2020

The Effects of Household Substrates on the Evaporation of Ignitable Liquids at Temperatures up to 210°C

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**The Effects of Household Substrates on the Evaporation of
Ignitable Liquids at Temperatures up to 210°C**

Caitlyn Wensel

Thesis submitted to the Eberly College of Arts and Sciences at West
Virginia University

in partial fulfillment of the requirements for the degree of

Master of Science in
Forensic and Investigative Science

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Morgantown, West Virginia
2020

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Abstract

The Effects of Household Substrates on the Evaporation of Ignitable Liquids at Temperatures up to 210°C

Caitlyn Wensel

In fire debris analysis, ignitable liquid residues are commonly identified using gas chromatography-mass spectrometry (GC-MS). The detection and identification of an ignitable liquid can help arson investigators determine whether a fire was intentional or accidental. To assist with the identification of ignitable liquid residues, chromatograms of questioned samples are typically compared to those of known ignitable liquids that have been weathered (evaporated) to different extents. Practitioners typically perform such weathering at room temperature and to a limited number of extents of weathering, so their database of weathered residues is likely to deviate markedly from casework residues. The ultimate goal of this project is to assist fire investigations by providing a stronger scientific basis for the observed weathering of ignitable liquid residues in casework samples.

The experiments were designed to elucidate the effects of three different weathering factors on the distribution of residues: 1) the temperature at which weathering occurs, and 2) the porosity of the substrate, and 3) the penetration depth of an ignitable liquid in the substrate. A nine-component synthetic gasoline simulant was experimentally evaporated to different extents at different temperatures on four different substrates, including cotton fabric, nylon carpet, plywood and pine wood. Additional experiments were conducted in which 30-s or 30-min delays were implemented between spiking the gasoline simulant on each substrate and initiating the weathering at 210°C. The weathered residues in the different substrates were collected using solid-liquid extraction in pentane and analyzed using gas chromatography-mass spectrometry (GC-MS).

The distribution of experimentally weathered residues were compared to a thermodynamic model that was previously developed by our group. In the absence of a substrate, the model provides accurate predictions of the relative peak areas for weathering conducted from 30-210°C and up to 95% weathering. For example, the root mean squared error of predictions (RMSEPs) of the model was on the order of 2% for N=180 predicted peak areas at 210°C. Although the weathering temperature significantly alters the relative distribution of volatiles remaining in the weathered residues, the model accounts for the effect of temperature and the accuracy remains quite constant at ~2% between 30-210°C. The presence of a relatively non-porous substrate like cotton fabric had a small effect on the accuracy of the model; the RMSEPs increased to ~2.9% for N=117 predictions. However, in the presence of more porous substrates, like pine wood and plywood, the RMSEPs increased to a low of 3.7% for pine wood with no delay between spiking and weathering to 7.8% for plywood with a 30-minute delay. The prediction errors indicate that porous substrates like untreated wood prevent the volatile components from evaporating at their normal rates, and that the relative distribution of weathered residues hardly changes beyond 50% weathering. The results indicate that the entrapment of ignitable liquids in porous substrates make them appear less weathered than one would expect for a thermodynamic model.

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I want to express my thanks to my family, especially my parents, whose belief in me never wavered, even when I started to doubt myself. From the day I decided I wanted to become a forensic scientist, they have been in my corner, and stood right beside me through all the ups and downs along this journey.

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1. Introduction

1.1 Statement of the Problem

Arson crimes cost billions of dollars annually in the US, but these crimes also cost lives, relationships, businesses and communities. The destructive nature of fires tends to limit the recoverable evidence at a fire scene. Once all accidental and natural causes of a fire have been eliminated, investigators often rely on detecting the presence of trace amounts of ignitable liquid residues (ILR) in the fire debris to establish a case for arson. The detection of trace levels of ignitable liquid residues is confounded by several factors: 1) the ignitable liquids partially evaporate (weather) during the fire, so they change composition; 2) household items oftentimes contain background contamination of the same petroleum distillates that are used as ignitable liquids; and 3) pyrolysis of organic matter during the structure fire produces many of the same compounds found in ignitable liquids. To solve the first problem, analysts have to reproduce evaporative weathering in the laboratory setting, but for practical purposes, such weathering is typically only performed at room temperature in the absence of substrates and at a select number of different weathering extents. If fire debris analysts could better understand the evaporative changes of ignitable liquids at elevated temperatures and in the presence of household substrates, they could make more reliable inferences about whether or not an ignitable liquid was present in the debris. They might also be better positioned identify or exclude possible sources of the ignitable liquid. This project aims to better understand the nature of ignitable liquid evaporation in the presence of household substrates through the comparison of experimental data and mathematical modeling of evaporations conducted at elevated temperatures (up to 210°C) and in the presence of different substrates.

1.2 Fire scene and fire debris

In a recent study published by the National Fire Protection Association (NFPA) regarding intentional fires during the period between 2010 and 2014, the US has documented more than \$1 billion in property damage and more than 1,700 people deaths or injuries [1]. From a forensic standpoint, it can be difficult to tell the difference between accidental fires, intentionally set fires and arson. Intentional fires are fires that are started deliberately, but not with the intent to cause harm or damage [1]; examples include a burn pile that accidentally sets fire to a shed, or a wood-burning fireplace that accidentally spreads outside the fireplace. Over the years, the definition of arson has evolved in differently in different jurisdictions, but most laws include language regarding the malicious and willful burning of property [2].

1.2.1 History

In the early part of the 20th century, fire scene investigation was rudimentary, with investigators relying on the smell and taste of fire debris [3]. It was not until 1938 that Professor Marc Bischoff first wrote about the presence of ignitable liquids at the scene [reference]. In 1949 Ralph Turner discussed the collection of control samples with the questioned samples to enable the differentiation between samples with background contamination vs elevated levels of ignitable liquids. The earliest mention of fire investigation in the United States comes from a letter written by Thomas Edison, where he discusses the potential for electricity to start a fire [3]. Figure 1.1 shows a brief timeline of advancements in fire debris extraction and analysis.

Figure 1.1: Timeline of milestones in fire debris and ignitable liquid residue extraction and analysis. Adapted from *Fire Debris Analysis* by Eric Stauffer [3].

1.2.2 Scene investigation

Fire scene investigation is often called origin and cause investigation, and its main purpose, like many other types of investigation, is to determine whether a crime has been committed (Fig 1.2).

Figure 1.2: Steps in a fire investigation.

To perform a thorough investigation, a fire investigator should have an understanding of the necessary conditions for fire initiation and maintaining a fire, fire dynamics, conditions influencing the spread and development of a fire, types of fuel packages, auto-ignition temperatures, burn and smoke patterns and proper protocols for crime scene investigation and sampling [2,4].

At a fire scene, before the investigation begins, the fire investigator in charge needs to gather as much information as possible, to determine the state and conditions of the scene before, during and after the fire. Witness interviews are an integral part of any investigation, but especially in a fire investigation because evidence can be destroyed in the blaze and the fire fight. Fire fighters will provide some of the best information, as they get information from the 9-1-1 call, they were present during the fire and they can speak to the state of the scene before it was disturbed. Investigators then enter the scene perform an initial walkthrough, documenting and noting areas they believe are important to the investigation. While conducting the investigation, the fire investigators will create multiple hypotheses based on the evidence they find and will test all of them to determine the cause of the fire. It is important to eliminate all natural and accidental causes of fire before trying to prove a fire is intentional and arson.

1.2.3 Sample collection

When preparing to collect evidence, fire investigators must first determine what evidence may or may not be important. If an investigator believes that an arsonist is at work, the most common types of evidence to be collected are flooring, carpet, baseboards, and furniture [2]. The type of packaging for the evidence will depend on the evidence itself, but paint cans are the most common package types [2–4]. Paint cans provide a tight seal and prevent the loss of any vapors that may be coming off the evidence. The loss of vapors could affect the evaporation pattern, as the evaporation of the fire will be different than the evaporation at ambient temperature. It is important that control

samples are also collected, if possible, from any type of evidence. This ensures that any background interference from the substrates will be accounted for during the analysis of the evidence.

1.3 Ignitable Liquids and Analysis

1.3.1 Definition

Ignitable liquids are defined as a “liquid or liquid phase of any material that is capable of fueling a fire, including a flammable liquid, combustible liquid, or any other material that can be liquified and burned” [4]. However, the presence of ignitable liquids in debris samples does not mean that a fire is arson and the absence of ignitable liquids does not mean that the fire was accidental or natural [5].

1.3.2 Neat v. weathered

The volatile nature of ignitable liquids makes them prone to evaporation, or weathering, when left over time. The ability to recognize and classify a neat, unweathered, liquid can build a foundation for more complex data interpretation [3]. The neat liquids can be categorized into eight classes and three sub-classes (Table 1.1) [4].

Table 1.1: Classification scheme and examples for known ignitable liquids (adapted from ASTM E1618-19 [5]). This list is not all-inclusive, and some examples can be placed in more than one classification based on brand or performance.

Class	Light (C ₄ – C ₉)	Medium (C ₈ – C ₁₃)	Heavy (C ₉ – C ₂₀)
Gasoline	Gasoline is typically in the C ₄ - C ₁₂ range		
Petroleum Distillates	Cigarette Lighter Fluid Camping Fuels	Charcoal Starters Paint Thinners Mineral Spirits	Kerosene Diesel Fuel Aviation Fuel
Isoparaffinic	Lighter Fluids Aviation Gasoline	Copier Toners Gun Oils	Spot Cleaners Insecticides
Aromatic	Solvent Cleaners Xylenes	Brush Cleaners Insecticides	Adhesives Insecticides
Naphthenic-Paraffinic	Cyclohexane-Based Solvents	Automotive Part Cleaners	Lamp Oils Insecticides
Normal Alkane		Candle Oils Wax Cleaners	Carbonless Forms Copier Toners
Oxygenated	Alcohols Ketones Lacquer Thinners	Metal Cleaners Gloss Removers Degreasers	Biodiesels Fuel Additives Floor Finishes
Miscellaneous	Enamel Reducers Lacquer Thinners Racing Gasoline	Turpentine Products Spray Lubricants Citrus Cleaners	Lamp Oils Citrus Cleaners Kerosene

The classification provided in ASTM E1618-19 is based upon chemical composition and boiling point ranges [5].

1.3.3 Detection at the scene

Detection of ignitable liquid residues at the scene can help investigators ensure that the correct evidence is collected. Fire investigators often detect based on visual recognition of burn patterns, pour patterns and the smell. However, most of these techniques are not based on scientific evidence and are prone to errors, especially after full room involvement [4]. Detectors can react to ignitable liquids in one of two ways: reacting to the presence of volatile organic compounds from the headspace above the sample or reacting to the fluorescence produced by aromatics in the sample [3].

Common detection techniques include canines, electronic sniffers and portable gas chromatography-mass spectrometry (GC-MS) [2,3]. Dogs are known for their incredible sense of smell, and when trained properly, they can differentiate between the ignitable liquid and the background of pyrolysis products. However, there is limited research on the olfactory system of canines and the admissibility of their detection in court has been argued extensively [2,6,7]. Electronic sniffers are instruments that can be used on scene and perform in a similar fashion to an accelerant detection canine. Like with the accelerant detection canines, there is limited research into the use and validation of these instruments. The instruments can also be expensive with low sensitivity and specificity, which makes them an undesirable option for detection [2].

GC-MS is the method of choice for laboratory analysis. Though advances in the technology has led to a miniaturization of the instrument to allow for portability to the scene, which can be invaluable to investigators, the higher complexity of the instrument would require more training for the investigators or the presence of lab personnel on scene. Also, studies have shown that portable instruments do not perform to the level of bench-top instruments, necessitating more thorough analysis in lab [3,8].

1.3.4 Extraction from debris

To properly analyze the ignitable liquids, the residues must be extracted from the fire debris. There are three main categories in which residues can be extracted from debris: distillation, solvent extraction, headspace analysis/headspace extraction [2,3,5,9–12] (Table 1.2). Distillation was one of the first techniques used to separate ignitable liquids from fire debris, but has been replaced with techniques that are less complex, cheaper and faster. Solvent extraction is destructive and uses the largest volumes of organic solvent, whereas passive headspace extraction techniques are by far the easiest and most commonly used approach.

Table 1.2: Common techniques used for the extraction of ignitable liquids from fire debris [3,10–13].

Method	Advantages	Drawback	Desorption	Sensitivity
Distillation	Obtain neat liquid from sample	Destructive Contamination potential Labor-intensive Analysis time	N/A	100-500 uL
Solvent	Limits competitive adsorption Not skewed by differences in vapor pressure Better extraction of non-volatile components	Destructive Can create by-products Loss of low boiling point components during concentration Efficiency is controversy High cost	N/A	1 uL
Static headspace	Nondestructive Rapid Good for volatiles	Poor recovery of heavy compounds Low sensitivity	N/A	10 uL
Passive headspace with activated charcoal	Nondestructive	Analysis time	Solvent	0.1 uL
Passive headspace with SPME	Nondestructive	Contamination potential High cost	Thermal	0.1 uL
Dynamic headspace	Destructive	More expensive than passive techniques	Thermal or Solvent	<0.1 µL

1.3.5 Analysis

As previously stated, GC-MS is commonly used to the analysis of ignitable liquids in the lab. The standard test method published by ASTM International, outlines parameters for analyzing a sampling using GC-MS [5]. Data analysis from a GC-MS uses components from GC chromatograms and MS spectra.

Classifications and identifications are made from chromatographic patterns and mass spectra that correspond to classes of ignitable liquids. The total ion chromatogram (TIC) can be compared to known reference collections, if the reference is collected under the same conditions [5]. The

boiling range of most of the compounds present can be used to separate the ignitable into either a light, medium or heavy qualifier within the classification. Analysts will classify the ignitable liquid present into one of the eight ASTM classes, but differentiating between liquids into a class is not always possible [3,5] because they sometimes fall into two different classes.

Interpretation of ignitable liquids and comparison to reference collections or samples can be confounded by the evaporation of the ignitable liquids and the presence of substrates. Current research is attempting to study the evaporation of different ignitable liquids and the interferences substrates can cause.

1.4 Current Research

Ignitable liquids are known to weather over time, and previous research has shown that as the extent of weathering increases, the most volatile components decrease in concentration and the least volatile components tend to become more concentrated. [1,14,15]. Only a few studies have applied mathematical modeling approaches to the weathering, even fewer groups incorporating a temperature component [16–20]. But there are reasons to think that the models are oversimplifications of reality. For example, in casework, ignitable liquids are exposed to significantly higher temperatures than the room-temperature simulations of a typical laboratory setting, so the simulations have questionable relevance to casework. Also, most laboratory-based weathering is usually conducted in non-porous substrates like glass or metal containers, and hardly ever in the presence of realistic, domestic, porous materials like wood or carpet.

In 2009, the National Research Council (NRC) published *Strengthening Forensic Science in the United States: A Path Forward*, in which it stated “[e]xperiments should be designed to put arson investigations on a more solid scientific footing” [2]. The report discussed an experimental

design in which variables or conditions should be altered to determine how the independent variables impacted the burn pattern on materials with and without ignitable liquids.

After the NAS report, reference databases became a staple across many forensic science disciplines. The most comprehensive ignitable liquid reference databases is hosted by the National Forensic Science Center (NCFS) at the University of Central Florida. The NIJ-funded database includes GC-MS chromatograms of common pristine ignitable liquids, as well as replicates that have been evaporated to varying extents [5,9,21,22]. The NCFS also hosts a substrate database, which includes background levels and pyrolysis products in substrates that are both pristine and deliberately burned.

Many techniques have been developed over the years to evaporate ignitable liquids [3,5,9,23–25]. Some research groups have also studied the background interference that substrates and matrixes can have on the patterns found in ignitable liquids, but not how they directly affect the evaporation. [26–29]. However, due to the large number of variables associated with the weathering of the liquids, including volatility, method, temperature and substrate interferences, a complete reference collection is impractical. Attempting to create a reference collection that would include the infinite number of combinations is a time-consuming process. Being able to compare unknown case samples to a prediction model could reduce the need for the reference collections.

Chemometrics, a discipline that combines mathematics, statistics and chemistry to optimize the extraction of chemical information from complex data, is a necessary practice in fire debris analysis. Chemometric approaches have established a strong basis for classifying and discriminating ignitable liquids, even when in the presence of matrixes [15,16,35–37,17,18,28,30–34]. However, at present, these methods have not been very successful in associating weathered residues to the pristine residues of the same samples.

Jasper *et al.* have proposed using isotope ratio mass spectrometry (IRMS) to link weathered and pristine ignitable liquid residues [38,39]. IRMS can be highly specific, as most ignitable liquids will have multiple compounds, each with unique isotope ratios. The unique profile for each compound multiplied potentially across tens or hundreds of compounds can lead to higher possibilities identifications between known and unknown samples. The study provided preliminary data but required more research before any definite conclusions could be made. Though this method works well for pristine liquid comparison and low temperature evaporation, weathering at high temperatures are unpredictable in terms of isotope ratios [40,41].

Multiple groups are looking at developing models for predicting the evaporation patterns of gasoline, both kinetically and thermodynamically, at elevated temperatures [16–20,30,31]. However, no studies have yet been done to document the high temperature evaporation patterns in conjunction with the substrate interferences. Studying the effect of elevated temperatures and substrate interferences on ignitable liquid weathering will best replicate actual fire debris samples and will lead to a more practical approach to identifying ignitable liquid residues in fire debris samples. The study of physical properties to predict accelerant weathering will place fire debris analysis on a more scientific path, satisfying the goals set forth by the NRC.

Kinetic-based models have been developed to predict evaporation patterns of ignitable liquids. Okamoto *et al.* measured vapor pressures of bulk gasoline and kerosene over a temperature range of 10°C to 40°C in 5°C increments [42,43]. The vapor pressures were used to predict the evaporation of the different ignitable liquids. However, the prior work did not extrapolate the model to temperatures that are typical in structure fires, so the models lack some practicality.

A second kinetic model was developed by McGuffin and Smith at Michigan State University (MSU). This model, based on first order kinetics, has been used to predict the evaporation of diesel

fuel, torch fuel, lamp oil, kerosene, paint thinner and unleaded gasolines [16,30,31]. The ignitable liquids studied included three classes of gasoline; gasoline, petroleum distillates and isoparaffinic [44]. The model employed the GC retention index for each compound as a model variable instead of the boiling point, which greatly facilitates the application of the model to complicated mixtures and reduces inter-laboratory variability. Evaporation rate constants were determined using normalized abundances and can be found for any retention index. Thus, identities of the compound does not need to be known, only the retention index.

Additional work by the same group extended the model to operate over the narrow temperature range of 5-35°C [31]. The expanded temperature range was used for development and validated using kerosene. It was then used to create a reference collection of predicted chromatograms and compared to test sets. Using Pearson-product moment correlation (PPMC), the predicted fraction remaining (or inversely, the percent weathered) can be determined.

The group at MSU has begun predicting chromatograms for liquids from other ASTM classes including aromatic and naphthenic. The predictions have high accuracy, PPMC coefficients between 0.95 and 0.98, when compared to experimentally weathered data. Similar to Okamoto *et al.*, this kinetic model has yet to be tested or validated at temperatures above 40°C.

Most recently, our group has proposed a thermodynamic-based model that is based on the measured vapor pressures of pure compounds at different temperatures and Raoult's Law [17,18]. In the published work by Birks *et al.*, the model closely fitted the experimental weathering results up to 90 °C, and the model was then extrapolated to 500 °C to show that at the higher temperatures a greater fractional composition of the more volatile compounds remained in the gasoline residues [17]. A second publication by Willis *et al.*, experimental weathering expanded to 210 °C and provided evidence that temperature plays an important role in the residue pattern from the

weathering of ignitable liquids [18]. Willis et al. also showed that adaptation of the model to Henry's law instead of Raoult's law improved the accuracy of peak area predictions from a RMSEP of 2.0 to 1.3 for ~120 peak area predictions in weathering range of 50-95%. This model is significant for fire debris application because surface temperatures in typical structure fires often exceed 500 °C [4].

Distillation curve methods also uses thermodynamics to predict evaporation patterns [19,20]. Their application has been applied to a variety of ignitable liquids; however, they suggest that the method should not replace all evaporation studies, but should be used in conjunction with weathering [20]. In one study, Bruno and coworkers looked into the effect of substrates (wood chips and carpet) on the distillation curves [19]. Previously, it had been believed that the moderated weathering patterns in structure fires was due to entrapment of volatile components in the pores of porous substrates; however, distillation curves of gasoline on wood and carpet suggest that entrapment has little effect on evaporation [19].

At present, there have been studies on the substrate and matrix interferences of the burn patterns [26–29]. Multiple studies from the last four decades of the 20th century began to investigate the effect of substrates pyrolysis products, with all concluding that the pattern seen by substrate pyrolysis was distinguishable from ignitable liquids [29]. Pyrolysis products and ignitable liquids could be differentiated based upon non-Gaussian peaks, irregular distribution, unresolved groups of peaks and presence of compounds like styrene and methylstyrenes [29].

Almirall and Furton studied the chemical composition of materials that are commonly found in structures where fires occur [27]. The authors burned over 20 different substrates, including carpet, wood, plastic, cotton, paper and food and identified major components based upon retention time and mass spectra. They determined that many of the combustion and pyrolysis products are

also target compounds for ignitable liquid residue analysis. However, like previous studies, they concluded that the pattern in which they appear as background products is different and distinguishable from the pattern present in ignitable liquid residues [27].

Two studies from Smith and McGuffin at MSU group also investigated the effect of matrix interferences. In one study, Baerncopf *et al.* studied the effect of nylon carpet on six ignitable liquids [28]. The nylon carpet was analyzed with and without the ignitable liquids present and burned for either 10 or 20 seconds. All ignitable liquids were discriminated from matrix interferences at both burn levels using PPMC coefficients and principal component analysis (PCA) [28]. In the other study, Prather *et al.* performed similar experiments, except kerosene was the only ignitable liquid chosen and six burn times were used; 0, 10, 20, 30, 60 and 120 seconds [15]. This study also looked at the added component of weathering the kerosene. Results showed that association to the correct ignitable liquid was possible, but the degree of weathering was not always possible. Their work provided evidence that PCA could be used to eliminate the effect of potential matrix interferences, as long as the interferences do not fall at the same retention time as compounds in the standards [15].

1.5 Project Outline

This project aims to better understand the nature of ignitable liquid evaporation in the presence of household substrates through the comparison of experimental data and mathematical modeling of evaporations conducted at elevated temperatures (up to 210°C) and in the presence of different substrates.

Weathering of a synthetic gasoline mixture was performed in the presence of common household substrates including wood and carpet. Time delays were added between spiking and weathering to imitate the time it takes between administering an ignitable liquid and igniting it.

Root mean square error of predictions (RMSEP) and Pearson product moment correlations (PPMCs) were used to evaluate the effectiveness between experimental data and the mathematical models. The results indicate that porous substrates interfere with the normal evaporation of a liquid and temper the evaporation rates of the more volatile components. The overall effect is that liquids that evaporated in the presence of a porous substrate like pine wood hardly alter their fractional composition at extents of weathering above ~50% weathering.

2. Materials and Methods

2.1 Materials

Untreated wood and carpet samples were purchased from a local Lowe's Home Improvement. White, untreated cotton fabric was purchased from a local Michaels. Each substrate was cut to 1.5 in by 1.5 in (3.8 cm by 3.8 cm) pieces (Fig 2.2). The synthetic gasoline was made in-house at West Virginia University according to previous studies described below [17,18].

2.1.1 Synthetic Gasoline

The synthetic gasoline is a nine component mixture similar to that previously used by Birks et al. and Willis et al. [17,18]. The mixture contains toluene, ethylbenzene, o-xylene, nonane, 1,2,4-trimethylbenzene, indane, naphthalene, hexadecane and eicosane (Fig 2.1 and Table 2.1).

Figure 2.1: A total ion chromatogram (TIC) of unweathered synthetic gasoline mixture and with an expanded region of the trace peaks found beyond 5 minutes.

Table 2.1: Recipe of the nine-component synthetic gasoline mixture.

Component	Volume (mL)	Density (mg/mL)	Boiling Point (°C)	Retention Index	Retention Time (min)
Toluene	359	867	110	760	1.51
Ethylbenzene	100	866	136	850	2.28
O-xylene	150	880	144	880	2.60
Nonane	29.8	718	151	900	2.70
1,2,4-trimethylbenzene	285	876	169	990	3.73
Indane	62	964	176.5	1020	4.17
Naphthalene	4.93	1150	218	1170	5.74
Hexadecane	4.9	770	286.8	1600	9.45
Eicosane	4.93	790	343.1	2000	12.26
Total	1000.56				

The nine components were chosen because they are common to different ignitable liquid classifications (Table 1.1) [12]—especially gasoline—and because they provide a range of volatilities and chemical classes, including aromatics, alkanes and indanes.

To avoid unintentional weathering losses of the gasoline simulant, the 1 L stock solution of synthetic gasoline was stored in five 200-mL glass containers with screw on lids at room temperature.

2.1.2 Wood

Two types of wood were used as substrates for the porosity studies: pine wood and plywood. Pine wood is a soft wood and is commonly found in furniture and building components. Plywood is a manufactured product, equivalent to a medium-density wood, that is found in both furniture and flooring products. Both are likely to be found at the scene of an architectural fire such as a house, office building or school.

2.1.3 Carpet

Nylon carpet was used during the project. Nylon carpets are the most common carpets in residential buildings due to their durability and affordability. Nylon carpet is also a common fiber used in the upholstery of vehicle seating and as a blend in furniture upholstery.

2.1.4 Cotton

A swatch of 100% cotton was used to emulate common items that are doused with ignitable liquids in a fire. Cotton is a ubiquitous material in rags, clothing, toweling and bedding materials, and these materials are often used as media to soak ignitable liquids in incendiary fires [1].

2.1.5 Substrate pre-treatment

To enable weathered residues in the substrate to be detected by mass difference, and to prevent chemical residues in the substrates interfering with any of the spiked samples, we had to demonstrate that the substrates had constant mass over the range of experimental temperatures. To minimize outgassing and contamination from the substrates, replicates of each substrate were weighed, then heated in an aluminum weight boat in the oven to the desired temperature; e.g.

210°C. The substrates were cooled and weighed again to ensure they had not outgassed and that they had reached constant mass. If the substrates showed signs of outgassing, they were heated for extended periods until they reach constant mass. Only substrates that reached constant mass were used for subsequent experiments. As a negative control, replicates of each substrate were also solvent extracted using the pentane extraction procedure described for the weathering experiments in section 2.4.

Figure 2.2.2: The four substrates used for the weathering of the synthetic gasoline, from left to right: plywood, pine wood, nylon carpet and cotton fabric.

2.2 Method validation

Before performing any experiments, the methodological procedures for making and evaporating the mixtures required validation. A series of experiments were therefore conducted to ensure the reliability of the experimental protocols. The homogeneity of the synthetic gasoline had to be confirmed between the five bottles by analyzing an unweathered sample from each bottle and comparing the relative peak areas of each substance. We also had to establish the density of

the synthetic mixture so that we could determine the weathering losses by mass. The results in section 3.1 confirm that the containers were homogeneous.

Previous work performed weathering experiments of the synthetic gasoline in aluminum weighing boats on an aluminum block, both of which had been heated to a desired temperature before spiking with the synthetic gasoline [17,18]. Unlike the current research, the previous weathering experiments were performed in a fume hood after the block had been removed from the heated oven. However, the previous researchers noted that condensates were visible on the walls of the aluminum weighing boats, and the previous work had not validated that the condensates had the same chemical composition as the residues in the bottom of the weighing boat. We were concerned that the compositions of the two residue locations might be slightly different because the walls might condensate the volatiles at a lower temperature than the bottom, which is in direct contact with the aluminum block. The results in Section 3.1 show that the composition on the sides and bottom of the aluminum weighing boats are largely similar, but that small significant differences occur for a few of the abundant volatile components like ortho-xylene.

To ensure a fair comparison of the model to the new method, synthetic gasoline was separately weathered in the fume hood and in the oven. Weathering was performed at $90\pm 2\%$ weathering in five replicates. The relative peak areas of the total residue (from the sides and bottom of the weigh boat) of the fume-hood and oven evaporations were compared using a paired t-test. A similar test was performed to compare residues collected from the bottom of the weight boat and the sides of the weight boat for the fume-hood experiments.

2.3 Collection of weathered synthetic gasoline samples

A 1 mL aliquot of the synthetic gasoline, placed in an aluminum weighing boat, was placed on a heated aluminum block that has been pre-heated to the desired temperature, e.g. 30°C, 120°C or 210°C (Fig. 2.3).

Figure 2.3: The aluminum blocks and weigh boat used for the weathering of the synthetic gasoline.

For the various weathering experiments, the synthetic gasoline was typically weathered to between 9 and 17 varying extents of weathering between approximately 50% and 95.5% to provide various points of comparison between the mathematical model and the experimental data points. The extent of weathering was determined by mass difference. Each weigh boat was pre-baked in a kiln at 400°C to remove all residual lubricants. The mass of each boat was then recorded. Each weathering experiment began with pipetting precisely 1 mL of simulant into the weight boat, which corresponded to 0.8653 g (see section 3.1). The mass loss during evaporation could then be established by subtracting the mass of the weigh boat + residue from the combined mass of the weight boat + original liquid. After recording the mass of the weighing boat, the residues were collected with three replicate rinses of 1 mL of pentane (Fig 2.4). The collected washings typically summed to ~600 μ L because of the rapid evaporation of pentane during the washing. However,

Raoult's law suggests that the large dilution factor of the residues in pentane should prevent the diluents from undergoing significant evaporation during the collection procedure.

Figure 2.4: An example of the pentane rinsing procedure used to collect residues from the weigh boat following weathering. Credit: Glen P Jackson.

The washings were then diluted to a final volume of 1 mL before diluting to a suitable concentration for analysis on the GC-MS. The relative peak area ratios of each component in the unweathered and weathered residues were compared to the evaporation model, as described by Birks et al. [17] (Fig 2.5).

Figure 2.2.5: (a) An overlaid comparison of the components in experimentally collected weathering data (circles) and the mathematically modeled predictions (lines) for the synthetic gasoline mixture weathered at 210°C, and (b) a close-up of the same data from 70-100% weathered (plots courtesy of Willis, Fan, and Jackson [reference]).

2.4 Recovery Calculations

Before performing weathering experiments, it is important to determine the length of time needed to reach complete or equilibrium extraction of the residues from the substrates. A 1-mL aliquot of the synthetic gasoline mixture was spiked onto a substrate and then the substrate was placed into a 250-mL glass jar at room temperature. The substrate was extracted using a sufficient volume of pentane to submerge the samples, which was different for each substrate; 25 mL for the control (i.e. no substrate) and cotton, 50 mL for nylon carpet and 70 mL for pine wood and plywood. At set time intervals of 0, 10, 20, 30, 40, 50, 60, 120 and 180 min, 500 μ L of the extractant was removed to a GC vial and diluted 1:5 in pentane for analysis.

2.5 Effect of substrates on the weathering of synthetic gasoline

The next phase of the weathering studies was designed to establish whether the substrate matrix influenced the evaporation rates of the different components, while minimizing the effects of porosity and entrapment. Towards this end, the experiments in section 2.3 were repeated with each of the different substrates in the weighing boat. The substrates were preheated to the desired weathering temperature, 210 °C, to ensure that any and all weathering takes place at the elevated temperature. If the synthetic gasoline was spiked on room-temperature substrates and then placed in the oven, some weathering would take place while the substrate was changing temperature in the oven. Our model is designed to simulate weathering at a fixed temperature, not necessarily a wide range of changing temperatures. The time between spiking the substrate with the synthetic gasoline and weathering was as short as possible to prevent the penetration of gasoline within the substrate.

2.6 Effect of substrate absorption/entrapment on the apparent weathering of synthetic gasoline

When ignitable liquids are used in arson cases, there is probably a delay of tens to hundreds of seconds lapse between when the ignitable liquid is administered on a substrate and when the perpetrator ignites the fire. The more time that passes between administering and igniting, the deeper the ignitable liquid can penetrate into the substrate. To visualize penetration of the ignitable liquid in the different substrates, a portion of the synthetic gasoline was spiked with a strong red dye called Alizarin (Sigma-Aldrich, St. Louis MO). Alizarin (Fig 2.6) is a prominent, naturally-occurring red dye that has been used for centuries to dye or stain textiles, fibers and wood [45]. Alizarin is an aromatic and neutral compound that is soluble in benzene, toluene and xylene.

Figure 2.6: Chemical structure of alizarin.

The experiments described in section 2.3 were repeated with the dye-spiked simulant, but with a range of delay times between the spiking and weathering. The gasoline simulant was allowed to penetrate the substrates for zero seconds (e.g. section 2.3), 30 seconds and 30 minutes in a sealed container with minimal headspace. The absence of headspace was designed to prevent unwanted weathering during the penetration period.

Figure 2.7: *One of the metal tins used for the weathering of the synthetic gasoline with the time delay. The lid of the tin is closed during the delay to prevent unwanted weathering.*

One replicate at each penetration time was cross-sectioned and examined to observe the pattern and penetration depth of gasoline in the substrate.

The remaining replicates, spiked with the un-dyed simulated gasoline, were weathered to different extents (50-95.5%) at 210 °C, as described previously. Once the approximate desired extent of weathering had been accomplished, the substrates were cooled and weighed to determine the actual extent of weathering in each replicate. The swatches were then be extracted using the solid/liquid extractions using pentane described above.

2.7 Gas chromatography/mass spectrometry

Analysis of the samples was performed on an HP 5977A Agilent Gas Chromatograph-Mass Spectrometer (GC/MS) with a 30 m x 0.25 mm diameter x 0.25 μ m film thickness HP-5 column (Agilent). Parameters for the GC/MS were as follows: a 1 μ L injection volume with an injector temperature at 250°C and 1:20 split ratio; the oven was held at 50°C for 2 min, then ramped up to 280°C at 15°C/min, then held for 5 min. The carrier gas was helium at a flow rate of 1.8 mL/min, and the transfer line was set to 270°C. The mass spectrometer had a solvent delay of 1.5 min and had a scan range of m/z 30-450. Data was extracted using Agilent MSD Productivity ChemStation Software Enhanced Data Analysis (Agilent, Santa Clara, CA, USA) and analyzed in Excel 2019

for Windows (Microsoft, Redmond, WA, USA).

3. Results and Discussion

3.1 Density and homogeneity of simulated gasoline mixture

The average of mass of five replicate 1-mL aliquots of the simulant mixture provided a density of 0.865 ± 0.008 g/mL (1 sd). To ensure that the synthetic mixture was homogenous before separating into the five bottles, replicate 1 mL aliquots were diluted to 1:500 in pentane and analyzed on the GC-MS. The relative peak areas for each component was compared to the average of the five bottles, and most of components for all five bottles fell within 95% confidence interval of that mean (Table 3.2). At most, the components that fall outside of the interval are only by ~1%.

Table 3.1: Comparison of relative peak areas for each bottle.

Component	Bottle 1	Bottle 2	Bottle 3	Bottle 4	Bottle 5	Mean	Standard Deviation	95% Confidence Interval
Toluene	33.4%	30.9%	32.8%	30.7%	31.6%	31.9%	1.18%	30.8% - 32.9%
Ethylbenzene	10.4%	12.0%	11.8%	11.5%	10.7%	11.3%	0.71%	10.7% - 11.9%
O-xylene	15.7%	15.8%	15.6%	16.1%	15.3%	15.7%	0.29%	15.5% - 16.0%
Nonane	3.0%	2.8%	2.7%	2.8%	2.8%	2.8%	0.12%	2.7% - 2.9%
1,2,4-trimethylbenzene	28.4%	28.0%	27.9%	28.5%	29.1%	28.4%	0.48%	28.0% - 28.8%
Indane	7.7%	8.7%	7.5%	8.6%	8.8%	8.3%	0.60%	7.7% - 8.8%
Naphthalene	0.5%	0.6%	0.7%	0.6%	0.7%	0.6%	0.06%	0.6% - 0.7%
Hexadecane	0.4%	0.5%	0.5%	0.5%	0.5%	0.5%	0.05%	0.5% - 0.5%
Eicosane	0.4%	0.5%	0.5%	0.5%	0.5%	0.5%	0.05%	0.5% - 0.5%

To compare the effects of weathering in the fume hood to weathering in the oven, we weathered the synthetic gasoline mixture five times to 90 ± 2 % weathering. In both cases, the residues were collected from the sides and bottom of the weigh boat. Paired t-tests determined that there was no statistical difference at $\alpha=0.05$ between the two approaches, with values ranging from 0.371 to 0.829 (Table 3.3). Thus, the new method of weathering within the oven can be compared to the previously proposed model.

Table 3.2: Table of paired t-test p values from comparison of components from residues weathered in the fume hood and in the oven. Number of samples for the comparison includes five samples weathered in the fume hood and five samples weathered in the oven.

Component	Paired t-test results
Toluene	0.67
Ethylbenzene	0.43
O-xylene	0.37
Nonane	0.44
1,2,4-trimethylbenzene	0.62
Indane	0.83
Naphthalene	0.52
Hexadecane	0.75
Eicosane	0.69

Similarly, a comparison of the washings from the bottom and the sides of weigh boats weathered in the fume hood was also conducted. When the weathering was performed in the fume hood, five of the nine components showed no statistical difference between the relative abundance of residues on the bottom and the sides of the weigh boat. Ethylbenzene, o-xylene, nonane and 1,2,4-trimethylbenzene did show statistical differences, with p values of 0.005, 0.003, 0.03 and 0.01, respectively (Table 3.4). However, when performed in the oven, only o-xylene showed a statistical difference, with a value of 0.003. These results provide some concern that the walls and bottom of the weigh boat are not in thermal equilibrium during the evaporation studies.

Table 3.3: Table of paired t-test p-values from the comparison of relative peak areas of components from the bottom and the sides of the weigh boat for fume hood and oven weathering at 90±2 % weathering. N=5 replicates for both the fume hood and oven weathering. * Indicates relative peak areas that are significantly different at the 95% confidence interval.

Component	Fume hood: bottom vs sides	Oven: bottom vs sides
Toluene	0.45	0.96
Ethylbenzene	0.005*	0.07
O-xylene	0.003*	0.003*
Nonane	0.03*	0.10
1,2,4-trimethylbenzene	0.01*	0.22
Indane	0.77	0.92
Naphthalene	0.26	0.43
Hexadecane	0.54	0.28
Eicosane	0.51	0.33

We then established the mass ratio of the amount of residue remaining in the weigh boat provided evidence that a majority of the residues are found on the bottom of the weigh boat. In the fume hood, the mass ratio of residue on the bottom of the weigh boat to the walls of the weigh boat was 1.4, with 59% on the bottom and 41% on the sides (Table 3.5 and Fig 3.1). The mass ratio of residues in the bottom to the walls of the weigh boat for samples weighed in the oven had an average of 3.9, with 80% on the bottom and 20% on the sides (Table 3.6 and Fig 3.2). Given that the oven weathering experienced less condensation on the walls, and given that the fractional composition of the residues on the walls and bottom were more similar in the oven, the oven method was selected as the method of choice.

Table 3.4: Comparison of the relative peak areas of the nine components from the residues collected from the bottom of the weigh boat and the sides of the weigh boat. The residues being compared were collected from the same weigh boat with residues weathered in the fume hood.

Percent of total mass of residue	59%	41%
Component	Bottom	Sides
Toluene	1.3%	0.4%
Ethylbenzene	3.9%	1.8%
O-xylene	10.5%	6.3%
Nonane	1.3%	0.8%
1,2,4-TMB	51.7%	58.7%
Indane	18.9%	18.9%
Naphthalene	1.6%	1.3%
Hexadecane	4.9%	1.5%
Eicosane	5.9%	6.3%

Figure 3.1: Comparison of chromatograms from residues collected from the a) bottom and b) sides of the weigh boat from weathering conducted in the fume hood. See table 2.1 for peak identities.

Table 3.5: Comparison of the relative peak areas of the nine components from the residues collected from the bottom of the weigh boat and the sides of the weigh boat. The residues being compared were collected from the same weigh boat with residues weathered in the oven.

Percent of total mass of residue	80%	20%
Component	Bottom	Sides
Toluene	0.7%	2.5%
Ethylbenzene	2.6%	1.9%
O-xylene	8.8%	5.7%
Nonane	1.1%	0.8%
1,2,4-TMB	58.2%	58.6%
Indane	17.6%	17.1%
Naphthalene	4.7%	3.4%
Hexadecane	4.8%	4.8%
Eicosane	5.5%	5.2%

Figure 3.2: Comparison of chromatograms from residues collected from the a) bottom and b) sides of the weigh boat from weathering conducted in the oven. See table 2.1 for peak identities.

3.2 Baseline weathering

Previously, our group proposed a mathematical model based on Raoult's law and Dalton's law to simulate the evaporation of a mixture [17,18]. Raoult's law states that the partial vapor

pressure, p_A , of A is proportional to the mole fraction, x_A and the vapor pressure of the pure liquid, P_A^* [46].

$$p_A = x_A P_A^* \quad (1)$$

Dalton's law states that the total pressure is equal to the sum of the partial pressures in a mixture [46]. These laws are based on ideal liquids and ideal gases and account for the fact that there are multiple components in the solution, none of which are major components.

The model works as follows; First, the vapor pressure of each component in the mixture is estimated from their Antoine constants, which describes the log of the vapor pressure as a function of temperature for each substance. Then Raoult's law and Dalton's law are used to calculate partial and total pressures of the headspace above the mixture. The mixture is comprised of a hypothetical total of 1 mole of components and contains different known mole fractions of each. Then, a stepwise loss of five percent (0.05 moles) of the vapor phase is subtracted from the original vapor phase to simulate an irreversible evaporative loss. The 5% loss is applied proportionally to the partial pressure of each component in the mixture to the partial number of moles in the original mixture. For example, if toluene made up 50% of the mixture (0.5 moles) and made up 80% of the vapor pressure—because it is more volatile than the other components in the mixture—then the first stepwise loss of toluene would be $80\% \times 5\% = 4\%$ of 0.5 moles, or 0.02 moles. After the first stepwise loss of each component, the remaining number of moles is renormalized to a sum total of 1 mole and the new mole fractions of each substance are computed. The process is then repeated by calculating new partial and total pressures from the new mole fractions in the mixture. The process is repeated until the total amount of residue remaining reached a desired percent weathering. The total percent weathering is tracked as follows; After the first 5% loss of the original solution, the fraction remaining is 95%. The second 5% loss is only 4.75% of the original

number of moles, so the total number of moles remaining after two 5% losses is 92.5%. Thus, the decay of consecutive 5% losses is exponential, not linear.

Fig. 3.3 shows the mathematical model with experimentally collected weathering data for the synthetic gasoline. For the three temperatures measured, the mathematical model provides an accurate fit for the experimentally observed data, as defined by root mean squared errors of predictions (RMSEP) of 1.9%, 2.6% and 2.5%, respectively, at 210°C , 120°C and 30°C.

$$RMSEP = \sqrt{\sum_{i=1}^n \frac{(\hat{y}_i - y_i)^2}{n}} \quad (2)$$

In the absence of a substrate, the model is a reliable estimator for the weathering patterns of the synthetic gasoline mixture up to 210°C. The validity of the model to a nine-component mixture provides some confidence that the model would also work on more complex solutions, like real gasoline, although such validation is still under development.

One of the remarkable findings of the previous experiments and modeling is that the temperature at which the solution evaporates has a significant effect on the distribution of weathered residues. For example, Figure 3.3 shows that at 30°C, toluene reaches threshold levels before 70°C evaporation of the mixture, whereas at 210°C toluene makes up ~9% of the mixture at 70°C and doesn't reach threshold until >90% weathering. A detailed explanation is provided in the previous work, but the basics are that at elevated temperatures, all the components are similarly volatile, so they evaporate at more similar rates.

Figure 3.3: (a) A comparison of experimentally collected weathering data (circles) for the nine components and the mathematical model (lines) for the synthetic gasoline mixture at 210°C, and (b) a close-up of the same data set from 70-100% weathered. (c), (d), (e) and (f) show the same comparisons for synthetic gasoline weathered at 120°C, a close-up of 120°C, synthetic gasoline weathered at 30°C, and a close-up of 30°C, respectively.

3.3 Potential contamination from substrates

In the pre-treatment of each substrate to prevent outgassing and achieve constant mass, we noted that substrates heated to 210°C showed significant outgassing, as noted by a decrease in mass of 1.3 grams relative to the plywood mass of 15.2 grams, 1.2 grams relative to the pine wood mass of 16.3 grams, 0.05 grams relative to the nylon carpet mass of 6.4 grams, and 0.01 grams relative to the cotton mass of 2.8 grams. The plywood, pine wood, nylon carpet and cotton reached constant mass after baking for 6.5 hours, 6.5 hours, 1.5 hours and 30 minutes, respectively. Extractions from a piece of each substrate showed that no substrate had any interfering peaks with the synthetic gasoline, nor does the solvent used for extraction and dilution (Fig 3.4-3.8).

Figure 3.4: Background chromatogram of plywood extract. The plywood was previously baked to constant mass at 210°C.

Figure 3.5: Background chromatogram of pine wood extract. The pine wood was previously baked to constant mass at 210°C.

Figure 3.6: Background chromatogram of nylon carpet extract. The nylon carpet was previously baked to constant mass at 210°C.

Figure 3.7: Background chromatogram of cotton extract. The cotton was previously baked to constant mass at 210°C.

Figure 3.8: Background chromatogram of pentane. Pentane is the solvent used for the extraction of the residue from the substrate and the dilution of the residue for analysis.

3.4 Recovery Calculations

For the control experiments, the jar volume was fixed at 250 mL and 1 mL of synthetic gasoline was spiked onto each substrate or no substrate (negative control). The substrates were left to soak for 0, 5 or 30 minutes to simulate different absorption times. After soaking, different volumes of pentane were then added to each substrate to ensure the substrates were submersed in the solvent. To monitor the kinetics of extraction, aliquots of the extract were removed at 0, 10, 20, 30, 40, 50, 60, 120 and 180 min and the total ion chromatogram (TIC) relative peak areas of each substance were determined using the GC-MS. A plot of absolute peak area vs extraction time for each substance is shown in Figure 3.9.

Figure 3.9: Plot of the peak area for each substance at each extraction time for a) plywood, b) pine wood, c) nylon carpet, d) cotton and e) no substrate (negative control).

A paired t-test of the peak areas for each substance between the negative control and each of the four substrates showed a significant difference for at least 50% of the compounds at an alpha value of 0.05 (Table 3.6). However, most of the differences can be explained by evaporative losses to the different headspace volumes.

Table 3.6: Paired-t test values comparing the relative peak areas of the negative control to each of the four substrates. Highlighted boxes indicate values that are significantly different.

Component	Plywood	Pine wood	Nylon carpet	Cotton
Toluene	5.6 x 10 ⁻⁴	1.2 x 10 ⁻⁵	1.3 x 10 ⁻⁶	6.7 x 10 ⁻³
Ethylbenzene	5.0 x 10 ⁻³	6.3 x 10 ⁻³	3.5x 10 ⁻⁵	1.3x 10 ⁻⁶
O-xylene	8.6 x 10 ⁻⁶	4.3 x 10 ⁻⁵	7.5x 10 ⁻⁵	1.6 x 10 ⁻³
Nonane	8.6 x 10 ⁻²	5.1 x 10 ⁻²	4.2x 10 ⁻²	1.5 x 10 ⁻²
1,2,4-trimethylbenzene	1.9 x 10 ⁻¹	9.3 x 10 ⁻²	5.2x 10 ⁻¹	5.7 x 10 ⁻⁴
Indane	1.2 x 10 ⁻⁴	9.9 x 10 ⁻⁸	5.3x 10 ⁻⁶	1.2 x 10 ⁻⁴
Naphthalene	9.3 x 10 ⁻⁵	6.2 x 10 ⁻⁷	2.5 x 10 ⁻⁴	2.8 x 10 ⁻¹
Hexadecane	7.5 x 10 ⁻²	1.3 x 10 ⁻³	3.4x 10 ⁻⁷	4.8 x 10 ⁻⁷
Eicosane	9.8 x 10 ⁻¹	7.5 x 10 ⁻²	1.8 x 10 ⁻⁶	1.8 x 10 ⁻⁷

We did not anticipate that the relative composition of the residues would be so sensitive to the differences in headspace volume in the jars (Fig 3.10 and Table 3.7). However, the plots in Figure 3.8 show that after an extraction time of 30 minutes, there is a correlation with the headspace volume. If the headspace had no effect, then there should be no difference in the relative peak areas between the unweathered liquid and the “no substrate” results. In effect, the only difference between these two is a dilution of 1:25. However, the relative peak area of toluene is significantly reduced in the no-substrate results because some of the toluene has been lost to the headspace of the jar. Ortho-xylene is affected similarly, but the difference is attenuated because ortho-xylene is less volatile than toluene and it comprises a smaller mole fraction in the headspace.

Figure 3.10: Visual representation of the substrates and the amount of headspace above them in the glass jars used for extraction.

Table 3.7: Volume of the glass jar and amount of headspace above substrates when in the jar and submerged in pentane.

Substrate	Volume of glass jar (mL)	Approximate volume of substrate (mL)	Volume of synthetic gasoline (mL)	Volume of pentane (mL)	Est. volume of headspace (mL)
No substrate	250	0	1	25	224
Plywood	250	10	1	70	168
Pine wood	250	10	1	70	169
Nylon	250	5	1	50	194
Cotton	250	0.5	1	25	224

Figure 3.11: Relative abundances of each component extracted from each substrate average across all times collected during time study.

The jars with the smallest headspace volume, which were the two types of wood, had the largest mole fractions of toluene and the smallest mole fractions of non-volatiles retained relative to no substrate. Substrates with the greatest headspace volume, such as no substrate and cotton, had the smallest mole fractions of volatiles retained and the largest mole fractions of non-volatiles retained. These results indicate that although the headspace has a small but measurable effect on the relative peak areas of components in the extract, the substrates themselves have almost no effect on the peak areas. The plots in Figures 3.9 and 3.11 provide evidence that the extraction efficiencies at 30 minutes are the same for each substrate, have reached equilibrium for most of the substances, and are unaffected by the presence of a substrate.

3.5 Weathering on substrates

Figure 3.12 shows the mathematical model plotted against the weathering experiments performed on each substrate at 210°C. In these experiments, the substrate was pre-heated to the weathering temperature, and there was no delay between spiking with the simulated gasoline and weathering in the oven. For comparison, the fitness of the model in the absence of any substrate is provided in Figure 3.2. In the presence of substrates, the RMSEPs for each substrate yielded predicted errors of 6.3%, 3.7%, 3.1% and 2.9% for plywood, pine wood, nylon carpet and cotton, respectively. The model does not perform as well in the presence of substrates—and especially the more porous substrates like wood—compared to non-porous substrates.

Figure 3.12: (a) A comparison of experimentally collected weathering data (circles) for the nine components and the mathematical model (lines) for the synthetic gasoline mixture spiked onto cotton at 210°C. (b), (c) and (d) show the same comparisons for synthetic gasoline weathered but spiked onto nylon carpet, pine wood and plywood, respectively, at 210°C.

3.6 Penetration of synthetic gasoline into the substrates

Figure 3.13 shows photographs of the different substrates under different conditions. In these photographs, the simulated gasoline spiked with alizarin was used to spike the substrates, which is why they appear the yellow/orange. The images show the substrates before spiking (column 4) and after 30-s (column 1) and 30-min (column 2) time delays. The third column shows a cross section of each substrate after 30 min of penetration and drying.

For both the plywood and the pine wood, there are some unwetted areas of the wood at 30 s, but after 30 min, the entire block has been soaked with the synthetic gasoline mixture. The cross sections of each wood sample in column 3 show that the dye is evenly distributed throughout the entire cross section of the samples. The nylon carpet appears to have a darker shade of yellow at the 30-s mark than at the 30-min mark, suggesting that the synthetic gasoline did not uniformly wet the entire carpet sample as it did the wood samples. The cotton fabric wetted very quickly and did not change appearance between 30-s and 30-min.

Figure 3.13: Images of a) plywood 30 seconds after spike, b) plywood 30 minutes after spike, c) cross-section of plywood 30 minutes after spike, d) plywood before spike, e) pine wood 30 seconds after spike, f) pine wood 30 minutes after spike, g) cross-section of pine wood 30 minutes after spike, h) pine wood before spike, i) nylon carpet 30 seconds after spike, j) nylon carpet 30 minutes after spike, k) cross-section of nylon carpet 30 minutes after spike, l) nylon carpet before spike, m) cotton 30 seconds after spike, n) cotton 30 minutes after spike, o) cut cotton 30 minutes after spike and p) cotton before spike. Note that images in the first two columns are taken with one swatch. Images taken in the third and fourth columns are taken with a different swatch than the first two images.

3.6 Weathering with substrates and time delay

Similar to previous plots, Figures 3.14 and 3.15 provide the comparison of the mathematical model to the experimentally weathered data for each substrate, with a 30-s time delay (Figure 3.13) and a 30-min time delay (Figure 3.14). The RMSEPs for each substrate with the 30 s time delay yielded predicted errors of 7.2%, 5.6%, 2.5% and 2.5% for plywood, pine wood, nylon carpet and cotton, respectively. For reference, the RMSEPs for weathering at the same temperature in the absence of a substrate was 1.9%. For the two wood substrates, the time delay increases the predicted error, whereas for the nylon carpet and the cotton fabric the delay decreases the RMSEPs.

Figure 3.14: (a) A comparison of experimentally collected weathering data (circles) for the nine components and the mathematical model (lines) for the synthetic gasoline mixture spiked onto cotton at room temperature, sealed for 30 seconds and weathered at 210°C. (b), (c) and (d) show the same comparisons for synthetic gasoline spiked onto nylon carpet, pine wood and plywood, respectively, at room temperature, sealed for 30 seconds and weathered at 210°C.

The additional time delay of 30 minutes again increases the RMSEPs for plywood and pine wood, to 7.8% and 7.2%, respectively. For the two wood substrates, the increase in RMSEPs from 30-s to 30-min time delays is smaller than from no time delay to 30 seconds. At 30 minutes, nylon carpet has an RMSEP of 3.3%, which is only slightly worse than 0 or 30 seconds. The RMSEP for cotton was virtually unchanged at 2.4% at 30 min. The residues for each substrate appear to hardly change in composition above 50%. This indicates that the substrates are inhibiting the evaporation of higher volatility substances that typically evaporate quicker when in the absence of substrates. The model no longer fits the data as well because the proportional loss that is applied to each step is no longer applicable with the presence of the substrates. Thus, residues that are weathered to a higher extent appear to be similar to those at a lower extent.

Figure 3.15: (a) A comparison of experimentally collected weathering data (circles) for the nine components and the mathematical model (lines) for the synthetic gasoline mixture spiked onto cotton at room temperature, sealed for 30 minutes and weathered at 210°C. (b), (c) and (d) show the same comparisons for synthetic gasoline spiked onto nylon carpet, pine wood and plywood, respectively, at room temperature, sealed for 30 minutes and weathered at 210°C.

Table 3.8 summarizes the RMSEP for all weathered experiments conducted in this study. As the table moves from left to right, the volume and porosity of each substrate increases and the RMSEP increases. In the absence of a substrate, or in low volume non-porous substrates like cotton fabric, the accuracy of the model is at its best.

Table 3.8: Root mean squared error of predictions (RMSEP) for each substrate at no delay time, 30 second delay and 30 minute delay. Number in the parentheses correspond to the number of samples used in each calculation.

	No substrate	Cotton	Nylon	Pine wood	Plywood
No delay	1.9 (180)	2.9 (117)	3.1 (108)	3.7 (90)	6.3 (108)
30 seconds	--	2.5 (90)	2.5 (72)	5.6 (81)	7.2 (81)
30 minutes	--	2.4 (90)	3.3 (72)	5.9 (81)	7.8 (99)

As the porosity of the substrate increases and as the wetting time increases, deviations from the model become more notable. These trends suggest that the more porous substrates are soaking and trapping more of the synthetic gasoline mixture and preventing the vapors from reaching the surface to evaporate the in the same way that it does when no substrate is present. Whereas the pre-baking procedure of wooden substrates up to $\sim 230^{\circ}\text{C}$ has been shown to slightly alter the hydrophobicity, acidity and wettability of the wood towards water [47], the changes are modest and the wettability towards hydrocarbons like aromatics and alkanes etc. is not well known. Therefore, although the physical properties of the wood may have been altered but the baking procedure, we do not anticipate that baking significantly impacts the findings.

It is quite obvious from Figure 3.14 that the inaccuracies in the fitness of the model are not random but systematic. The absolute errors in predictions were therefore assessed in more detail below. Figures 3.16 through Figure 3.20 compare the absolute residuals for each substrate across the nine components and the three delay times. The residuals for no substrate in each scenario are the same, no time delays were added when weathering without a substrate present. Also, all plotted residuals have been multiplied by 100, as this makes for an easy transition to a RMSEP percentage in the later calculation steps. An overall trend seen in all plots is that the magnitude of the residuals tends to increase with the percent weathering. As the liquid become less like the original mixture, the model has a harder time accurately predicting the remaining residues. In

conjunction, as the amount of time for penetration increases, so do the residuals, which corresponds to the increase in RMSEP as time delay increases.

Toluene appears to have one of the largest spreads in the residuals, with components having both positive and negative residuals (Fig 3.16). The large spread is most likely the result of the high volatility and thus the natural variability in remaining residuals compared to other components. For all four substrates the smaller extents of weathering have a positive residual, meaning the model has over predicted the amount of toluene remaining. This finding can be explained by the fact that during the extraction procedure, some of the toluene is lost to the headspace of the glass container, as described previously. However, at greater extents of weathering, the model under predicts the residual composition of toluene, which can only be explained by excess retention of toluene in the substrate during the weathering procedure. For the majority of the experiments, the weathering with no substrate had positive residuals for toluene, which is consistent with the small evaporative loss to the headspace during the extraction procedure.

Figure 3.16: Plots of absolute errors of predictions for toluene and ethylbenzene weathering in the presence of no substrate, plywood, pine wood, nylon carpet and cotton with (a) no time delay, (b) 30 second time delay and (c) 30 minute time delay.

Ethylbenzene is the next most volatile substance after toluene, and it has a smaller spread of residuals than toluene (Fig 3.16). A larger proportion of the residuals are negative for two reasons. First, because toluene undergoes more loss than expected during the extraction, the

other compounds are enhanced relative to the model. The model therefore tends to underestimate ethylbenzene and the other compounds. At extents of weathering greater than 60%, the absolute error of predictions correlates with the extent of weathering. The trend towards negative residuals at greater extents of weathering is consistent with less evaporation than expected relative to the other compounds.

O-xylene follows the trend of the other volatile components, toluene and ethylbenzene; most of the residuals are negative because of preferential toluene losses to the headspace during extraction, and the largest negative residuals are at extents of weathering greater than 80% (Fig 3.17). Much like the residuals for ethylbenzene, most points below 70% weathering have little deviation from zero. Figure 3.17 shows that nonane follows a similar trend as o-xylene.

1,2,4-trimethylbenzene has some of the largest residuals across all the substrates and all the time delays, with the largest prediction errors occurring above 80% weathering (Fig 3.18). These residuals are consistently positive and are largely influence by the larger-than-expected retention of volatiles at large extents of weathering. For the non-volatiles naphthalene through eicosane in Figures 3.19 through 3.20, the residual errors are dominate by the behaviors of the volatiles like toluene. At extents of weathering below 50%, the volatiles are less abundant than expected because of weathering losses to the headspace, therefore, the non-volatiles are less abundant than predicted and have consistently negative residual errors. At extents of weathering above 50%, the volatiles are prevented from evaporating at the predicted rate and are higher in abundance than predicted. Therefore, the non-volatiles have to be less abundant than predicted to ensure that the sum total number of moles remains constant at one.

Hexadecane has a large increase in the spread of the residuals between the no time delay and 30-s and 30-min time delay experiments (Fig 3.19). While none of the percent weatherings are

exactly the same between different delay times, comparisons between similar percent weatherings show a decrease in some of the residuals for nylon carpet and cotton, whereas for plywood and pine wood they increase.

Eicosane appears to be the most consistent in the residuals, with the few exceptions of pine wood at no time delay (Fig 3.20). Eicosane is the least volatile component in the mixture and also lowest abundant component in the mixture, thus it has the lowest probability of evaporating, even at the high temperatures. Because of this, the difference in the substrate chemistry and porosity have the least amount of effect on its evaporation and is the most consistent in remaining residue.

Figure 3.17: Plots of absolute errors of predictions for ortho-xylene and nonane weathering in the presence of no substrate, plywood, pine wood, nylon carpet and cotton with (a) no time delay, (b) 30 second time delay and (c) 30 minute time delay.

Figure 3.18: Plots of absolute errors of predictions for 1,2,4-trimethylbenzene and indane weathering in the presence of no substrate, plywood, pine wood, nylon carpet and cotton with (a) no time delay, (b) 30 second time delay and (c) 30 minute time delay.

Figure 3.19: Plots of absolute errors of predictions for naphthalene and hexadecane weathering in the presence of no substrate, plywood, pine wood, nylon carpet and cotton with (a) no time delay, (b) 30 second time delay and (c) 30 minute time delay.

Figure 3.20: Plots of absolute errors of predictions for eicosane weathering in the presence of no substrate, plywood, pine wood, nylon carpet and cotton with (a) no time delay, (b) 30 second time delay and (c) 30 minute time delay.

4. Conclusions

This research provides the controlled studies of weathering at elevated temperatures in the presence of a substrate. These conditions are closest to those experienced in real structure fires. The results show that the properties of substrates have a significant effect on the weathering pattern of a synthetic gasoline mixture at elevated temperatures. In less than 30 seconds, a synthetic gasoline mixture permeated all the way through 2"x2"x1" samples of plywood and pine wood, and when the wood was then heated to 210°C volatiles like toluene and o-xylene evaporated at rates that were significantly slower than those predicted by their native vapor pressures.

In the absence of any substrate, an in-house thermodynamic model based on Raoult's law and Dalton's law predicted the fractional composition of a weathered residue with a RMSEP of ~2%. In the presence of a porous substrate like untreated wood, the substrate increased the RMSEP to ~7%. Nylon carpet and cotton fabric also effected the evaporation rates of the components in the gasoline simulant, but to a lesser extent than the wood substrates.

Based upon on the absolute error of predictions of peak areas, it appears that the presence of the substrates have a larger effect on the evaporation rates of the volatile components than the amount of time the synthetic gasoline is provided to penetrate into the substrate. If the wood was treated, or if the wood was a hard wood, the penetration time may be more important, but the softwoods were significantly wetted in ~30 s. Delayed penetration times from 30 s to 30 min had little effect on the RMSEPs of the model. The results show that, as a general rule of thumb, the fractional composition of weathered residues in porous wooden substrates remains fairly consistent with a mixture that is weathered to ~50%. This finding helps explain why, when ignitable liquids are extracted from casework samples, anecdotally they often appear to be weathered between 50-70%, despite having been exposed to extreme temperatures of a structure fire [2,3,5].

5. Future Work

Now that we have provided direct evidence for the effects of substrate porosity on the weathering of the ignitable liquids, the next phase of the future work could focus on a model or correction factor to accommodate the porosity of the substrate. If so, future work might also have to assess the effects of the other substrate materials, like hardwoods, absorbent materials like furniture batting, foam, carpet padding and other absorbent flooring materials. The expansion of substrates should also include investigating the differences in finished and unfinished woods. One way to theorize the mechanism of entrapment is through resistance to mass transfer in the substrate.

On one level, entrapment of volatile components in the pores of the substrate might be influenced by the diffusion rate of each substance through the substrate. However, it would be very difficult to describe a concentration gradient through the substrate, and a concentration gradient is one of the required variables in calculation diffusion rates [48].

On the other hand, the mechanism might behave more like effusion, in which the volatiles are entrapped in a large pore and must escape out of a relatively small hole to evaporate. In effusion, the loss rate (Q) of a volatile through an orifice is proportional to the square root of the molecular mass (M) and the temperature (T):

$$Q_{\text{effusion}} \propto \frac{1}{\sqrt{MT}} \quad (3)$$

Either way, as long as the movement of compounds through the substrate is slower than the evaporation rate, the evaporation rates of the volatile components will be attenuated to a greater extent than the non-volatiles, and the results will be similar to those observed experimentally in our work.

Another area of ongoing work in our laboratory is to extend the model to predict the evaporation of any liquid, not just a simple one, and not just one where the chemical identities and vapor pressure are well characterized. Our group has begun to take the mathematical model and generalize it to use retention index instead of known substances. By using retention index instead of known substances, the model can be applied to a more complicated mixture and to mixtures whose identity is unknown. This model can then be used to predict chromatograms at different extents of weathering, as long as the fresh molar ratios are known. To validate the model, a blind comparison with a weathered sample could be compared using RMSEP and PPMC to test the predictive accuracy.

Along the same lines, future work could study the presence of pyrolysis products on the fitness of the model. In this work, we had no background contamination because the substrates were heated to a constant mass and were not burned or pyrolyzed during the weathering experiments. However, in actual fires, substrates could be partially or completely burned and may contain pyrolysis products. Previous studies have concluded that pyrolysis products can be differentiated from the weathering pattern of a particular liquid, but there has not been any study that tests that conclusion against a model that attempts to predict the chromatograms for weathered ignitable liquids.

To provide a more robust and accurate model for practitioners, the subsequent step would attempt to combine the prediction power of the model developed in our group with the kinetic model currently being developed at MSU. Comparison of the model's accuracy on data weathered as described in this study, as well as the laboratory at MSU could point out further limitations of the model and provide guidance for the improvement of the model.

6. References

- [1] R. Campbell, Intentional Fires, 2017. www.nfpa.org/arson.
- [2] J.R. Almirall, K.G. Furton, Analysis and interpretation of fire scene evidence, CRC Press, 2004.
- [3] E. Stauffer, J.A. Dolan, R. Newman, Fire debris analysis, Academic Press, 2008.
- [4] Technical Committee on Fire Investigations, NFPA 921: Guide for Fire and Explosion Investigations, Quincy, MA, 2017. <https://www.nfpa.org/codes-and-standards/all-codes-and-standards/list-of-codes-and-standards/detail?code=921>.
- [5] ASTM, E1618-19: Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry, (2019).
- [6] M.L. Henneberg, N.R. Morling, Unconfirmed accelerants: Controversial evidence in fire investigations, n.d. <https://www.innocenceproject.org/cases/william-dillon/>.
- [7] S.R. Katz, C.R. Midkiff, Unconfirmed Canine Accelerant Detection: A Reliability Issue in Court, 1998. www.astm.org.
- [8] S. Casamento, E. Konza, E. Du Pasquier, D. Royds, E. DU Pasquier, Evaluation of a Portable Gas Chromatograph for the Detection of Ignitable Liquids, Can. Soc. Forensic Sci. J. 38 (2005) 191–203. doi:10.1080/00085030.2005.10757591.
- [9] ASTM, E1412-16: Standard Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration With Activated Charcoal, (2016).
- [10] ASTM, E1386-15: Standard Practice for Separation of Ignitable Liquid Residues from Fire Debris Samples by Solvent Extraction, (2015).
- [11] ASTM, E1388-17: Standard Practice for Static Headspace Sampling of Vapors from Fire Debris, (2017).
- [12] ASTM, E2154-15: Standard Practice for Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Passive Headspace Concentration with Solid Phase Microextraction (SPME), (2015).
- [13] ASTM, E1385-00: Standard Practice for Separation and Concentration of Ignitable Liquid Residues from Fire Debris Samples by Steam Distillation, 2000.
- [14] N.R. Council, Strengthening Forensic Science in the United States: A Path Forward, 2009.
- [15] K.R. Prather, S.E. Towner, V.L. McGuffin, R. Waddell Smith, Effect of Substrate Interferences from High-Density Polyethylene on Association of Simulated Ignitable Liquid Residues with the Corresponding Liquid, (2013). doi:10.1111/1556-4029.12305.
- [16] R.W. Smith, R.J. Brehe, J.W. Mcilroy, V.L. McGuffin, Mathematically modeling chromatograms of evaporated ignitable liquids for fire debris applications, (2016). doi:10.1016/j.forc.2016.08.005.
- [17] H.L. Birks, A.R. Cochran, T.J. Williams, G.P. Jackson, The surprising effect of temperature on the weathering of gasoline, Forensic Chem. 4 (2017) 32–40. doi:10.1016/j.forc.2017.02.011.
- [18] I.C. Willis, Z. Fan, J.T. Davidson, G.P. Jackson, Weathering of ignitable liquids at elevated temperatures: a thermodynamic model, based on laws of ideal solutions, to predict weathering in structure fires, Forensic Chem. (2020) 100215. doi:10.1016/j.forc.2020.100215.
- [19] T.J. Bruno, S. Allen, Weathering Patterns of Ignitable Liquids with the Advanced Distillation Curve Method, 118 (2013). doi:10.6028/jres.118.003.

- [20] T.J. Bruno, T.M. Lovestead, M.L. Huber, Prediction and Preliminary Standardization of Fire Debris Constituents with the Advanced Distillation Curve Method, *J. Forensic Sci.* 56 (2011). doi:10.1111/j.1556-4029.2010.01628.x.
- [21] National Center for Forensic Science, Ignitable Liquids Database, (n.d.).
<http://ilrc.ucf.edu/>.
- [22] U. of C.F. National Center for Forensic Science, Substrate Database, (n.d.).
<http://ilrc.ucf.edu/substrate>.
- [23] P.M.L. Sandercock, Fire investigation and ignitable liquid residue analysis-A review: 2001-2007, *Forensic Sci. Int.* 176 (2008) 93–110. doi:10.1016/j.forsciint.2007.09.004.
- [24] Analysis of Fire Debris Reference List Fire Debris and Explosives Subcommittee, n.d.
https://www.nist.gov/sites/default/files/documents/2018/06/14/osac_-_fire_debris_references_list.pdf.
- [25] S.S. Hetzel, Survey of American (USA) Gasolines (2008), *J. Forensic Sci.* 60 (2015).
<https://onlinelibrary.wiley.com/doi/epdf/10.1111/1556-4029.12595>.
- [26] K.R. Prather, V.L. McGuffin, R.W. Smith, Effect of evaporation and matrix interferences on the association of simulated ignitable liquid residues to the corresponding liquid standard, *Forensic Sci. Int.* 222 (2012) 242–251. doi:10.1016/j.forsciint.2012.06.010.
- [27] J.R. Almirall, K.G. Furton, Characterization of background and pyrolysis products that may interfere with the forensic analysis of fire debris, *J. Anal. Appl. Pyrolysis.* 71 (2004) 51–67. doi:10.1016/S0165-2370(03)00098-6.
- [28] J.M. Baerncopf, V.L. McGuffin, R.W. Smith, Association of Ignitable Liquid Residues to Neat Ignitable Liquids in the Presence of Matrix Interferences Using chemometric Procedures, *J. Forensic Sci.* 56 (2011) 12.
<https://onlinelibrary.wiley.com/doi/epdf/10.1111/j.1556-4029.2010.01563.x>.
- [29] E. Stauffer, Identification and characterization of interfering products in fire debris analysis, Florida International University, 2001.
- [30] N.K. Eklund, B.A. Capistran, V.L. McGuffin, R.W. Smith, Improvements in a kinetic-based model to predict evaporation of gasoline, *Forensic Chem.* 17 (2020). doi:10.1016/j.forc.2019.100194.
- [31] J. McIlroy, R. Smith, V. McGuffin, Fixed- and Variable-Temperature Kinetic Models to Predict Evaporation of Petroleum Distillates for Fire Debris Applications, *Separations.* 5 (2018) 47. doi:10.3390/separations5040047.
- [32] J.W. McIlroy, A.D. Jones, V.L. McGuffin, Gas chromatographic retention index as a basis for predicting evaporation rates of complex mixtures, *Anal. Chim. Acta.* 852 (2014) 257–266. doi:10.1016/j.aca.2014.08.055.
- [33] M.E. Sigman, M.R. Williams, Covariance mapping in the analysis of ignitable liquids by gas chromatography/mass spectrometry, *Anal. Chem.* 78 (2006) 1713–1718. doi:10.1021/ac058040e.
- [34] M. Sigman, M. Williams, Application of Chemometrics and Fast GC-MS Analysis for the Identification of Ignitable Liquids in Fire Debris Samples, 2012.
<https://www.ncjrs.gov/pdffiles1/nij/grants/240684.pdf>.
- [35] N.A. Sinkov, P.M.L. Sandercock, J.J. Harynuk, Chemometric classification of casework arson samples based on gasoline content, *Forensic Sci. Int.* 235 (2014) 24–31. doi:10.1016/j.forsciint.2013.11.014.
- [36] M.E. Sigman, M.R. Williams, R.G. Ivy, Individualization of Gasoline Samples by Covariance Mapping and Gas Chromatography/Mass Spectrometry, (2007).

- doi:10.1021/ac062230n.
- [37] R. Brehe, Overcoming Challenges in Fire Debris and Analysis Caused by Evaporation, 2015.
 - [38] J.P. Jasper, J.S. Edwards, L.C. Ford, Molecular Isotope Technologies-Arson Stable Isotope Analysis A Novel Method for Arson Accelerant Analysis: Gas Chromatography/Isotope Ratio Mass Spectrometry, n.d.
<http://www.molecularisotopes.com/asia.html>.
 - [39] J. Jasper, J. Edwards, L. Ford, R. Corry, Putting the Arsonist at the Scene: “DNA” for the fire investigator, *Fire Arson Investig.* 51 (2002) 30–34. www.micromass.co.uk.
 - [40] Z. Schwartz, Y. An, K.I. Konstantynova, G.P. Jackson, Analysis of household ignitable liquids and their post-combustion weathered residues using compound-specific gas chromatography-combustion-isotope ratio mass spectrometry, (n.d.).
doi:10.1016/j.forsciint.2013.10.010.
 - [41] S.A. Harris, M.J. Whitticar, M.K. Eek, Molecular and isotopic analysis of oils by solid phase microextraction of gasoline range hydrocarbons, n.d.
 - [42] K. Okamoto, N. Watanabe, Y. Hagimoto, K. Miwa, H. Ohtani, Changes in evaporation rate and vapor pressure of gasoline with progress of evaporation, *Fire Saf. J.* 44 (2009) 756–763. doi:10.1016/j.firesaf.2009.03.004.
 - [43] K. Okamoto, M. Hiramatsu, H. Miyamoto, T. Hino, M. Honma, N. Watanabe, Y. Hagimoto, K. Miwa, H. Ohtani, Evaporation and diffusion behavior of fuel mixtures of gasoline and kerosene, (2012). doi:10.1016/j.firesaf.2011.12.013.
 - [44] ASTM International, Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry, (2014).
<https://compass.astm.org/download/E1618.9374.pdf> (accessed April 22, 2019).
 - [45] R.W. Sabnis, Handbook of Biological Dyes and Stains: Synthesis and Industrial Applications, John Wiley and Sons, Ltd. Publication, Hoboken, NJ, 2010.
 - [46] P. Atkins, J. de Paula, J. Keeler, Atkins’ Physical Chemistry, 11th ed., Oxford University Press, 2018.
 - [47] V. Jirouš-Rajković, J. Miklečić, Heat-Treated Wood as a Substrate for Coatings, Weathering of Heat-Treated Wood, and Coating Performance on Heat-Treated Wood, *Adv. Mater. Sci. Eng.* 2019 (2019).