OVERCOMING CHALLENGES IN FIRE DEBRIS ANALYSIS CAUSED BY EVAPORATION

By

Rebecca Brehe

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ABSTRACT

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The comparison of chromatograms from fire debris and known ignitable liquid reference collections is complicated by the evaporation of the ignitable liquids during a fire, which causes chemical changes in the evaporated liquids. Although forensic laboratories include evaporated standards in their reference collections of ignitable liquids and there has been an increasing interest in the study of evaporation, there is currently no standardized method for evaporating ignitable liquids. This research investigated different factors that affect evaporation and the application of a mathematical model to fire debris analysis.

Gasoline was evaporated under different agitation conditions and in vessels with different surface areas to determine the effect of these parameters on the evaporation process. Fraction remaining plots were generated for several characteristic compounds in gasoline with a range of volatility to assess the reproducibility associated with the different factors. Ultimately, agitation was determined to generate the most reproducible data.

A previously developed mathematical model was used with three petroleum distillates and gasoline to generate theoretical chromatograms of the evaporated liquids. Pearson productmoment correlation (PPMC) coefficients were used to assess the correlation between the theoretical and experimental chromatograms. Strong correlation was observed for all three petroleum distillates, while the model showed potential for predicting the evaporation of gasoline as well.

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Chapter 1: Introduction

1.1 Arson

Arson is the intentional setting of a fire, with the intent to cause damage and destruction. According to the National Fire Incident Reporting System, approximately 1,835 intentional fires were reported in Michigan during 2014¹. These fires resulted in six deaths, over 22 injuries, and \$16,213,642 in property damage¹. Arson incidents typically involve the use of an accelerant, which is any material that increases the spread and intensity of a fire. As ignitable liquids, such as gasoline, are commonly used as accelerants, residue from these liquids can often be detected on debris from the scene of an intentional fire. Fire debris analysts are responsible for determining if an ignitable liquid is present in fire debris samples submitted to the forensic laboratory.

1.2 Fire Debris Analysis

In the laboratory, ignitable liquids are typically extracted from fire debris samples through passive-headspace extraction before being analyzed by gas chromatography-mass spectrometry (GC-MS) with the primary goal of determining if an ignitable liquid is present in the debris. To do this, the total ion chromatograms (TICs) of the submitted sample and suitable reference standards are compared based on retention time. In addition, for every compound present in the sample, a mass spectrum is obtained, which can be used to identify the compounds. Once the identities of all major compounds in the submitted sample are known, the chemical class of the liquid can be determined, following the classification system defined by the American Society for Testing and Materials (ASTM) International². The eight ASTM classes (Table 1-1) are based on chemical composition of the liquid and include gasoline, petroleum distillates, isoparaffinics, naphthenic paraffinics, aromatics, normal alkanes, oxygenated solvents, and miscellaneous.

Table 1-1. ASTM Classification²

Class	Composition	Light (C ₄ – C ₉)	Medium $(C_8 - C_{13})$	Heavy $(C_8 - C_{20+})$
Gasoline – all brands, including gasohol	$\begin{array}{c c} C_{3} \ \ alightarrow constraints} \\ C_{3} \ \ alightarrow constraints} \\ C_{3} \ \ alightarrow constraints} \\ \hline \\ C_{3} \ \ alightarrow constraints} \\ \hline \\ Fresh \ gasoline \ is \ typically \ in \ the \ range \ of \ constraints \\ \hline \\ C_{3} \ \ alightarrow constraints \\ \hline \ alightarrow constraints \\ \hline \\ C_{3} \ \ alightarrow constraints \\ \hline \\ C_{3} \ \ alightarrow constraints \\ \hline \ alightarrow c$		ge of $C_4 - C_{12}$	
Petroleum Distillates	Homologous series of <i>n</i> -alkanes; other compounds less abundant	Petroleum ether, cigarette lighter fluids, camping fuels	Charcoal starters, paint thinners, dry cleaning solvents	Kerosene, diesel, jet fuels, charcoal starters
Isoparaffinic products	Branched chain (isoparaffinic); cyclic and <i>n</i> -alkanes absent or insignificant	Aviation gas, specialty solvents	Charcoal starters, paint thinners, copier toners	Commercial specialty solvents
Aromatic products	Aromatic compounds; aliphatic compounds absent or insignificant	Paint and varnish removers, automotive parts cleaners, xylenes	Automotive parts cleaners, insecticides; fuel additives	Insecticides, industrial cleaning solvents
Naphthenic paraffinic products	Branched chain and cyclic alkanes; <i>n</i> -alkanes absent or insignificant	Cyclohexane-based solvents/products	Charcoal starters, insecticides, lamp oils	Insecticides, lamp oils, industrial solvents
<i>n</i> -Alkane products	Only <i>n</i> -alkanes, usually less than 5	Solvents, pentane, hexane, heptanes	Candle oils, copier toners	Candle oils, carbonless forms, copier toners
Oxygenated solvents	Alcohols, esters, ketones; major components include xylene and toluene	Alcohol, ketones, lacquer thinners	Lacquer thinners, industrial solvents	
Miscellaneous	Liquids that cannot be classified	Single component liquids, blended products	Turpentine and blended products	Specialty and blended products

For example, petroleum distillates are dominated by normal (*n*) alkanes with other compounds present at substantially lower abundance (Table 1-1). In contrast, a naphthenic paraffinic contains mainly branched and cyclic alkanes with *n*-alkanes present at substantially lower abundance (Table 1-1). Each class, with the exception of gasoline, can be further subcategorized based on the range of *n*-alkanes present in the liquid. For example, a petroleum distillate containing butane (C_4) – nonane (C_9) would be a light petroleum distillate, while one containing *n*-alkanes ranging from octane (C_8) – tridecane (C_{13}) would be a medium petroleum distillate (Table 1-1). Finally, a petroleum distillate containing octane (C_8) – eicosane (C_{20}) would be considered a heavy petroleum distillate (Table 1-1). Some liquids may contain a range of normal alkanes that spans two subclasses. For example, a petroleum distillate containing *n*-alkanes from heptane (C_7) – undecane (C_{11}) would be classified as a light to medium petroleum distillate (Table 1-1).

Using these procedures, any ignitable liquid present in the fire debris can be identified. However, the interpretation of the fire debris evidence can be extremely difficult due to several factors that can easily complicate the comparison of chromatograms and mass spectra and the subsequent identification of ignitable liquids. Although pyrolysis and substrate interferences affect the interpretation, the focus in this research will be on evaporation and the challenges this can cause in the interpretation of ignitable liquids in fire debris.

During a fire, the temperature increases, causing the compounds within a liquid to change from a liquid into a gas, through a process known as evaporation (Figure 1-1). Compounds with a lower boiling point will evaporate first, as their boiling point will be reached before those compounds with higher boiling points. Although the compounds can become gaseous regardless of their position in the liquid, only those at the surface of the liquid can evaporate. As the more

volatile compounds, or those with low boiling points, completely evaporate from the liquid, the less volatile compounds will begin to evaporate until only the most stable compounds remain.



Figure 1-1. General diagram of evaporation: the lower phase is liquid, the upper phase is gas, the star represents a volatile molecule moving from the liquid phase to the gas phase, and the equation representing the shift from liquid to gas

Ignitable liquids evaporate readily, making them ideal accelerants. However, evaporation changes the chemical composition of the liquids, resulting in chromatograms of fire debris that look completely different, depending on the concentration or volume of liquid present, from the chromatograms of the reference standards (Figure 1-2). The more volatile compounds, which have lower boiling points, will evaporate at a faster rate than compounds with higher boiling points (Figure 1-2). As a result, depending on the ignitable liquid used in an arson, the majority of the liquid may be completely evaporated by the time the fire is extinguished and the debris is sent to the laboratory for analysis. For example, gasoline is commonly used as an accelerant due to its accessibility and high volatility (Figure 1-2). Unevaporated gasoline, shown in Figure 1-2A, contains toluene, C_2 -alkylbenzenes including ethylbenzene, *p*-xylene, and *o*-xylene,



Figure 1-2. Chromatogram of (A) unevaporated and (B) 90% evaporated gasoline. The axis of chromatogram B is expanded to show the characteristic compounds of gasoline

C₃-alkylbenzenes including propylbenzene and 1,2,4-trimethylbenzene, C₄-alkylbenzenes including 1,2,4,5-tetramethylbenzene and 1-methyl-4-(2-propenyl)benzene, and two methylnaphthalenes (1-methylnaphthalene and 2-methylnaphthalene) in relatively high abundance. The presence of these compounds is required to identify a liquid as gasoline, according to ASTM guidelines². Additionally, certain ratios of peak abundances for alkylbenzenes (e.g. 1:3:1 ratio for the C₂-alkylbenzenes) must be observed along with the presence of the methylnaphthalenes in a 2:1 ratio³. However, in 90% evaporated gasoline (Figure 1-2B), toluene and all of the compounds are substantially reduced in abundance compared to the unevaporated liquid. As a result, at this high level of evaporation (90%), it can be extremely difficult to identify the liquid as gasoline due to the effects of evaporation.

1.3 Evaporation of Ignitable Liquids

To address this issue of evaporation, forensic laboratories include evaporated and unevaporated standards in their reference collection of ignitable liquids. The National Center of Forensic Science (NCFS) maintains the national Ignitable Liquid Reference Collection (ILRC) in compliance with the Scientific Working Group/Technical Working Group for Fire and Explosions (SWG/TWGFEX). This reference collection contains over 500 liquids that represent all eight ASTM classes⁴. Additionally, for each unevaporated standard in the database, there are 2 - 4 samples of the liquid that have been evaporated to different levels (*e.g.* 25, 50, 75, 90, or 95% evaporated by volume). The database includes the chromatogram for each unevaporated and evaporated standard for comparison to the chromatogram of submitted samples. In addition to the chromatogram, analysts can request samples of liquids for analysis in their own laboratories for inclusion into their individual reference collections.

However, evaporation affects not only the evaporation of ignitable liquids in the fire debris samples but also the evaporation of the ignitable liquid standards in the laboratory reference collections. Regardless of the controlled environment used to generate the evaporated standards, chemical changes will occur, altering the overall composition of the evaporated liquid. Depending on the conditions used for evaporation, the accuracy and reproducibility of the evaporation process could be affected. Although each forensic laboratory has its own protocol for generating a reference collection of ignitable liquids, there is no standardized method used by all forensic laboratories. In fact, although a few laboratories provide their standard operating procedures (SOPs) for the analysis of fire debris evidence, there is no mention of how the ignitable liquids in the reference collection are evaporated^{5, 6, 7}.

Many research groups have conducted experiments in the area of evaporation. Although the majority of the research was conducted on oil samples for environmental applications, it is still relevant to the discussion of the evaporation of ignitable liquids as many of the ignitable liquids in the ASTM classes originate from crude oil. Throughout the literature on the study of evaporation, many different methods are used to generate the evaporated liquids.

The liquids may be evaporated passively or actively under nitrogen⁸. Passive evaporation involves allowing a liquid to evaporate at its natural rate, without any additional air flow. As a result, the volatile molecules will accumulate and evaporate above the liquid surface. Active evaporation involves the flow of nitrogen blowing down onto the liquid, creating a vortex at the surface of the liquid. The vortex at the surface agitates the upper portion of the liquid, allowing the evaporation of additional volatile molecules trapped below the surface of the liquid. As more molecules rise to the surface and evaporate into the atmosphere, their abundances in the resulting chromatogram will be lower. As with passive evaporation, the evaporating volatile molecules

will accumulate above the surface of the liquid. However, the flow of nitrogen removes the accumulated volatile molecules, shifting the equilibrium reaction toward evaporation. Therefore, active evaporation causes the volatile molecules to evaporate at their natural rate without the limitations caused by diffusion. While the NCFS generates evaporated standards for the ILRC using active evaporation³, only Kuk and Spagnola actively evaporated their samples under nitrogen⁹. The other research groups, including Hetzel, Malmquist *et al.*, and Zorzetti and coworkers, used passive evaporation for their evaporated samples^{10, 11, 12}.

There is currently no standard vessel used for evaporation. For example, liquids may be evaporated in a graduated cylinder, a beaker, or a Petri dish⁸. Not only do the vessels themselves differ in size and shape, but the exposed surface area available for evaporation and the thickness, or depth, of the liquid varies as well, depending on the dimensions of the vessel being used. For example, 10 mL of a liquid in a Petri dish with dimensions 60 x 15 mm would resemble a thin film covering the bottom of the dish with an exposed surface area of $\sim 32.9 \text{ cm}^2$, while 10 mL of that same liquid in a 10-mL graduated cylinder with a diameter of 1.2 cm and a height of 7.80 cm would have a very narrow surface area of ~ 1.1 cm² available for evaporation. Furthermore, the thickness of the liquid in this particular Petri dish might be ~ 0.1 cm, while the thickness of this same liquid might be 7.80 cm in the graduated cylinder. A smaller exposed surface area combined with a larger distance for the molecules to travel in order to evaporate will decrease the rate of evaporation, resulting in more abundant compounds in the chromatogram. The NCFS evaporates the liquid standards for the ILRC in graduated microvials⁴, while Sandercock and coworkers generated evaporated samples of gasoline in 7 mL vials¹³. Hetzel used 18 x 150 mm test tubes as vessels for evaporation¹⁰. All three of these vessels have exposed surface areas and liquid thicknesses similar to that of a graduated cylinder. However, Malmquist et al. performed

their evaporation experiments in Petri dishes¹¹, while Okamoto *et al.* performed multiple studies using liquid samples evaporated in an open tray, which has an exposed surface area similar to that of a Petri dish^{14, 15, 16}.

Another factor that can affect evaporation is the use of agitation. Molecules can only evaporate into the environment from the surface of the liquid. By changing the rate of agitation, the evaporation rate for each compound may be altered. For example, increasing the agitation rate will allow volatile molecules near the bottom of the liquid to rise to the surface, evaporating into the environment. As a result, the evaporation rate will not be limited by diffusion, decreasing the amount of time necessary for evaporation to occur. Although the studies performed by both Fingas and Heymes *et al.* involved evaporating samples under windy and non-windy conditions^{17, 18}, no studies used agitation during the evaporation process.

Although there are multiple ways to address the need for a standardized method for evaporating liquids, only two methods will be addressed in this thesis. The first method focuses on investigating the different factors that are known to affect the rate of evaporation to ensure the most accurate representation of the ignitable liquid standards possible. The second method involves the use of a model to mathematically generate chromatograms of evaporated liquids based only on the unevaporated ignitable liquid standard. By using a mathematical model, all of the potential influences on the evaporation process are eliminated.

1.4 Development of the Mathematical Model

The mathematical model developed by McIlroy *et al.* was originally developed for environmental purposes and used diesel fuel that was passively evaporated in a thin film as its basis^{19, 20}. The model, which can predict the fraction remaining for individual compounds, was originally designed for use in determining the behavior of crude oil in large scale oil spills. By

predicting the fraction remaining for each compound within the diesel fuel, the fraction remaining of the total fuel could be estimated at different time and temperature intervals.

To develop the model, a thin film of diesel fuel on top of water in a Petri dish was passively evaporated at room temperature inside an evaporation chamber. Samples were taken at nine different time points throughout the evaporation process^{19, 20}. The evaporated samples were then analyzed by GC-MS. Retention indices were calculated for all of the compounds in the diesel sample.

Decay curves were generated for four different classes of compounds (*n*-alkanes, branched alkanes, alkyl benzenes, and polycyclic hydrocarbons) present in diesel by plotting the evaporation time versus the abundance, which was normalized to the peak height of the *n*-alkane, C₂₁. Decay curves for the *n*-alkanes C₁₀, C₁₂, and C₁₄ are shown in Figure 1-3. Decane (boiling point 174.1 °C) evaporates rapidly and is almost fully evaporated after 150 hours. Dodecane (boiling point 216.2 °C) and tetradecane (boiling point 253.5 °C) do not evaporate as readily. From these data, the first-order kinetic rate constants, k, were calculated using non-linear regression, shown in Equation 1-1,

$$C_t = C_0 \exp(-kt)$$
 Equation 1-1

where C_t is the concentration of the compound at a certain time (t) and C_0 is the initial concentration of the compound. The calculated rate constants decrease as the volatility of the compound decreases. For example, C_{10} has a faster rate constant than C_{12} , and C_{14} has a rate constant of zero, indicating that its concentration does not change noticeably over 300 hours.

The rate constants were plotted as a function of retention index and modeled using multiple linear regression (Equation 1-2),

$$\ln(k) = -1.04 \times 10^{-2} I + 6.70$$
 Equation 1-2

where ln (k) is the natural log of the rate constant, -1.04×10^{-2} and 6.70 are constants representing the slope and intercept, respectively, and I is the retention index. Retention index was used for the model because it has a linear relationship with boiling point, making it advantageous over retention time. Retention index is based on the number of carbons in the *n*alkane (n), the retention time of the compound of interest (t_x), and the retention times of the normal alkanes eluting before and after the compound (t_n and t_{n+1}, respectively), shown in Equation 1-3.



$$I = 100n + 100 \times \frac{(t_x - t_n)}{(t_{(n+1)} - t_n)}$$
 Equation 1-3

Figure 1-3. Decay curve for decane (C₁₀), dodecane (C₁₂), and tetradecane (C₁₄) in diesel evaporated at 20 °C^{19, 20}

Retention index has several advantages compared to retention time because retention index is not affected by many gas chromatography parameters that affect retention time, such as mobile phase flow rate, column dimensions, and oven temperature program. The regression models for each of the four chemical classes were then combined into a comprehensive regression model (Figure 1-4).



Figure 1-4. Rate constant (k) as a function of retention index (I) for compounds in diesel: *n*-alkanes (squares), branched alkanes (circles), alkyl benzenes (diamonds), and polycyclic hydrocarbons (triangles)^{19, 20}

The rate constants were then used to predict the fraction remaining for each individual compound in diesel. The fraction remaining (F) of each compound was calculated using the rate constant (k) calculated from Equation 1-2, and time (t), shown in Equation 1-4.

$$F = \exp(-kt)$$
 Equation 1-4

The fraction remaining ranged from 0 to 1, with 1 indicating no evaporation and 0 indicating complete evaporation. The fraction remaining for each individual retention index was then used to generate the fraction remaining curve, which showed the fraction remaining for the total fuel.

The fraction remaining curve was used to generate the compound distribution in the chromatogram after evaporation using just the chromatogram of the unevaporated liquid.

The chromatogram of an unevaporated liquid, such as diesel (Figure 1-5A), was multiplied by the fraction remaining curve for that liquid (Figure 1-5B) to generate theoretical chromatograms of the liquid corresponding to different evaporation levels. These theoretical chromatograms were compared to the corresponding experimental chromatogram (Figure 1-6). McIlroy *et al.* used Pearson product-moment correlation (PPMC) coefficients (discussed in Chapter 2, Section 2.4) to assess the similarity between the theoretically derived chromatograms and the experimentally obtained chromatograms^{19, 20}. A strong correlation was observed between each set of experimental and theoretical chromatograms, indicating that the model was extremely accurate at predicting the evaporation of diesel.

Although the model was validated with kerosene (a petroleum distillate) and marine fuel stabilizer (a naphthenic paraffinic product), the primary focus was on the environmental applications, which involves determining the time necessary for evaporation, rather than the forensic applications, which emphasizes the level of evaporation instead of the time. As a result, the model needs to be applied to additional classes of ignitable liquids, particularly gasoline, to be applicable in forensic laboratories.

1.5 Research Objectives

The first objective in this research was to investigate the effect of various factors on the reproducibility of the evaporation process. Gasoline was selected for this initial investigation due to its high volatility and common use as an accelerant. Gasoline was actively evaporated under nitrogen to different levels by volume, under different conditions, before being analyzed by GC-MS. The evaporated samples were generated with and without agitation in both a graduated



Figure 1-5. (A) Experimental unevaporated diesel chromatogram and (B) Fraction remaining (F) curve calculated according to equation 1-3 and 1-4



Figure 1-6. Overlaid experimental and theoretical chromatograms for diesel evaporated for 100 hours at 20 °C

cylinder and a Petri dish, and the mass lost for each sample was determined. For the agitated samples, three different agitation rates and three different shaped stir bars were investigated.

The second objective in this research was to investigate the application of the previously developed mathematical model for fire debris analysis. The model was used to mathematically generate chromatograms for three petroleum distillate standards and one gasoline standard based solely on the corresponding chromatogram of the unevaporated liquid. Chromatograms corresponding to four different evaporation levels were generated using the model based on the experimental fraction remaining by mass. PPMC coefficients were then used to compare the theoretical chromatograms to experimentally derived chromatograms to assess the utility of the mathematical model for this application.

By determining the factors that affect the evaporation of ignitable liquid reference standards, this research will provide the first step in developing a standardized method for generating reference standards evaporated to different levels for inclusion in databases. This research will also be the first step in assessing the utility of a previously generated mathematical model for applications in fire debris analysis. REFERENCES

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Chapter 2: Instrument and Data Analysis Theory

2.1 Instrumentation: Gas Chromatography (GC), Mass Spectrometry (MS), and Flame Ionization Detector (FID)

2.1.1 Gas Chromatography (GC)

Chromatography techniques involve the separation of compounds that is achieved via interactions with a stationary and a mobile phase. The mobile phase is typically a gas or a liquid that carries the compounds through the stationary phase, which is usually a liquid or a solid. Although there are many types of chromatography, gas chromatography is most commonly used for the analysis of fire debris evidence. Gas chromatography (GC) is based primarily on the partitioning of an analyte between a gaseous mobile phase and a liquid stationary phase, which is thinly coated onto the inner wall of a capillary column. The general diagram of a GC coupled to a mass spectrometer, which is commonly used in forensic laboratories, is shown in Figure 2-1.

A liquid sample is injected into the instrument through a heated (typically 250 °C) injector port using a microsyringe. There are two different types of injection: splitless and split. A splitless injection refers to the injection of the entire volume of the sample, with none of the sample being sent to waste. A split injection (typically 50:1 or 100:1) involves the division of the sample being injected into the column. As the ratio of the split increases, the amount of sample that enters the column decreases. A split injection is commonly used when a sample is concentrated or if the concentration is unknown, in order to avoid overloading or contaminating the system, while a splitless injection is necessary for low concentration samples.

The vaporized sample is then carried through the column by the flow of the mobile phase (typically 1 mL/min). Helium is commonly used as the mobile phase, or carrier gas, because it is inert and does not interact with the compounds being separated. However, the choice of carrier



Figure 2-1. General diagram for a gas chromatograph-mass spectrometer

gas may depend on the type of detector being used. The compounds within the sample will elute, or travel through the column to the detector, at different rates based, primarily, on boiling point and, secondarily, on the interactions between each compound and the column stationary phase. Depending on the composition of the column stationary phase, certain compounds will interact more than others. A column containing a 5%-diphenyl-95%-dimethylpolysiloxane stationary phase is commonly used in forensic laboratories. The phenyl groups give the stationary phase slightly polar characteristics, which influences the elution of certain types of compounds such as aromatics and polycyclic hydrocarbons. A column with a 100% poly(dimethylsiloxane)

stationary phase is the most non-polar commercially available stationary phase, resulting in compounds eluting based solely on boiling point. Additionally, oven temperature programs are commonly used to improve the separation and reduce the amount of time a sample spends in the column.

As GC is a separation-based technique, it is subject to the effects of the Golay equation (Equation 2-1), which is typically utilized to optimize the separation of analytes in the sample.

$$H = \frac{B}{\mu} + (C_s + C_m)\mu \qquad \text{Equation 2-1}$$

The B term, which is related to the longitudinal diffusion caused by the migration of analytes from an area of high concentration to an area of low concentration, is extremely important in GC separations. The diffusion rate depends on numerous variables, including temperature and the solute-solvent system. As the samples in GC are gaseous in the mobile phase, the rate of diffusion is much faster (1 to 0.1 cm²/sec) than if the compounds were liquid. The use of lower oven temperatures or an oven temperature program can minimize the B term by lowering the diffusion coefficient of the analytes. The C terms are related to the mass transfer between the mobile and stationary phases. The C_s term is affected by the thickness of the stationary phase film, while the C_m term is related to the mass transfer in the mobile phase. As the films used in this GC system are very thin, the C_s term is negligible. However, the C_m term is still a factor. One way to reduce the C_m term is to use a column with a narrower inner diameter.

The sample moves through the column, and analytes are separated based on boiling point. Each separated analyte reaches the detector, taking a different amount of time to travel through the system, which is known as the retention time of the analyte. The more volatile analytes, or those with lower boiling points, will reach the detector before the less volatile analytes. One of the outputs from a GC analysis is a chromatogram, which is a plot of abundance on the y-axis

and retention time on the x-axis. Each separated analyte is present as a peak in the chromatogram, shown in Figure 2-2. The ideal chromatographic peak will be Gaussian in appearance, although misshapen peaks are not uncommon due to the effects of non-linear isotherms and some extra-column sources, such as the injection and detection volumes. The x-axis represents the retention time, or the time it takes for each compound to travel through the column to the detector. The height of each peak is dependent on the concentration, or amount, of that compound present in the original sample. Therefore, the relative abundances, or peak heights, can provide information about the ratio of compound concentrations within the sample.

While GC separates compounds and provides qualitative and quantitative information about each compound, GC alone cannot be used to definitively identify a compound because it does not provide structural information. Therefore, it must be combined with some type of detector that can be used for identification purposes. One such type of detector is the mass spectrometer.



Figure 2-2. Chromatogram generated from gas chromatographic analysis

2.1.2 Mass Spectrometry (MS)

As the sample moves through the column encased within the transfer line, it passes through the heated interface (typically 280 °C) between the GC and the MS detector. This allows a continuous introduction of sample into the MS from the GC column. Although there are many types of detectors, ionization methods, and mass analyzers, only the system most commonly used in forensic laboratories will be discussed here. The entire system is under vacuum to achieve low pressure, which is essential to generate ions and electrons. Pressures typically range from 10^{-2} to 10^{-5} Pa to minimize the chance for collisions within the mass analyzer.

Once the sample moves completely through the interface, it enters the ionization chamber (Figure 2-3), where electron ionization occurs. In electron ionization, a high-energy beam of electrons (e⁻) bombards the sample (M) entering the chamber, causing the sample to lose electrons, resulting in positively charged ions. The molecular ions (M⁺) then fragment due to an excess of energy, producing fragment ions. However, each molecule will fragment differently, resulting in unique fragmentation patterns.



Figure 2-3. General diagram of electron ionization chamber

The charged ions then travel into the quadrupole mass analyzer (Figure 2-4), which consists of four rods arranged in a diamond shape. Each pair of parallel rods has the same charge, with one pair being positively charged and the other pair being negatively charged. Due to the different charges, an electromagnetic field forms and is able to separate ions based on their massto-charge (m/z) ratio due to a combination of radiofrequency (RF) and direct-current (DC) fields. Depending on the m/z of the ions, certain ions with collide with the rods and be pumped away by the vacuum system, while other ions will maintain a steady trajectory and pass through the center of the mass analyzer to the detector. For each set of RF/DC voltages, only a specific range of m/z values will be allowed through the entire mass analyzer. By scanning all RF/DC voltages, ions with different m/z values will be allowed to reach the detector. This method results in the full mass range being scanned in order to generate the mass spectrum of the sample.



Ion Source



Once the ions with different m/z ratios have been separated, they enter the detector, which detects the relative abundance of each ion. In order to accurately detect all of the ions flowing through, the detector converts the signal from the ions into an electric current, which represents the abundance of the detected ions at a specific m/z value at any given point in time. In order to increase the sensitivity of the MS detector, an electron multiplier is used to magnify the signal from each ion. An electron multiplier, shown in Figure 2-5, consists of a series of flat metal dynodes coated with lead oxide, arranged in a funnel-like pattern. As each ion enters the detector, it will collide with one of the plates, resulting in the emission of electrons. Due to different potentials applied to each plate, the electrons will collide with the next plate, resulting in additional emissions of electrons. As each collision occurs, the quantity of electrons emitted increases, causing an amplification effect. The amplified current from the electrons can then be detected. Although the electron multiplier does result in increased sensitivity, it does not uniformly respond to ions of all masses.



Figure 2-5. General diagram of electron multiplier

Mass spectrometry can be used to definitively identify compounds because it provides structural information about the chemical composition of the compound. When each compound fragments during the ionization process, the resulting fragmentation pattern is unique to that
compound under those specific conditions. As a result, the mass spectrum, shown in Figure 2-6, for each compound can be viewed as that compound's fingerprint, allowing for definitive identification. The mass spectrum consists of a series of peaks, each of which correspond to a specific m/z ratio. Each m/z ratio, in turn, represents a specific fragmented portion of the original compound. The height of each peak represents the abundance of that particular fragment ion. The molecular ion peak (M^+) corresponds to the molecular mass of the compound, helping with identification. The most abundant peak, known as the base peak, is the most commonly formed fragment ion for a specific compound.



Mass-to-charge (m/z)



Each peak in the chromatogram results in its own mass spectrum. The mass spectrum of each peak is then compared to known mass spectra in a reference library in order to identify the compound. By looking at each mass spectrum, all of the compounds in the sample can be identified.

2.1.3 Flame Ionization Detector (FID)

Another type of detector used with gas chromatography is the flame ionization detector (FID). Like the mass spectrometer, which is considered a universal detector, the FID is also a universal detector and is very sensitive with a dynamic range of 10^7 and a sensitivity range of 10 – 100 pg.

A general schematic for the FID is shown in Figure 2-7. As the compounds exit the column, they enter the FID where they are combusted by a hydrogen flame, forming ions. Although ions are formed in both FID and MS detectors, the ions are not separated prior to entering the FID and, therefore, are detected all at the same time. As a result, FID cannot be used for definitive identification as structural information is not provided due to the lack of separation. The ions move to the collector, which contains two plates. A potential difference is applied to the plates. As analyte ions begin to enter the collector, the current increases, and the new current is detected. Therefore, the current is dependent on the presence of ions in the collector. Although the FID is insensitive to water and carbon dioxide, the temperature of the detector must be high enough that condensation does not occur due to the combustion process. The resulting signal is determined by the number of carbon atoms in the flame.

2.2 Correlation Optimized Warping (COW) Alignment

Correlation optimized warping (COW) alignment is a type of retention-time alignment, designed to correct for natural shifts in the apex of chromatographic peaks due to drifts in

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Figure 2-7. General diagram of flame ionization detector (FID)

retention time. These drifts in retention time can be caused by changes in the mobile phase flow rate, injection volume, and column length. This process aligns chromatographic data by performing piecewise linear stretching and warping of the retention time axis in each chromatogram². One chromatogram is used as the target and must contain all of the compounds present in the chromatograms being aligned. The other chromatograms are then adjusted to align with the target, one at a time. Each chromatogram is split into equal-sized segments, which may vary depending on the software program being used. In order to properly align the chromatograms, a certain number of data points, known as the warp or slack, are either added or subtracted until the apex of each peak in every segment of the chromatogram is aligned with the corresponding peak apex in the target chromatogram segments. Although data points are added or removed, no chemical information is lost or added, and each individual segment remains in the same position in the overall chromatogram. The alignment is then evaluated by determining the correlation coefficient between each individual segment in the chromatogram compared to the corresponding segment in the target chromatogram².

The segment size and warp are user-defined parameters, although guidelines exist for selecting these features. Typically, the segment size is first chosen to match the number of data points across a peak, and a small warp, which consists of only a few data points, is used. Depending on the amount of adjustment necessary, the segment size and warp are varied one at a time until the optimal parameters are determined³. To assess the alignment, local correlation of each segment is determined, followed by global correlation of the aligned data.

2.3 Retention index

Kováts introduced the concept of retention indices, after demonstrating the linear relationship between retention of normal alkanes on a non-polar stationary phase and boiling point (Figures 2-8 to 2-10)⁵. As a result, retention indices can be calculated for compounds in a chromatogram based on the retention times of the compounds of interest (t_x) and the retention times of the normal alkanes eluting before and after the compounds (t_n and t_{n+1} , respectively), within the same injection, as shown in Equation 2-2. This equation is only applicable for separations under temperature programmed conditions.

$$I = 100n + 100 * \frac{(t_x - t_n)}{(t_{(n+1)} - t_n)}$$
 Equation 2-2



Figure 2-8. Plot of retention index versus boiling point showing linear relationship^{6,7}



Figure 2-9. Chromatogram of unevaporated diesel with retention time on the x-axis⁷



Figure 2-10. Chromatogram of unevaporated diesel with retention index on the x-axis⁷

Retention index is broadly applicable and advantageous over retention time. It is independent of many GC parameters, including changes in the mobile phase flow rate, stationary phase film thickness, column diameter and length, injection volume, and oven temperature programs, which greatly affect retention time. Retention index can then be used to compare chromatograms obtained using different GC methods or instrumentation.

2.4 Pearson Product-Moment Correlation (PPMC) Coefficients

Pearson product-moment correlation (PPMC) coefficient (r) is commonly used to measure the extent of association between two data sets. In this study, PPMC coefficients are used to assess similarity, or otherwise, between two chromatograms. Specifically, they perform a pointby-point comparison between each point in one chromatogram (x_i) and the corresponding point in the second chromatogram (y_i) . The equation for calculating PPMC coefficients is shown in Equation 2-3.

$$r = \frac{\sum[(x_i - \bar{x})(y_i - \bar{y})]}{\sqrt{\sum(x_i - \bar{x})^2} \sqrt{\sum(y_i - \bar{y})^2}} \qquad \text{Equation 2-3}$$

The variables x_i and y_i represent the same specific data point in each of the chromatograms being compared, while the \overline{x} and \overline{y} represent the average data points in the two chromatograms, respectively. In essence, the PPMC coefficients are calculated by dividing the summation of the differences between each specific data point and the averages in both chromatograms by the summation of the standard deviations from each chromatogram. Therefore, the PPMC coefficients demonstrate how the two variables vary together by determining the covariance, or the numerator, and how they vary independently by determining the variance, or the denominator (Equation 2-3)⁴. Although instrument replicates should theoretically have a correlation of 1, indicating perfect correlation, this will only rarely occur due to instrumental drift and other minute differences. PPMC coefficients range from 1 to 0 with any value $\pm 0.99 - 0.8$ indicating a strong correlation. Moderate correlation relates to PPMC coefficients ranging from $\pm 0.79 - 0.5$, and weak correlation relates to PPMC coefficients $< \pm 0.5$. A correlation value of 0 indicates no correlation between the two variables. A positive correlation indicates that both points of comparison have similar behavior, while a negative correlation indicates that one point is rising while the other is falling.

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Chapter 3: Factors Influencing the Evaporation of Gasoline

3.1 Introduction

Numerous factors, such as the rate of agitation and the exposed surface area available for evaporation, influence the evaporation of gasoline. In this chapter, several studies were conducted to determine the effect of each of these factors on the reproducibility of gasoline after evaporation. As evaporation can complicate the identification of ignitable liquids, especially for volatile liquids such as gasoline, the standards used for comparison need to be as accurate and reproducible as possible. By determining the effect of these different factors on the evaporation process, forensic laboratories can begin to develop a more standardized method for the evaporation of the standards in the ignitable liquid reference collections.

3.2 Materials and Methods

3.2.1 Collection and Preparation of Gasoline Samples

Two samples of gasoline, collected approximately six months apart, were used for these experiments. Both gasolines were collected from the same gas station in the East Lansing, MI area.

A ten-milliliter graduated cylinder (product number 70075-10, Corning, Inc., Corning, NY), containing a stir bar and covered with a piece of aluminum foil, was weighed on an analytical balance (serial number 60403, Mettler H80, Columbus, OH), and the mass recorded. Ten milliliters of gasoline were poured into the graduated cylinder, and the new mass was recorded. The cylinder was then placed in the center of a stir plate (model number S130815, Thermo Scientific, Waltham, MA) in the fume hood. The gasoline was actively evaporated using house nitrogen for all experiments, but was agitated at different rates using different stir bars and vessel dimensions, depending on the specific conditions of the experiment. Samples of gasoline were

individually evaporated to approximately 25%, 50%, 75%, and 90% by volume. Once the desired volume was reached, the graduated cylinder was removed from the fume hood and the remaining liquid was poured into a pre-weighed vial and capped. The vial was re-weighed, and the new mass recorded. Finally, the foil was replaced on top of the cylinder, and the cylinder was reweighed to determine the mass of residual gasoline present. Based on these masses, the mass of gasoline evaporated was determined and recorded. Although evaporation level was determined by volume and by mass, the latter was used throughout to increase the accuracy of the denoted evaporation level. The graduated cylinder and stir bar were then thoroughly rinsed with dichloromethane (HPLC/UHPLC grade, J.T. Baker, Avantor Performance Materials, Inc., Center Valley, PA) before being left to air dry.

Following evaporation, ten microliters of each sample were transferred into a two-milliliter volumetric flask and diluted with dichloromethane to the calibrated mark. The diluted liquid was transferred into a vial and analyzed by GC-MS.

3.2.2 Evaporation of Gasoline Samples

The first two studies were conducted using a small stir plate (model number S130815, Thermo Scientific), which enabled the evaporation of one experimental replicate at a time. The first study investigated the effect of agitation rate on the evaporation of gasoline. Three separate experiments were performed, in each case using a spinfin® stir bar (product number F371250012, Bel-Art Products, Inc., Wayne, NJ) with different agitation rates, corresponding to speed settings of 7 (109 \pm 2 rpm), 9 (134 \pm 2 rpm), and 11 (199 \pm 2 rpm), respectively. For each agitation rate, the gasoline was evaporated to the aforementioned levels in triplicate, generating three experimental replicates.

The second study investigated the effect of different shaped stir bars, shown in Figure 3-1, on

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the evaporation of gasoline. Three experiments were performed, one using a spinfin® stir bar (product number F371250012, Bel-Art Products, Inc.), one using a spinvane® stir bar (product number F371340000, Bel-Art Products, Inc.), and one using a micro stir bar (product number F371190002, Bel-Art Products, Inc.). Again, the gasoline was evaporated to the four different levels in triplicate, generating three experimental replicates for each stir bar shape.



Figure 3-1. Images of the spinfin[®], the spinvane[®], and the micro stir bars, respectively¹

Non-agitated samples of evaporated gasoline were obtained for comparison to the agitated samples from the two agitation studies. The gasoline was actively evaporated under nitrogen in the same graduated cylinder to the four different levels in triplicate, resulting in three experimental replicates.

The final study involved the evaporation of gasoline in a Petri dish (part number 3160-60BO, Corning, Inc., Corning, NY) without agitation. Again, the gasoline was evaporated to the four different levels in triplicate, generating three experimental replicates.

3.2.3 GC-MS Analysis

The unevaporated and evaporated gasoline samples were analyzed using an Agilent 6890N GC coupled to a 5975 MSD with an Agilent 7683B automatic liquid sampler (Agilent Technologies, Palo Alto, CA). A 1 μ L injection volume was injected in pulsed (0.25 min at pressure 15.0 psi) splitless mode into the injection port, which was heated to 250 °C. Ultra high-purity helium (Airgas Great Lakes, Independence, OH) was used as the carrier gas with a

nominal flow rate of 1 mL/min. A 5% diphenyl-95% dimethylpolysiloxane stationary phase (30 m × 0.25 mm × 0.25 μ m), was used with the following oven temperature program: 40 °C for 3 min, 10 °C/min to 280 °C, with final hold for 4 min. A transfer line temperature of 280 °C was also used. The mass spectrometer used electron ionization (70 eV, 230 °C) and a quadrupole mass analyzer (150 °C), with a mass scan range of 50 – 550 amu and a scan rate of 2.91 scans/s. *3.2.4 Data Analysis*

The total ion chromatograms (TICs) were exported from the ChemStation software (version E.01.01.335, Agilent Technologies) to Microsoft Excel 2007 (Microsoft Corporation, Redmond, WA) for further processing. The data were normalized to the maximum peak height of 2methylnaphthalene with the assumption that 2-methylnaphthalene does not evaporate. However, this is not completely true. Due to its boiling point of 241.1 °C, 2-methylnaphthalene is somewhat volatile and will be affected by evaporation. Therefore, the normalization may be affected by the slight evaporation of 2-methylnaphthalene.

To investigate the effect of each parameter on the evaporation of gasoline, the following compounds were considered: toluene, *p*-xylene (a C_2 -alkylbenzene), 1,2,3-trimethylbenzene (a C_3 -alkylbenzene), and 1,2,4,5-tetramethylbenzene (a C_4 -alkylbenzene). These compounds are considered characteristic of gasoline and cover a wide range in volatility.

Initially, the mean peak area and peak height for each compound of interest, along with the associated relative standard deviation (RSD) were calculated for each set of experimental replicates. However, the RSDs do not provide an accurate representation of the experimental replicates because of differences in the mass lost in each replicate. Due to variability in the evaporation process, the mass lost varies for different replicates. Fraction remaining by mass values account for these slight differences, while RSDs do not. For example, the fraction

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remaining by mass for three experimental replicates of 25% evaporated gasoline was 0.764, 0.768, and 0.773, respectively. The RSD for these three replicates is 0.59. The fraction remaining by mass for three experimental replicates of 90% evaporated gasoline was 0.0620, 0.0928, and 0.107, respectively. The RSD for these three replicates is 26%. The RSD of the experimental replicates was extremely high at 90% evaporated, due to the variability in the evaporation process at low volumes and, thus, provided a false representation of the relationship among the experimental replicates.

Because of the differences in mass lost among experimental replicates, the fraction of each gasoline remaining after evaporation was also taken into account. The experimental fraction remaining by mass was determined by dividing the mass remaining after evaporation by the initial mass of gasoline. The abundance of the compound of interest in a particular replicate was then plotted against the fraction of gasoline remaining for that replicate. These plots were generated for each compound to allow an assessment of the effect of the parameter under investigation on the reproducibility of the evaporation.

3.3 Results and Discussion

3.3.1 Effect of Evaporation on the Chemical Composition of Gasoline

The chromatogram of unevaporated gasoline, shown in Figure 3-2, contains a characteristic pattern of abundant aromatic compounds, which typically consists of toluene, C_2 -alkylbenzenes (including ethylbenzene, *p*-xylene, and *o*-xylene), C_3 -alkylbenzenes (including propylbenzene and 1,2,4-trimethylbenzene), C_4 -alkylbenzenes (including 1,2,4,5-tetramethylbenzene and 1-methyl-4-(2-propenyl)benzene), and two methylnaphthalenes (1-methylnaphthalene and 2-methylnaphthalene). The composition of the gasoline standard used in this research was in accordance with ASTM guidelines², which requires the presence of toluene, the C_2 -, C_3 -, and C_4 -

alkylbenzenes, and the methylnaphthalenes as well as specific ratios of the peak heights of these compounds (e.g. C_2 -alkylbenzenes 1:3:1 ratio of abundance, methylnaphthalenes 2:1 ratio of abundance) for the definitive identification of gasoline.

As evaporation occurs, compounds with lower boiling points evaporate at a faster rate than those with higher boiling points, due to their high volatility. Therefore, the compounds eluting at the beginning of the chromatogram, such as toluene and the C_2 -alkylbenzenes, will decrease in abundance relatively quickly as evaporation progresses.



Figure 3-2. Chromatogram of unevaporated gasoline

However, as these compounds begin to completely evaporate, the compounds with higher boiling points, such as the C_3 - and C_4 -alkylbenzenes and the methylnaphthalenes, will begin to decrease in abundance as well, though at a slower rate than the more volatile compounds. Based on the volatility and the boiling points of the compounds in gasoline, toluene will evaporate at the

fastest rate, followed by the C_2 -, C_3 -, and C_4 -alkylbenzenes and the methylnaphthalenes, respectively.

At 25% evaporated by volume, shown in Figure 3-3, the abundance of the compounds with boiling points less than 138.4 °C, including toluene and the C₂-alkylbenzenes, have decreased compared to the abundance of these compounds in the unevaporated gasoline sample (Figure 3-2). Additionally, due to the higher boiling points and slower rates of evaporation for the C₃- alkylbenzenes, the C₂- and C₃-alkylbenzenes now have approximately the same abundance.

In fact, the overall abundance of the compounds in the chromatogram of 25% evaporated is actually higher than the overall abundance of the compounds in the chromatogram of the unevaporated gasoline (Figure 3-3A). This discrepancy in the overall abundance is due to a dilution error introduced during sample preparation. Ten microliters of each evaporated gasoline sample were used for analysis, regardless of the volume remaining after evaporation. This leads to a preconcentration of the more evaporated gasoline samples, causing an increase in the abundance of the compounds in the chromatograms of the more evaporated samples. To address this preconcentration issue, a chromatographic adjustment was performed, which is explained fully in Chapter 4, Section 4.3.1.2.4. The chromatograms for the four different evaporation levels have all been adjusted (Figures 3-3B to 3-6).

At 50% evaporated by volume (Figure 3-4), the abundance of toluene has decreased further, while the abundances of the C_2 - and C_3 -alkylbenzene peaks only slightly decreased. There are also several compounds present at low abundance that elute before toluene and between toluene and the C_2 -alkylbenzenes, with boiling points lower than that of the C_2 -alkylbenzenes (138.4 °C). At 75% evaporated by volume (Figure 3-5), the abundances of these compounds have decreased and are almost completely evaporated. Toluene has also decreased in abundance

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Figure 3-3. Chromatogram of gasoline evaporated to 25% by volume (A) with no dilution adjustment and (B) with dilution adjustment

due to evaporation and is approximately the same height as the C₂- and C₃-alkylbenzene peaks. At 90% evaporated by volume (Figure 3-6), all of the compounds eluting before the C₂alkylbenzenes with boiling points below 138.4 °C, are completely evaporated, and the remaining compounds are significantly lower in abundance.



Figure 3-4. Chromatogram of gasoline evaporated to 50% by volume



Figure 3-5. Chromatogram of gasoline evaporated to 75% by volume



Figure 3-6. (A) Chromatogram of gasoline evaporated to 90% by volume and (B) Zoomed in chromatogram of gasoline evaporated to 90% by volume

3.3.2 Effect of Agitation Rate on Evaporation of Gasoline

Fraction remaining plots for representative compounds from each characteristic group of compounds in gasoline were generated. The fraction remaining by mass was calculated by dividing the measured mass after evaporation by the measured mass before evaporation for each of the evaporation levels (Figures 3-2 - 3-6). The abundance of the compound in each experimental replicate was then plotted against the calculated fraction remaining value for each replicate. These plots were used to evaluate the data for each of the studies.

The plot of abundance versus fraction remaining for toluene at each agitation rate is shown in Figure 3-7. The abundance of toluene decreases as the evaporation level increases, with full evaporation observed at fraction remaining values of 0.06 - 0.11, which correspond to 90% evaporated by volume. This trend is observed for all three agitation rates as well as the nonagitated samples (Figure 3-8). The spread in the replicates on the y-axis is more noteworthy than the spread on the x-axis as the y-axis indicates differences in the abundance of the compound for specific fraction remaining values. The spread of the replicates on the x-axis does not provide information about the precision of the data as it only generates a more accurate representation of the individual fraction remaining for each experimental replicate. There is less precision with the non-agitated samples at the higher evaporation levels (75% and 90% evaporated by volume), indicating that agitation produces better reproducibility at the higher evaporation levels. In fact, at 90% evaporated by volume, toluene is completely evaporated for the agitated samples, while there is still some toluene present in the non-agitated samples. There are no noticeable differences in the reproducibility of the data for the different agitation rates, indicating that, for toluene, agitation is necessary to generate reproducible data at the higher evaporation levels.

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Figure 3-7. Fraction remaining plots for toluene using agitation rates of (A) 109 ± 2 rpm, (B) 134 ± 2 rpm, and (C) 199 ± 2 rpm

Figure 3-7 (cont'd)



Figure 3-7. Fraction remaining plots for toluene using agitation rates of (A) 109 ± 2 rpm, (B) 134 ± 2 rpm, and (C) 199 ± 2 rpm



Figure 3-8. Fraction remaining plot for toluene using all three agitation rates and no agitation

The fraction remaining plot for a representative C_2 -alkylbenzene using all three agitation rates and no agitation is shown in Figure 3-9. In general, the abundance of this C_2 -alkylbenzene remains relatively constant for the 25% - 50% evaporated by volume for the agitated samples. However, for the non-agitated samples, there is a marked decrease in abundance as the evaporation level increases from 25% to 50% evaporated by volume. There is a decrease in the abundance at 75% - 90% evaporated by volume, although complete evaporation does not occur. This trend is observed for all three agitation rates as well as the non-agitated samples, although the non-agitated samples appear to have a more linear decrease in abundance as the evaporation level increases. The precision of the experimental replicates at 90% evaporated by volume is poorer for two of the agitation rates as well as the non-agitated samples, indicating that there is more variation at this particular high evaporation level. However, the precision for the high agitation rate is actually slightly higher at the 90% evaporated by volume level compared to the 75% evaporated by volume level. The non-agitated samples do appear to have the poorest precision at the 90% evaporated by volume level, suggesting that agitation produces better reproducibility at this evaporation level. These data indicate that agitation is necessary to generate reproducible data at the higher evaporation levels.



Figure 3-9. Fraction remaining plot for *p*-xylene (a C_2 -alkylbenzene) using all three agitation rates and no agitation

The fraction remaining plot for a representative C_3 -alkylbenzene using all three agitation rates and no agitation is shown in Figure 3-10. In general, the abundance of this C_3 -alkylbenzene remains relatively constant for the 25% - 50% evaporated by volume for the agitated samples, while the abundance of the non-agitated samples appear to markedly decrease between these two evaporation levels. However, there is a decrease in the abundance at 75% - 90% evaporated by volume, although complete evaporation does not occur. This trend is observed for all three agitation rates as well as the non-agitated samples, although the non-agitated samples appear to have a more linear decrease in abundance as the evaporation level increases. The precision of the experimental replicates at 90% evaporated by volume is lowest for the low agitation rate, indicating that a faster agitation rate is needed to produce reproducible data. The non-agitated samples appear to have better precision at the 90% evaporated by volume level than that of the low agitation rate. However, the medium and high agitation rates appear to have better precision than the non-agitated samples, suggesting that faster agitation may be required to generate better reproducibility for this particular compound. Additionally, the abundance of the non-agitated samples is higher than the abundance of the agitated samples, which indicates that agitation allows additional volatile molecules to evaporate compared to non-agitation.



Figure 3-10. Fraction remaining plot for 1,2,3-trimethylbenzene (a C₃-alkylbenzene) using all three agitation rates and no agitation

The fraction remaining plot for a representative C₄-alkylbenzene using all three agitation rates and no agitation is shown in Figure 3-11. In general, the abundance of this C₄-alkylbenzene appears to remain relatively constant for 25% - 75% evaporated by volume with a slight decrease in abundance at 90% evaporated by volume. This trend is observed for all three agitation rates as well as the non-agitated samples. The precision of the experimental replicates at 90% evaporated by volume is poorest for the low agitation rate, indicating that the medium and high agitation rates are again necessary to produce reproducible data. For this compound, the non-agitated samples appear to have poorer precision at the 50% evaporated by volume level, suggesting that faster agitation may be required to generate better reproducibility for this particular compound at every evaporation level.



Figure 3-11. Fraction remaining plot for 1,2,4,5-tetramethylbenzene (a C_4 -alkylbenzene) using all three agitation rates and no agitation

Overall, agitation appears to improve the reproducibility of the experimental replicates, especially at 90% evaporated by volume. However, for the less volatile compounds, there is a similar decrease in precision at 90% evaporated by volume for both the low agitation rate and the non-agitation replicates. This indicates that a faster rate of agitation is necessary to generate reproducible data for the more stable compounds at the highest evaporation level. The necessity of a faster agitation rate is most likely caused by the increased variation in the evaporation process at such high levels of evaporation.

3.3.3 Effect of Stir Bar Shape on Evaporation of Gasoline

Although the agitation rate study used a spinfin® stir bar, the effects of two other stir bars were also evaluated (Figure 3-1). Each stir bar has a unique shape and purpose. The dimensions of the stir bar itself can impact the agitation, and subsequently, the evaporation process. For example, the micro stir bar is uniform in length and diameter, resulting in more continuous agitation compared to the spinvane® stir bar, which has a triangular shape that could affect the uniformity of the agitation. Due to the triangular shape of the spinvane[®] stir bar, the wider edge of the stir bar could agitate a larger volume of the liquid than the narrow edge, resulting in disproportionate stirring. As the micro stir bar is smaller than the spinfin® stir bar, it does not interfere with the determination of the liquid volume at extremely high evaporation levels as the spinfin® stir bar does. As the volume of the liquid remaining was used to determine when the desired evaporation level was reached, the reading error was more prominent with the spinfin® stir bar than with the micro stir bar because the micro stir bar has smaller dimensions than that of the spinfin® stir bar. As a result, the fraction remaining by mass values were more variable for the spinfin[®] stir bar compared to the values for the micro stir bar. Additionally, the spinfin[®] stir bar is most effective for round bottom flasks as well as cylinders and test tubes. The spinvane®

stir bar is most useful in test tubes, micro vials, and centrifuge tubes with cone-shaped bottoms, and the micro stir bar is ideal for stirring small volumes in small vessels, including vials and tubes¹. Based on the specific uses for each stir bar, the micro stir bar is likely to generate the most reproducible data compared to the other stir bars.

The trends observed for both the spinvane[®] stir bar and micro stir bar are similar to those shown in Figures 3-7 - 3-11 for the spinfin[®] stir bar. The plot of abundance versus fraction remaining of toluene using all three stir bars at the low agitation rate is shown in Figure 3-12. There is less precision with the spinvane[®] stir bar at the 25% - 75% evaporation levels, indicating that a stir bar with a more uniform shape produces more reproducible data for toluene. However, at 90% evaporated by volume, toluene is completely evaporated. These data indicate that, for toluene, agitation with either the spinfin[®] or the micro stir bar is necessary to generate reproducible data at all evaporation levels.



Figure 3-12. Fraction remaining plot for toluene using three different stir bars

The fraction remaining plot for a representative C_2 -alkylbenzene using all three stir bars is shown in Figure 3-13. All three stir bars show moderate to high precision for the 25 – 75% evaporation levels, with the exception of the spinvane® stir bar at 25% evaporated. However, the precision of the experimental replicates at 90% evaporated by volume is poorer for all three stir bars, indicating that there is more variation at this particular evaporation level. Although the micro stir bar appears to have the best precision at 90% evaporated by volume, it is possible that the similarity in the fraction remaining values for the micro stir bar leads to less variation in the abundance of this C₂-alkylbenzene when compared to the spinfin® and spinvane® stir bars.



Figure 3-13. Fraction remaining plot for *p*-xylene (a C₂-alkylbenzene) using three different stir bars

The fraction remaining plot for a representative C_3 -alkylbenzene using all three stir bars is shown in Figure 3-14. The precision is similar with all three stir bars at 50% and 75% evaporated by volume. While the micro stir bar appears to exhibit the highest precision at 90% evaporated by volume, it is possible that the similarity in the fraction remaining values for the micro stir bar leads to less variation in the abundance of this C_3 -alkylbenzene when compared to the spinfin® and spinvane® stir bars.

The fraction remaining plot for a representative C_4 -alkylbenzene using all three stir bars is shown in Figure 3-15. The precision is similar with all three stir bars at 50% and 75% evaporated by volume. While the micro stir bar appears to exhibit the highest precision at



Figure 3-14. Fraction remaining plot for 1,2,3-trimethylbenzene (a C₃-alkylbenzene) using three different stir bars

90% evaporated by volume, it is possible that the similarity in the fraction remaining values for the micro stir bar leads to less variation in the abundance of this C_4 -alkylbenzene when compared to the spinfin® and spinvane® stir bars.

Overall, the micro stir bar seems to generate the most reproducible data for every compound at each evaporation level, although this could be due to similarity in the fraction remaining values leading to less variation in abundance compared to the other two stir bars. This could indicate that using the micro stir bar, which is designed to agitate small volumes, is ideal for generating reproducible data for all of the compounds at all evaporation levels.



Figure 3-15. Fraction remaining plot for 1,2,4,5-tetramethylbenzene (a C₄-alkylbenzene) using three different stir bars

3.3.4 Effect of the Exposed Surface Area on Evaporation of Gasoline

The agitation rate and stir bar studies were all conducted in a graduated cylinder, which has an exposed surface area of 1.13 cm^2 available for evaporation of molecules out of the liquid into the environment. In the absence of agitation, Equation 3-1 shows the time (t) necessary for molecules at the bottom of the graduated cylinder (Figure 3-16) to diffuse to the surface using a typical diffusion coefficient (D) for the liquid phase.

$$t = \frac{d^2}{2D} = \frac{(7.80)^2}{2(10^{-5})} = 845 h$$
 Equation 3-1

For a distance (d) of 7.80 cm (which is the distance from the bottom of the cylinder to the 10 mL mark), it would take 845 hours for the molecules at the bottom to diffuse (Equation 3-1). As a result, the use of agitation and active evaporation is essential in order to decrease the time necessary to evaporate gasoline. However, a molecule only needs to diffuse ~0.1 cm to reach the surface of the liquid and evaporate in a Petri dish (Figure 3-16). As diffusion takes only 8.3 min, agitation is not necessary (Equation 3-2).

$$t = \frac{d^2}{2D} = \frac{(0.1)^2}{2(10^{-5})} = 8.3 min$$
 Equation 3-2

The evaporation of gasoline in a Petri dish is also more realistic as it simulates the surface area available for evaporation and the thickness of a liquid during a fire. The ignitable liquid is spread out over the surface of the scene, resulting in a thin film of liquid. Therefore, the evaporation of standards in a Petri dish is more comparable to the evaporation of an ignitable liquid occurring during a fire compared to evaporation in a graduated cylinder.

The trends observed for this study are similar to those shown in Figures 3-7 - 3-11 for the agitation rate study. The plot of abundance versus fraction remaining for toluene in a graduated cylinder with and without agitation and in a Petri dish without agitation is shown in Figure 3-17. It appears that the graduated cylinder without agitation samples have better precision than the other two data sets at each evaporation level, although the Petri dish without agitation has similar precision at the 50% evaporation level. If a curve was drawn through each set of samples, then



Figure 3-16. Illustration of dimensions of a graduated cylinder versus a Petri dish, each containing 10 mL of gasoline

the Petri dish without agitation and the graduated cylinder with agitation samples actually appear to be more accurate and reproducible. Additionally, the abundance of toluene at each evaporation level is consistently higher for the graduated cylinder without agitation samples compared to the other two data sets. At 90% evaporated by volume, toluene is completely evaporated for the Petri dish without agitation and the graduated cylinder with agitation, while toluene is still present in the graduated cylinder without agitation. This indicates that agitation in a graduated cylinder or the use of a Petri dish without agitation result in the evaporation of additional volatile toluene molecules compared to the graduated cylinder without agitation samples.

The fraction remaining plot for a representative C_2 -alkylbenzene is shown in Figure 3-18. Although the precision of the experimental replicates at 90% evaporated by volume is lower



Figure 3-17. Fraction remaining plot for toluene in a graduated cylinder with and without agitation and in a Petri dish without agitation

for both sets of samples in the graduated cylinder, the non-agitated samples in the graduated cylinder have the poorest precision, suggesting that agitation is necessary for evaporation in a graduated cylinder to produce better reproducibility at this evaporation level. However, agitation does not seem necessary to produce reproducible data in the Petri dish at this evaporation level.

The fraction remaining plot for a representative C_3 -alkylbenzene is shown in Figure 3-19. The precision of the replicates was similar for the graduated cylinder with agitation and the Petri dish without agitation, with slight differences observed at each evaporation level. However, the abundance of the replicates for each evaporation level is higher for the graduated cylinder without agitation compared to the other data sets, suggesting that the other two methods of evaporation result in the evaporation of additional volatile molecules compared to the graduated



Figure 3-18. Fraction remaining plot for p-xylene (a C₂-alkylbenzene) in a graduated cylinder with and without agitation and in a Petri dish without agitation

cylinder without agitation samples. Furthermore, the precision of the replicates for the graduated cylinder without agitation decreases as the evaporation level increases.

The fraction remaining plot for a representative C_4 -alkylbenzene is shown in Figure 3-20. Although the graduated cylinder without agitation data appear to have less precision at the 50% and 75% evaporated by volume levels, the precision is similar to that of the other data sets for the 25% and 90% evaporation levels. The similarity in precision at the high evaporation levels indicates that the use of agitation or an increased surface area may not be necessary for more stable compounds.

Overall, agitation appears to improve the reproducibility of the experimental replicates evaporated in the graduated cylinder. Additionally, the Petri dish data appear to be comparable to that of the agitated graduated cylinder data, suggesting that the evaporation processes occurring


Figure 3-19. Fraction remaining plot for 1,2,3-trimethylbenzene (a C_3 -alkylbenzene) in a graduated cylinder with and without agitation and in a Petri dish without agitation



Figure 3-20. Fraction remaining plot for 1,2,4,5-tetramethylbenzene (a C_4 -alkylbenzene) in a graduated cylinder with and without agitation and in a Petri dish without agitation

in each vessel are similar.

Determining the various factors that affect the evaporation of gasoline may improve the reproducibility of the evaporation process, which could lead to the development of a standardized method for the evaporation of ignitable liquid standards. However, the factors influencing the evaporation process will still exist and affect the evaporation of the standards. Furthermore, there is no true standard for what the chromatogram of evaporated gasoline should look like. As a result, another method for generating evaporated standards that is not affected by these factors and can accurately simulate the evaporation process is needed.

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Chapter 4: Mathematical Modeling of Evaporated Ignitable Liquid Standards

4.1 Introduction

As the evaporation process is affected by various factors, a method for generating evaporated standards that is unaffected by these factors is needed. A mathematical model previously developed by McIlroy *et al.* based on first-order kinetics has the potential for forensic applications¹. This model was used to predict the fraction remaining of the individual compounds of three petroleum distillates and gasoline, which was plotted versus retention index to generate chromatograms of the liquids at four different evaporation levels. The modeled chromatograms were then compared to the corresponding chromatograms derived experimentally, using Pearson product moment-correlation (PPMC) coefficients. This chapter will focus primarily on the application of the model to kerosene and gasoline. Kerosene contains compounds that include a wide range of retention indices, making kerosene less volatile than gasoline. Gasoline is highly volatile and is commonly encountered in fire debris analysis.

4.2 Materials and Methods

4.2.1 Sample Collection, Evaporation, and Preparation

Two of the petroleum distillate standards were commercial ignitable liquids obtained from local stores. These petroleum distillate standards were lamp oil (Lamplight® Medallion®, Lamplight Farms, Inc., Menomenee Falls, WI) and torch fuel (Tiki®, Lamplight Farms, Inc., Menomenee Falls, WI). The third petroleum distillate standard, kerosene, and gasoline were collected from gas stations in the East Lansing, MI area.

A ten-milliliter graduated cylinder, containing a spinfin® stir bar and covered with a piece of aluminum foil, was weighed in an analytical balance (Mettler H80, Serial no. 60403), and the mass recorded. Ten milliliters of ignitable liquid were poured into the graduated cylinder, and the

new mass was recorded before the cylinder was placed in the center of a stir plate (Thermo Scientific, model S130815) in the fume hood. Each liquid was actively evaporated using house nitrogen and agitated at 109.3 ± 1.5 rpm. Each liquid was individually evaporated to 26%, 52%, 78%, and 94% by volume, which corresponds to 7.5, 5.0, 2.5, and 1.0 milliliters, respectively. Once the desired volume was reached, the graduated cylinder was removed from the fume hood and the remaining liquid was poured into a pre-weighed vial and capped. The vial was reweighed, and the new mass recorded. Finally, the foil was replaced on top of the cylinder, and the cylinder was reweighed to determine the mass of residual ignitable liquid present. Based on these weighings, the mass of the ignitable liquid evaporated was also determined and recorded. Although the liquids were evaporated by volume, the mass loss was determined to increase the accuracy of the experimental evaporated liquids. The cylinder and stir bar were then thoroughly rinsed with dichloromethane (CH₂Cl₂) (HPLC/UHPLC grade, J.T. Baker, Avantor Performance Materials, Inc., Center Valley, PA) before being left to air dry. This process was repeated for each liquid, resulting in three experimental replicates per evaporation level. Ten microliters of each evaporated liquid were transferred into a two-milliliter volumetric flask. Forty microliters of the internal standard solution (0.1162 g octadecane (Sigma Chemical Company, St. Louis, MO) in 50 mL DCM) were then added before the sample was diluted with DCM to the calibrated mark. The diluted liquid was poured into a labeled vial and analyzed by gas chromatographymass spectrometry (GC-MS).

4.2.2 GC-MS Analysis

All ignitable liquids, unevaporated and evaporated, were analyzed using an Agilent 6890N gas chromatograph(GC) coupled to a 5975 mass spectrometer detector (MSD) with an Agilent 7683B automatic liquid sampler (Agilent Technologies, Palo Alto, CA). A 1 µL volume of each

liquid was injected in pulsed splitless mode into the injection port, which was heated to 250 °C. Ultra high-purity helium (Airgas Great Lakes, Independence, OH) was used as the carrier gas with a nominal flow rate of 1 mL/min. A DB-1 column, which has a 100% poly(dimethylsiloxane) stationary phase (30 m × 0.25 mm × 0.25 μ m) was used with an oven temperature program of: 40 °C for 3 min, 10 °C/min to 280 °C, with final hold for 4 min. A transfer line temperature of 280 °C was also used. The mass spectrometer used an electron ionization ion source (70 eV, 230 °C) and a quadrupole mass analyzer (150 °C), with a mass scan range of 50 – 550 amu and a scan rate of 2.91 scans/s.

4.2.3 Data Analysis

The total ion chromatograms (TICs) were exported from the ChemStation software (version E.01.01.335, Agilent Technologies) to Microsoft Excel 2007 (Microsoft Corporation, Redmond, WA). The data were normalized to the maximum peak height of the internal standard, octadecane.

4.2.3.1 Correlation Optimized Warping (COW) Alignment

The normalized data were retention-time aligned to the chromatogram of the corresponding unevaporated liquid using a correlation optimized warping (COW) algorithm (Version 10.2, The Unscrambler® X, CAMO Software AS, Woodbridge, NJ) (discussed in Chapter 2, Section 2.2). Most of the chromatograms were acquired over a short time period and, due to their similarity in alignment, were all aligned using a warp of 5 data points and a segment size of 50 data points. However, other chromatograms were acquired after routine column maintenance and had more variability in retention times. These chromatograms required a two-step procedure to align them to the target chromatogram. Of these chromatograms, the majority started with a warp of 20 data points and a segment size of 75 data points, followed by a warp of 5 data points and segment size of 50 data points, while the last six chromatograms started with a warp of 30 data points and a segment size of 75 data points, followed by a warp of 5 data points and segment size of 50 data points. This realignment is illustrated in Figure 4-1.



Figure 4-1. (A) Peak misalignment between unevaporated and evaporated chromatograms of kerosene and (B) Peak alignment between same two chromatograms following an initial COW alignment with a warp of 20 data points and a segment size of 75 data points and a second alignment with a warp of 5 data points and a segment size of 50 data points

4.2.3.2 Removal of the Internal Standard, Octadecane (C_{18})

The next step in the modification of the model involved the removal of the peak corresponding to the internal standard used for normalization. When PPMC coefficients were initially calculated, the chromatograms consisted of retention indices 800 – 2200, including the internal standard with a retention index of 1800. The resulting PPMC coefficients showed a moderate to strong correlation at the 94% evaporation level.

As octadecane was added as the internal standard after evaporation was completed, the same volume and concentration of internal standard was used for each unevaporated and evaporated liquid. However, the model attempted to predict the behavior of octadecane as though it was undergoing evaporation. According to the fraction remaining curves for kerosene at all four evaporation levels (Figure 4-2), octadecane is unaffected by evaporation, even at 94% evaporated. Therefore, when the abundance of octadecane in the chromatogram of unevaporated kerosene was multiplied by the fraction remaining for octadecane, the abundance of the internal standard peak in the theoretical chromatograms was over-predicted by the model. As the primary interest for the model application was to assess the model's ability to predict the evaporation of each ignitable liquid, zeroes were entered into the chromatographic data for the compounds in the RI range 1780 – 1810. The PPMC coefficients would then account for differences in the more volatile compounds rather than the less volatile compounds. After removing the C₁₈ peak, the PPMC coefficients for all three petroleum distillates improved, especially at 94% evaporated by volume, resulting in strong correlation for all three liquids.

4.2.3.3 Area Adjustment of Aligned Data to Address Sample Dilution Error

The final issue encountered during the application of this model involved a sample dilution error for the experimentally derived data. During preparation, 10 μ L of each evaporated liquid are diluted in dichloromethane. By using the same volume of liquid for analysis, regardless of

the original volume of the evaporated liquid, the more evaporated liquids are preconcentrated, compared to the less evaporated liquids. For example, in the 94% evaporated liquid, only 1 mL of liquid remains and 10 μ L of this remaining liquid is diluted, while for the 26% evaporated liquid, 7.5 mL of liquid remains but only 10 μ L are used for analysis. As the evaporation level increases, the preconcentration of the diluted sample increases as well. This preconcentration resulted in the presence of compounds whose abundances were inflated due to the increased concentration. As a result, the experimental chromatograms contained more compounds than the theoretical chromatograms (illustrated in Figure 3-3). To address this issue, an area adjustment of the chromatographic data for the evaporated liquid (F_e) and the ratio of the evaporated and unevaporated areas (A_e and A_u, respectively) to adjust for the dilution error, shown in Equation 4-1,

$$D_f = F_e \times \frac{\sum A_u}{\sum A_e} \times D_0$$
 Equation 4-1

where D_0 and D_f are the initial abundance of the data point and the adjusted abundance of the data point, respectively. This area adjustment did correct the experimental chromatograms so that the data were on the same order of magnitude as the theoretical chromatograms. However, the adjustment could not eliminate the compounds artificially inflated due to the evaporation and dilution error. Although this dilution/preconcentration error does affect the magnitude of the abundance of the compounds, it does not invalidate the overall conclusions of this research.

4.2.4 Modifications of the Theoretical Model

4.2.4.1 Determination of Experimental Fraction Remaining

Retention indices were calculated for each liquid, based on the maximum peak height for each *n*-alkane in the aligned chromatograms. The model was originally developed as a function of time with evaporation being predicted at specific times, rather than at different levels of evaporation. However, in order to determine the forensic applications of the model, the model needed to be modified until it was based on a function of fraction remaining, rather than time. To successfully modify the model, the experimental fraction remaining by mass was determined for each experimental replicate at all four evaporation levels by dividing the final mass by the initial mass. The theoretical time for evaporation was then systematically adjusted by changing the time necessary for evaporation until the theoretical fraction remaining was similar to the experimental fraction remaining.

The fraction remaining was originally determined based on the signal, which was determined by dividing the signal in the chromatogram of the evaporated liquid by the signal in the chromatogram of the unevaporated liquid. As the experimentally derived chromatograms were evaporated by volume, the fraction remaining for the theoretical chromatograms was determined by the experimental fraction remaining by volume. However, the model was more accurate when the fraction remaining was determined by mass because the individual mass lost for each replicate caused by variation in the evaporation process was addressed. Although differences in the fraction remaining were observed when determined by mass, they were more prominent when determined by volume. For example, three experimental replicates of gasoline at 94% evaporated gave fraction remaining by mass values of 0.06, 0.09, and 0.10. However, the fraction remaining was assumed to be 0.06 for all three replicates, as it was the nominal fraction remaining value for 90% evaporated. By accounting for the mass lost for each replicate, variation in the evaporation process can be addressed. Therefore, the chromatograms generated by the model were based on the mass, rather than the volume of the remaining

ignitable liquid. As there were three experimental replicates for each evaporation level, the average fraction remaining of the three replicates was used in the model.

Both the original and modified mathematical models used the normalized, unevaporated chromatograms of each of the ignitable liquid standards to calculate the retention index (I) and evaporation rate constant (k) for all of the compounds in each liquid between octane (C_{8}) and docosane (C_{22}), shown in Equation 4-2,

$$k = m_I \times I + m_T \times \frac{1}{T} + b_T$$

$$k = -0.0103 \times I + 6409.52 \times \frac{1}{292.88} + 28.66$$
 Equation 4-2

where m_I and m_T are the slopes with respect to retention index and temperature, respectively, T is the temperature, and b_T is the intercept with respect to temperature. The rate constants were then used to calculate the fraction remaining for each individual compound in the liquid (Equation 1-4). Fraction remaining curves were generated by plotting the individual fraction remaining for each compound against retention index. Changing the time necessary for evaporation will result in a different curve. Therefore, each time, which results in a specific evaporation level, will generate its own unique fraction remaining curve. The fraction remaining curve was then multiplied by the chromatogram of the unevaporated ignitable liquid to generate a theoretical chromatogram at a certain evaporation level.

The normalized experimental chromatogram for each evaporated sample was compared to the corresponding chromatogram generated by the model using Pearson product moment-correlation (PPMC) coefficients (Equation 2-3). The model is able to determine the rate constants for each compound in the liquid, generating theoretical chromatograms that are essentially the true "standard" for the evaporated liquid at different evaporation levels. Therefore, the PPMC

coefficients can assess how accurately the experimentally derived chromatograms compare to the "true standards".

4.3 Results and Discussion

4.3.1 Petroleum Distillates

4.3.1.1 Chemical Composition and Evaporation of Kerosene

The unevaporated kerosene has a unimodal distribution of normal alkanes (Figure 4-1A), ranging from nonane to heptadecane. The less abundant compounds consist of branched alkanes, aromatics, and polycyclic hydrocarbons. As there are so many compounds in kerosene, the chromatogram cannot be baseline resolved. According to ASTM standard E1618¹, kerosene is classified as a "petroleum distillate" due to the dominance of the *n*-alkanes and as "heavy" based on the range of *n*-alkanes present (i.e. $C_8 - C_{20}$), as shown in Table 1-1.

Fraction remaining curves corresponding to the different evaporation levels were generated for kerosene, shown in Figure 4-1B. The fraction remaining is based on the rate constant and time. Therefore, changing the length of time required for evaporation provides a different fraction remaining curve. As the evaporation level increases, the range of compounds that have completely evaporated also increases. The fraction remaining curve for kerosene at 26% evaporated shows that all compounds from RI 800 – 900 are completely evaporated, while the compounds from RI 900 – 1300 experience evaporated, all compounds from RI 800 – 1050 are completely evaporated, compounds from RI 1050 – 1600 evaporate to different extents, and compounds after RI 1600 are unaffected by evaporation. The curve for 78% evaporated shows the complete evaporation of all compounds in the RI range of 800 – 1200, with the compounds from RI 1200 – 1700 evaporated to different extents. At 90% evaporated, all of the compounds



Figure 4-2. (A) Chromatogram of unevaporated kerosene and (B) Fraction remaining curves for kerosene at 26%, 52%, 78%, and 94% evaporated

from RI 800 – 1350 are completely evaporated, and all compounds from RI 1350 – 1800 are partially affected by evaporation. Only those compounds after RI 1800 do not evaporate. Although the same general evaporation trends are observed for the other two petroleum distillates, the fraction remaining curves differ slightly for each liquid due to differences in chemical composition.

The evaporation of kerosene predicted by the fraction remaining curves is consistent with the evaporation observed in the experimental chromatograms at each of the four evaporation levels (Figures 4-3 – 4-6). Therefore, only the evaporation observed in the 26% evaporated chromatogram will be discussed in detail. At 26% evaporated by volume, shown in Figure 4-3, the more volatile compounds, with boiling points less than 151 °C, are completely evaporated, from RI 800 – 900. Only a few extremely low abundant compounds eluting before C₁₀ are still present. The abundances of the compounds between C₉ and C₁₃ (RI range 900 – 1300), with boiling points ranging from 151 °C – 234 °C, also show signs of evaporation, with the loss in abundance decreasing as the boiling point of the compound increases.

The chromatograms generated by the model are theoretically correct and avoid variability introduced during the experimental evaporation process. Therefore, this model provides a potential method for generating evaporated standards. Furthermore, evaporating kerosene to different evaporation levels for a reference collection is extremely time-consuming. In this research, the evaporation process took approximately three days for 26% evaporated kerosene and one month for 94% evaporated kerosene. The same trend in evaporation was observed in the torch fuel and lamp oil standards analyzed in this research (Appendices B and C, respectively). As a result, this mathematical model will address the need for a quicker method for generating evaporated standards for comparison to fire debris samples.



Figure 4-3. Overlay of experimental and theoretical chromatograms of kerosene evaporated 26% by volume



Figure 4-4. Overlay of experimental and theoretical chromatograms of kerosene evaporated 52% by volume



Figure 4-5. Overlay of experimental and theoretical chromatograms of kerosene evaporated 78% by volume



Figure 4-6. Overlay of experimental and theoretical chromatograms of kerosene evaporated 94% by volume

4.3.1.2 Application of Mathematical Model for Predicting the Fraction Remaining

Once the model was modified (Sections 4.2.3 and 4.2.4), PPMC coefficients were recalculated. The mean PPMC coefficients for the different evaporation levels of kerosene ranged from 0.9942 ± 0.0005 to 0.954 ± 0.002 (Table 4-1). A strong correlation between the theoretical and experimental chromatograms of kerosene at each evaporation level was observed. However, the correlation between the experimental and theoretical chromatograms decreased slightly as the evaporation level increased, which could be due to variation in the evaporation of the experimental replicates at the higher evaporation levels or to the additional compounds present in the experimental chromatograms as a result of the dilution error discussed in Section 4.2.3.3.

	Mean PPMC Coefficient ± Standard Deviation (n = 9)			
% Evaporated by Volume	Kerosene	Lamp Oil	Torch Fuel	
26	0.9942 ± 0.0005	0.9979 ± 0.0006	0.987 ± 0.003	
52	$0.9881 \pm 0.0019 *$	0.9900 ± 0.0006	0.991 ± 0.004	
78	0.976 ± 0.004	0.966 ± 0.003	0.988 ± 0.004	
94	0.954 ± 0.002	0.88 ± 0.03	0.973 ± 0.005	

 Table 4-1. Mean PPMC coefficients for petroleum distillates

*n = 12

This same trend was also observed in lamp oil, with strong correlation being observed for all four evaporation levels and the PPMC coefficients decreasing slightly from 0.9979 ± 0.0006 to 0.88 ± 0.03 (Table 4-3) as the evaporation level increased. After model modification, the mean PPMC coefficient for the 94% evaporated lamp oil was only 0.88, which, while still indicating strong correlation, is substantially lower than the PPMC coefficients for the other petroleum distillate standards at this same evaporation level. This unexpected decrease in correlation is due to a lower correlation between the theoretical chromatogram and one of the three experimental replicates. When the chromatograms were visually examined, the abundances of the two most dominant peaks (C₁₁ and C₁₂) in lamp oil were lower in one replicate compared to the other two As a result, this one replicate was lowest in abundance compared to the abundance of the theoretical. The abundances of the rest of the compounds were actually higher in this particular replicate compared to the other two, shown in Figure 4-7, with the third replicate now being highest in abundance compared to the abundance of the theoretical.



Figure 4-7. Overlaid theoretical and experimental chromatograms of Medallion lamp oil 94% evaporated by volume with the third replicate shown in purple and the theoretical in red; left inset shows region of the third replicate with lowest abundance and right inset shows region of the third replicate with lowest abundance and right inset shows region of the third replicate with highest abundance

These differences in abundance can be partially explained by the differences in the fraction remaining of the third replicate compared to the other two replicates. The first two replicates had fraction remaining values of 0.10 and 0.09 by mass, while the third replicate had a fraction remaining value of 0.07 by mass. Differences in the mass fraction remaining are more influential at the higher evaporation levels due to error in reading the volume on the graduated cylinder and the small volumes remaining at such high evaporation levels. Slight differences in the volume of

the remaining liquid result in slight differences in the mass lost. The differences in abundance could also be due to different rates of evaporation. However, at small volumes, these differences are more influential than at larger volumes. Therefore, although the differences are very small, the variation in the chromatograms caused by these slight differences cause a loss in correlation between the theoretical and experimental chromatograms.

In order to examine this issue, a theoretical chromatogram for 94% evaporated lamp oil was generated for each replicate based on the individual experimental fraction remaining of that replicate, rather than the average fraction remaining. By using the actual fraction remaining for each experimental replicate, the differences in evaporation and the fraction remaining by mass can be addressed. Although the correlation at 94% evaporated is not as high for lamp oil as it is for kerosene, there is still a strong correlation at all four evaporation levels for lamp oil (Table 4-1).

Strong correlation was also observed for all four evaporation levels of torch fuel. Initially, torch fuel did not appear to follow the same trend as kerosene and lamp oil. The other two petroleum distillates exhibited a substantial decrease in correlation as the evaporation level increased, e.g. from 0.99 for 26% evaporated to 0.88 for 94% evaporated lamp oil. However, the mean PPMC coefficients for torch fuel only ranged from 0.987 ± 0.003 for 26% evaporated by volume to 0.973 ± 0.005 for 94% evaporated by volume. In fact, the PPMC coefficient for the comparison of the experimental and theoretical 52% evaporated (0.991) was actually higher than for the coefficients were not statistically different. Upon performing t-tests comparing the mean PPMC coefficients for all four evaporation levels, the only statistical difference among the PPMC coefficients was between the 52% and 94% evaporated liquids. As there are no statistical

differences among the PPMC coefficients, with the exception of the 52% and 94% evaporated liquids, it is impossible to determine if the trend is present in the torch fuel standard. Additionally, in general, the standard deviation was small for the replicates of all three petroleum distillates, indicating good precision among the experimental replicates.

The trend observed in both kerosene and lamp oil with the PPMC coefficients decreasing as the evaporation level increased indicates that the correlation between the experimental and theoretical chromatograms decreased as the evaporation level increased. There are two potential explanations for this trend. First, the decrease could be due to differences in the evaporation process between the model (developed based on passive evaporation of a thin film) and the experiment (active evaporation under nitrogen in graduated cylinder).

When the ignitable liquid is present as a thin film, the entire surface of the liquid is exposed to the environment, allowing the more volatile compounds spread throughout the liquid to evaporate more quickly. However, during active evaporation, the liquid is in a graduated cylinder and there is less surface area available for evaporation, as discussed in Chapter 3, Section 3.3.4. The nitrogen blowing onto the liquid combined with the agitation allow the more volatile compounds present near the bottom of the cylinder to diffuse to the surface where they can evaporate into the environment. As more of the compounds within each liquid are evaporated by the higher evaporation levels, the differences between the passive and active evaporation is more pronounced, resulting in lower PPMC coefficients. However, due to the similarities in reproducibility and precision of the samples evaporated in a graduated cylinder and a Petri dish (Chapter 3, Section 3.3.4), this potential error is unlikely to be the primary source of error.

Second, the dilution error in the sample preparation contributed to this decrease in correlation as evaporation increased. Due to the preconcentration of the evaporated samples, especially at

the higher evaporation levels, additional compounds were observed in the experimental chromatograms compared to the corresponding theoretical chromatograms. The dilution error caused compounds that would normally be present below the threshold of detection to reach a concentration level detectable by GC-MS. These compounds were especially noticeable at the higher evaporation levels due to the small volumes involved. As the theoretical chromatograms were based on the unevaporated chromatogram, these additional compounds were not present in the theoretical chromatograms. This discrepancy in the presence of these compounds due to the dilution error is the most likely cause of the slight decrease in correlation as the evaporation level increased.

Despite these issues and the slight decrease in PPMC coefficients, there is still a strong correlation between the theoretical and experimental chromatograms even at the highest evaporation level. This indicates that the model is able to accurately predict the fraction remaining of different compounds in the petroleum distillates, regardless of the evaporation level. Based on these results, the model is able to accurately predict the evaporation of multiple petroleum distillates and not just diesel, the liquid used for the initial development of the model¹.

4.3.2 Gasoline

4.3.2.1 Chemical Composition and Evaporation of Gasoline

The chromatogram of unevaporated gasoline, shown in Figure 4-8A, contains a characteristic pattern of abundant aromatic compounds, which typically consists of toluene, C_2 -alkylbenzenes including ethylbenzene, *p*-xylene, and *o*-xylene, C_3 -alkylbenzenes including propylbenzene and 1,2,4-trimethylbenzene, and two methylnaphthalenes (1-methylnaphthalene and 2-methylnaphthalene). The composition of the gasoline standard used in this research was in accordance with ASTM guidelines² (Table 1-1).

Fraction remaining curves corresponding to the different evaporation levels were generated for gasoline (Figure 4-8B). As the evaporation level increases, the range of compounds that have completely evaporated also increases. The evaporation of the compounds is discussed in detail later in the chapter.

At 26% evaporated by volume (Figure 4-9), the abundance of toluene and the C_{2} alkylbenzenes has decreased compared to their abundance in the unevaporated chromatogram. In contrast, the abundance of the C_3 -alkylbenzenes has increased so that now, the C_2 - and C_3 alkylbenzenes have approximately the same abundance. At 52% evaporated by volume (Figure 4-10), the abundance of toluene has decreased, while the abundances of the C_2 - and C_3 alkylbenzene peaks only decreased. There are also several low abundance compounds present before toluene and between toluene and the C_2 -alkylbenzenes. These compounds, including toluene, have lower boiling points than the C_2 -alkylbenzenes, so they will evaporate before the alkylbenzenes. At 78% evaporated by volume (Figure 4-11), the abundances of the compounds eluting before and after toluene have significantly decreased and are almost completely evaporated. Toluene has also decreased in abundance due to evaporated by volume (Figure 4-12), all of the compounds eluting before RI 800 are completely evaporated, and the remaining compounds are significantly lower in abundance.

As with the petroleum distillates, the model could provide a more accurate representation of the evaporation with no variability due to various factors that affect the evaporation process. However, all of the compounds present in gasoline have boiling points below 253.5 °C and are greatly affected by evaporation, whereas most petroleum distillates contain compounds that are less volatile. As a result, gasoline is more affected by evaporation due to the volatile nature of



Figure 4-8. (A) Chromatogram of unevaporated gasoline and (B) Fraction remaining curves for gasoline at 26%, 52%, 78%, and 94% evaporated

the compounds present. Although gasoline evaporates more quickly than the petroleum distillates, ranging from approximately five minutes for 26% evaporated to three hours for 94% evaporated, it is still time-consuming to generate evaporated standards at every evaporation level.



Figure 4-9. Chromatogram of gasoline evaporated to 26% by volume



Figure 4-10. Chromatogram of gasoline evaporated to 52% by volume



Figure 4-11. Chromatogram of gasoline evaporated to 78% by volume



Figure 4-12. Chromatogram of gasoline evaporated to 94% by volume

4.3.2.2 Application of Mathematical Model for Predicting Fraction Remaining

The modified model was applied to the normalized, aligned chromatogram of unevaporated gasoline. The experimental chromatograms compared to the corresponding theoretical chromatograms at each evaporation level for gasoline are shown in Figures 4-9 – 4-12. PPMC coefficients were calculated to assess the correlation between the theoretical and experimental chromatograms (Table 4-2). The trend that was present in the petroleum distillate standards, with the correlation decreasing in relation to the increase in evaporation level, is also observed in gasoline. However, the decrease is substantially more pronounced with the mean PPMC

coefficients decreasing from a strong correlation of 0.9620 ± 0.0014 for 26% evaporated to a moderate correlation of 0.535 ± 0.015 for 94% evaporated.

% Evaporated by Volume	Mean PPMC Coefficient ± Standard Deviation* (n = 9)
26	0.9620 ± 0.0014
52	0.779 ± 0.004
78	0.61 ± 0.03
94	0.535 ± 0.015

Table 4-2. Mean PPMC coefficients for gasoline

By visually assessing the overlaid experimental and theoretical chromatograms (Figures 4-9 – 4-12), noticeable differences between the experimental and theoretical chromatograms are visible, especially in the region between retention indices 600 - 900 that contains toluene and the C₂-alkylbenzenes. Based on the chromatogram of unevaporated gasoline, the model predicted that these compounds should be much lower in abundance at each evaporation level than is actually observed in the experimental chromatogram, with the model over-predicting the evaporation of these compounds.

To understand the origin of this error, the number of compounds present in gasoline that elute prior to toluene must be determined. Unleaded gasoline, which was used as the standard for the gasoline evaporations, contains numerous compounds that evaporate at a faster rate than toluene and the alkylbenzenes. Unfortunately, due to the GC-MS method used, the compounds are undetected because the GC oven temperature program starts too high (40 °C) and the MS detector is turned off for the first three minutes of the analysis as a solvent delay in order to

prevent the solvent from saturating the source. Although the compounds are present in the sample, they are not accounted for by the chromatogram, shown in Figure 4-13A. As a result, further investigation was necessary to determine how many compounds are present in the gasoline standard being used.

The gasoline sample was analyzed by GC using a flame ionization detector (FID) in order to determine the number of compounds eluting before toluene. As the sample is instantly combusted in the flame, a solvent delay is not necessary. The chromatogram for unevaporated gasoline (Figure 4-13B) revealed the presence of numerous compounds that are unaccounted for by the GC-MS method used. The compounds were not definitively identified. However, they are eluting prior to toluene and are not being detected by the mass spectrometer (MS) detector due to the solvent delay. Although the retention times of the compounds in the FID chromatogram differ from those in the MS chromatogram due to differences between the instruments used, the compounds still elute in the same relative order.

At 26% evaporated by volume, the FID chromatogram showed that the abundances of the compounds between 3 and 3.5 minutes, which elute prior to toluene (~6.3 min), only slightly decrease. However, by 94% evaporated, all of the compounds prior to toluene have completely evaporated, and the abundance of toluene has decreased significantly. This difference is most likely the primary contributor to the lack of correlation between the experimental and theoretical chromatograms for gasoline, although differences in other regions of the chromatograms also contribute to the lack of correlation.



Figure 4-13. (A) Chromatogram of unevaporated gasoline using MS detector and (B) Chromatogram of unevaporated gasoline using FID detector. Note that the x-axis is retention time rather than retention index for this comparison

As the model is based on the chromatogram of the unevaporated gasoline standard, the model cannot accurately predict the evaporated chromatograms because only two or three compounds prior to toluene are accounted for in the chromatogram of unevaporated gasoline. Additionally, the compounds eluting prior to toluene contribute substantially to the overall mass of the remaining liquid, which is not addressed by the model.

Figure 4-14 shows the chromatogram of unleaded gasoline, obtained using a cryogenic oven, which allows the GC-MS method to begin at 0 °C. In contrast, the lowest temperature possible with a conventional GC oven is 10 °C above room temperature (~35 °C). The GC-MS method used in this research, which is typical for fire debris analysis, begins at 40 °C with a three-minute solvent delay. The compounds eluting before toluene consist of benzenes and other aliphatic compounds, among others.





One solution for addressing the lack of correlation involves the optimization of the PPMC coefficients, which is possible as the model can predict evaporation at any level. This is accomplished by systematically increasing the theoretical fraction remaining until the PPMC coefficients are optimized. By increasing the theoretical fraction remaining, the predicted abundance of the compounds in gasoline will increase until the overall area of the theoretical evaporated liquid matches that of the experimental liquid. To test this theory, the fraction remaining for each evaporation level of gasoline was increased in increments of 0.01 to determine the difference between the fraction remaining predicted by the model and the actual fraction remaining by mass determined experimentally. The difference in fraction remaining would indicate the portion of the experimental fraction remaining provided by the undetected compounds. The fraction remaining determined experimentally for 94% evaporated gasoline was 0.108, while the fraction remaining necessary to optimize the PPMC coefficient was 0.360, which increased the mean PPMC coefficient from 0.535 to 0.986 (Figure 4-15).

The difference between the optimal and initial fraction remaining is 0.252. This indicates that ~25% of the mass is due to the compounds unaccounted for by the model due to their absence in the chromatographic data. This is consistent with the number of compounds typically present in gasoline that elute prior to toluene (Figure 4-14). Figure 4-16 shows the overlaid chromatograms of the experimental, initial theoretical, and optimal theoretical chromatograms for 94% evaporated gasoline. The abundances of the detected compounds in the optimal theoretical chromatogram are higher in abundance compared to the experimental chromatogram because they are less evaporated in the theoretical chromatogram due to the evaporation of the undetected compounds. The original and optimal fraction remaining and PPMC coefficient for each evaporation level are shown in Table 4-5. The PPMC coefficients increase from moderate

correlation for 52% - 94% evaporated to strong correlation at all four evaporation levels, indicating that optimizing the PPMC coefficients successfully addresses the contributions from the undetected compounds that elute prior to toluene.



Figure 4-15. Plot of fraction remaining for 94% gasoline versus PPMC coefficient

% Evaporated	Initial Fraction	Optimal Fraction	Initial PPMC	Optimal PPMC
by Volume	Remaining	Remaining	Coefficient	Coefficient
26	0.774	0.970	0.945	0.999
52	0.536	0.910	0.779	0.999
78	0.265	0.710	0.61	0.992
94	0.108	0.360	0.535	0.986

Table 4-5. Change in fraction remaining and PPMC coefficient for gasoline


Figure 4-16. Overlay of chromatograms of experimental, initial theoretical (FR 0.108), and optimal theoretical (FR 0.360) 94% evaporated gasoline

Based on the mean PPMC coefficients for gasoline, the model is applicable to gasoline and has the potential to predict the evaporation of gasoline at any evaporation level. The optimization of the PPMC coefficients increases the correlation between the theoretical and experimental chromatograms by adjusting the theoretical fraction remaining to account for the mass of compounds not detected by the GC-MS method. This optimization is beneficial to forensic laboratories. The exact evaporation level of ignitable liquids in fire debris is typically unknown, and analysts are not interested in predicting specific evaporation levels. By generating theoretical chromatograms until the PPMC coefficients are optimized, the exact evaporation level of the fire debris does not need to be determined. However, additional modifications are required before the model can be as accurate for gasoline as for the petroleum distillates the model was originally developed for.

APPENDICES

APPENDIX A: UNEVAPORATED AND EVAPORATED TORCH FUEL



Figure A-1. Chromatogram of unevaporated Tiki torch fuel



Figure A-2. Chromatogram of Tiki torch fuel evaporated 26% by volume



Figure A-3. Chromatogram of Tiki torch fuel evaporated 52% by volume



Figure A-4. Chromatogram of Tiki torch fuel evaporated 78% by volume



Figure A-5. Chromatogram of Tiki torch fuel evaporated 94% by volume

APPENDIX B: UNEVAPORATED AND EVAPORATED LAMP OIL



Figure B-1. Chromatogram of unevaporated Medallion lamp oil



Figure B-2. Chromatogram of Medallion lamp oil evaporated 26% by volume



Figure B-3. Chromatogram of Medallion lamp oil evaporated 52% by volume



Figure B-4. Chromatogram of Medallion lamp oil evaporated 78% by volume



Figure B-5. Chromatogram of Medallion lamp oil evaporated 94% by volume

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Chapter 5: Conclusions and Future Work

5.1 Conclusions

Evaporation of an ignitable liquid during a fire greatly impacts the analysis of fire debris by altering the chemical composition of the evaporated liquid. Many forensic laboratories now include evaporated and unevaporated standards in their reference collections of ignitable liquids. However, there is currently no standardized method for generating the evaporated standards. This research investigated different factors that affect the evaporation process as well as the utility of a mathematical model for fire debris applications.

Based on the results of the first two studies, agitation appears to improve the reproducibility of the evaporation process, especially at the higher evaporation levels. However, for those compounds with lower volatility, a higher rate of agitation is required to generate reproducible data at the highest evaporation level, which is most likely due to increased variation in the evaporation process at such high levels of evaporation. The use of the spinfin® and micro stir bars resulted in higher precision than the spinvane® stir bar, indicating that using a stir bar with a more uniform shape is necessary to generate reproducible data at all evaporation levels.

When comparing the agitated and non-agitated samples from the graduated cylinder to the non-agitated samples in the Petri dish, similar precision was observed for the graduated cylinder with agitation and the Petri dish without agitation data sets. This indicates that changing the surface area available for evaporation and decreasing the thickness of the liquid may negate the need for agitation.

Although determining the different factors that affect the evaporation of gasoline may result in improved reproducibility of the evaporation process and lead to the development of a standardized method for evaporation, the factors affecting evaporation will still affect the

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evaporation of the standards. Furthermore, no true standard for the evaporated liquids actually exists. Therefore, an alternative method that is unaffected by these factors and can accurately simulate the evaporation process was investigated.

A previously developed mathematical model was applied to three petroleum distillates and gasoline, and theoretical chromatograms at four different evaporation levels were generated. The chromatograms were then compared to corresponding experimental chromatograms to assess the correlation between the chromatograms. Strong correlation was observed for the three petroleum distillates at all four evaporation levels, although the correlation did decreases slightly as the evaporation level increased. However, the strong correlation observed at each evaporation level, including the 90% evaporation level, indicates that the model can accurately predict the evaporation of multiple petroleum distillates at any evaporation level.

The trend observed in the petroleum distillates was also observed for gasoline, although the trend was more prominent in gasoline with only moderate correlation at the higher evaporation levels. This lack of correlation is due to a limitation in the GC-MS method used for analysis. The compounds present in gasoline that elute prior to toluene were not observed in the chromatographic data due to a solvent delay at the start of the analysis. As a result, approximately 25% of the compounds in gasoline were unaccounted for by the model. To address this issue, the PPMC coefficients were optimized by increasing the theoretical fraction remaining until the optimal PPMC coefficient was obtained. The difference between the initial and optimal fraction remaining values corresponds to the unaccounted compounds, indicating that these compounds contribute to the overall mass lost during the evaporation process.

Based on the optimal PPMC coefficients for gasoline, the model is applicable to gasoline and has the potential to predict the evaporation of gasoline at any evaporation level. As the exact

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evaporation level of the ignitable liquids in fire debris is typically unknown, this optimization is beneficial to forensic laboratories because the exact evaporation level of the fire debris does not need to be determined.

Ultimately, the model provides an alternative method for evaporating standards that is unaffected by the factors affecting the evaporation process. The model eliminates the need for experimental evaporated reference standards, saving time and resources.

5.2 Future Work

Although the mathematical model is able to accurately predict the evaporation of multiple petroleum distillates at any evaporation level, additional modifications are required before the model can be as accurate for gasoline as for the petroleum distillates. The optimization of the PPMC coefficients shows potential for improving the prediction of evaporation for gasoline. However, this method does not address the compounds undetected during GC-MS analysis.

By modifying the GC-MS method so that the detector was only off during the time that the solvent eluted, these compounds could be detected. As a result, the TIC would show all of the compounds present in gasoline, including those that elute before toluene, without the danger of saturating or overloading the detector. With a more representative TIC of unevaporated gasoline, the model could more accurately predict the fraction remaining of the compounds present. The correlation between the theoretical and experimental chromatograms would improve without the need for optimization of the PPMC coefficients.

Further investigation into the applicability of the model may focus on the other ASTM classes of ignitable liquids as well as simulated fire debris samples to determine the universal utility of the model.

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