye Shellac Clear, were used for this
project (Section 3.2, Table 5). Initially, all five wood treatment products were spiked onto KimWipes before three of them were chosen on the basis of varying content. These three wood treatment products were then spiked onto maple, white oak and pine wooden blocks.

Table 5: Summary of the five oxygenate-containing wood treatment products analyzed

<table>
<thead>
<tr>
<th>Brand and Product Name</th>
<th>Ethanol</th>
<th>Isopropanol</th>
<th>Acetone</th>
<th>Spiked on KimWipes</th>
<th>Wood</th>
</tr>
</thead>
<tbody>
<tr>
<td>Howard54 Restor-A-Finish</td>
<td>Absent</td>
<td>5-10%</td>
<td>3-7%</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Minwax®55 Clear Aerosol Lacquer Clear Satin</td>
<td>Absent</td>
<td>Absent*</td>
<td>Absent*</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Zinsser®56 Bulls Eye Shellac Clear</td>
<td>35%</td>
<td>5%</td>
<td>30%</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Varathane57 Polyurethane Semi-Gloss</td>
<td>Absent</td>
<td>Absent</td>
<td>30%</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Minwax®58 Water-based Polycrylic® Protective Finish Clear Satin</td>
<td>Absent</td>
<td>5%</td>
<td>Absent</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>

*: Compound was not listed in material safety data sheet (MSDS), but was identified after instrumental analysis.
2.2 Extraction parameters

2.2.1 Sample preparation and initial characterization process

The initial characterization process involved diluting samples with MeOH, before analyzing the samples by GC/MS. Without any extraction process performed, the products were diluted to a total volume of 1mL. Dilution ratios employed included 1:100, 1:200 and 1:1000.

2.2.2 Passive heated headspace with single- and dual-mode adsorptions

Beyond the initial characterization stage, passive heated headspace extraction was employed, rather than sample dilution. From previous thesis research, it was established that the volume of the paint cans had no bearing on the recovery of oxygenates.\textsuperscript{42} Rather than the traditional choice of quart-sized cans, pint-sized paint cans were used instead.

To aid in the development of the reference library, a piece of KimWipe, spiked with 5µL of sample, was placed in a pint-sized can. After setting up the ACS or zeolite packet (described later in this section), the can underwent an incubation period, followed by a desorption period (parameters listed in Section 2.2.3). After the preparation, the extract was then analyzed using GC/MS. It should be noted that unless stated otherwise, 5µL of oxygenates was added to the substrate in this project. The extent of compounds lost through oven incubation could be understood by comparing the chromatograms generated by diluted samples versus the samples analyzed using heated passive headspace extraction.
The first phase (Sections 3.1 and 3.2) of the project only employed single-mode adsorption (i.e. either ACS or Z in each can; Figure 4 left). It should be noted that only half a piece of ACS was used in each can with a razor blade. The extraction procedure followed the existing ASTM International protocols.\textsuperscript{10}

Zeolites were used to compare its recovery with ACS. The extraction procedure followed what was understood from previous thesis research: A porous teabag containing approximately 510mg of zeolites was suspended within the headspace of the cans. Using a razor blade, the excess material of the tea bag was removed to facilitate the creation of the zeolite packets.\textsuperscript{40–42}

The second phase of the project employed a dual-mode adsorption (i.e. both ACS and Z in each can; Figure 4 right). Similar to the previous setup, only half a piece of ACS was used. The ACS and zeolite packet were suspended separately in the can.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4.png}
\caption{Comparison between single-mode adsorption (left) and dual-mode adsorption (right)}
\end{figure}
2.2.3 Oven extraction parameters

The samples from Section 2.2.2 were incubated at approximately 90°C for two hours. Afterwards, the adsorbents were removed from the cans and added to separate black top vials, containing 995µL of MeOH. The vials were then placed on a shaker for 15 minutes, before transferring the solution into a GC vial for analysis.

2.2.4 Setup for the application of wood treatment products onto wooden blocks

Previously described processes regarding single-mode adsorption, incubation and desorption parameters were applied (Sections 2.2.2 and 2.2.3), with the exception that three types of wooden blocks (i.e. maple, white oak and pine) replaced KimWipes as the substrate. Unless stated otherwise, 5µL of wood treatment products was pipetted onto the wooden blocks, as listed in Table 5.

2.2.5 Setup for the preferential oxygenate recovery study using cypress blocks

After considering the results and the parameters used in previous experiments, an oxygenate specificity study was also performed to understand if oxygenates displayed a preference for an adsorbent. Dual-mode adsorption was utilized in this study, and the injection volume was increased to 20µL. Due to availability, 1cm³ cypress wooden blocks were used instead of the previously used wood species (i.e. maple, white oak and pine). The heated passive headspace extraction process remained unchanged at 90°C for
two hours. Desorption with MeOH followed the incubation period. Purchased solvents were used in this study, instead of previously discussed commercial products.

2.2.6 Setup for the incubation period study using cypress blocks

In addition to the preferential oxygenate recovery study, a study on the effects of the length of incubation period on the oxygenates’ recovery was conducted as well. Parameters of this study were the same as the oxygenate specificity study (Section 2.2.5), with the exception of the incubation time, which varied from two, eight and 16 hours.

2.2.7 Setup for the oxygenate recovery comparison study between KimWipes and cypress blocks

Dual-mode adsorption was again applied, with equal volumes (i.e. 20µL) of acetone applied to the substrates (i.e. KimWipes or cypress blocks). The paint cans were then immediately incubated at 90°C for two hours, before undergoing a desorption process to extract the compounds from the adsorbents.

2.3 Quality standard and controls

A quality standard sample containing 5µL of EtOH, 5µL of IPA, 5µL of acetone and 985µL of MeOH was analyzed prior to each sample sequence on the GC/MS. The purpose of analyzing this sample was to provide a system suitability standard for oxygenate detection, since retention times might change due to various reasons, including
instrument maintenance, the instrumental methods applied, etc. Moreover, by analyzing a quality standard sample initially, any adjustments required to the solvent delay could be performed prior to the analysis of samples. Solvent delay refers to the amount of time at the beginning of a sample sequence prior to turning on the detector, allowing the solvent to pass through the detector without being detected. This can extend the lifespan of the ion source filament. Moreover, without the use of a solvent delay, the solvent peak will cause the relative abundances of compounds of interest to appear as minor contributions in a chromatogram, given its high concentration in the mixture analyzed. Therefore, a solvent delay can improve analysts’ ability to identify peaks and increase the longevity of the MS filament.

In addition to the quality standard, positive and negative controls were included in each sample sequence as well. Due to the two possible adsorbents that can be used, separate controls were set up for each of them. Similar to the quality standards, the positive controls for the heated passive headspace extraction consisted of 5µL each of EtOH, IPA and acetone spiked onto a substrate, while the negative control only consisted of a substrate in the can. The substrates were KimWipes in the first phase and wooden blocks in the second phase.
2.4 Gas chromatography/mass spectrometry method

Two instrumental methods were employed throughout the duration of this research (Table 6). BFEMARSON2ISOMEOH.M was a short isothermal (40°C) method optimized for detecting oxygenates. With a run time of four minutes, the method had a solvent delay of approximately 1.68 minutes. ARSON.M, a method that was used to detect petroleum-based compounds was provided for reference.

The second method used was KTARSON1MEOH.M. It was a combination of both BFEMARSON2ISOMEOH.M and ARSON.M, but with minor modifications. This method was developed to identify both oxygenates and petroleum-based compounds contained within the samples.

<table>
<thead>
<tr>
<th>Table 6: Oven parameters of different GC/MS methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>BFEMARSON2ISOMEOH.M</td>
</tr>
<tr>
<td>----------------------</td>
</tr>
<tr>
<td><strong>Oven program</strong></td>
</tr>
<tr>
<td>Initial</td>
</tr>
<tr>
<td>Ramp</td>
</tr>
<tr>
<td>Final</td>
</tr>
<tr>
<td><strong>Injection port temperature</strong></td>
</tr>
<tr>
<td><strong>Pressure</strong></td>
</tr>
<tr>
<td><strong>Flow rate</strong></td>
</tr>
<tr>
<td><strong>Injection volume</strong></td>
</tr>
<tr>
<td><strong>Split Mode</strong></td>
</tr>
<tr>
<td><strong>Split ratio</strong></td>
</tr>
<tr>
<td><strong>Solvent delay</strong></td>
</tr>
<tr>
<td><strong>Scan range</strong></td>
</tr>
<tr>
<td><strong>Run time</strong></td>
</tr>
</tbody>
</table>
2.5 Data Analysis

After obtaining the data from the GC/MS, the ChemStation software was used to analyze the data collected. Using the software, mass spectrometry data was extracted from the TIC, and compounds were identified after undergoing a search using the National Institute of Standards and Technology Mass Spectral Search Program (National Institute of Standards and Technology, U.S.A.). Comma-separated values (CSV) files were extracted using the ChemStation software. With the use of Excel, developed by Microsoft (Redmond, Washington, U.S.A.), the chromatograms were reproduced using data from the CSV files.
3. RESULTS AND DISCUSSION

3.1 Characterization of commercial products

3.1.1 Summary of commercial products collected

Figure 5: Breakdown of commercial products collected based on usage

Figure 5 shows the oxygenated components of the commercial products divided based on how they are used. From the dilution study, all six of the automotive products contained acetone. Many petroleum-based products are used in the production of various
automotive parts. Solvents are often required to keep the parts clean and lubricated. Compounds used to produce automotive products tend to be non-polar to generate the desirable interactions between the product and the surface applied, or volatile to reduce drying time. The two non-polar methyl groups and its high volatility make acetone a valuable component in automotive products.

Similar to automotive products, only one oxygenate (EtOH) was found in the three food products examined. Both IPA and acetone are listed on the “Food Additive Status List” maintained by the U.S. Food and Drug Administration, regulating their use in food products. Given the regulated nature of these two compounds and their low concentration in food products, their presence in food products should bear little forensic significance. As for EtOH, its consumption and the problems associated with excessive drinking have been well-documented. Given alcohol content can be up to approximately 80% in some liquor and the public accessibility to food products, it is more likely that ethanol would be a common oxygenate encountered in the analysis of food products.

Unlike the previous two groups of products, a mixture of several oxygenates was found in household and personal care products. The variety exhibited by these products suggests that an in depth characterization effort could be beneficial. Household products, similar to those tested, are often applied to the surface of most furniture. Regardless of substrate contribution, the prior application of these products to furniture can alter the chromatogram generated from the debris. Therefore, analysts should attempt to
differentiate contributions from the wood and contribution from the commercial products applied.

Overall, given that some oxygenates are absent from certain types of commercial products, analysts should be able to eliminate certain categories of products based on the oxygenates identified. However, the variable compositions in personal care products and household products suggested that more studies should be performed to reach a more definitive conclusion.

3.1.2 Partial separation between acetone and ethanol

Figure 6 shows the chromatograms generated by analyzing acetone, ethanol and their mixture during the analysis of the quality standards. Individually, acetone (approximately 1.814 minutes) eluted first, followed by EtOH (approximately 1.818 minutes). Acetone had a lower resolution, as its peak ranged from 1.779 minutes to 1.9 minutes. Ideally, a peak with high resolution will be narrow in shape, allowing the peak to have a clear separation from other compounds in the mixture. From the figure, there is evidence of only partial separation between EtOH and acetone. Partial separation refers to the phenomenon that a second compound begins to elute out of the column before the first compound finishes its eluting process. Partial separation is different from co-elution, which refers to the phenomenon that the compounds elute out of the column at the same time due to similar chemical properties. Unlike the latter, the MS data can differentiate the partially separated compounds.
It should be noted that a non-polar GC/MS column was used for this project, which is common among forensic laboratories. A non-polar column will retain non-polar molecules longer than polar molecules in the column due to the existing attractive intermolecular forces. This longer retention on the column leads to better separation of non-polar molecules. Since arsonists tend to use petroleum-based ILs (e.g. gasoline), this justifies the use of a non-polar column to separate the non-polar compounds found in these ILs. Therefore, by switching to a polar column, polar molecules will be retained longer in the column, which can improve the separation. However, using a non-polar column in a forensic laboratory can also eliminate the need to change columns, which can reduce time required to process evidence. Based on the initial results using a non-polar column, analysts can assess whether there is a need to reanalyze the compounds using a polar column.

Considering that the concentrations of both compounds analyzed were the same, analysts should be aware of the possibility of partial separation between acetone and ethanol as a result of the poor resolution shown in Figure 6. Based on these results, further adjustments (e.g. starting at a lower temperature, introducing a ramp in the oven program, etc.) to the method could improve the separation.
3.1.3 Poor peak shapes from 1:1000 dilutions

Figure 7 was generated by analyzing a dilution of Klean-Strip Lacquer Thinner in MeOH. The inset of the figure shows a chromatographic comparison between 1:200 and 1:1000 dilutions, while the main figure shows an enlarged version of the chromatogram generated at 1:1000 dilution. In addition to the two dilution levels, 1:100 dilutions were also performed during the initial characterization effort. However, the chromatogram from the 1:1000 dilutions (here using the Klean-Strip Lacquer Thinner as an example) suggested that low solute concentration and background noise affects the peak shapes relative to the 1:200 dilution, which is not unexpected (Figure 7). Using pre-defined integration criteria, the software failed to integrate these peaks automatically.
The lack of numerical values for area count produced using the software prevented any following recovery comparison studies to be performed at 1:1000 dilution. Nonetheless, this could be addressed by manual integration of the peaks. Manual integration refers to the process where integration parameters are adjusted manually. Therefore, the user can set a threshold that the software can use to include peaks that are above the threshold and exclude those that are below the threshold. However, common problems associated with manual integration are the inclusion of background noise, consistency issues and human errors. Therefore, careful consideration should be made when setting the threshold.
The poor peak shapes prompted the necessity to question whether the dilution level was approaching the limit of detection (LOD) for oxygenates when using the isothermal method. In the study conducted by Armbruster et al., the authors looked into two different methods to define LOD using commonly abused drugs (e.g. methamphetamine). The first method, the empirical method, was considered more difficult to generate data, since it involved lowering the concentration until the background noise and the target peaks could no longer be differentiated. The second method, the statistical method, involved analyzing blanks. In this method, the LOD is defined as the addition of three standard deviations to the mean value of the blanks. They concluded that the empirical method was a better method for studying LOD than the statistical method using GC/MS in forensic settings. Although this study was performed using drug samples, there is no reason to believe that it could not be applied to fire debris analysis to establish a LOD for oxygenated ILs. Being able to properly establish a LOD for oxygenated ILs will aid in an investigation. As a result, it will be important for future research to establish the LOD for the instrumental method employed in this project (i.e. BFEMARSON2ISOMEOH.M).
3.1.4 Zeolites’ performance as an adsorbent for oxygenates

Commercial products collected were extracted using single-mode adsorption and analyzed using the isothermal instrumental method. Figures 8 and 9 represent four of the 32 products analyzed. Based on both qualitative (i.e. chromatographic data) and semi-quantitative (i.e. area count) data collected, zeolites could recover more oxygenates than ACS from KimWipes (Figures 8 and 9), which solidified zeolites’ role in recovering oxygenates from commercial products. Moreover, the data reaffirmed previous findings regarding zeolites being a better adsorbent for oxygenates (e.g. acetone, 2-butanone, etc.) and ACS excelling in recovering petroleum-based compounds (e.g. methylhexanes, heptanes, etc.) (Figures 8 and 9).
3.2 Characterization and application of wood treatment products

3.2.1 Inconsistent product composition information

Some of the oxygenates in the wood treatment products tested were identified through instrumental analysis, despite not being listed on the MSDS, namely in Minwax® Clear Aerosol Lacquer Clear Satin, as displayed in Table 5. The MSDS of this product only listed 2-(2-butoxyethoxy)-ethanol and 1-methyl-2-pyrrolidone in its composition (Figure 10). However, the GC/MS data indicated the additional presence of IPA and acetone. Unreported compounds in MSDS or unexpected product formation during the storage periods were considered possible explanations.
The Occupational Safety & Health Administration (OSHA) of the Department of Labor currently requires that certain information be included in the MSDSs under the Hazard Communication Standard.\textsuperscript{65} OSHA developed a voluntary format for MSDSs in 1985, before endorsing the 16-section format established by the American National Standards Institute. However, some question the emphasis on voluntary cooperation rather than enforced regulation.\textsuperscript{66} In 2007, a facility exploded in Valley Center, Kansas exploded and 6000 residents were forced to evacuate. The U.S. Chemical Safety and Hazard Investigation Board (CSB) reported that, along with several other factors, the MSDSs of chemicals located at the factory failed to provide enough information on the possible dangers and precautionary measures.\textsuperscript{66} Consequently, the CSB conducted an investigation on the MSDSs of some of the more commonly used flammable liquids. The investigation showed 97\% of the chemicals included a warning regarding ignitable vapors, while 98\% of them failed to include the potential of forming an ignitable mixture inside a storage tank. The report also questioned whether OSHA should provide manufacturers with so much flexibility when preparing MSDSs. Analysts should be aware of the possible deficiencies and limitations of MSDSs and be cautious when extracting information from the documents.

\textbf{Figure 10: Compounds listed in Minwax® Clear Aerosol Lacquer Clear Satin}

[Diagram of compounds]
Recently, OSHA has made the decision to unify the formats of MSDSs to align with the Globally Harmonized System of Classification and Labeling of Chemicals (GHS), an international standard developed by the United Nations. In addition to the change in format, the MSDS will also be renamed as the Safety Data Sheet (SDS). The SDS consists of the same 16 sections that OSHA endorsed previously, with some minor modifications. This change provides an opportunity for employers to arrange additional training to employees and update the information listed on these data sheets. OSHA also provided a series of dates and requirements for manufacturers and employers to comply with during this transition period, with full compliance from employers expected by June 2016. It is believed these changes can address some of the deficiencies of MSDSs.
3.2.2 The effects of applying wood treatment products on KimWipes and wooden blocks

Figure 11: Chromatographic comparison of oxygenate recovery from KimWipes (top) and pine blocks (bottom) using single-mode adsorption

Figure 11 was generated using single-mode adsorption after applying Zinsser Bulls Eye Shellac (Clear). The top figure was generated by the application of the product on KimWipes, while the bottom figure was generated using pine blocks as the substrate. Both insets show the TICs, while the two main figures show the chromatograms up to the retention time of approximately 2 minutes. A reduced abundance was observed when attempting recovery from wooden blocks in comparison to KimWipes (Figure 11). This
observation was consistent with a study performed by St. Pierre. It was believed that the composition of the wooden blocks could explain the reduced abundance. The applied oxygenates may have had a higher affinity to the wooden blocks, rather than the adsorbents.

Figures 12 and 13 show the selected chromatograms generated from analyzing the controls using maple and white pine blocks. Both positive and negative controls were included in the figures. The negative controls suggested there was no detectable contribution from the wooden blocks (i.e. no detectable substrate contribution) when analyzed using the isothermal GC/MS method. However, components of the wooden blocks could still interfere with the chromatograms generated using a different GC/MS method.

St. Pierre suggested that either the complicated matrix within the wood prevented acetone from vaporizing or the volume applied was too little. From comparing past project parameters and performing a literature search, it was deemed possible that both the wood matrix and spiking volume contributed to the reduced abundances. It is well documented that changing environmental conditions (e.g. moisture content) can alter wood dimensions. Hagstrom and Wengert listed moisture content as one of the six factors carpenters should be aware of when dealing with the dimensional change in wood. The dimensional change originates from the interaction between water and the components of the plant cell wall. The cell wall consists of three different types of highly hydroscopic polymer, namely hemicellulose, cellulose and lignin. All three polymers contain hydroxyl groups to form hydrogen bonds that trap water. Given that the wooden
blocks used in this experiment were stored at a low humidity environment (approximately 30%), the moisture content of the wood should be approximately less than 9%. It could be postulated that the polymers within the cell wall had the capacity and the affinity to form hydrogen bonds with the polar oxygenates at the time of testing. Given only 5µL of wood treatment products was applied and the high affinity displayed by the hydrosopic compounds in the cell wall, it makes sense that lower levels of oxygenates were recovered using either ACS or Z as adsorbents.

Figures 11-13 also show the unexpected results of ACS recovering more oxygenates from wood than zeolites. Previous thesis research attempted to study the effect of pine wood on oxygenate recovery. The Gugliotta study showed that zeolites resulted in a better recovery of oxygenates in comparison to ACS when using pine wood. Unfortunately, a direct comparison was not possible, as different extraction parameters were used in the set-ups (Table 7), with the differences being a much higher volume applied and the use of an oxygenate-specific desorption solvent. The extensive study performed by Rodgers showed that using Z/MeOH had better oxygenate recovery than ACS with MeOH as the desorption solvent (ACS/MeOH) in both single- and dual-mode extractions. However, KimWipes were used in these experiments rather than wooden blocks.
Table 7: Comparison of different "spiked, unburnt" studies that were performed on pine wood

<table>
<thead>
<tr>
<th></th>
<th>St. Pierre (2011)\textsuperscript{40}</th>
<th>Gugliotta (2012)\textsuperscript{41}</th>
<th>Hayward (2013)\textsuperscript{53}</th>
<th>Current Experiment</th>
</tr>
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<tbody>
<tr>
<td>Drying time</td>
<td>3mins</td>
<td>Not available</td>
<td>None</td>
<td>5mins</td>
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<tr>
<td>Compounds of interest</td>
<td>Acetone only</td>
<td>Acetone, EtOH, IPA, etc.</td>
<td>Petroleum products</td>
<td>Commercial products</td>
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<tr>
<td>Volume used</td>
<td>10μL</td>
<td>1mL</td>
<td>5μL</td>
<td>5μL</td>
</tr>
<tr>
<td>Oven parameters</td>
<td>90°C for 4hrs</td>
<td>120°C for 4hrs</td>
<td>90°C for 2hrs</td>
<td>90°C for 2hrs</td>
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<tr>
<td>Desorption</td>
<td>MEK for 5-10mins</td>
<td>MEK or MeOH for 5-10mins</td>
<td>CS\textsubscript{2} for 15mins</td>
<td>MeOH for 10mins</td>
</tr>
</tbody>
</table>

Figure 12: Chromatograms for controls using ACS and zeolites as adsorbents and maple blocks as substrate
Figure 13: Chromatograms for controls using ACS and zeolites as adsorbents and white pine blocks as substrate

3.3 Preferential oxygenate recovery, incubation time and substrate comparison investigations

Zeolites recovered more oxygenates in comparison to the ACS for all of the commercial products tested using KimWipes as a sample substrate (Section 3.1.4). However, ACS recovered more oxygenates using wooden blocks as the sample substrate (Section 3.2.2), prompting a need to re-assess the extraction parameters. Therefore, the following set of experiments attempted to investigate, using dual-mode adsorption (Figure 4 right), whether there was any oxygenate specificity of the adsorbent when encountering unburned wood samples and the effects of heated passive headspace extraction on recovery. It was believed these studies could address the unexpected
oxygenate recovery results in comparison to previous experimental results from our group.

Prior experiments in this project involved single-mode adsorption as the sole method of extraction (Figure 4, left). Previously, single-mode adsorption (i.e. ACS/MeOH or Z/MeOH) studies have been performed using both KimWipes and wood.\textsuperscript{40–42} However, for dual-mode adsorption studies under the same extraction parameters, only KimWipes were used.\textsuperscript{41,42} A dual-mode study could resolve whether the competitiveness between ACS and Z caused the unexpected recovery result, or an optimal oxygenate IL extraction procedure was substrate-specific.

The heated passive headspace extraction study could address whether compound loss during the incubation period was responsible for the unexpected results. This, in combination with dual-mode adsorption, could also address whether zeolites are more temperature-sensitive than ACS when attempting to recover oxygenates from wood.
3.3.1 Dual-mode adsorption study on the preferential recovery of oxygenates using cypress blocks

In order to assess whether there was a preferential adsorption for oxygenates in the wood matrix, a specificity experiment was performed using dual-mode adsorption. Results agreed with previously obtained data (Section 3.2.2) and suggested that the ACS was the better adsorbent for oxygenates when working with wood substrate samples (Figure 14). Based on area count, ACS recovered 34% more acetone and 8.5% more IPA in comparison to zeolites. However, the conclusion of the ACS being the better adsorbent was not comprehensive, as zeolites were 20% more effective in recovering ethanol than the ACS. Thus, it would be important for future researchers to understand if this behavior was oxygenate-specific.

![Dual-mode adsorption study on oxygenate specificity using cypress blocks](image)

Figure 14: Dual-mode adsorption study on oxygenate specificity using cypress blocks
3.3.2 Dual-mode adsorption study on the effects of incubation time on oxygenate recovery using cypress blocks

The experiments involving wooden blocks suggested that the ACS was the better adsorbent for oxygenates than zeolites (Sections 3.2.2 and 3.3.1). Originally, the higher temperature (approximately 90°C) was chosen as an alternative to the lower temperature (approximately 60°C), because the lower temperature would require a longer incubation period (12-16 hours) when compared to a shorter period (two hours) for the higher temperature. Although Rodgers had performed a study on incubation period, it was performed with KimWipes and zeolites only. A dual-mode adsorption study using MeOH as the desorption solvent (i.e. ACS/MeOH and Z/MeOH in the same container) was performed to determine whether incubation time was a factor in this unexpected result. The study was performed with cypress wood blocks to eliminate variables arising from using multiple wood species, with three commercial products providing oxygenates of interest. The oven temperature was kept at 90°C, while the incubation time was varied (i.e. two, eight or 16 hours).
The recovery summaries suggested that the ACS was significantly better for recovering oxygenates from wooden blocks (Figure 15). More importantly, the results suggested a longer incubation time would not necessitate a better recovery. Therefore, at $90^\circ C$, ACS could recover more oxygenates from wooden blocks than zeolites, even with the varying incubation times.
3.3.3 Dual-mode adsorption study for substrate comparison using KimWipes and cypress blocks

After eliminating incubation time as a factor for the enhanced recovery obtained by the ACS, a dual-mode adsorption experiment comparing the recovery from KimWipes and wood samples using acetone was performed to better understand if this was a substrate-specific behavior.

The results suggest that zeolites recovered 99 times more acetone from KimWipes than the ACS (Figures 16 and 17). However, the ACS recovered twice as much acetone as zeolites from wood.

3.3.4 Summary of extraction parameters studies

Considering the results obtained throughout this project, it could be concluded that the competitiveness in dual-mode adsorption had no bearing on the recovery ability of the adsorbents. Using KimWipes as sample substrate, zeolites recovered more acetone (Figures 8, 9 and 11 top), while ACS recovered more acetone from wood, regardless of the adsorbent setup (Figures 11 bottom and 14). Therefore, more research is needed with regard to the performance of adsorbents when encountering different types of substrates.
Figure 16: Chromatographic comparison for the dual-mode recovery of acetone using ACS and zeolites with KimWipes and cypress blocks as substrates

Figure 17: Area count comparison of dual-mode recovery of acetone using ACS and zeolites with KimWipes and cypress blocks as substrates
4. CONCLUSIONS AND FUTURE DIRECTIONS

From the characterization effort, acetone and EtOH were the sole oxygenates found in automotive and food products, respectively. However, all three oxygenates (i.e. acetone, EtOH and IPA) were found in household and personal care products. Zeolites were able to recover oxygenates from the commercial products that could potentially be used as ILs in arson cases, which supports their application in casework. In the studies using KimWipes, the results were consistent with previous research, with zeolites being the better choice for extracting oxygenates, and ACS excelling in recovering petroleum-based compounds.

Although the majority of the dilution study was performed at the 1:200 dilution level the 1:100 and 1:1000 dilution studies were also performed. The 1:1000 samples suggested a LOD study could be performed based on the qualitative cues within the chromatograms. Previous research utilizing zeolites has focused on method development and studied the feasibility of their involvement in forensic casework. Establishing an LOD and limit of quantitation (LOQ) for the EtOH, IPA and acetone using the isothermal GC/MS method would be a relevant next step. This could be achieved by establishing a baseline signal-to-noise level.

Partial separation of acetone and EtOH within the isothermal method displayed by analyzed the quality standard suggested that further method development is necessary. The resolution between two closely eluting compounds can be improved by starting the isothermal GC/MS method at 30°C or 35°C, before ramping up to 40°C, decreasing the flow rate of the mobile phase or increasing the polarity of the stationary phase. Given the
abundance of acetone and ethanol in commercial products, these two compounds should receive additional attention in future oxygenate studies.

Information obtained from a MSDS of a chemical is not always consistent with the total composition of a given commercial product as supported by one sample within this project. This should serve as a warning to analysts when comparing similarities and differences between the available literature and obtained analytical results.

The isothermal GC/MS method employed was able to recover oxygenates (provided by the wood treatment products) from the wooden blocks. It should be noted that the products were pipetted onto the wooden blocks, rather than covering the whole surface in this research. The results confirmed the validity of using zeolites to recover oxygenates, however, applying the products multiple times on the whole surface of the blocks, rather than a drop on part of the block, would be more realistic.

No substrate contribution from the four types of wooden blocks was detected using the isothermal GC/MS method (Figures 11 and 12). The oxygenates were detected using the isothermal method. However, given the limited wood species used in this project, additional substrates are required before a more definitive statement can be made regarding the wood substrate contribution. In addition, more effort should be dedicated to studying wood chemistry to understand the interaction between ILs and the wood matrix. Previous research examined the retention capabilities of petroleum-based ILs of various wood species.\(^\text{53}\) It is important to note that the study concluded that no relationship existed between density of the wood species and their retention capabilities. Yet, it remains to be seen whether oxygenated ILs will display the same trend.
ACS was found to be the better adsorbent when using wood as a substrate. This may help analysts decide which adsorbent to use. Therefore, a dual-adsorption study investigating the recovery from various types of commonly encountered fire debris samples (e.g. carpet) should be conducted. Also, after eliminating the length of the incubation period as a factor, further analysis should be done with regards to the effects of oven temperature on the recovering preference of oxygenates.

In conclusion, common commercial products can generate chromatographic peaks similar to those generated by oxygenated ILs. In addition, zeolites displayed generally better recovery of oxygenates in these commercial products than ACS. However, ACS managed to recover more from wooden blocks than zeolites, which was unexpected.
## APPENDIX 1: LIST OF PRODUCTS TESTED

<table>
<thead>
<tr>
<th>Category (No.)</th>
<th>Brand and Product Name</th>
<th>Vial no.</th>
<th>EtOH</th>
<th>IPA</th>
<th>Acetone</th>
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<td>Hi Tech Pharmacol Clobetasol Propionate 0.05% w/w</td>
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<td>CVS Pharmacy Isopropyl Rubbing Alcohol</td>
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<td>Bath + Body Works Pleasures Perfume - Country Apple Scent</td>
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<td></td>
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<td>Victoria's Secret Secret Garden Love Spell Refreshing Body Mist</td>
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<td>Automotive Products (6)</td>
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<td>Vick's NyQuil Cherry Flavored Cough Syrup</td>
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<td>Clorox Green Works All-purpose Cleaner</td>
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<td>Howard Restor-A-Finish</td>
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<td>Minwax Water-based Polycrylic Protective Finish Clear Satin</td>
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<td>Watco Rejuvenating Oil</td>
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ND: Not detected
APPENDIX 2: SELECTED CHROMATOGRAMS FOR AUTOMOTIVE PRODUCTS

x-axis: Retention time (minutes), y-axis: Abundance (in thousands)
Valucraft Brake Parts Cleaner

Acetone

Cyclo- & Methylhexanes

Methylpentanes

Heptane

Aurozone Brake Cleaner

Acetone

Methylhexanes

Heptane

x-axis: Retention time (mins); y-axis: Abundance (thousands)
APPENDIX 3: SELECTED CHROMATOGRAMS FOR FOOD PRODUCTS

x-axis: Retention time (minutes), y-axis: Abundance (in thousands)
APPENDIX 4: SELECTED CHROMATOGRAMS FOR HOUSEHOLD PRODUCTS

x-axis: Retention time (minutes), y-axis: Abundance (thousands)
APPENDIX 5: SELECTED CHROMATOGRAMS FOR PERSONAL CARE PRODUCTS

x-axis: Retention time (minutes), y-axis: Abundance (in thousands)
L'Oréal Professional Texture line curling hair spray

Bath and Body Works Body Spray

Victoria's Secret Secret Garden
Love Spell Refreshing Body Mist
<table>
<thead>
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<th>Journal Abbreviation</th>
<th>Full Name</th>
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<tr>
<td>Clin Chem</td>
<td>Clinical Chemistry</td>
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<tr>
<td>Drug Alcohol Depend</td>
<td>Drug and Alcohol Dependence</td>
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<tr>
<td>Forensic Sci Int</td>
<td>Forensic Science International</td>
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<tr>
<td>Ind Eng Chem Res</td>
<td>Industrial &amp; Engineering Chemistry Research</td>
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<tr>
<td>J Forensic Sci</td>
<td>Journal of Forensic Sciences</td>
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<td>J Subst Abuse Treat</td>
<td>Journal of Substance Abuse Treatment</td>
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<tr>
<td>J Univ Chem Technol Metall</td>
<td>Journal of the University of Chemical Technology and Metallurgy</td>
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<tr>
<td>PhysMathCentral Phys B</td>
<td>PMC Physics B</td>
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<td>Prog Org Coat</td>
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<tr>
<td>Sci Justice</td>
<td>Science &amp; Justice</td>
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</table>
BIBLIOGRAPHY


5. Massachusetts General Laws Chapter 266 Section 1 [Internet]. Available from: https://malegislature.gov/laws/generallaws/partiv/titlei/chapter266/section1


11. ASTM International. Standard Practice for Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Dynamic Headspace Concentration. 2007;


15. James SH, Nordby JJ, Bell S. Forensic Science: An Introduction to Scientific and Investigative Techniques [Internet]. 1st ed. [cited 2014 Mar 3]; Available from: http://books.google.com/books?id=KMfs_ezuWdMC&pg=PA501&lpg=PA501&dq=metal+paint+cans+rust+forensic+evidence&source=bl&ots=LS7_SFzo1B&sig=scBDwOLtJk0EsI1WOHg1x1d5ta&hl=en&sa=X&ei=XaoUU7eTBayO1AHpjYCwCA&ved=0CDwQ6AEwAQ#v=onepage&q=rust&f=false


26. MSDS MeOH. Sciencelab.com, Inc.,


41. Alison L Gugliotta. The recovery and analysis of oxygenated ignitable liquids by competitive adsorption utilizing zeolites and activated carbon.

42. Corissa L Rodgers. Improving oxygenated ignitable liquid recovery by dual-mode heated passive headspace extraction using zeolites and activated charcoal strips.


53. Hayward A. Retention Capabilities of Different Genera of Wood for Common Ignitable Liquids.


56. MSDS Spray Shellac with 3C Alcohol. 2011;

57. MSDS VARA SSPR 6PK HD POLY SEMI-GLOSS. 2012;


63. Ingestion of Isopropanol. toxtidbits, 2009;


65. Recommended Format for Material Safety Data Sheets (MSDSs) [Internet]. [cited 2013 Dec 11]; Available from: https://www.osha.gov/dsg/hazcom/msdsformat.html


CURRICULUM VITAE

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Year of Birth: 1989
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Education:
M.S. in Biomedical Forensic Sciences (Anticipated May 2014) Boston University, Boston, MA 02118

B.S. in Biochemistry and Medical Biology (summa cum laude) University of New England, Biddeford, ME 04005
2008 - 2012

Research:
Research Assistant
Advisor: Dr. Adam Hall, Ph.D.
Department of Anatomy and Neurobiology
Division of Graduate Medical Sciences
Boston University
January 2013 – Present
• Developed a reference library illustrating the contribution from oxygenated commercial products
• Evaluated the recovery efficiencies of zeolites and activated charcoal strips in the recovery of oxygenated ignitable liquids

Research Assistant
Advisor: Dr. John Stubbs, Ph.D. & Dr. Amy Deveau, Ph.D.
Department of Chemistry and Physics
University of New England
October 2009 – May 2012
• Utilized quantum chemical calculations to understand the different reaction mechanisms involved in the attempted synthesis of 6-desoxynaltrexone
• Confirmed the identity of synthetic products using nuclear magnetic resonance spectroscopy
• Developed an experimental protocol to train rats in operant chambers to understand the correlation between pain and feeding behavior

Research Assistant
Advisor: Dr. Glenn Stevenson, Ph.D
Department of Psychology
University of New England
September 2008 – February 2010

Instrumental Experience:
Gas Chromatography-Mass Spectrometry
Fourier Transform Infrared Spectroscopy with
- Horizontal Attenuated Total Reflectance Microscopy
Thin Layer Chromatography
Microscopy
- Compound light microscopy
- Stereomicroscopy
- Comparison microscopy
- Polarized light microscopy

Computer Experience:
Proficient in Microsoft office (Word, Excel & Powerpoint), ChemBio Draw, Spartan, Thermo OMNIC, Agilent ChemStation