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INFLUENCE OF EVAPORATION AND MATRIX
INTERFERENCES ON THE ASSOCIATION AND
DISCRIMINATION OF IGNITABLE LIQUIDS USING
CHEMOMETRIC PROCEDURES

presented by

Tiffany Paige Van De Mark

has been accepted towards fulfillment
of the requirements for the

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Criminal Justice

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**INFLUENCE OF EVAPORATION AND MATRIX INTERFERENCES ON THE
ASSOCIATION AND DISCRIMINATION OF IGNITABLE LIQUIDS USING
CHEMOMETRIC PROCEDURES**

By

Tiffany Paige Van De Mark

A THESIS

**Submitted to
Michigan State University
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ABSTRACT

INFLUENCE OF EVAPORATION AND MATRIX INTERFERENCES ON THE ASSOCIATION AND DISCRIMINATION OF IGNITABLE LIQUIDS USING CHEMOMETRIC PROCEDURES

By

Tiffany Paige Van De Mark

In arson investigations, fire debris is collected, extracted, and analyzed by gas chromatography-mass spectrometry (GC-MS). The resulting chromatograms are visually assessed to identify an ignitable liquid residue (ILR). However, the ILR may differ in chemical composition from the original neat liquid due to evaporation and thermal degradation as well as interference effects from the burned debris. As a result, visual inspection of the chromatograms is highly subjective and prone to misinterpretation. The goal of this research is to develop an objective method using chemometric procedures, such as principal components analysis (PCA), Pearson product moment correlation (PPMC) coefficients, and hierarchical cluster analysis (HCA), to identify an ignitable liquid in the fire debris despite evaporation, matrix interferences, and combustion.

The first study investigated successful association of six ignitable liquids at four levels of evaporation to the corresponding neat liquid standard using PCA, PPMC coefficients, and HCA. In the second study, ignitable liquid mixtures containing gasoline and kerosene at two levels of evaporation were investigated to assess the ability to associate to the corresponding mixed liquid standard, despite the presence of evaporation, matrix interferences, and combustion. Using chemometric procedures, such as PCA, PPMC coefficients, and HCA, the mixed liquid samples were unable to be associated to the mixed liquid standard.

This thesis is dedicated to my Granny, Virginia Vogel Van De Mark.
I love you so much and miss you dearly.

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CHAPTER 1

Introduction

According to the United States Fire Administration (USAF), the estimated 30,500 intentionally set structure fires in 2008 killed 315 civilians and caused an estimated \$866 million in property damage [1]. The criminal act of setting a fire with malicious intent to destroy the property of another is considered arson. Most commonly at an arson scene, ignitable liquids are used as accelerants in order to rapidly ignite and spread a fire in a given area. The presence of an ignitable liquid would indicate that the fire was intentionally ignited in order to cause extensive damage. To confirm the presence of an ignitable liquid in fire debris collected from a suspected arson scene, a fire debris analyst must identify the ignitable liquid through visual comparison to a known ignitable liquid.

1.1 Classification of Ignitable Liquids

As defined by the American Society of Testing and Materials (ASTM), there are eight classes of ignitable liquids which, are classified based on the types of hydrocarbons present [2]. The major classes of ignitable liquids along with the chemical compounds that are present in each ignitable liquid are shown in Table 1.1.

Table 1.1 ASTM ignitable liquid classes and major components within each class.

Class	Light	Medium	Heavy
Gasoline	Gasoline falls in the range of C ₄ -C ₁₂		
Aromatic Products	Some toluene-based products	Specialty cleaning solvents	Industrial cleaning solvents
N-Alkane Products	Solvents such as pentane and hexane	Copier toners	Candle fuels
Isoparaffinic Products	Aviation gas	Some paint thinners	Some commercial specialty solvents
Naphthenic Paraffinic Products	Cyclohexane based solvents	Some charcoal starters	Industrial solvents
Petroleum Distillates	Petroleum ether	Some charcoal starters	Kerosene, Diesel fuel
Oxygenated Solvents	Alcohols	Some lacquer thinners	
Miscellaneous	Some blended products	Turpentine products	Some blended products

Within each ignitable liquid class except for gasoline, three subclasses are used to separate the ignitable liquids based on boiling point, which relates to the number of carbons present in each hydrocarbon. The three subclasses are light, medium, and heavy. The light class has low boiling point compounds from C₄-C₉. The medium class contains compounds from C₈-C₁₃, which have boiling points higher than those of the light class. The heavy class has the compounds C₉-C₂₀₊, which have higher boiling points than those of the medium class. If an ignitable liquid contains a wider range of hydrocarbons than a subclass, it can be classified into two subclasses, such as “light to medium” or “medium to heavy”. Shown in Table 1.2 are examples of ignitable liquids categorized into the corresponding classes and subclasses.

1.2 Extraction of Ignitable Liquid Residues from Fire Debris

When fire debris is collected from a suspected arson scene, the crime scene investigator collects the fire debris, which contains multiple matrices, into a paint can. The fire debris is then submitted to a forensic laboratory for analysis. Upon receiving the evidence, the fire debris analyst opens the fire debris evidence container and writes a description of the evidence received. Then, the fire debris analyst decides on an extraction procedure in order to extract any ignitable liquid residue (ILR) from the fire debris. Three extraction procedures recommended by ASTM are solvent extraction, active headspace extraction, and passive headspace extraction [3-5].

Table 1.2 Examples of ignitable liquids in each ASTM class.

Class	Alkanes	Cycloalkanes	Aromatics	Polycyclic Aromatic Hydrocarbons
Gasoline	Present	Present	Present, abundant	Present
Aromatic Products	Not present	Not present	Present, abundant	Present, abundant
N-Alkane Products	Normal alkanes present, abundant	Not Present	Not Present	Not Present
Isoparaffinic Products	Branched alkanes present	Not Present	Not Present	Not Present
Naphthenic Paraffinic Products	Branched alkanes present	Present, abundant	Not Present	Not Present
Petroleum Distillates	Branched and normal alkanes present	Present	Present	Present
Oxygenated Solvents	Oxygenated organic compounds present with other classes of compounds			
Miscellaneous	A combination of compounds that do not fit into the previous classes			

A solvent extraction is performed by adding an organic solvent, such as pentane or carbon disulfide, to the evidence [3]. The sample collected from the scene is placed in a beaker and a sufficient volume of solvent is added. The extraction is performed for one minute. Then the solvent is removed from the sample and concentrated to 1.0 mL for analysis by gas chromatography-mass spectrometry (GC-MS). This extraction method is advantageous for the heavy carbon compounds due to their low volatility.

Another extraction method recommended by ASTM is an active headspace extraction where the sample is heated in an unlined paint can between 50°C to 80°C for 2-24 hours [4]. The heating of the fire debris volatilizes any compounds that have a low boiling point. Once the paint can has been thoroughly heated, a gas-tight syringe is inserted through a small hole in the top of the paint can, and 1.0 µL of sample is drawn into the syringe. Immediately, the sample is injected and analyzed by gas chromatography-mass spectrometry (GC-MS). This extraction procedure favors compounds with low volatility. However, heavier compounds, which have a high boiling point, will not volatilize into the headspace and will not be detected in the analysis of the extract.

The most common extraction method is a passive headspace extraction with activated carbon strip. With this ASTM recommended procedure, an activated carbon strip is suspended in the headspace of the paint can which contains the fire debris [5]. The can is closed, then placed in the oven at a temperature between 50°C to 80°C, and extracted for 2 to 24 hours. Once the extraction is complete, the activated carbon strip is removed from the paint can and eluted with a solvent, such as carbon disulfide or pentane, at a volume of 50 to 1000 µL. The extract is then analyzed by GC-MS. As with

the active headspace extraction, the passive headspace extraction also favors compounds with low boiling points. However, the compounds in the headspace must compete with one another for absorption and adsorption onto the activated carbon strip. Thus, some of the compounds may not be as concentrated on the strip as they are in the sample. When eluting the carbon strip, some of the compounds may adhere to the strip and decrease the concentration in the extract analyzed.

1.3 Analysis of Ignitable Liquid Residues

Once the ILR has been extracted from the fire debris, it is analyzed by GC-MS, which will be discussed in more detail in Chapter 2. Briefly, liquid extracts are volatilized upon injection into the instrument. Any ignitable liquids in the extract are then separated into individual compounds based on their hydrocarbon content as observed in Table 1.1. For example, the normal alkanes in gasoline will be separated from the aromatic compounds. Once the compounds have been separated, they are detected using mass spectrometry. Using GC-MS, the compounds are separated and can be definitively identified. However, the compounds in the extract must be volatile and thermally stable to be analyzed by GC.

Along with the analysis of the ILR extract, extracts of the unburned debris and burned debris, which are not suspected to contain any ignitable liquid, should also be analyzed. Due to the manufacturing process, inherent hydrocarbons, which are similar to those found in ignitable liquids, could be present in the unburned matrices [6]. Also, the

burned matrices contain thermal degradation products that are similar to the compounds present in an ignitable liquid [7].

The final output of GC-MS is a total ion chromatogram (TIC), which shows abundance of the separated compounds on the y-axis and retention time on the x-axis. The chromatogram contains peaks which indicate the different compounds present in the ILR extract. Furthermore, each peak is also represented by a mass spectrum in order to identify the compound present. The chromatogram is then compared to a reference collection of chromatograms. Each forensic laboratory typically has an in-house reference collection of known ignitable liquids. In certain cases, an ignitable liquid from a suspect can be analyzed by GC-MS, and the resulting chromatogram can be used as a point of reference. The ILR chromatogram and the reference chromatogram are then compared visually by the analyst. When the ILR chromatogram is assessed to determine the presence or absence of an ILR, the peak ratios of the compounds must be similar to those in the reference chromatogram of the ignitable liquid.

The identification of peaks in the TIC along with the relationship of these peaks to each other can identify an ILR present in the fire debris [8]. When determining the presence or absence of an ignitable liquid present in the fire debris, the analyst must identify the compounds in the chromatogram by their mass spectrum. Once the compounds have been identified, the relationship, or pattern, among the peaks indicates the class of ignitable liquid present. For example, the presence of the C₁₂ normal alkane along with ethylbenzene will not identify the ILR as a petroleum distillate. The presence of the C₁₂ normal alkane could classify the liquid as gasoline, petroleum distillate, or n-alkane. The presence of ethylbenzene could classify the liquid as gasoline, petroleum

distillate, or aromatic. However, the presence of a chain of normal alkanes in a Gaussian distribution including the C₁₂ normal alkane along with the presence of ethylbenzene with other aromatic, branched, and cyclic compounds would classify the liquid as a petroleum distillate.

1.4 Problems in Identifying Ignitable Liquid Residues in Fire Debris

The problems with identifying an ILR from fire debris begin before the ignition of the fire. Sometimes, an ignitable liquid is spread around the scene and ignited at a later time in order to create an alibi for the arsonist. Once the ignitable liquid is spread, the more volatile compounds present in the liquid will evaporate, thus decreasing the presence of these compounds in the resulting chromatogram. With the decrease or loss of these compounds, the ignitable liquid, even before burning, has become more difficult to identify. Once the ignitable liquid has been ignited, more compounds are lost from the ignitable liquid due to thermal degradation and evaporative loss due to burning. The loss of the compounds further changes the chromatogram making identification even more difficult.

Since any ignitable liquid present will act as a fuel, other matrices, along with oxygen, must be present to sustain the fire. The interferences present from both the unburned and burned matrices contribute to the difficulty in the identification of the presence of the ILR. Due to the manufacturing process, household products, from flooring to upholstery, contain many inherent hydrocarbons. These hydrocarbons in the matrix can mask or coelute with the hydrocarbons in the ILR. Furthermore, additional

interferences are present due to thermal degradation of the matrices as a result of burning. These additional matrix interferences further complicate the chromatogram.

After extraction and analysis, the ILR chromatogram is compared to the reference chromatogram by a fire debris analyst. Although fire debris analysts are trained to identify the patterns present, the pattern recognition performed through visual assessment is subjective. Furthermore, there are no statistical procedures applied to the ILR chromatogram and the reference chromatogram in order to assess similarity between them. The application of statistical procedures would further confirm or deny the presence of an ILR in the chromatogram and show the similarity of the ILR chromatogram to the reference chromatogram. Furthermore, the National Academy of Sciences report on forensic science states that statistical evaluation of forensic evidence, including fire debris evidence, is necessary in order to strengthen the conclusions made by fire debris analysts [9].

1.5 Literature Review

1.5.1 Procedures to Reduce Non-Chemical Sources of Variance in Chromatographic Data

In order to limit non-chemical sources of variance that are introduced into a data set when samples are analyzed by GC-MS, both the GC temperature program and data pretreatment procedures must be investigated. Common data pretreatment procedures include smoothing, retention time alignment, and normalization.

In a study by Baerncopf *et al.*, the influence of six different GC temperature programs on association and discrimination of five diesel samples analyzed in triplicate was investigated [10]. The diesel samples were analyzed using temperature programs with varying ramp rates. The resulting chromatograms were then subjected to data pretreatment procedures, specifically retention time alignment and normalization. The chromatograms were then subjected to principal components analysis (PCA) and Pearson product moment correlation (PPMC) coefficients in order to assess the effect of temperature program on association and discrimination of the diesel samples. The results of the chemometric procedures showed similar association and discrimination of the diesel samples for each temperature program. Since chemometric procedures were not significantly affected by the temperature program, the recommended temperature program was 10°C/min to decrease the analysis time of the diesel samples. While the effect of the temperature program on association and discrimination was investigated for diesel, the data pretreatment procedures were not thoroughly examined in this study.

In order to remove instrumental noise introduced during analysis, smoothing can be applied to each chromatogram in the data set. Of the smoothing filters available, the Savitzky-Golay algorithm is commonly used [11]. In order to smooth a chromatogram using this algorithm, two parameters must be specified by the user: order of the polynomial and window size. The window size is the number of data points to which the polynomial is fitted. To smooth a chromatogram using the Savitzky-Golay algorithm, the polynomial is fitted to the data points in the window. Then, the algorithm calculates the value for the data point in the middle of the window using the polynomial and replaces the experimental data point with the calculated point. The algorithm shifts the window

and repeats the process for each data point in the chromatogram. Since the peaks in a chromatogram are curved, a second or third order polynomial is usually chosen. The other polynomial degrees do not represent the shape of the peaks and would reduce the abundance of them. Also, a small window size is usually chosen since a large window size usually reduces the peak height and peak width [12].

Due to variation of the flow rate within the instrument, the chromatograms within a data set should be retention time aligned to correct for slight shifts in retention times of peaks. Many studies on retention time alignment have been published in the literature. Two of the more common retention time alignment algorithms are the peak matching algorithm and the correlation optimized warping (COW) algorithm.

Johnson *et al.* developed the peak matching algorithm using diesel samples in order to correct for retention time variation among chromatograms [13]. For the study, two data sets of diesel samples were investigated. The first set contained chromatograms of 20 diesel samples analyzed in triplicate by gas chromatography-flame ionization detection (GC-FID). For a given peak, the maximum range that a peak was shifted was 300 ms. The second data set contained chromatograms of 21 diesel samples analyzed in duplicate by GC-FID. In this case, the maximum range that a peak was shifted was 10 s. Through visual assessment of the data sets before and after alignment, the peak matching algorithm improved the alignment of the peaks with similar retention times in the chromatograms. In order to further investigate the alignment, PCA was applied to both the unaligned and aligned data sets. The replicates of each diesel sample were associated to each other and differentiated from the other diesels for both the aligned and unaligned

data sets. However, the replicates of each diesel were more closely associated to each other in the aligned data sets than in the unaligned data sets.

Nielsen *et al.* developed the COW algorithm that optimizes the correlation between chromatograms in order to align the peaks [14]. Within this study, two experiments were performed to investigate improvement in peak alignment using the COW algorithm. In the first experiment, two chromatograms were constructed using mathematical software. The chromatograms differed in the number of data points, noise levels, and baseline drift. The chromatograms were then aligned using the COW algorithm. Through visual assessment, the peaks within the chromatograms were well aligned to each other indicating that the COW algorithm is not sensitive to common variations in chromatographic data (i.e. differences in data points, noise levels, and baseline drift). In the second experiment, 16 fungal cultures were analyzed by high performance liquid chromatography. The resulting chromatograms were compiled into a data set and aligned using the COW algorithm. Overall, the alignment of the chromatograms was improved in the two experiments, as determined through visual assessment.

Tomasi *et al.* investigated the effect of retention time alignment, using the COW algorithm, on association and discrimination of 84 coffee extracts packaged under different conditions [15]. The extracts were analyzed by GC-MS, and the chromatograms were compiled into a data set and background subtracted. The chromatograms were retention time aligned using the COW alignment. Both the aligned and unaligned data sets were subjected to PCA. The scores plot for the unaligned coffee extracts showed a 'horseshoe' shape, which indicated that the association and discrimination of the samples

was mainly based on retention time shifts observed in the chromatograms. The scores plot for the aligned data did not exhibit a 'horseshoe' pattern, indicating that the association and discrimination of the aligned coffee extracts was due only to chemical variation. Overall, the COW algorithm improved alignment of the chromatograms and removed non-chemical sources of variation such that association of the samples was based only on chemical similarities among the samples and discrimination was based only on chemical differences.

In order to minimize variation in injection volume and instrument response between analyses of each sample, normalization can be applied to the entire data set. To normalize a data set, the chromatograms are scaled to a similar order of magnitude depending on the type of normalization [11]. For example, total area normalization is performed by summing the abundance under the chromatogram and dividing each data point by that sum. Through normalization, the variability in abundance among peaks is reduced since the abundance of each peak is a fraction of the total abundance. Normalization is performed prior to data analysis in order to reduce the influence of a sample in the data set contributing more to the variance than the chemical variance.

1.5.2 Evaporation of Ignitable Liquids

Few studies in the literature have addressed the effect of evaporation on the identification of ignitable liquids in fire debris. A study by Barnes *et al.* investigated the association of evaporated gasoline samples to the neat gasoline samples using target compound analysis [16]. Sixteen gasoline samples were evaporated to the 50% and 75% evaporation levels. The neat gasoline samples and the 75% evaporated gasoline were

spiked onto a Kimwipe® inside a paint can and extracted using an active headspace extraction procedure. The 50% evaporated gasolines were spiked onto a piece of charred pine inside a paint can and extracted in a similar manner. Three headspace samples from each of the extracts were analyzed by GC-MS. For target compound analysis, ratios of aliphatic compounds common to neat gasoline were compared to the corresponding ratios in the 50% and 75% evaporated gasoline chromatograms. The compounds that gave reproducible ratios within a set of replicates and the most variable ratios among neat and evaporated samples were chosen. The 75% evaporated gasolines and 50% evaporated gasolines recovered from the charred pine were associated to the original gasoline using four compound ratios and six compound ratios, respectively. However, the entire chromatogram was not utilized in this study, only the ratios of specific compounds. Furthermore, only gasoline was investigated which decreases the applicability of target compound analysis to other ignitable liquid classes.

A study by Sandercock and Du Pasquier was performed to determine if evaporated gasoline samples could be associated to the corresponding neat gasoline sample [17]. Thirty five gasoline samples, varying in grade, were obtained from 24 gas stations over a seven month period. Each gasoline sample was evaporated to four different levels of evaporation (25%, 50%, 75%, and 90%) by weight. The samples were then diluted and analyzed in replicate (n=5) using GC-MS with selected ion monitoring for the C₀-C₂ naphthalene compounds. The resulting chromatograms were normalized using a natural logarithmic transformation; however, no retention time alignment was reported. Principal components analysis and linear discriminant analysis (LDA) were applied to a data set containing all chromatograms. Using a combination of PCA and

LDA, the 35 gasolines formed 18 groups, where 11 groups contained one gasoline sample, which included both neat and evaporated samples, and the remaining 24 samples were classified into seven groups. The seven groups contained gasoline of similar grade and brand, irrespective of evaporation. Through this study, the differences in the abundance of the C₀-C₂ naphthalenes were used to discriminate different gasoline samples, while associating the evaporated gasoline sample to the corresponding neat gasoline. However, this study did not investigate the effect of evaporation on other ignitable liquid classes. Furthermore, only a section of the chromatogram was used, limiting the discrimination of the liquids to only a few compounds. Also, the gasoline samples were directly injected and not extracted, which would simulate the procedure used for fire debris.

In a study by Tan *et al.*, the effect of evaporation of an ignitable liquid on a matrix was investigated using soft independent model classification analogy (SIMCA) [18]. One ignitable liquid was selected from each class investigated: light petroleum distillate, gasoline, medium petroleum distillate, kerosene, and heavy petroleum distillate. Each ignitable liquid was spiked onto a piece of polyolefin carpet in triplicate. The samples were evaporated in a temperature regulated tank for up to seven days at specified temperatures of 0°C, 20°C, or 35°C. The ignitable liquids were extracted from the carpet using a solvent extraction procedure and analyzed by GC-MS. The resulting chromatograms were normalized to an internal standard and subjected to PCA and SIMCA.

Principal components analysis was first applied to the neat liquids. Then, two of the replicates of the neat liquids were used as a training set in order to form a

classification model using the SIMCA procedure. The third replicate was used to test the classification ability of the model. Then, the evaporated liquids were classified using the developed model. Through classifying the liquids, the researchers observed that at higher temperatures, the ignitable liquid was more difficult to classify due to evaporative losses. However, the researchers gave no indication of which compounds were lost from the evaporated liquids leading to the misclassification in the SIMCA model. Except for normalization, data pretreatment procedures, such as smoothing and retention time alignment, were not applied to the chromatogram, which could have lead to misclassification of the evaporated samples by SIMCA.

Each of the studies described above investigated the effect of evaporation on the association of an evaporated ignitable liquid to a neat ignitable liquid. However, none of these studies investigated which compounds were lost from an ignitable liquid due to evaporation. Furthermore, these studies did not investigate matrix interferences present in fire debris, with the exception of Tan *et al.* whose study consisted of mainly unburned matrices.

1.5.3 Matrix Interferences

Most matrix interference studies in the literature do not address the difficulty in identifying an ILR from fire debris. In a study by Lentini *et al.*, unburned matrices were investigated in order to determine which ignitable liquid profiles, if any, were present in household products [6]. Matrices, such as flooring, clothing, paper products, and shoes, were collected. Each matrix was placed in separate paint cans, extracted using the passive headspace extraction procedure, and analyzed by GC-MS. Within the chromatograms of

certain household products, ignitable liquid profiles were observed. For example, spandex shorts were observed to contain a profile resembling that of kerosene. Also, newspaper was observed to contain medium to heavy petroleum distillates, which could cause false positives in ignitable liquid determinations. However, fire debris collected at a scene has been burned, which would change the interferences present in the household products, and this was not investigated by Lentini *et al.*

Due to burning, the fire debris collected at a suspected arson scene contains pyrolysis and thermal degradation products. In order to clarify the mechanisms by which pyrolysis occurs in fire debris, Stauffer investigated common polymers found in matrices, such as carpet and plastic bags [19]. Samples of pure polymers, such as polyethylene, polyvinyl chloride, and polystyrene, were collected, burned, and then extinguished with water. The samples were then extracted using a passive headspace extraction and analyzed by GC-MS. Using these pyrolyzed samples, the three major mechanisms of degradation (random scission, side group scission, and monomer reversion) were demonstrated. Random scission occurred when the polymer backbone was broken in random places. The pyrolysis products common to random scission are alkanes, alkenes, and alkadienes. This mechanism of degradation commonly occurs in polyethylene. Side group scission occurred when side groups attached to the polymeric backbone were cleaved. Many aromatic compounds, such as benzene, toluene, ethylbenzene, styrene, and naphthalene, are formed due to side group scission. This mechanism commonly occurs in polyvinyl chloride. Monomer reversion occurred when the polymer breaks apart into the original monomers. This mechanism commonly occurs in polymethylmethacrylate. A combination of these mechanisms could occur in polymers as well. For example, the

pyrolysis of polystyrene produced compounds such as styrene, toluene, ethylbenzene, and naphthalene. Styrene was present due to monomer reversion, while the other compounds were present due to side group scission. With this study, the mechanisms of degradation by which pyrolysis products are formed were investigated using pure polymers. However, the matrices collected at an arson scene are composed of a combination of polymers and other materials, such as adhesives and wood.

In a study by Almirall and Furton, household matrices were collected and burned in order to determine the pyrolysis and thermal degradation products common to these matrices [7]. Thirty five matrices, such as carpet, wallpaper, and plastic products, were collected and burned under controlled conditions. The burned matrices were then extracted using a passive headspace procedure in an unlined paint can and analyzed by GC-MS. The compounds from the burned matrices were identified by their retention time and mass spectra. Almirall and Furton found that many of the compounds in the burned matrices, such as normal alkanes, cyclic alkanes, alkylbenzenes, and naphthalenes, are also used to identify an ILR. However, the chromatographic patterns of the burned matrices were different than those of an ILR.

In another study, Fernandes *et al.* investigated the pyrolysis of partially burned household matrices in order to determine the pyrolytic compounds present [20]. For this study, common household matrices, such as flooring, adhesives, and spray paint were collected and assembled as they would be in a house. For example, a spray paint was applied to wood in order to simulate furniture. The assembled items were burned until approximately half was consumed and then extinguished using water. The burned matrices were then extracted and analyzed by GC-FID. The chromatograms of the burned

matrices showed the presence of volatile compounds that were similar to those present in ignitable liquids. However, the pattern of these compounds was not representative of an ignitable liquid. With the studies by Fernandes *et al.* and Almirall and Furton, the identification of an ignitable liquid in the presence of an ignitable liquid was not investigated.

In a study by Bertsch, the effect of matrix interferences on the identification of an ignitable liquid was investigated using visual assessment of chromatograms [21]. Carpet and carpet padding were collected from various sources and charred under various conditions. Some of the burned carpet and carpet padding were spiked with gasoline. The spiked and non-spiked matrices were extracted using a passive headspace procedure and analyzed by GC-MS. Chromatograms of the spiked and non spiked matrices were visually compared. The burned matrices contained some similar compounds to gasoline, such as alkylbenzenes and naphthalenes, as well as other pyrolysis products. Within the burned matrices spiked with gasoline, the pyrolysis products coeluted with some of the compounds from gasoline. However, the pattern of alkylbenzenes from gasoline was different from those present in the burned matrix. This study only employed visual assessment and did not apply any statistical or chemometric procedures to the data.

In a study by Borusiewicz *et al.*, various factors, such as type of accelerant, type of matrix, time of burning, and availability of air, were investigated to assess their influence on the identification of an ignitable liquid from fire debris [22]. For the study, three matrices (carpet, deciduous wood, and chipboard) and five ignitable liquids, including gasoline, kerosene, and diesel were collected. Each matrix was spiked with an ignitable liquid and burned using various conditions. The burned matrix was then

extracted using a passive headspace procedure and analyzed using GC-MS. Through visually assessing the chromatograms, Borusiewicz *et al.* determined that the type of matrix influenced the identification of an ignitable liquid most. Since carpet is more absorbent than wood or chipboard, more of the compounds from the ignitable liquids were able to be identified, thus increasing the likelihood of identifying the ignitable liquid. However, as with the study by Bertsch, no statistical or chemometric procedures were applied to the data.

All of the studies previously mentioned have used visual assessment of chromatograms in order to draw conclusions from their results. A study conducted by Baernkopf *et al.* investigated the influence of matrix interferences on the association of a simulated ILR to the corresponding neat liquid using chemometric procedures [23]. Six liquids from different ASTM classes were selected for the study. Each liquid was spiked onto separate pieces of carpet and burned in triplicate using both light and heavy burn conditions. The simulated ILRs were extracted using a passive headspace extraction procedure and analyzed by GC-MS. The extracts were separated into two data sets according to their burn conditions and then retention time aligned and normalized. Pearson product moment correlation coefficients and PCA were applied to the data sets to assess the association of the simulated ILRs to the neat liquids. For both sets of burning conditions, the simulated ILRs were associated to the corresponding neat liquid using both PCA and PPMC coefficients. Although chemometric procedures were used, the PCA scores plot was visually assessed with no statistical measure of the association and discrimination observed. Furthermore, the matrix interferences in the chromatograms, even under the heavy burn conditions, were limited.

While matrix interferences from both burned and unburned matrices have been investigated, many of these studies did not utilize chemometric procedures in order to associate the ILR to the corresponding neat ignitable liquid. However, Baerncopf *et al.* did use chemometric procedures in associating an ILR to the corresponding ignitable liquid, but very few matrix interferences were observed even under heavy burning conditions.

1.5.4 Statistical and Chemometric Analysis of Ignitable Liquids

Statistical and chemometric procedures have been applied to ignitable liquids in order to differentiate according to grade, brand, or service station location [24-28]. In each of these studies, only one ignitable liquid, either gasoline or diesel, was investigated, limiting the application of the chemometric procedures used in these studies.

In a study by Gaines *et al.*, peak ratios of compounds in diesel samples were investigated in order to discriminate the diesels from each other using PCA [24]. The 14 diesel samples were diluted and analyzed by GC-MS. The peaks from the extracted ion chromatograms were integrated and used to calculate peak ratios. Due to the large number of peak ratios calculated, PCA was applied to the data set in order to reduce the number of ratios necessary to differentiate the diesels. Of the 313 peak ratios, nine contributed most to the variance and could be used to differentiate the diesel samples.

In a study by Sandercock and Du Pasquier, gasoline samples were investigated in order to determine which compounds within these samples could differentiate them by grade and brand [25]. Firstly, the polycyclic aromatic hydrocarbons (PAH) and the polar compounds present in the 35 gasoline samples were isolated from each other using a solid

phase extraction procedure with activated alumina. The PAH extract and the polar compound extract were analyzed in replicate (n=5) by GC-MS, and for the PAHs, selected ion monitoring was also utilized. The chromatograms were visually assessed and subjected to PCA and LDA. When the chromatograms were visually assessed, the polar compounds were similar in relative ratios for all samples, while the PAHs varied among samples, specifically the C₀-C₂ naphthalenes. Through PCA, the gasoline samples were able to be differentiated based on the abundance of the C₀-C₂ naphthalenes. The gasoline samples were also classified into 32 groups with most groups containing a single sample. The researchers were able to discriminate most gasoline samples through the C₀-C₂ naphthalenes. However, this study along with the study by *Gaines et al.* was only based on a small number of compounds in the chromatogram. Using the entire chromatogram would offer more discrimination among samples.

In another study in the literature, ignitable liquids were associated and discriminated based on peak area of specific compounds using statistical and chemometric procedures. Doble *et al.* investigated the classification of gasoline samples using PCA, LDA, and artificial neural networks (ANN) [26]. Eighty eight gasoline samples of various grades were collected and analyzed by GC-MS. The peak area of 44 target compounds for each gasoline sample were calculated and subjected to PCA. The gasolines were differentiated by grade using PCA, and 93% of the gasolines were classified correctly by grade using LDA. When the grades were further classified into summer and winter gas using LDA, 62% of the gasolines was classified correctly. Once trained to classify gasolines by grade and by season, the ANNs were able to classify 97%

of the samples correctly. As with previous studies, only gasoline was investigated, and only a select number of peaks were used for the study, rather than the full chromatogram.

In a study by Hupp *et al.*, diesel samples of various brands were discriminated from each other using PCA and PPMC coefficients [27]. Twenty five diesel samples were collected, and each sample was diluted and analyzed in triplicate by GC-MS. Total ion chromatograms along with extracted ion chromatograms (EIC) for the alkane (m/z 57) and aromatic (m/z 91) profiles were generated. The resulting chromatograms were retention time aligned using the peak matching algorithm developed by Johnson *et al.* and normalized using total area normalization [10]. Principal components analysis and PPMC coefficients were applied to the diesel samples. The PPMC coefficients for diesel samples of the same brand were higher than PPMC coefficients among different brands for both the TICs and the EICs. This indicates that diesel samples from the same brand are more similar in chemical composition than diesels of different brands. Within the PCA scores plot for the TICs, samples were differentiated into four groups. The first group contained samples from the same brand. Two of the groups each contained a single diesel, and the last group contained the remaining 19 diesels. The discrimination was similar for the scores plots of the EICs; however, more discrimination among samples was observed in the scores plot for the aromatic EICs, which was also reflected in the PPMC coefficients calculated. The aromatic compounds in the diesel samples varied more in abundance than the alkane compounds thus contributing to the differentiation observed in the PCA scores plot and PPMC coefficients.

A study by Marshall *et al.* also investigated the association and discrimination of diesel samples using PPMC coefficients and PCA [28]. Five diesel samples of various

brands were collected and analyzed in triplicate using GC-MS. Total ion chromatograms along with extracted ion profiles (EIP) for the alkane (m/z 57+71+85+99) and aromatic (m/z 91+105+119+133) profiles were generated. The TICs, alkane EIPs, and aromatic EIPs formed three data sets, respectively. The chromatograms in each data set were baseline corrected, retention time aligned using the peak matching algorithm developed by Johnson *et al.*, and normalized using total area normalization [10]. The data sets were then subjected to PPMC coefficients and PCA. For each data set, most of the diesel samples were distinguishable from each other using PPMC coefficients. The PCA scores plot for each data set showed the replicates of each diesel were clustered together and discriminated from the other diesels. Spread was observed among replicates, which was due to misalignments in the data set. Marshall *et al.* determined that derivative shaped peaks in the loadings plot indicate misalignments in the data set. The studies conducted by Hupp *et al.* and Marshall *et al.* only investigated one ignitable liquid, which limits the applicability of these studies to other classes of ignitable liquids. Furthermore, the visual assessment of the PCA score plots is subjective. In order to remove this subjectivity, other chemometric procedures must be investigated to allow a statistical measure of association and discrimination observed in the scores plot.

1.6 Research Objectives

The present literature has a variety of limitations. For evaporated ignitable liquids, the studies did not utilize the entire chromatogram for association of the evaporated ignitable liquids to the corresponding neat ignitable liquid. Furthermore, the studies did

not indicate which compounds in the ignitable liquids were lost due to evaporation. Most matrix interferences studies relied only on visual assessment of chromatograms and did not apply any statistical or chemometric procedures to the data. Furthermore, very few of these studies investigated simulated ILRs. In addition, ignitable liquid mixtures have not been investigated, and currently no literature on them exists. The studies on statistical and chemometric procedures only investigated one ignitable liquid, limiting the application of these procedures to other ignitable liquids. With the limitations of previous studies, the objectives of this research were:

- To associate the evaporated liquids to the corresponding neat liquid using chemometric procedures based on the full chromatogram.
- To associate an evaporated ignitable liquid mixture to the corresponding mixture even in the presence of matrix interferences.
- To associate an evaporated ignitable liquid mixture to the corresponding mixture even in the presence of matrix interferences and combustion.

The first study investigated the effect of evaporation on the association and discrimination of ignitable liquids. A subset of six ignitable liquids from six different ASTM classes were chosen and evaporated to four levels of evaporation. The evaporated liquids along with the neat liquids were extracted by passive headspace extraction with activated carbon strip and then analyzed by GC-MS. The chromatograms of the neat and evaporated liquids were subjected to data pretreatment procedures, such as smoothing, retention time alignment, and normalization, to eliminate any non-chemical sources of variance. Then PCA, PPMC coefficients, and hierarchical cluster analysis (HCA) were

applied to the chromatograms in order to investigate the association of the evaporated liquids to the corresponding neat liquid.

With more than one ignitable liquid present in some ILRs, the second objective of this research was to investigate the association of a mixed ignitable liquid to the original mixed liquid, in the presence of matrix interferences, evaporation, and thermal degradation products. Two liquids were selected and evaporated to two levels of evaporation then mixed in various combinations. The mixtures were spiked onto burned carpet to investigate the association of the mixed liquids to the original mixed liquid despite matrix interferences. The mixtures were also spiked onto unburned carpet and burned to investigate the association of the simulated ILR to the original mixed liquid despite matrix interferences and evaporation. The different combinations of the neat and evaporated liquids, along with the mixtures spiked onto burned carpet and the simulated ILRs, were extracted using a passive headspace extraction with activated carbon strip and analyzed by GC-MS. Data pretreatment procedures were applied to the chromatograms to remove non-chemical sources of variance. Then, PCA, PPMC coefficients, and HCA were used to investigate the association of the mixed liquids even in the presence of matrix interferences, evaporation, and thermal degradation.

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CHAPTER 2

Instrumental, Statistical, and Chemometric Techniques

2.1 Gas Chromatography-Mass Spectrometry

Gas chromatography-mass spectrometry (GC-MS) is used by fire debris analysts for the analysis of the ignitable liquid residues (ILR) from fire debris. It is one of the most common analytical instruments used in a forensic laboratory. In basic terms, the gas chromatograph separates the mixture into individual compounds, while the mass spectrometer fragments and detects the separated compounds from the gas chromatograph.

Overall, chromatography is the separation and detection of the compounds present in a mixture. With all chromatographic techniques, a mobile phase and a stationary phase are present and effect the separation of a mixture [1]. The mobile phase carries the compounds within the mixture through the stationary phase, while the interaction of the compounds between the mobile phase and the stationary phase separates them. For gas chromatography, the mobile phase is a carrier gas, such as helium, while the stationary phase is a thin film, which contains nonpolar compounds.

The mixtures that can be analyzed by GC-MS must be easily volatilized so that thermal degradation does not occur. One of the ways of introducing a mixture into the GC-MS is through dissolving it in a solvent and injecting it by a syringe. The solvent must not interact with the mixture and also be volatilized upon injection [1]. In order to inject the mixture, a syringe is cleaned with the solvent in order to prevent contamination, and then typically one microliter of the sample is drawn up into the syringe. An

additional microliter of air is also drawn up into the syringe. This prevents the mixture from volatilizing inside the needle prior to injection.

The mixture is introduced into the instrument through a heated inlet (Figure 2.1) and travels onto the GC column along with the carrier gas. The temperature of the inlet is set between 150°C -300°C in order to volatilize the mixture upon injection into the instrument, which is determined by the boiling point of the least volatile compound in the mixture [1].

Along with the temperature of the inlet, the split mode is set by the analyst in order to allow a portion or the entire mixture onto the GC column. This is done to prevent highly concentrated mixtures from traveling onto and contaminating the GC column. In split mode, a split ratio must be determined by the analyst, where a part of the mixture injected is allowed onto the column while the other part is diverted to waste. So, for a 50:1 split, one part of the mixture passes onto the column and the other 50 parts pass into waste. For mixtures where the analytes are in trace amounts, splitless mode is chosen instead of split mode. With splitless mode, all of the mixture travels onto the column and is separated and analyzed. With a splitless injection, the split valve remains closed so that the mixture can travel onto the column and then reopens to allow the carrier gas to clean the inlet.

One of the other parameters in the inlet that can be adjusted is the pressure. For a set period of time, the pressure in the inlet can be increased in order to force more of the sample onto the column. A pressure pulse is employed to limit peak broadening and to make the injection more reproducible.

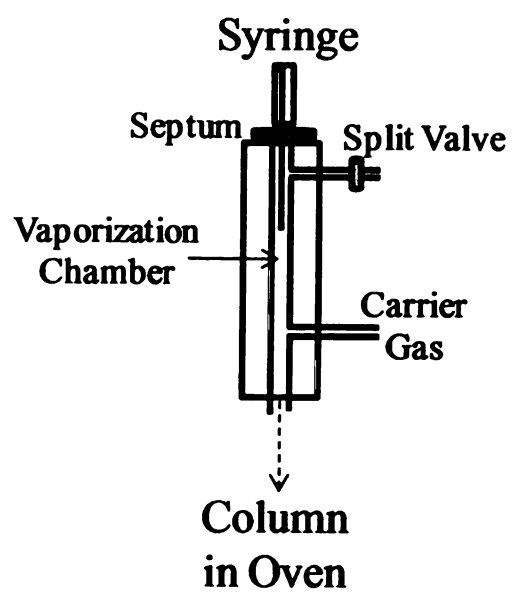


Figure 2.1: Diagram of GC inlet.

From the inlet, the analytes pass onto the GC capillary column contained within a temperature-controlled oven (Figure 2.2). Within the GC column, the analytes are separated by boiling point and interaction with the stationary phase. The main contributor to the separation of the analytes is boiling point. When they pass onto the column, the analytes with a lower boiling point will travel through the column faster than those with a higher boiling point.

In order to more efficiently separate the analytes, a temperature program can be set for the oven. With some mixtures, an isothermal temperature program, where the oven temperature remains constant throughout the entire analysis, is sufficient. However, the concern with an isothermal temperature program is that some of the analytes will condense on the column, thus causing contamination. Furthermore, mixtures which contain analytes with a wide range of boiling points will not be sufficiently separated. For most analyses, a GC temperature program with a single ramp rate is used. With a low ramp rate, such as 4°C/min, the resolution of the analytes may be improved, since analytes with similar boiling points will be separated more efficiently. However, the low ramp rate will extend the time of analysis and possibly subject the analytes to peak broadening. With a high ramp rate, such as 30°C/min, the analytes will travel through the GC column faster; however, many of the analytes will coelute and not be distinguished from each other when they are detected. So, a temperature program must be found that sufficiently separates the analytes in the mixture without causing peak broadening.

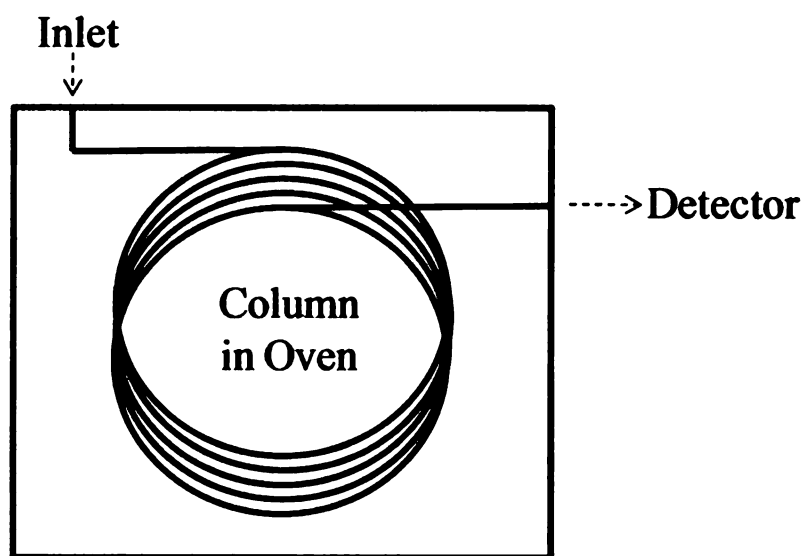


Figure 2.2: Diagram of GC column in temperature controlled oven.

Along with boiling point, the interaction with the stationary phase of the analytes will affect separation, which is based on the polarity. The stationary phase can be nonpolar and made of a thin liquid layer of polymethylsiloxanes. The thin layer coats the inside of the GC column and is no more than 0.25 micrometers thick [1]. When the compounds pass through the column, the analytes interact with the stationary phase. Furthermore, the nonpolar analytes have more interaction with the stationary phase than the polar analytes. So, the nonpolar analytes are retained on the GC column longer than those that are polar, thus causing separation.

Once they have been separated in the GC column, the analytes pass from atmospheric pressure through a heated transfer line (300°C) into a vacuum. This is possible due to the low flow rate and to the GC column fitting directly into the detector.

Of the many detectors available, the most common detector in a forensic laboratory is the mass spectrometer. The mass spectrometer contains three parts: the ionization source, the mass analyzer, and the detector. In the ionization source, the analytes are ionized and fragmented. Then, the fragments are separated by mass-to-charge (m/z) ratio in the mass analyzer, and are finally detected by the detector. The entire mass spectrometer is maintained under vacuum in order for the ions to remain stable. The mass spectrometers in forensic laboratories usually contain an electron ionization source, a quadrupole mass analyzer, and a continuous dynode electron multiplier detector.

Of the many ionization sources available, electron ionization is the most common ionization used in forensic laboratories. Upon entering the mass spectrometer, analytes are ionized through a stream of electrons that are emitted from a filament (Figure 2.3).

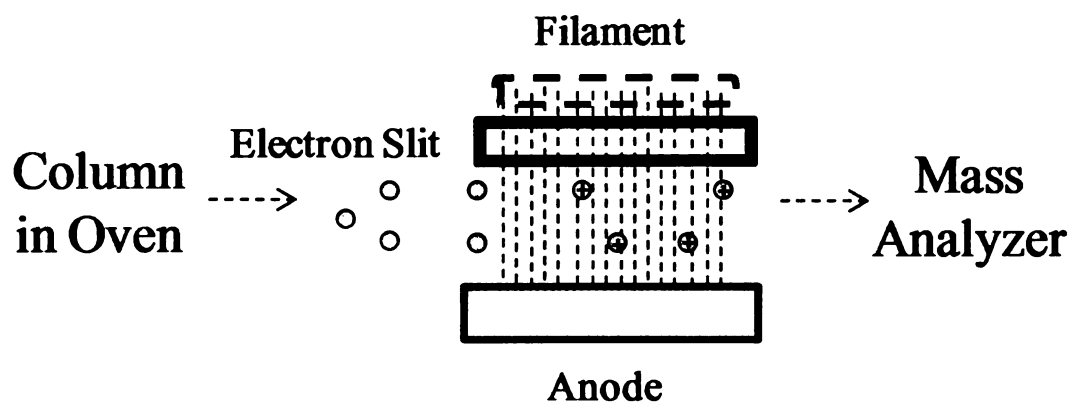


Figure 2.3: Diagram of electron ionization of compounds in mass spectrometer.

The electrons emitted from the filament typically have a voltage of 70 eV and are focused through the electron slit and travel towards the anode. A voltage of 70 eV is advantageous since the maximum energy from the electron is transferred to the analytes. As the stream of electrons is passed perpendicularly to the analytes, interactions occur between them. The primary interaction is where the analyte loses an electron and becomes positively charged, thus forming a molecular ion. Other positively charged fragments will also be formed from the molecular ion interacting with other ions or other electrons within the electron stream [1].

Once the analyte has been ionized and fragmented, the molecular ion and corresponding fragments are focused through electrostatic lenses and accelerated into the mass analyzer (Figure 2.4).

For most forensic analyses and this research, a quadrupole mass analyzer is used. As inferred by its name, the quadrupole mass analyzer has four poles, or rods, that form a diamond shape inside the mass analyzer. The pairs of rods are orthogonal to each other and are oppositely charged with one pair containing a positive charge and the other pair containing a negative charge. The charges on the rods continually alternate. For each set of rods, the charge is applied from a direct current (DC) power source. Along with DC, radio-frequency (RF) voltages are also applied to the rods. As the ions enter and pass through the quadrupole, the DC and RF voltages are increased, while the ratio between them remains constant. As the voltages are increased, the ions oscillate in between the rods because of the alternating positive and negative charges [1]. Due to the increase in RF and DC voltages, some ions will develop unstable trajectories while passing through the quadrupole, impact the rods, and be neutralized. Other ions with stable trajectories

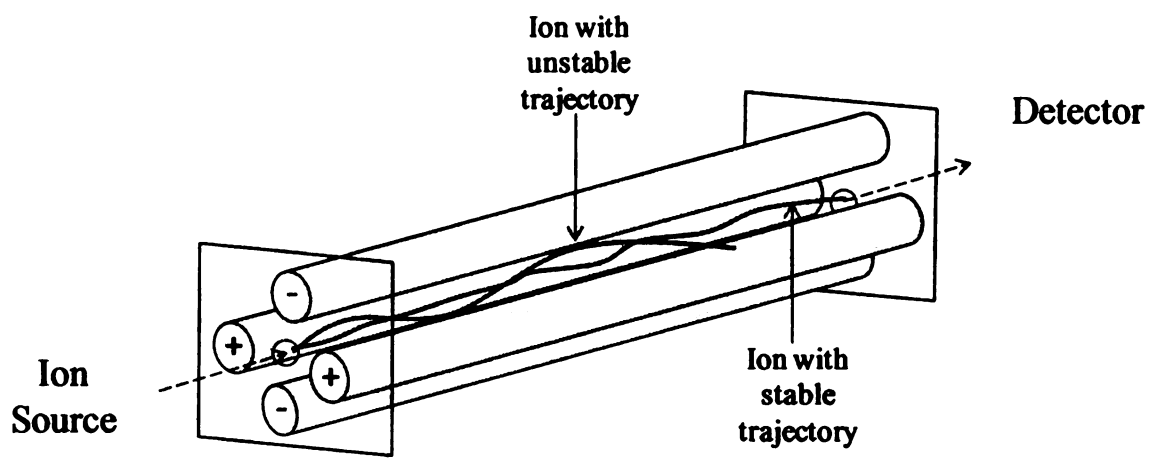


Figure 2.4: Diagram of quadrupole mass analyzer.

will successfully oscillate between the pairs of rods and pass through the quadrupole to the detector. Each RF and DC voltage applied to the rods corresponds to an m/z ratio, thus increasing the voltages across the rods while keeping the ratio between them constant allows for a full mass scan (e.g. m/z 50-550).

The detector within the mass spectrometer detects the ions that have passed through the mass analyzer. Of the detectors that are available, the continuous-dynode electron multiplier is one of the more commonly used detectors (Figure 2.5). It is made of glass that contains a high amount of lead which allows it to maintain an electrical potential of 1.8 to 2 kV [1]. The electron multiplier is shaped in the form of a curved cylinder that has a large opening on one side and narrows to a small enclosure on the other side. When the ions enter the detector through the larger opening, they are attracted to the negatively charged sides of the multiplier. Upon impact, the ions eject secondary electrons which are attracted to higher voltages present further into the multiplier. As the number of impacts increase, the number of secondary electrons increases exponentially [1]. After multiple impacts with the sides of the transducer, the secondary electrons produced are detected at the closed end of the cylinder.

The output of GC-MS analysis is the total ion chromatogram (TIC), which is the sum of all of the ions detected in the mass spectrometer. The TIC is a plot of retention time on the x-axis and abundance of the analytes on the y-axis. Within the chromatogram are peaks, and each peak indicates a different analyte that was separated in the mixture. From each peak, a mass spectrum can be obtained. The mass spectrum is a plot of the molecular ion and the fragmented ions where m/z is on the x-axis and abundance of the

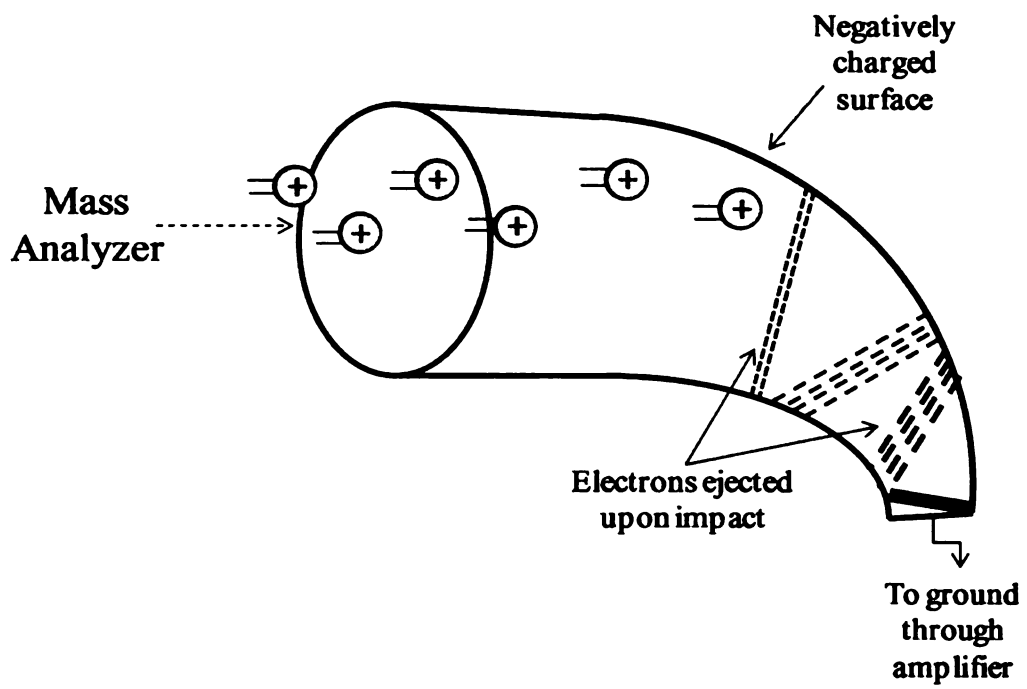


Figure 2.5: Diagram of continuous-dynode electron multiplier.

peaks is on the y-axis. From each mass spectrum, the analyte can be identified since the fragmentation pattern under the same conditions is specific to that analyte.

2.2 Data Pretreatment Procedures

Before subjecting the chromatograms to data analysis, data pretreatment procedures can be applied in order to eliminate non-chemical sources of variance, such as variation in injection volume as well as instrumental drift. The data pre-treatment procedures investigated in this research were smoothing, retention time alignment, and normalization.

2.2.1 Savitzky-Golay Smoothing

Before retention time alignment and normalization of the data set, the chromatograms can be smoothed in order to reduce the instrumental noise introduced during analysis. The algorithm used in this research is known as the Savitzky-Golay smooth [2], which is a least squares polynomial smooth. The algorithm reduces the noise in the chromatogram through recalculating each data point in the experimental chromatogram using a polynomial, which is fitted to a section at a time.

Before smoothing, two parameters must be defined by the user: order of the polynomial and window size. The order of the polynomial defines the equation which will be used to fit each section. A second or third order polynomial is usually selected since the graphs of these polynomials are similar to the peak shape in a chromatogram [3]. With smaller or larger orders, the peaks in the chromatogram may over-smoothed,

thus broadening them. The window size is the number of data points within the chromatogram to which the polynomial is fitted. A window size less than the number of data points contained within a peak will usually provide the best smooth for the chromatogram. However, an extremely small window size will not remove much of the noise in the chromatogram. With a large window size, the peaks in the chromatograms will be over-smoothed, thus reducing the peak height and broadening the peak width. An odd numbered window size is always chosen since the algorithm will average the two data points in the middle of an even numbered window and replace those two points with only one. From this, the number of data points is decreased, thus reducing the chemical information from that chromatogram.

Once the two parameters are determined, the polynomial is fitted to the window at the beginning of the chromatogram. This is done by the algorithm solving the polynomial and recalculating the data point in the middle of that window. Next, the new data point replaces the experimental one, thus smoothing that point. The process repeats one data point at a time until each data point is smoothed.

Although the Savitzky-Golay smooth reduces the noise in the chromatogram, over-smoothing can occur due to a polynomial order that does not fit the chromatographic peak shape or a large window size. Also, the algorithm does not smooth the first and last data points in a chromatogram. For example, with a window size of 15, the first 7 and the last 7 points in a chromatogram will not be smoothed. Thus, not all of the data points in the chromatogram will be smoothed.

2.2.2 Retention Time Alignment

Retention time alignment corrects for minor shifts in the peaks within a chromatogram due to slight variation in the stationary phase and flow rate within the instrument. Multiple retention time alignment algorithms are available, but only two, the peak matching algorithm and the correlation optimized warping (COW) algorithm, are investigated in this research. Along with selecting the alignment algorithm, a target chromatogram to which the peaks are aligned in the sample chromatograms must be chosen.

2.2.2.1 Target Selection

Multiple options are available for the target chromatogram. One of the more common options is to use a sample chromatogram from the data set which has many similar peaks to the other chromatograms [4]. The limitation of this selection is that the chromatograms in the data set may not contain all of the peaks necessary for alignment. Another option is a consensus target. The consensus target is a combination of all of the mixtures in the data set, which is analyzed in a same manner as the other mixtures. This is a better choice for a target, since all of the peaks present in the sample chromatograms are present in the target chromatogram. However, the peaks in the consensus target should not be at a low abundance and must be detectable by the algorithm in the alignment procedure. When a consensus target is not possible to form due to variation in chemical components among mixtures, an average target is also applicable to align the data set. An average target is an average of each data point at each retention time within a set of chromatograms. This average chromatogram contains all of the peaks from the

other chromatograms. As with the consensus target, the abundance of the peaks in the target chromatogram may not be at a high enough abundance for alignment of the sample chromatograms.

2.2.2.2 Peak Matching Algorithm

One of the alignment algorithms investigated in this research was the peak matching algorithm [4]. The algorithm identifies and aligns the peaks in the sample chromatograms and the target chromatogram through determining the zero crossing of the first derivative of each peak. The only parameter besides the target chromatogram that needs to be specified is the window size. The window size determines the number of data points that the zero crossing can be shifted in order to align a peak. With a small window size, such as 1 or 2, the algorithm may not be able to shift the peak in order to align them. However, large window sizes, such as 7 or 8, could align a peak within the sample chromatogram to a different peak in the target chromatogram.

In order to align the chromatograms, the peaks in the target chromatogram are identified through initially calculating the first derivative of the entire chromatogram. Then, the algorithm identifies the leading edge of a peak when the standard deviation surpasses a threshold of five times the standard deviation of the noise. The standard deviation of the noise is determined by a user defined number of points in the chromatogram. The algorithm then identifies the apex and the tailing edge of the peak through the zero crossing of the first derivative. The peak is then added to a list of peaks recognized by the algorithm for that chromatogram. Once all the peaks in the target chromatogram have been determined, the algorithm repeats the process for the sample

chromatograms. With all of the peaks within each chromatogram having been identified, the peaks in each sample chromatogram are compared to the peaks in the target chromatogram. In order to align a peak, the peak must be present in both the sample chromatogram and the target chromatogram and also be within the allotted window size. If these conditions are met, the peaks from the sample chromatogram and target chromatogram will be aligned through interpolation of data points so that the retention times of the two peaks are the same. If a peak is present in the target chromatogram and not present in the sample chromatogram, the peak is disregarded, and the algorithm moves to the next peak. This process is repeated for each peak in each of the sample chromatograms.

The peak matching algorithm can successfully align complex chromatograms, such as diesel samples [4]. However, a peak with a low signal-to-noise ratio may not be identified or aligned by the algorithm since it may be below the baseline noise. Also, the algorithm assumes that the closest peak in the sample chromatogram within a given window size should be aligned to the peak in the target chromatogram. Another disadvantage would be that the algorithm may not be able to align peaks that coelute, especially if one peak is substantially more abundant than the other.

2.2.2.3 Correlation Optimized Warping Algorithm

The correlation optimized warping (COW) algorithm optimizes correlation between the sample chromatogram and the target chromatogram in order to align the peaks within each chromatogram [5,6]. The algorithm divides the chromatogram into segments, and through adding or subtracting points, assesses correlation between these

segments in order to determine the best alignment between the sample and target chromatograms. Along with selection of the target chromatogram, two other parameters must be determined: the segment size and the warp size. The segment size is the number of data points contained within a segment of the chromatogram. When choosing a segment size, the segments formed must have at least the number of data points that define one peak. With a large segment size, such as 75, the segment could contain multiple peaks which would hinder alignment of individual peaks. With small segment sizes, such as 25, the peaks may be divided such that the apex of a peak could be separated from the peak edge. The warp size is the number of points that can be added or subtracted from each defined segment in order to align the peaks within the sample chromatogram to the target chromatogram. With a large warp size, such as six, the segment may be shifted further from the corresponding peaks in the sample chromatograms which would increase the number of misalignments. For a small warp size, such as two, the segment may not be shifted enough to align the sample chromatogram with the target chromatogram.

Once these parameters are chosen, the algorithm begins at the end of the chromatograms. For the first segment, the algorithm optimizes correlation between the target and sample chromatograms. This is done through adding and subtracting the warp size from the segment being aligned. With a warp size of n , n data points can be added or subtracted from that segment. For example, the algorithm can add or subtract one, two, or zero data points with a warp size of two. For each addition or subtraction, the algorithm interpolates points so that the target segment and the sample segment are the same length. Once the points have been interpolated, a local correlation coefficient between the sample

segment and the target segment is calculated for each warp performed. So for a warp size of two, five local correlation coefficients have been calculated. Then, the algorithm proceeds to the next segment and repeats the process. Each segment is aligned in the same manner until all local correlations for each segment have been calculated.

The local correlation coefficients from each segment are summed in all combinations in order to form global correlation coefficients. The best alignment between the sample chromatogram and the target chromatogram is determined by the global correlation coefficient with the highest value. The process is repeated for the other sample chromatograms.

As with the peak matching algorithm, the COW algorithm can be used to align complex chromatograms. Furthermore, the COW algorithm will still align chromatograms even if they differ in the number of data points, noise level, and baseline drift [5]. However, the COW algorithm can align the fronting or tailing edge of the peaks instead of the apices in order to optimize correlation between the target segment and the sample segment.

2.2.3 Normalization

Due to variation in injection volume, the raw chromatograms obtained vary in abundance of peaks among replicates. Through normalization, the variation in abundance observed can be reduced or eliminated. Multiple normalization procedures are available; however, a combination of the maximum peak area normalization followed by the total area normalization of each set of replicates is used for this research. The two normalizations are used to correct for differences in peak abundance among the samples

in the data set and also to correct for variation in abundance among replicates of those samples. The maximum peak area normalization is first applied to the chromatograms in order to scale all of the chromatograms within the data set to each other. Using this normalization, the larger peaks in the chromatograms are similar in abundance; however, the smaller peaks still vary in abundance among replicates. Total area normalization of the replicates is used to scale the smaller peaks in the chromatograms to a similar abundance. Due to the variation in the number of chemical components among samples, total area normalization could not be applied to the entire data set.

2.3 Principal Components Analysis

Principal components analysis (PCA) is a multivariate statistical technique that reduces the number of variables in a data set to those that contribute most to the variance [7]. This is done in order to determine the variables that can differentiate the samples from each other. Through PCA, the association and discrimination of samples can be assessed from a few variables rather than the entire data set.

In order to apply PCA, the data set must be mean-centered in order to ensure that the first principal component (PC) describes the maximum variance within the data set. In PCA, each data point in each sample is considered a variable. In order to mean-center the data, the average across each variable is calculated. Then, the average is subtracted from each data point in the data set. The process is repeated until every data point in each sample has been mean-centered.

Once the data is mean-centered, the covariance matrix is calculated. The covariance is a measure of the amount of variation from the mean between a pair of samples. To form the covariance matrix, the covariance is calculated between all variables, and the values form an $n \times n$ matrix, where n is the number of variables in the data set. Within the covariance matrix, the top to bottom diagonal is the covariance of the variable by itself. About that diagonal, the matrix is symmetric since the covariance of variables $a \times b$ is the same as the covariance of the variables $b \times a$.

From the covariance matrix, the eigenvectors and eigenvalues can be calculated. An eigenvector is a solution vector to the determinant of an $n \times n$ matrix. An eigenvalue is a value that when multiplied by the eigenvector and the $n \times n$ matrix, the resulting solutions are equal to each other. In order to calculate the eigenvalues, the determinant of the covariance matrix is set equal to zero and then solved. Once an eigenvalue has been determined, the eigenvector can be solved using both the covariance matrix and that eigenvalue. Other eigenvectors are calculated in the same manner and positioned orthogonally to the preceding eigenvector until $n-1$ eigenvectors have been calculated, where n is the number of samples in the data set. Each eigenvector calculated is considered a principal component (PC), and each PC has a corresponding eigenvalue. In order to determine which PC varies the most within a data set, the eigenvalues are ordered from highest to lowest. The PC with the highest eigenvalue is considered the first principal component, since it accounts for the most variance in the data set.

From the PCs, the scores for each sample in the data set can be calculated using the mean-centered data. For each PC, each variable from the mean-centered data is multiplied by the corresponding data point in that PC. Then, the resulting values are

summed in order to obtain the score for that sample. The calculated score represents the positioning of the sample on a specific PC. These calculations are repeated with each sample in the data set and with each calculated PC.

From the calculated scores, eigenvectors, and eigenvalues, the scores plots and the loadings plots can be generated to visually assess the differences in the data set. Typically, the scores for each sample on the first two PCs are plotted to form the scores plot. From the scores plot, the similarities and differences among the samples on those two PCs can be visually observed. Samples that are positioned closely in the scores plot are similar to each other on those two PCs while samples that are further apart are different. The loadings plots are formed by plotting the PC versus the original x-variable, such as retention times of chromatographic data. From the loadings plot, the variables that vary the most within that PC can be identified. Furthermore, the positioning of the samples on the scores plot can be explained using the loadings plot, since the variables present in the loadings plot are the ones that differ the most among samples.

The variables that contribute most to the variance in a data set can be established using PCA. However, since only the PCs with the highest percentage of variance are usually assessed, some of the variables which contribute to the variance in the data set are disregarded. Also, the scores plot is visually assessed, thus introducing subjectivity in interpretation of the association and discrimination of samples.

2.4 Pearson Product Moment Correlation Coefficients

Pearson product moment correlation (PPMC) coefficients assess the correlation between two samples [8, 9]. In order to determine the PPMC coefficient (r) between a pair of samples that are defined as x and y , the n data points within each sample are subjected to the following Equation 2.1:

$$r_{xy} = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2 \cdot \sum_{i=1}^n (y_i - \bar{y})^2}} \quad \text{Equation 2.1}$$

From this equation, correlations between -1 and +1 can be calculated. A perfect inverse correlation is indicated by -1 where the slope of one sample is increasing while the slope of other sample is decreasing. A perfect positive correlation of +1 indicates that both samples are increasing or decreasing with the same slope. No correlation between the samples is indicated by zero. From the PPMC coefficient calculated, varying degrees of similarity can be determined. A strong correlation is indicated by PPMC coefficients between 0.8 and 1; a moderate correlation is indicated by PPMC coefficients between 0.5 and 0.8, while PPMC coefficients less than 0.5 indicate a weak correlation [8,9].

When PPMC coefficients are calculated, all of the data points within each sample are compared. Furthermore, a numerical value is calculated using PPMC coefficients. However, the similarity of the samples in the entire data set to each other cannot be assessed, since only two samples can be compared using PPMC coefficients.

2.5 Hierarchical Cluster Analysis

Hierarchical cluster analysis (HCA) is a multivariate statistical procedure where the similarity of samples is determined through distance among samples in a multidimensional space [10]. With HCA, there are two types of grouping methods: agglomerative and divisive. In the agglomerative method, each sample is defined as its own group, and the samples are clustered together until all of the scores are contained into one group. With the divisive method, all of the samples are grouped together initially, and the samples are then divided until each sample forms its own group.

In order to group samples, the distance between pairs must be calculated. Of the equations available to calculate distance between the samples, the Euclidean distance is commonly used. The Euclidean distance is calculated using Equation 2.2.

$$d_{ab} = \left[\sum_j^m (x_{aj} - x_{bj})^2 \right]^{1/2} \quad \text{Equation 2.2}$$

The distance between the two samples is represented by d_{ab} . The first sample is represented by x_a , while the second sample is represented by x_b . The j to m represents the dimensions in the coordinate plane in which the samples are plotted.

Once the distances among all pairs of samples are calculated, the samples that have the shortest distance between them are linked. In order to link the samples, a linkage method must be selected. Of the many linkage methods available, the single linkage method and the complete linkage method are common methods. The single linkage method is also known as the nearest neighbor linkage method and is illustrated in Figure 2.6A. In this example, sample 3 is positioned between cluster 1 and cluster 2. The

distance between sample 3 and the sample in cluster 1 that is closest to sample 3 is calculated. Similarly, the distance between sample 3 and the sample in cluster 2 that is closest to sample 3 is calculated. Sample 3 is assigned to the cluster to which it has the shortest distance, which in this example is cluster 1.

The complete linkage method, also known as the farthest neighbor linkage method, connects the sample with the farthest neighbor closest to the sample. For example, sample 3 is positioned between cluster 1 and cluster 2. When the distances are calculated, sample 3 is observed to be closer to the farthest sample in cluster 2 than the farthest sample in cluster 1. So, sample 3 is linked to cluster 2 (Figure 2.6B). Once the samples with the shortest distance between them have been linked, the distances among the new cluster and the samples are recalculated. Again, the samples with the shortest distance between them are linked. This is repeated until all samples are clustered into a single group.

After the samples have been linked, the similarity of the samples to each other can be established using the distances calculated (Equation 2.3).

$$\text{similarity}_{ab} = 1 - \frac{d_{ab}}{d_{max}} \quad \text{Equation 2.3}$$

The distance between two samples is represented by d_{ab} , and the greatest distance between samples in the data set is represented by d_{max} . A similarity of 1 is assigned to samples that are identical, while a similarity of zero indicates the most dissimilar samples in the data set.

The output of HCA is a dendrogram, which shows the calculated similarities of the samples in the data set. On the x-axis of the dendrogram, the similarity from 1 to 0 is

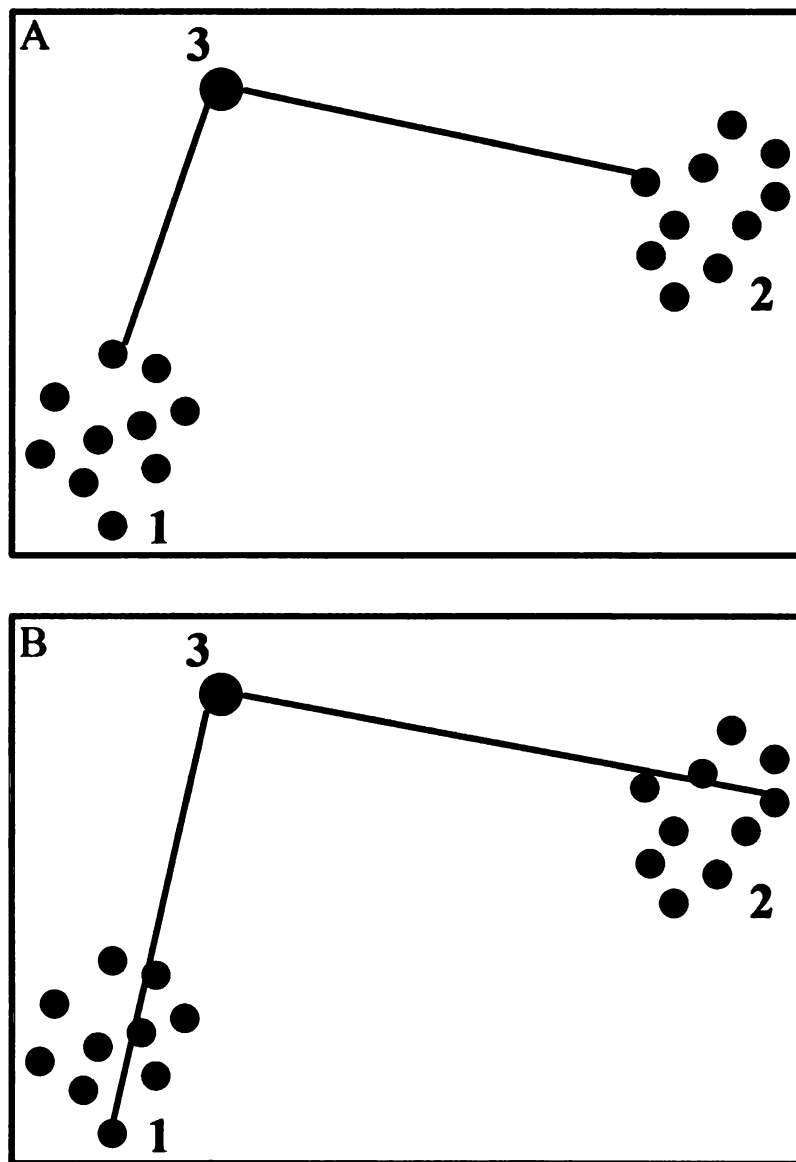


Figure 2.6: A) Diagram depicting the single linkage method used in HCA. B) Diagram depicting the complete linkage method used in HCA.

shown. The y-axis contains all of the samples in the data set. Within the dendrogram, samples that are similar will have a high similarity and be more closely linked to each other. Within the dendrogram each sample begins with its own branch, and samples are then connected according to the similarity calculated previously from highest similarity to lowest similarity.

Hierarchical cluster analysis shows the natural clusters of samples through assessing their similarity. Furthermore, a number which measures the similarity among samples is specified. However, HCA cannot determine which variables in the samples contribute to the similarity.

With PCA, the differences among samples are determined through the variables that vary the most within a data set. Through HCA, the similarities among samples are assessed, and samples are grouped by their similarity. However, HCA cannot determine which variables contribute the most to the differences in samples. Furthermore, in PCA, each PC only accounts for a certain percentage of the variance and only distinguishes the samples based on those variables.

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CHAPTER 3

Association of Evaporated Ignitable Liquids to Their Neat Counterparts Using Chemometric Procedures

3.1 Introduction

At suspected arson scenes, an ignitable liquid may be present at various levels of evaporation depending on the extent of the fire. Due to evaporation of the ignitable liquids during the fire, the more volatile compounds are lost, changing not only the abundance of the compounds, but also the number of compounds detected by gas chromatography-mass spectrometry (GC-MS). Since the overall profile of the chromatogram has changed, an arson investigator may not be able to identify the evaporated liquid used in the fire. In this research, chemometric procedures, such as principal components analysis (PCA), Pearson product moment correlation (PPMC) coefficients, and hierarchical cluster analysis (HCA), were used as an objective method to investigate the association of an evaporated ignitable liquid to its neat counterpart.

Firstly, six ignitable liquids, one from each of six different American Society of Testing and Materials (ASTM) classes [1], were evaporated to four levels of evaporation. The neat ignitable liquids along with the corresponding evaporated liquids were analyzed by GC-MS. The total ion chromatograms of the neat and evaporated liquids were compiled. The chromatograms were subjected to pretreatment procedures where the chromatograms were smoothed, retention time aligned, and normalized. Principal components analysis was used to discriminate the ignitable liquids in different classes,

while associating the evaporated, ignitable liquids to the corresponding neat ignitable liquid. The PPMC coefficients were used to assess both the precision of the extraction procedure as well as the degree of correlation of the evaporated ignitable liquids to the neat ignitable liquid. Hierarchical cluster analysis was used as a statistical measure to assess the similarity of the positioning of the evaporated liquid to the corresponding neat liquids in the scores plot.

3.2 Materials and Methods

3.2.1 Sample Collection

A subset of six ignitable liquids, one liquid from each of the six classes defined by ASTM, was collected from various locations. Gasoline and kerosene were collected from service stations in the Lansing, Michigan area. Lacquer thinner, lamp fuel, marine fuel stabilizer, and paint thinner were collected from local hardware stores, grocery stores, and online sources. The ignitable liquids in the subset, along with the class and major compounds present in each, are listed in Table 3.1.

3.2.2 Sample Preparation

Each of six ignitable liquids was evaporated to four different levels of evaporation (5%, 10%, 20%, and 50% by volume) using filtered air and magnetic stir bars for agitation. Once evaporated, liquids were stored in 7.4 mL amber screw cap vials (Fisher Scientific, Pittsburgh, PA) that were acid washed before use. Vials were labeled, wrapped in Parafilm[®] (American National Can, Menasha, WI), and stored at 16°C until analysis.

Table 3.1 Ignitable liquids investigated.

Ignitable Liquid	ASTM Class	Major Compounds
Gasoline	Gasoline	Toluene, Alkylbenzenes, Naphthalenes
Kerosene	Petroleum Distillate	Alkylbenzenes, Normal Alkanes (C ₉ -C ₁₈)
Lacquer Thinner	Aromatic	Toluene
Lamp Fuel	Alkane	Normal Alkanes (C ₁₂ -C ₁₅)
Marine Fuel Stabilizer	Naphthenic Paraffinic	Naphthalenes, Branched Alkanes (C ₁₀ , C ₁₁) Cyclic Alkanes (C ₆)
Paint Thinner	Isoparaffinic	Branched alkanes (C ₇ , C ₈ , C ₁₀)

All liquids (neat and evaporated) were diluted in dichloromethane (CH_2Cl_2) (spectrophotometric grade, Jade Scientific, Canton, MI). The liquids had different dilution factors so that the same order of magnitude for the abundance was observed in all chromatograms. Paint thinner and marine fuel stabilizer were diluted 1:350 (v/v), while gasoline was diluted 1:100 (v/v), kerosene was diluted 1:10 (v/v), lacquer thinner and lamp fuel were diluted 1:550 (v/v). A 250 μL aliquot of each diluted liquid was spiked onto a 5 x 5 cm^2 Kimwipe TM (Kimberly-Clark, Irving, TX) in a 1.0 L, unlined paint can (Arrowhead Forensics, Lenexa, KS). The liquids were then extracted in triplicate at 80°C for four hours using a passive headspace extraction with one fourth of an activated carbon strip (Albrayco Technologies, Inc. Cromwell, CT). After extraction, the activated carbon strip was eluted with 200 μL CH_2Cl_2 and analyzed by GC-MS.

A consensus standard was also prepared by combining 250 μL of each of the six neat liquids, diluted as described previously. The consensus standard was then extracted in triplicate and analyzed as previously described.

3.2.3 GC-MS Analysis

All extracts were analyzed using an Agilent 6890 gas chromatograph coupled to an Agilent 5975 mass spectrometer, with an Agilent 7683B automated liquid sampler (ALS) (Agilent Technologies, Santa Clara, CA). The GC was equipped with an Agilent HP-5MS capillary column (30 m x 0.25 mm internal diameter x 0.25 μm film thickness (df)). A 1 μL volume of sample was injected using the ALS in the pulsed, splitless mode, using a pressure pulse of 15.0 psi for 0.25 min. The inlet temperature was 250°C. The

carrier gas was ultra-high purity helium (Airgas, East Lansing, MI) and had a nominal flow rate of 1 mL/min. The GC temperature program was as follows: 40°C for 3 min, 10°C/min to 280°C, hold for 4 min at 280°C. The transfer line was maintained at 280°C, and the mass spectrometer was operated in electron ionization mode (70 eV) with a quadrupole mass analyzer operating in full scan mode (m/z 50-550) at a scan rate of 2.91 scans/s.

Before any extracts were analyzed, two equilibration runs were performed to minimize active sites in the inlet and on the column. For the equilibration runs, all of the instrument parameters were the same except the oven ramp rate, which was increased from 10°C/min to 20°C/min. The equilibration runs were always aliquots of the first sample to be analyzed on that day.

3.2.4 *Data Pretreatment*

Total ion chromatograms (TICs) were generated for all the neat and evaporated liquids. All of the chromatograms were smoothed using a Savitzky-Golay smooth in ChemStation software (version E.01.01.335, Agilent Technologies), then compiled into a data set.

Chromatograms were retention time aligned to a target chromatogram, which was generated by smoothing and averaging the triplicates of the consensus standard.

Both a commercially available correlation optimized warping (COW) algorithm (LineUp™, version 3.0, Infometrix, Inc., Bothwell, WA) and a peak matching algorithm available in the literature [2] were used to align the chromatograms. For each algorithm, various user-defined parameters were investigated as shown in Table 3.2. There are

Table 3.2 User defined parameters investigated for peak matching algorithm and COW algorithm.

	Peak Matching Algorithm	COW Algorithm	
	Window Size in Data Points	Warp Size in Data Points	Segment Size in Data Points
Data Points	2, 3, 4, 5, 6, 7	1, 2, 3, 4, 5, 6	15, 25, 45, 60, 65, 75

typically 13 points across a peak so that window size and warp size are smaller than the peak width, while the segment size is larger than the peak width.

For the COW algorithm, all combinations of the warp sizes and the segment sizes in Table 3.2 were investigated. In order to determine the optimal alignment, chromatograms were visually assessed for peak misalignments. The PPMC coefficients were also calculated in Matlab (version 7.7.0.471, The MathWorks, Inc., Natick, MA) and used to further evaluate the alignment of the chromatograms.

After retention time alignment, the chromatograms were normalized using Microsoft Excel (version 12.0.6524.5003, Microsoft Corp., Redmond, WA). Maximum peak normalization was first performed, whereby each data point in a chromatogram was divided by the abundance of the maximum peak and then multiplied by the average abundance of the maximum peaks for all chromatograms. Total area normalization was then performed among replicates for each neat and evaporated ignitable liquid. Each data point in the chromatogram was divided by the total area of that chromatogram and then multiplied by the average area of the replicate chromatograms for that liquid. This combination of normalization procedures reduced the differences in abundance observed within the chromatograms.

3.2.5 *Data Analysis*

Once the chromatograms had been aligned and normalized, PCA was initially performed on the neat liquids using MatLab (The Math Works, Inc.). The scores for the first principal component (PC1) and the second principal component (PC2) for each neat liquid were calculated in Matlab (The Math Works, Inc.) and plotted in Excel (Microsoft

Corp.) to generate a scores plot. The eigenvectors for PC1 and PC2 were also plotted against retention time in Excel to generate loadings plots. These plots were used to identify those compounds that were most variable and hence, most discriminating, among the liquids.

Scores for the evaporated liquids were then calculated in Excel (Microsoft Corp.). Prior to projection, chromatograms were mean-centered. To mean-center the chromatograms of the evaporated liquids, the abundance at each retention time was subtracted from the average abundance at the same retention time of the neat liquids. The mean-centered data were then multiplied by the eigenvector of PC1 and summed to obtain the score for the evaporated liquid on PC1. Scores for each evaporated liquid on PC2 were calculated in a similar manner using the eigenvector of PC2. The scores for the evaporated liquids were then projected onto the scores plot of the neat liquids. Using this approach, association and discrimination was based on chemical composition of the neat liquids rather than the evaporated liquids.

Pearson product moment correlation coefficients (Equation 2.1) were calculated for the aligned chromatograms using MatLab (The Math Works, Inc.). The PPMC coefficients were calculated among replicates of each liquid to assess the precision of the extraction and analysis procedure. The correlation between all levels of evaporation and the corresponding neat liquid was then calculated to assess the degree of similarity between the evaporated and neat liquids.

Using the scores calculated for the neat and evaporated liquids, hierarchical cluster analysis was performed in Pirouette (version 4.0, Infometrix, Inc., Bothwell, WA). The Euclidian distance (Equation 2.2) was calculated between all pair-wise combinations

of the PC scores. Using the agglomerative method, the scores were linked through the nearest neighbor linkage method. Using these parameters, two dendrograms were generated: a dendrogram of only the neat liquids and a dendrogram of the neat and evaporated liquids, from which similarity was assessed.

3.3 Results and Discussion

3.3.1 Optimization of Retention Time Alignment

With the peak matching algorithm, window sizes of two to seven data points were investigated. With the larger window sizes, specifically five to seven, more misalignments were observed among the neat and evaporated liquids. The most misalignments were observed using a window size of seven, since the peaks were shifted further with a larger window size. The chromatograms of marine fuel stabilizer showed major misalignments, especially with a window size of seven (Figure 3.1A). When window sizes of two to four were investigated, the number of misalignments decreased slightly. Of the remaining window sizes, the fewest misalignments among replicates of each liquid were observed using a window size of three (Figure 3.1B). Thus, for the peak matching algorithm, the optimal window size was three.

The optimal alignment for the COW algorithm was determined by investigating multiple warp sizes and segment sizes. For most combinations of warp size and segment size, misalignments were still present among the chromatograms of the neat and evaporated liquids. The most misalignments were observed with a large warp size and a large segment size. With large segment sizes, each segment contains multiple peaks.

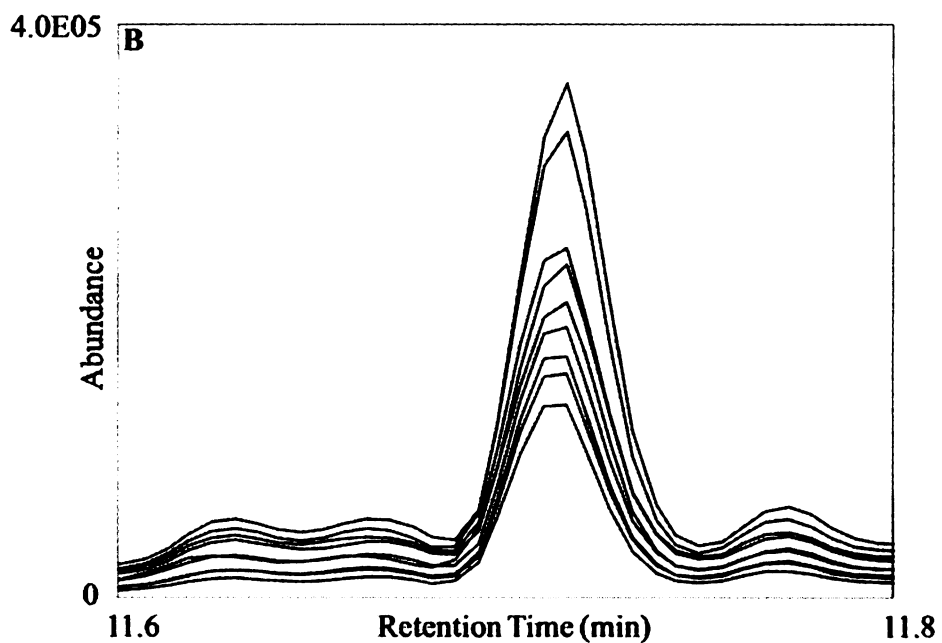
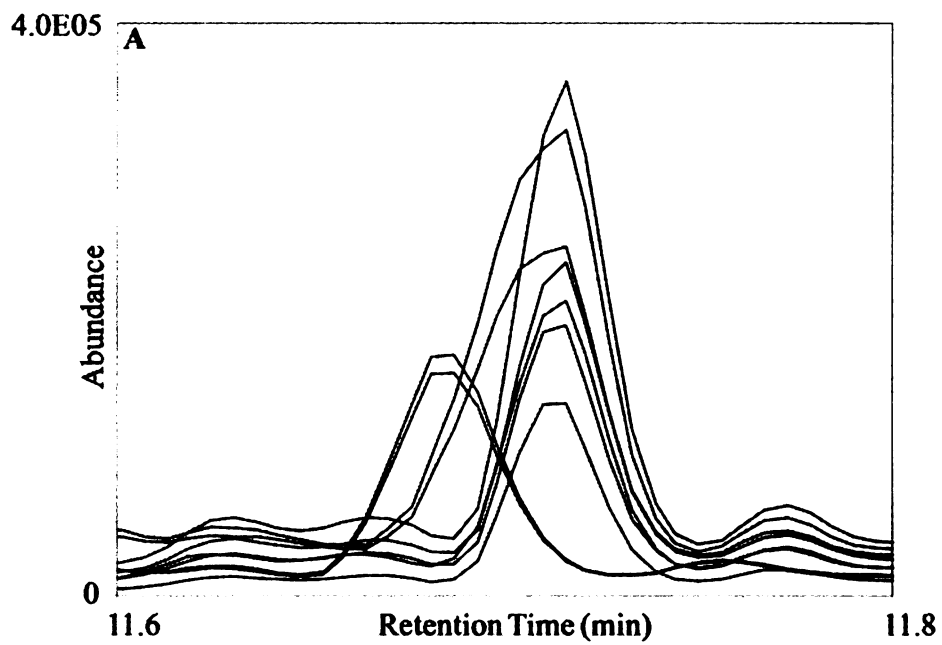


Figure 3.1: A) Poorly aligned 2,6-dimethylundecane peak in the TIC of neat and evaporated marine fuel stabilizer using a window size of seven. B) Well aligned 2,6-dimethylundecane peak in the TIC of neat and evaporated marine fuel stabilizer using a window size of three.

When a large warp size is also used, these large segments are shifted further, which results in misalignment of the peaks. For example, a warp size of six and a segment size of 45 showed major misalignments for the 2,2,3,5-tetramethylheptane peak in paint thinner (Figure 3.2A). Visual assessment of the chromatograms yielded optimal parameters of a warp size of three and a segment size of 65 for the COW alignment (Figure 3.2B).

The optimal COW alignment and the optimal peak matching alignment were then compared to determine the optimal alignment method. The COW alignment was observed to have fewer major misalignments than the peak matching alignment when chromatograms were compared visually (Figure 3.3A and B).

Higher PPMC coefficients were also observed among the replicates of the COW aligned chromatograms than the peak matching aligned chromatograms (Table 3.3). For each ignitable liquid, a two sample t-test was applied to compare the mean PPMC coefficients calculated for each alignment algorithm. The difference between the mean PPMC coefficients was found to be statistically significant at the 90% confidence level for all ignitable liquids except kerosene. Thus, the significantly higher PPMC coefficients indicated improved alignment with the COW algorithm compared to the peak matching algorithm.

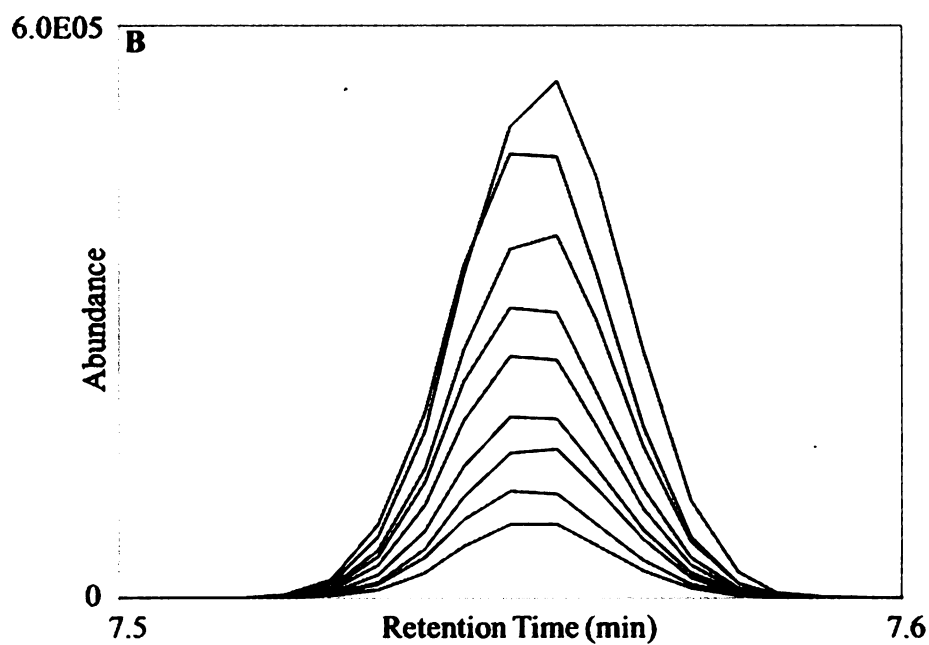
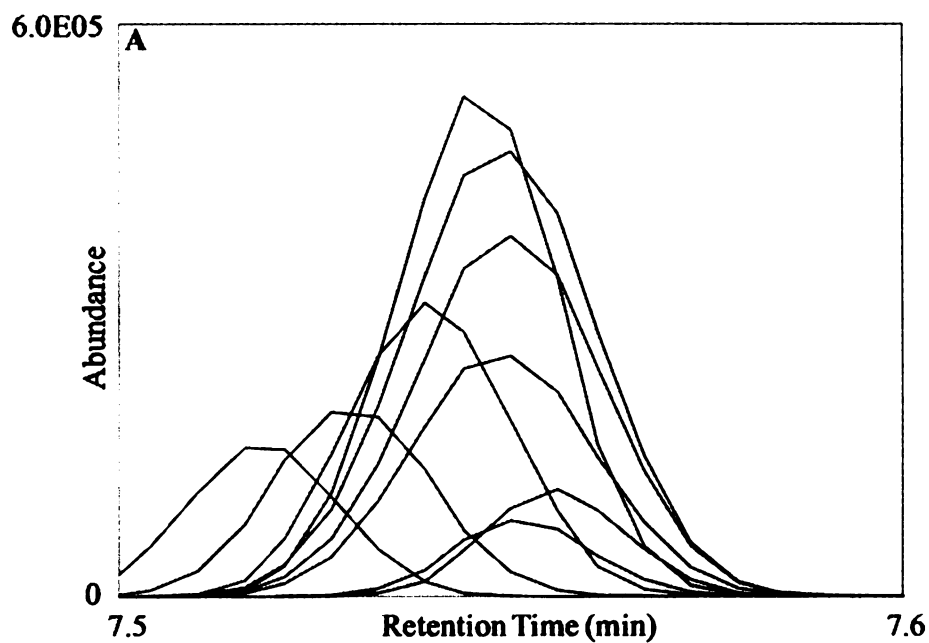


Figure 3.2: A) Poorly aligned 2,2,3,5-tetramethylheptane peak in the TIC of neat and evaporated paint thinner with a warp size of six and a segment size of 45. B) Well aligned 2,2,3,5-tetramethylheptane peak in the TIC of neat and evaporated paint thinner with a warp size of three and a segment size of 65.

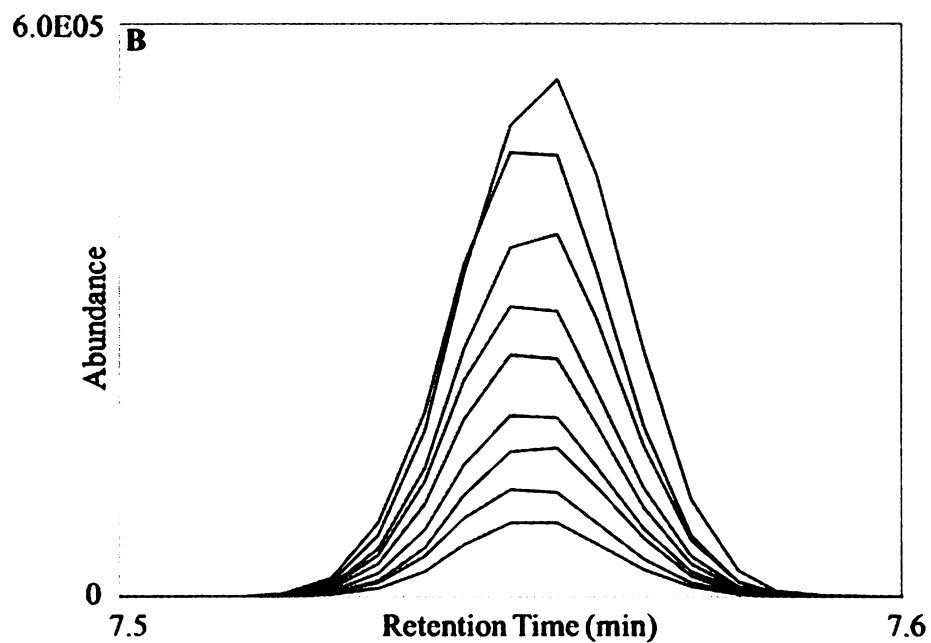
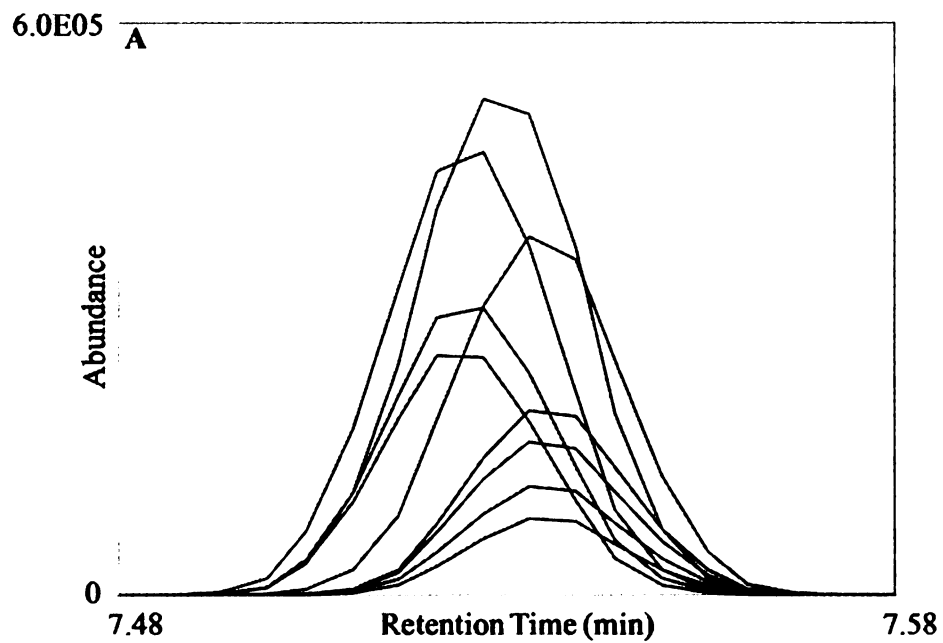


Figure 3.3: A) Poorly aligned 2,2,3,5-tetramethylheptane peak in the TIC of neat and evaporated paint thinner with a window size of three using the peak matching algorithm. B) Well aligned 2,2,3,5-tetramethylheptane peak in the TIC of neat and evaporated paint thinner with a warp size of three and a segment size of 65 using the COW algorithm.

Table 3.3: PPMC coefficients for all replicates (n=15) for optimal peak matching alignment and optimal COW alignment.

Ignitable Liquid	Mean PPMC Coefficient ± Standard Deviation Using COW Algorithm (Warp 3, Segment 65)	Mean PPMC Coefficient ± Standard Deviation Using Peak Matching Algorithm (Window Size 3)
Gasoline	0.9951 ± 0.0044	0.9915 ± 0.0042
Kerosene	0.9958 ± 0.0016	0.9954 ± 0.0018
Lacquer Thinner	0.9936 ± 0.0090	0.9822 ± 0.0178
Lamp Fuel	0.9964 ± 0.0018	0.9895 ± 0.0102
Marine Fuel Stabilizer	0.9972 ± 0.0018	0.9959 ± 0.0021
Paint Thinner	0.9949 ± 0.0044	0.9892 ± 0.0109

Combinations of the peak matching algorithm and the COW algorithm were also considered. However, preliminary investigation of the combination of the algorithms showed an increased number of misalignments in the chromatograms, and this approach was not further investigated.

Thus, through visual assessment of chromatograms and PPMC coefficients, the COW alignment with a warp of three and a segment size of 65 was chosen as the optimal alignment.

3.3.2 *Normalization*

The unnormalized chromatograms showed differences in abundance among triplicate extractions for both evaporated and neat liquids (Figure 3.4A). Maximum peak area normalization was first performed on the chromatograms, where the replicates were generally grouped by evaporation level, as illustrated for marine fuel stabilizer in Figure 3.4B. After maximum peak normalization, there was still some spread in the replicates. Total area normalization between each set of replicates was then performed in order to minimize these differences (Figure 3.4C). Through a combination of maximum peak area normalization and total area normalization of the replicates, differences in abundance of the triplicate extractions of the evaporated liquids were minimized.

3.3.3 *Association and Discrimination of the Neat Liquids using PCA*

The scores plot of the first principal component (PC1) and the second principal component (PC2) accounts for 67.5% of the variance among the neat liquids (Figure 3.5). As observed in Table 3.4, there is at least an order of magnitude difference between the

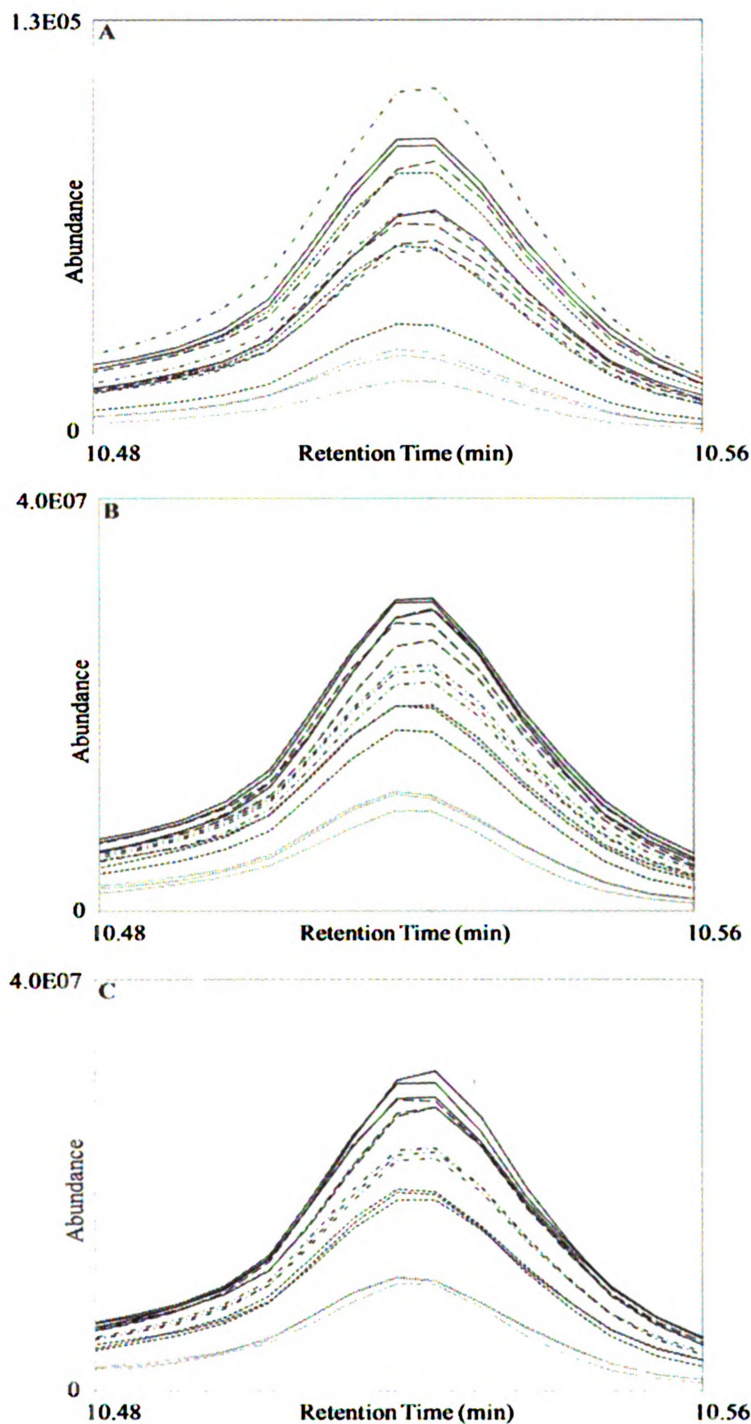


Figure 3.4: A) Unnormalized pentylcyclohexane peak in the TIC of neat and evaporated marine fuel stabilizer. B) Maximum peak normalized pentylcyclohexane peak in the TIC of neat and evaporated marine fuel stabilizer. C) Total area normalization of replicates of the pentylcyclohexane peak in the TIC of neat and evaporated marine fuel stabilizer. Neat (—), 5% Evaporated (---), 10% Evaporated (- · -), 20% Evaporated (— —), 50% Evaporated (····).

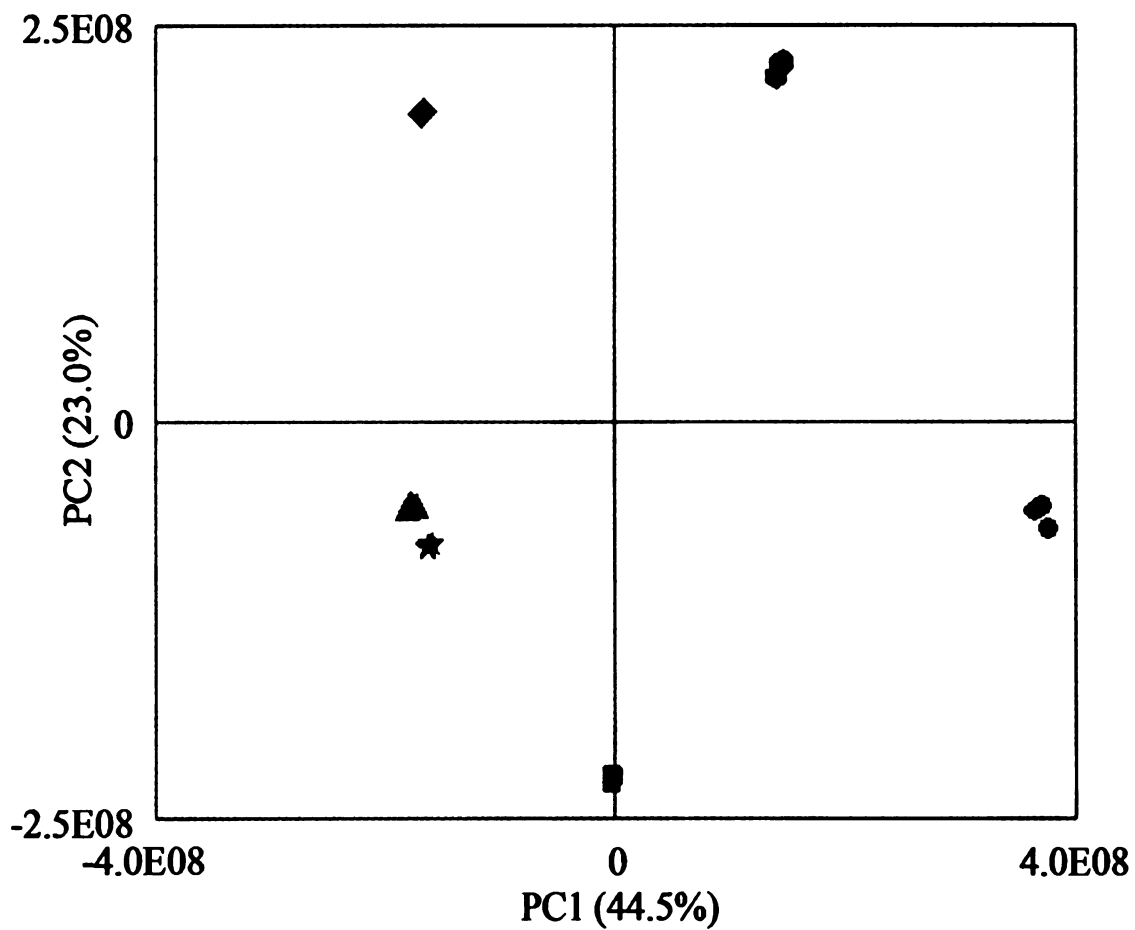


Figure 3.5: Scores plot of PC1 vs. PC2 based on the TIC for the six neat ignitable liquids. Liquids were indicated by symbol. Lamp Fuel (■), Kerosene (●), Marine Fuel Stabilizer (◆), Paint Thinner (◆), Gasoline (▲), and Lacquer Thinner (★).

Table 3.4: Mean PCA score for replicates (n=3) of each liquid class based on the TIC.

Ignitable Liquid	Mean PCA score on PC1	Mean PCA score on PC2
	\pm Standard Deviation for Replicates	\pm Standard Deviation for Replicates
Paint Thinner	$-1.48 \times 10^8 \pm 3.74 \times 10^5$	$1.56 \times 10^8 \pm 4.68 \times 10^5$
Marine Fuel Stabilizer	$1.24 \times 10^8 \pm 2.66 \times 10^6$	$1.78 \times 10^8 \pm 3.91 \times 10^6$
Kerosene	$3.24 \times 10^8 \pm 5.22 \times 10^6$	$-4.74 \times 10^7 \pm 5.64 \times 10^6$
Lamp Fuel	$-2.25 \times 10^6 \pm 8.75 \times 10^5$	$-1.80 \times 10^8 \pm 2.25 \times 10^6$
Lacquer Thinner	$-1.43 \times 10^8 \pm 1.29 \times 10^6$	$-6.24 \times 10^7 \pm 8.91 \times 10^5$
Gasoline	$-1.56 \times 10^8 \pm 3.64 \times 10^6$	$-4.39 \times 10^7 \pm 1.93 \times 10^6$

average and the standard deviation for the scores of the ignitable liquids on PC1 and PC2. The difference in order of magnitude indicates that the replicates of each ignitable liquid are not spread from each other in the scores plot. Very little spread is observed among the replicates of each of the liquids, indicating a precise analytical procedure.

Overall, the liquids are differentiated in PC1 and PC2, except for gasoline and lacquer thinner. Kerosene and marine fuel stabilizer load positively on PC1, while gasoline, lacquer thinner, lamp fuel, and paint thinner load negatively. In PC2, marine fuel stabilizer and paint thinner load positively, while gasoline, kerosene, lacquer thinner, and lamp fuel load negatively.

The loadings plots for PC1 and PC2 are shown in Figure 3.6. The first principal component (Figure 3.6A) discriminates the ignitable liquids based on toluene, C₂- and C₃-alkylbenzenes, and branched alkanes (C₇, C₈, and C₁₀), which load negatively on PC1 and naphthalenes, cyclic alkanes, and normal alkanes (C₉-C₁₈) that load positively. The second principal component (Figure 3.6B) discriminates the ignitable liquids based on toluene, C₂- and C₃-alkylbenzenes, and normal alkanes (C₁₂-C₁₇) that load negatively and branched alkanes, cyclic alkanes, and naphthalenes that load positively. The loadings plots of PC1 and PC2 can be used to explain the positioning of the liquids in the scores plot based on chemical composition.

Paint thinner, which contains only C₇, C₈, and C₁₀ branched alkanes (Appendix A, Figure A.4), is positioned negatively on PC1 and positively on PC2. The C₇, C₈, and C₁₀ branched alkanes are the only compounds contributing to the positioning of paint

thinner in the loadings plots. These branched alkanes load negatively on PC1 and positively on PC2.

Marine fuel stabilizer, which contains naphthalenes, cyclic alkanes, C₁₀ and C₁₁ branched alkanes, and 2,6-dimethylundecane (Appendix A, Figure A.3), is positioned positively on PC1 due to the presence of naphthalenes and cyclic alkanes that load positively on PC1. Marine fuel stabilizer is positioned positively on PC2 due to the presence of naphthalenes, cyclic alkanes, branched alkanes, and 2,6-dimethylundecane that load positively on PC2. Most of the positive variance described by PC2 is due to the compounds present in marine fuel stabilizer.

Kerosene is dominated by normal alkanes (C₁₀-C₁₉), but also contains naphthalenes and C₂- and C₃-alkylbenzenes (Appendix A, Figure A.2). In the scores plot, kerosene is positioned positively on PC1 and negatively on PC2. The normal alkanes and naphthalenes load positively on PC1 while the C₂- and C₃-alkylbenzenes load negatively on PC1. Since the naphthalenes and the C₁₂-C₁₈ normal alkanes are more dominant than the aromatic compounds, kerosene is positioned positively on PC1. The C₁₂-C₁₇ normal alkanes and the C₂- and C₃-alkylbenzenes are contributing more to the variance on PC2 than the early eluting naphthalenes, which positions kerosene negatively on PC2.

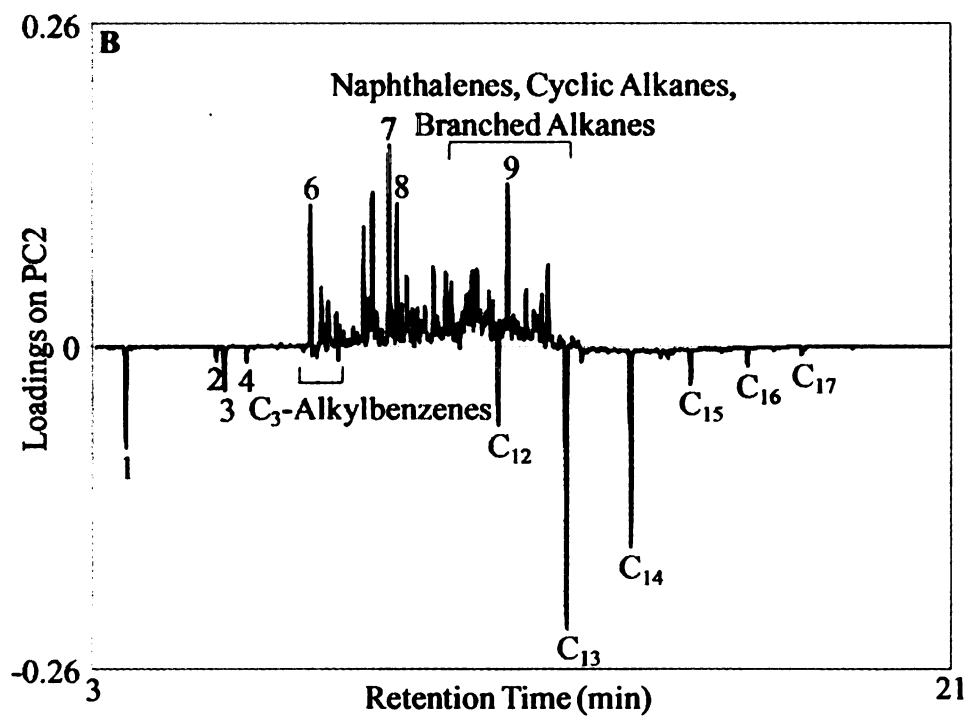
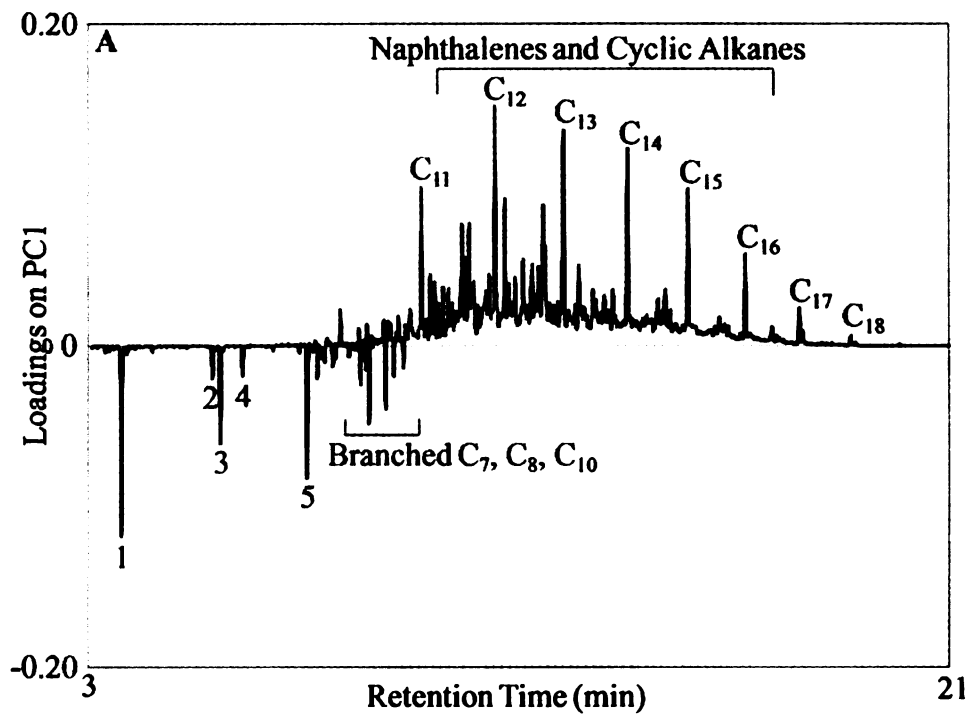


Figure 3.6: Loadings plots of (A) PC1 and (B) PC2 based on the TIC for six neat liquids. Major components are labeled: 1) toluene, 2) ethylbenzene, 3) *o*-xylene, 4) *p*-xylene, 5) 1-ethyl-3-methylbenzene, 6) 2,2,3,5-tetramethylheptane, 7) 5-ethyl-2,2,3-trimethylheptane, 8) 3,6-dimethylundecane, 9) 2,6-dimethylundecane.

Lamp fuel, which contains C₁₂-C₁₅ normal alkanes (Figure 3.7A)(Appendix A, Figure A.1), is positioned at zero on PC1. Within the loadings plot, the C₁₂-C₁₅ normal alkanes load positively on that PC (Figure 3.6A). The mean-centered chromatogram of lamp fuel contains both components from lamp fuel and components from other ignitable liquids (Figure 3.7B). These other components are present in the average chromatogram to which the lamp fuel is mean-centered. When multiplied by the eigenvector for PC1, the mean-centered chromatogram for lamp fuel contains similar peak areas loading positively and negatively, which offset one another (Figure 3.7C). Thus, components from the other liquids that load positively and negatively on PC1 contribute to the positioning of lamp fuel. Consequently, the scores for lamp fuel are positioned at zero on PC1. The C₁₂-C₁₅ normal alkanes load negatively on PC2, which contributes to the negative positioning of the liquids on that PC.

Gasoline, which contains toluene and C₂- and C₃-alkylbenzenes (Appendix A, Figure A.5), is positioned negatively on PC1 in the scores plot due to the dominance of these compounds, which load negatively on that PC. Gasoline is positioned slightly negatively on PC2 due to toluene and the C₂- and C₃-alkylbenzenes which have a small negative contribution to the loadings plot of PC2.

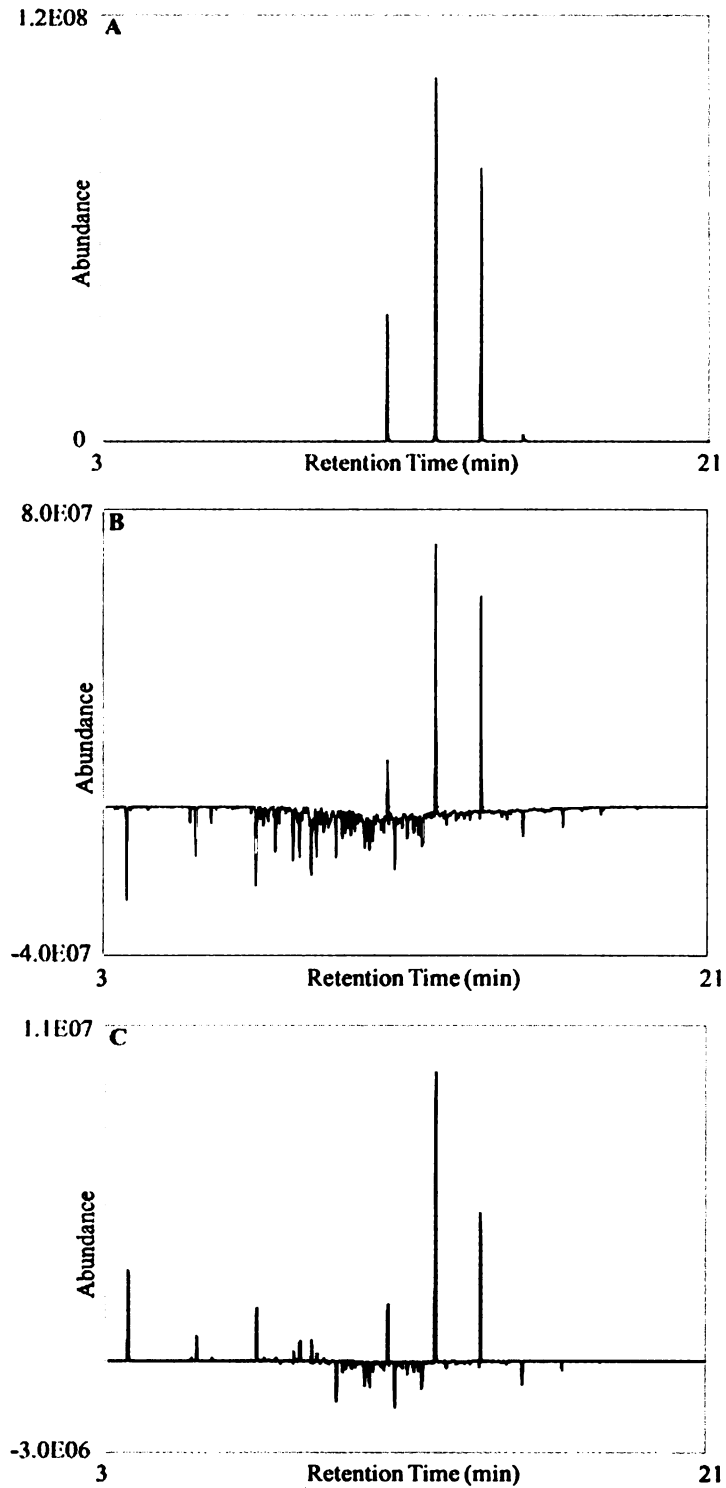


Figure 3.7: A) TIC of lamp fuel. B) Mean-centered chromatogram of lamp fuel. C) Mean-centered chromatogram multiplied by the eigenvector for PC1.

Lacquer thinner, which only contains toluene (Appendix A, Figure A.6), is positioned negatively on PC1 and PC2 since toluene loads negatively on both PCs.

Lacquer thinner and gasoline are positioned closely in the scores plot and cannot be visually distinguished. Lacquer thinner contains only toluene, while gasoline mainly contains toluene and the C₂- and C₃-alkylbenzenes. In the loadings plots for PC1 and PC2, toluene and the C₂- and C₃-alkylbenzenes load negatively on both PC1 and PC2. Although gasoline contains more components on PC1, toluene is contributing more to the positioning of the liquids on both PC1 and PC2 than the C₂- and C₃-alkylbenzenes. Thus, gasoline and lacquer thinner are positioned similarly in the scores plot.

Within the scores plot, the replicates of each liquid are well associated to one another indicating precision in the analytical methodology. With the exception of gasoline and lacquer thinner, the ignitable liquids are separated from one another in the scores plot due to their differences in chemical composition.

3.3.4 Association of Evaporated Liquids to Neat Liquids using PCA

When the evaporated liquids are projected onto the scores plot, the liquids are positioned closely to the corresponding neat liquid (Figure 3.8). The replicates of each evaporated liquid are also clustered closely together, indicating precision in the analytical methods.

Evaporated paint thinners at the 5%, 10%, and 20% evaporation levels (Appendix B, Figures B.13 to B.15) are positioned closely to the neat liquid. Due to evaporation, the 50% evaporated liquid (Appendix B, Figure B.16) contains a lower concentration of early

eluting C₇, C₈, and C₁₀ branched alkanes. As a result, these compounds contribute less to the negative variance of PC1, shifting the positioning of the 50% evaporated liquid more positive. Similarly, the compounds contribute less to the variance on PC2; hence, the 50% evaporated liquid is positioned less positively on PC2.

Evaporated marine fuel stabilizer at the 5% evaporation level is positioned closely to the neat liquid (Appendix B, Figures B.9 to B.12). As evaporation increases further, the evaporated liquids are positioned slightly less positively on both PC1 and PC2. This trend is due to the evaporation of early eluting naphthalenes, branched alkanes, and cyclic alkanes, which decrease the positive contribution of these compounds to the variance on PC1 and PC2.

Evaporated kerosenes (Appendix B, Figures B.5 to B.8), specifically the 5%, 10%, and 20% evaporated liquids, are closely associated with the neat liquid on both PC1 and PC2. At these evaporation levels, only the aromatic components have been evaporated. Since the C₂- and C₃-alkylbenzenes contribute only slightly to the variance described in the loadings plots, there is little change in positioning of the liquids on the scores plot. At the 50% evaporation level, the C₉-C₁₁ normal alkanes and early eluting naphthalenes have been evaporated, along with the aromatic components. Therefore, the C₁₂-C₁₇ normal alkanes, which load negatively on PC1 and PC2, are the compounds that contribute to the positioning of the 50% evaporated liquid. Due to the evaporation of the early eluting naphthalenes and the early eluting normal alkanes, the 50% evaporated liquids are positioned closer to zero on PC1 and less positively on PC2.

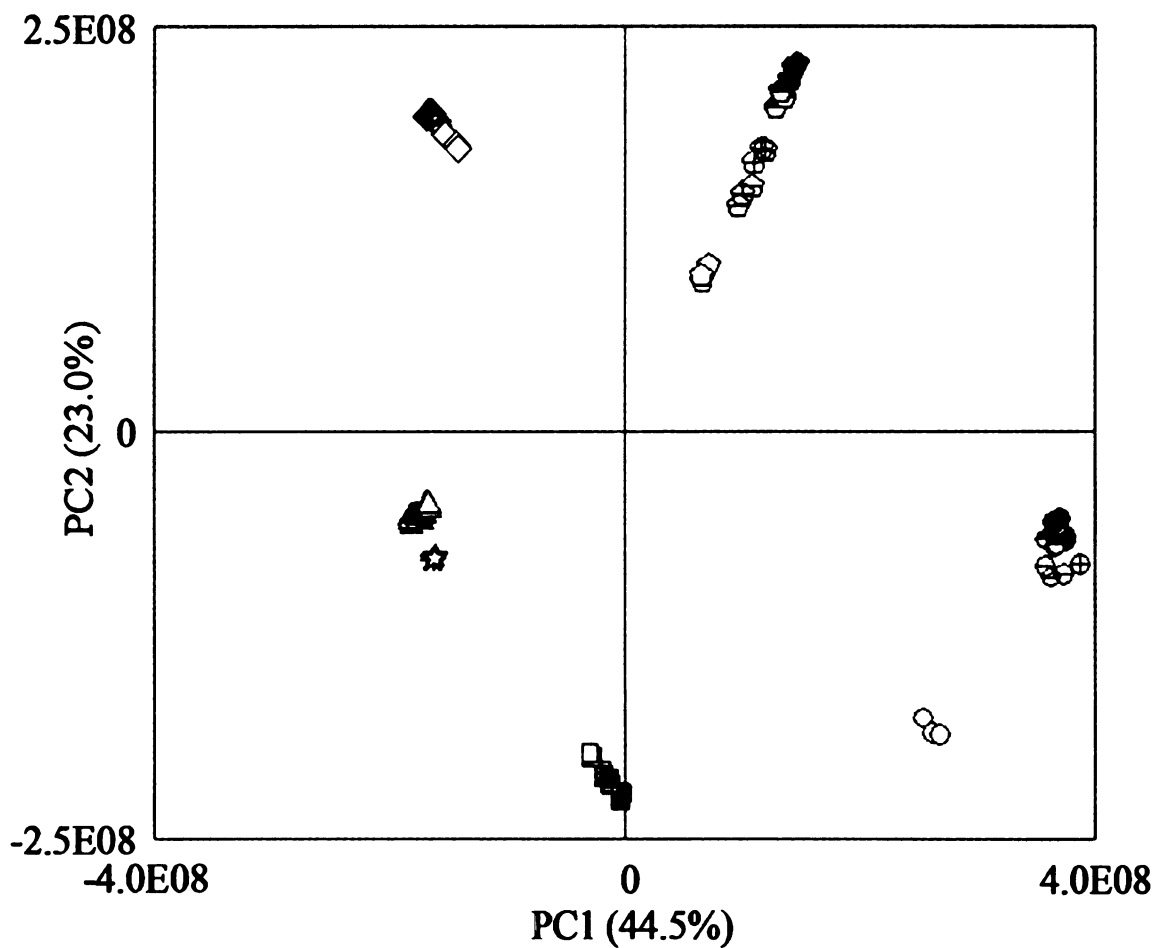


Figure 3.8: Scores plot of PC1 vs. PC2 based on the TIC for six ignitable liquids with projections of evaporated liquids. Liquids are indicated by symbol. Lamp Fuel (■), Kerosene (●), Marine Fuel Stabilizer (◐), Paint Thinner (◆), Gasoline (▲), and Lacquer Thinner (★). Each fill indicates a different level of evaporation. Neat (Filled e.g. ■), 5% evaporated (Half Filled e.g. ◐), 10% evaporated (Cross e.g. ◑), 20% evaporated (Line e.g. ◒), 50% evaporated (No Fill e.g. ◓).

Evaporated lamp fuels (Appendix B, Figures B.1 to B.4) are closely associated with the neat lamp fuel. However, as evaporation level increases, the liquids are positioned slightly more negatively on PC1 and slightly less negatively on PC2. This slight shift in positioning is due to the decrease in contribution of the C₁₂ and C₁₃ normal alkanes due to evaporation, which load positively on PC1 and negatively on PC2.

Evaporated lacquer thinners (Appendix B, Figures B.21 to B.24) are positioned closely to the neat lacquer thinner on both PC1 and PC2 since compounds that eluted in the solvent front were evaporated. As a result, the abundance of toluene is concentrated by evaporation. After normalization, the toluene abundance is similar for all levels of evaporation and also similar to the levels observed in the neat lacquer thinner. Within the scores plot, all evaporated lacquer thinners overlaid with the neat lacquer thinner.

Evaporated gasolines (Appendix B, Figures B.17 to B.20) are very closely associated with the neat liquid and are positioned negatively on both PC1 and PC2. Gasoline contains components more volatile than toluene that elute in the solvent front and are not detected by GC-MS. The presence of these components has been confirmed using GC with flame ionization detection. During evaporation, these more volatile components are evaporated, resulting in toluene and C₂- and C₃-alkylbenzenes being concentrated. However, after normalization, the evaporated and neat gasolines were similar in abundance. Hence, no differences in positioning of the evaporated liquids to the neat gasoline are observed.

Thus, the evaporated liquids are closely associated to the corresponding neat liquid, with the exception of 50% evaporated kerosene. The evaporated liquids are

differentiated from evaporated liquids in other ASTM classes, with the exception of gasoline and lacquer thinner. Evaporated gasolines and lacquer thinners are positioned closely since both contain toluene, which is contributing greatly to the variance in PC1 and PC2. As with the neat liquids, PCA can only be visually assessed, and there is not a statistical measure of the association of the evaporated liquids to the neat liquids. Therefore, PPMC coefficients and HCA were used to statistically evaluate the similarities among the evaporated and neat liquids

3.3.5 Association and Discrimination of Evaporated Liquids to Neat Liquids using PPMC coefficients

The precision of the analytical methods was investigated by calculating mean PPMC coefficients between the neat replicates of each liquid (Table 3.5) (Appendix D, Table D.1).

For all neat liquids, the mean PPMC coefficients are greater than 0.99, indicating a strong correlation and hence, acceptable precision in the extraction and analysis procedures. The PPMC coefficients of the replicates are not 1.0000 due to slight instrument variations in the analyses of the replicates and slight variability in the extraction procedure.

The PPMC coefficients were also calculated to investigate the chemical similarities between the evaporated ignitable liquids and their neat counterparts, as well as differences between ignitable liquid classes. While each principal component accounts for a certain percentage of the variance, PPMC coefficients take into account the entire chromatogram and are an alternative method for comparison of the ignitable liquids.

Table 3.5: PPMC coefficients for replicates (n=3) and range of coefficients for each liquid class based on the TIC.

Ignitable Liquid	Mean PPMC Coefficient ± Standard Deviation for Neat Replicates	Range of PPMC Coefficients between Neat & Evaporated Liquids in Each Class
Gasoline	0.9944 ± 0.0007	0.9994 - 0.9759
Lacquer Thinner	0.9984 ± 0.0013	1.0000 - 0.9593
Lamp Fuel	0.9953 ± 0.0018	0.9997 - 0.9716
Paint Thinner	0.9920 ± 0.0013	0.9998 - 0.9157
Marine Fuel Stabilizer	0.9982 ± 0.0010	0.9994 - 0.8535
Kerosene	0.9954 ± 0.0006	0.9992 - 0.8744

A strong correlation (Section 2.4) is observed between the neat and the evaporated liquids for all six liquids at all levels of evaporation (Table 3.6) (Appendix C, Tables C.1 to C.6). For gasoline, lacquer thinner, lamp fuel, and paint thinner, all PPMC coefficients are greater than 0.9000, which indicates that, even at the 50% evaporation level, the evaporated liquids are still sufficiently similar to yield strong association to the neat liquid. For marine fuel stabilizer, there is a wider range of PPMC coefficients due to the loss of earlier eluting compounds from the chromatogram. However, a strong correlation is still observed between the neat and 50% evaporated liquids. Like marine fuel stabilizer, kerosene shows a wider range of PPMC coefficients which is due to the loss of all volatile compounds at the 50% evaporation level. As a result, the chemical composition of the neat and 50% evaporated kerosene is sufficiently different that a lower PPMC coefficient (0.8764) is observed. However, the correlation between the neat and the 50% evaporated liquid is still considered a strong correlation.

Although strong correlations between the evaporated liquids and the corresponding neat liquids are observed, PPMC coefficients for lacquer thinner are lower than expected. The only peak in the lacquer thinner chromatograms is toluene, which is concentrated during evaporation. The wide range of PPMC coefficients for lacquer thinner is due to the misalignment of toluene in the chromatograms even after optimizing alignment. With the low abundance of this peak in the consensus target, the algorithm is unable to optimize the correlation between the consensus target and the sample chromatogram. Thus, misalignments occur in the chromatograms of lacquer thinner.

For lamp fuel, the lower correlations observed between the neat and evaporated liquids are due to the evaporation of the C₁₂ and C₁₃ normal alkanes. Although PPMC

coefficients are not affected by overall peak height, the change in the relative peak heights will affect the correlation coefficient. As the level of evaporation increases, the peak height of the C₁₂ and C₁₃ normal alkanes decreases in relation to the other components; this decreases the correlation coefficient between the neat and evaporated lamp fuels

Neat and evaporated gasolines are positioned closely to lacquer thinner in the scores plot (Figure 3.8) and could not be differentiated by PCA. The PPMC coefficients were calculated between the gasoline and lacquer thinner to assess the degree of similarity between the two liquids (Table 3.6). Neat and 50% evaporated levels of each liquid were chosen to represent the two extremes in chemical composition.

When the 50% evaporated liquid was compared to the corresponding neat liquid, a strong correlation was observed. With all other combinations of the neat and 50% evaporated lacquer thinner and the neat and 50% evaporated gasoline, moderate to weak correlations were observed (Table 3.6) (Appendix C, Tables C.5 and C.6; Appendix D, Tables D.5 and D.6). Lacquer thinner only contains toluene, while gasoline contains not only toluene, but also the C₂- and C₃-alkylbenzenes. Hence, moderate to weak correlations are observed between these liquids, irrespective of the level of evaporation, indicating that the liquids can be distinguished using PPMC coefficients. However, the two liquids cannot be differentiated using PCA, because PC1 and PC2 only account for a percentage of the variance. Thus, the combination of PCA with PPMC coefficients can differentiate the classes of ignitable liquids from each other.

Table 3.6: PPMC coefficients (n=9) between neat and evaporated gasoline and neat and evaporated lacquer thinner.

Pair-wise comparison	Mean PPMC Coefficient ± Standard Deviation
Neat Gasoline vs. 50% Evaporated Gasoline	0.9848 ± 0.0028
Neat Lacquer Thinner vs. 50% Evaporated Lacquer Thinner	0.9978 ± 0.0031
Neat Gasoline vs. Neat Lacquer Thinner	0.5423 ± 0.0030
50% Evaporated Gasoline vs. Neat Lacquer Thinner	0.4424 ± 0.0422
Neat Gasoline vs. 50% Evaporated Lacquer Thinner	0.5408 ± 0.0046
50% Evaporated Gasoline vs. 50% Evaporated Lacquer Thinner	0.4414 ± 0.0423

3.3.6 Association of Evaporated Liquids to Neat Liquids using HCA

The scores plot (Figure 3.9) showed the association of the neat liquid replicates, while differentiating the liquids according to ASTM class. Using HCA, a statistical measure of the association and discrimination of the liquids in the scores plot was determined. Within the dendrogram of the neat liquids (Figure 3.8), replicates of each liquid are associated and separated from different liquids at a similarity greater than or equal to 0.959, which indicates the replicates are very similar to each other. However, replicates are expected to have a similarity closer to 1. This lower than expected similarity is due to variability in the extraction procedure of the neat liquids.

Gasoline and lacquer thinner are closely positioned in the scores plot (Figure 3.5) and could not be differentiated. Using HCA, these two liquids are associated at a similarity level of 0.900 (Figure 3.9). Kerosene and gasoline are positioned furthest apart on PC1 (Figure 3.5) and, using HCA, there is no similarity between these two liquids (similarity of 0.000 in Figure 3.8). Marine fuel stabilizer and lamp fuel are positioned furthest apart on PC2 in the scores plot (Figure 3.5) and, using HCA, there is no similarity between these two liquids (similarity of 0.083 in Figure 3.9).

Within the dendrogram of the neat and evaporated liquids (Figure 3.10), separation by class of the liquids is observed at a similarity level of 0.836. A high similarity between the evaporated liquids and the corresponding neat liquid is observed with the exception of 50% evaporated kerosene (0.494).

As observed in the scores plot (Figure 3.8), the 50% evaporated kerosene replicates are positioned between lamp fuel and kerosene on both PC1 and PC2. However, using HCA, the 50% evaporated kerosene is more similar to the neat kerosene

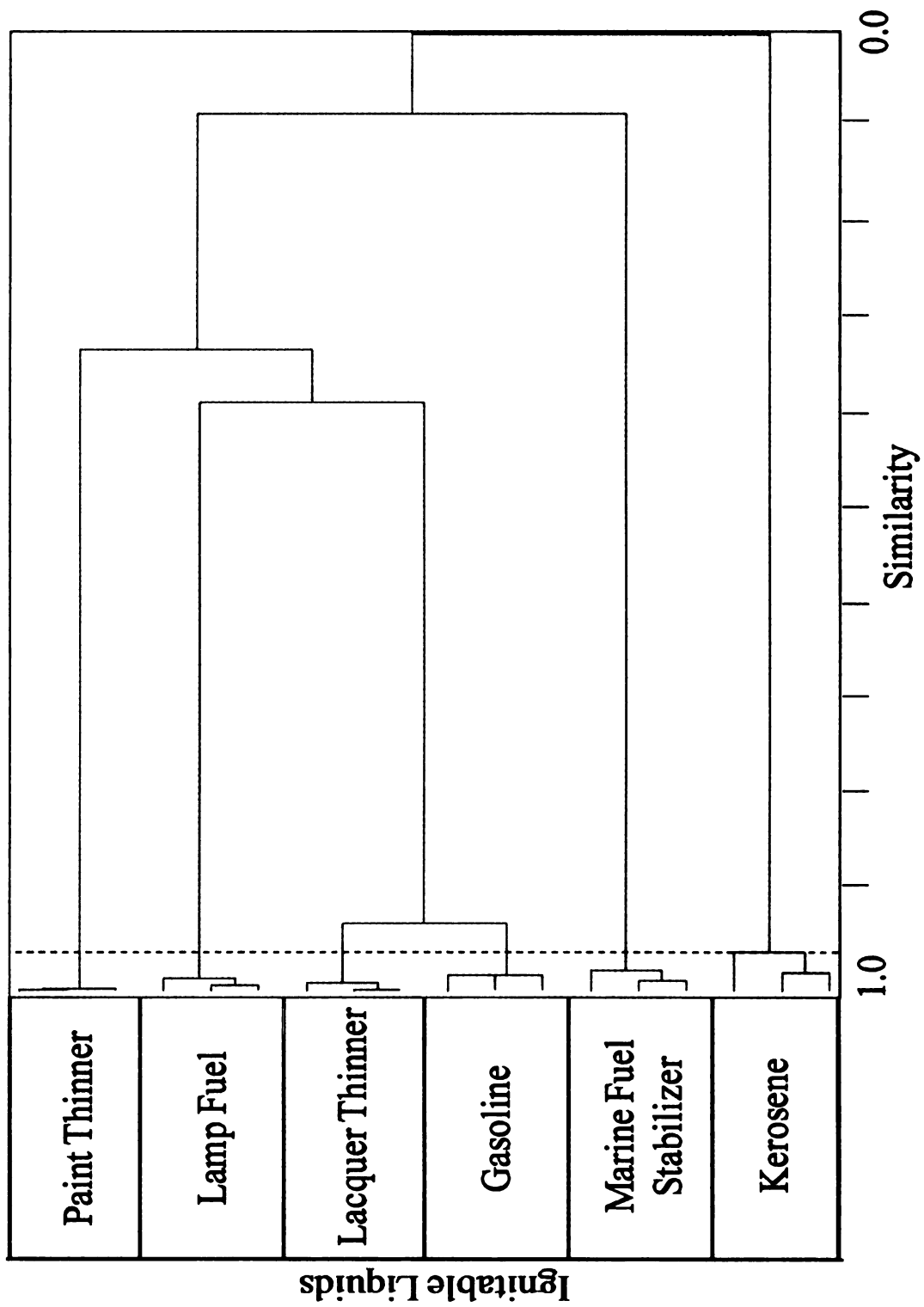


Figure 3.9: HCA Dendrogram of the scores of the neat liquids. Dashed line indicates similarity of 0.959.

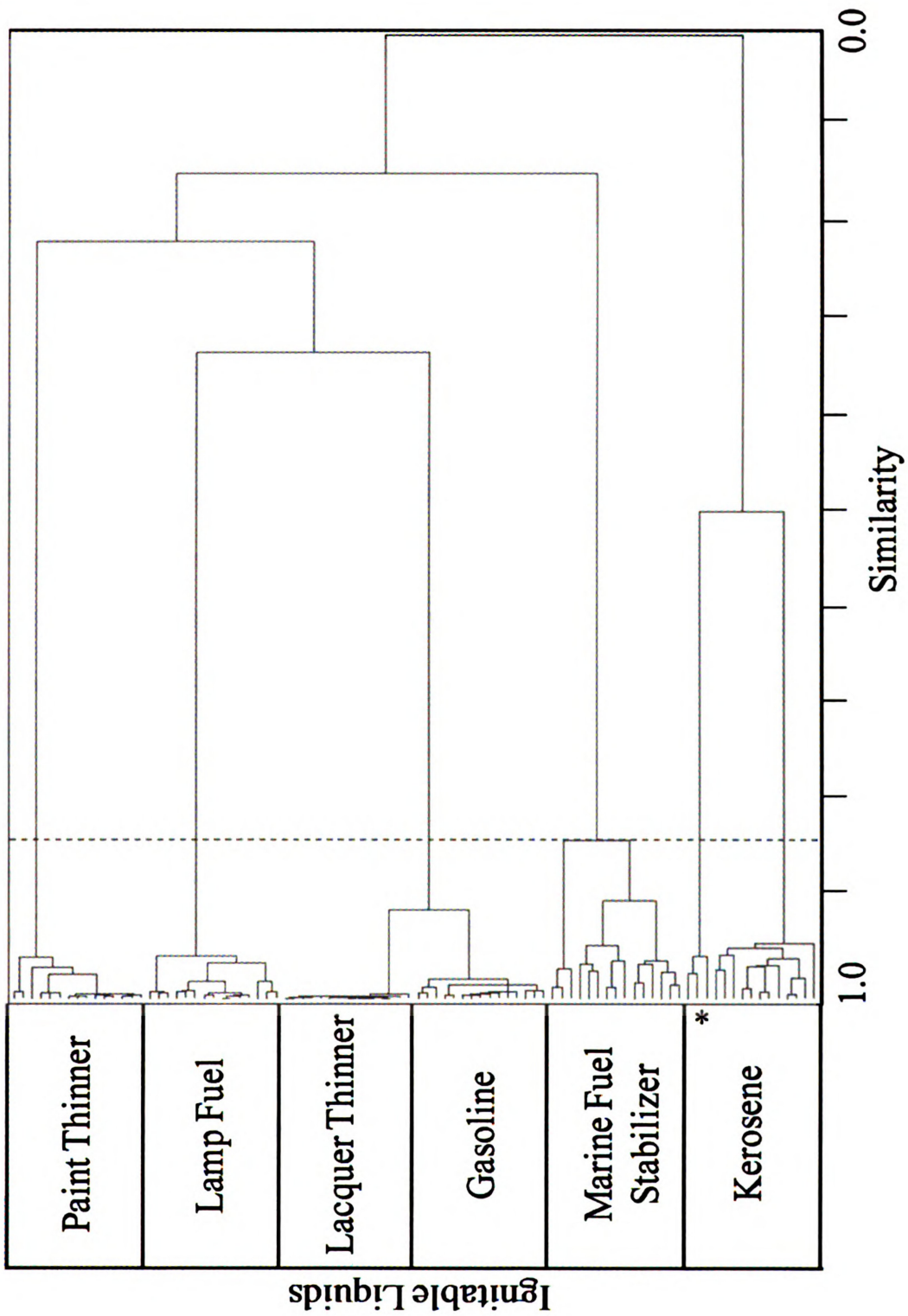


Figure 3.10: HCA Dendrogram of the scores of the neat and evaporated liquids. An asterisk indicates 50% evaporated kerosene. Dashed line indicates similarity of 0.836.

(similarity of 0.494) than to neat lamp fuel (similarity of 0.000). Hence, HCA can be used as a statistical measure of the association and discrimination of the neat and evaporated liquids by PCA.

3.4 Conclusions

Through the use of PCA, PPMC coefficients, and HCA, the ignitable liquids are distinguished by class with the replicates of each liquid associated to each other and separated from other ignitable liquids. Furthermore, the evaporated liquids are generally associated to the corresponding neat liquid.

The neat liquids were distinguished using PCA according to ASTM class, with the exception of gasoline and lacquer thinner. Through PPMC coefficients, all of the ignitable liquids were able to be distinguished from each other. Although they were positioned closely in the scores plot, gasoline and lacquer thinner were observed to only have a moderate correlation to each other with PPMC coefficients. Four of the six liquids were further distinguished from each other in the scores plot using HCA. Gasoline and lacquer thinner were not distinguishable through HCA, having a similarity greater than 0.900.

The evaporated liquids were associated to the corresponding neat liquid in the PCA scores plot. Based only on the scores plot, there was no measure of the degree of association. Using PPMC coefficients, a strong correlation was determined between the evaporated liquid and the corresponding neat liquid. A similarity level was also established between evaporated ignitable liquids and the corresponding neat liquid using

HCA. While PPMC coefficients evaluate correlation among pairs of samples, HCA statistically measures similarity of all of the samples. Through HCA, a value can be applied to assess the similarity of the scores in the scores plot. The combination of these three statistical procedures reduces the subjectivity of associating an evaporated ignitable liquid to the corresponding neat ignitable liquid.

3.5 References

1. American Society for Testing and Materials, ASTM E 1618-06e1. *Annual Book of ASTM Standards 14.02*.
2. Johnson KJ, Wright BW, Jarman KH, Synovec RE. High-speed peak matching algorithm for retention time alignment of gas chromatographic data for chemometric analysis. *J Chromatogr A* 2003;996:141-55.

CHAPTER 4

Effect of Matrix Interferences, Evaporation, and Combustion on the Identification of Mixed Ignitable Liquids in Fire Debris using Chemometric Procedures

4.1 Introduction

At a suspected arson, an arsonist may have used a mixture of ignitable liquids rather than a single ignitable liquid, as in Chapter 3. Under these conditions, the ignitable liquid residues (ILR) collected from an arson scene would contain matrix interferences from the fire debris and evaporative loss from the ignitable liquid mixture. With the profile of the ILR differing from that of the ignitable liquid mixture, an arson investigator may not be able to identify the ignitable liquids present. In this research, chemometric procedures, such as principal components analysis (PCA), Pearson product moment correlation (PPMC) coefficients, and hierarchical cluster analysis (HCA), were used as an objective method to associate mixed liquid samples to the corresponding mixed liquid standards even in the presence of matrix interferences, evaporative loss, and combustion.

Firstly, gasoline and kerosene were selected as the model liquids and evaporated to two levels of evaporation. Mixed liquid standards were prepared using different combinations of the neat and evaporated ignitable liquids. The mixtures were then spiked onto burned carpet in order to assess association of the mixed liquid in the presence of matrix interferences. Mixed liquids were also spiked onto unburned carpet and then burned to simulate an ILR. This was done to assess association of the mixed liquid in the presence of matrix interferences, evaporative loss, and combustion due to burning. All

samples were analyzed by gas chromatography-mass spectrometry (GC-MS). The chromatograms were compiled into two data sets and subjected to pretreatment procedures (smoothing, retention time alignment, and normalization). Principal components analysis, PPMC coefficients, and HCA were applied to assess association of the mixed liquid samples to the corresponding mixed liquid standard even in the presence of matrix interferences, evaporative loss, and combustion.

4.2 Methods and Materials

4.2.1 Sample Collection

Gasoline and kerosene were collected from service stations in the Lansing, Michigan area. The ignitable liquids, along with the class and major compounds present in each, are listed in Table 3.1 in Chapter 3.

4.2.2 Mixed Ignitable Liquids

Gasoline and kerosene were evaporated to two different levels of evaporation (10% and 50% by volume) using filtered air and magnetic stir bars for agitation. Once evaporated, the liquids were stored in 7.4 mL amber screw cap vials (Fisher Scientific, Pittsburgh, PA) that were acid washed before use. The vials were labeled, wrapped in Parafilm[®] (American National Can, Menasha, WI), and stored at 16°C until analysis.

A set of mixed gasoline and kerosene samples was prepared using different combinations of the neat, 10% evaporated, and 50% evaporated liquids (1:1 v/v), as shown in Table 4.1. The mixed ignitable liquids were diluted 1:50 (v/v), extracted, and

Table 4.1 Mixed Ignitable Liquids.

Gasoline	Kerosene
Neat	Neat
Neat	10% Evaporated
Neat	50% Evaporated
10% Evaporated	Neat
50% Evaporated	Neat

analyzed using the same procedure described in Chapter 3.

4.2.3 Matrix Interferences

Nylon carpet (source unknown) was cut into $5 \times 5 \text{ cm}^2$ squares, burned for 40 sec with a propane blow torch (Benzomatic, Medina, NY), and allowed to burn further for 1.0 min. The flame was extinguished through inverting a 1000 mL beaker and placing it over the burning carpet. The pieces of burned carpet were extracted using the same passive headspace extraction and eluted with CH_2Cl_2 , as described previously in Chapter 3 Section 2.2. The process was repeated twice more, using fresh pieces of carpet.

Additional samples of $5 \times 5 \text{ cm}^2$ carpet were burned and extinguished as described previously. A $1 \mu\text{L}$ aliquot of each mixed liquid, except for the neat gasoline: neat kerosene mixture, was spiked onto separate pieces of the burned carpet and extracted, as described previously in Chapter 3 Section 2.2. This process was repeated twice more for each mixed liquid. The chromatograms collected are subsequently referred to as the “burned then spiked” samples.

A $750 \mu\text{L}$ aliquot of each mixed liquid, except for the neat gasoline: neat kerosene mixture, was spiked onto separate pieces of $5 \times 5 \text{ cm}^2$ unburned carpet. The carpet was burned following the previously described procedure and extracted following the method described in Chapter 3 Section 2.2. The chromatograms collected are subsequently referred to as the “simulated ILR” samples.

4.2.4 GC-MS Analysis

The experimental parameters for the GC-MS analysis are exactly the same as those described in Chapter 3 Section 2.3.

4.2.5 Data Pretreatment

Total ion chromatograms (TICs) were generated and smoothed for the mixed ignitable liquids, the burned carpet, the burned then spiked samples, and the simulated ILR samples using the same procedure described in Chapter 3 Section 2.4. Two data sets were compiled, where both data sets contained the TICs of mixed ignitable liquid standards and the burned carpet, one data set contained the TICs of burned then spiked samples, while the other data set contained the TICs of the simulated ILR samples.

Chromatograms in each data set were retention time aligned to a target chromatogram. The target chromatogram was generated by averaging the replicates of the mixed ignitable liquid standards and the burned carpet. The chromatograms were averaged due to the difficulty in forming a consensus target that included the compounds from the mixed liquids and matrix inferences. The TIC of the average target was added to each data set for alignment purposes.

The two data sets were aligned using the same algorithms described in Chapter 3 Section 2.4. For each algorithm, various user-defined parameters were investigated, as shown in Table 4.2. There are typically 13 points across a peak such that window size and warp size are smaller than the peak width, while the segment size is larger than the peak width.

Table 4.2 User defined parameters investigated for peak matching algorithm and COW algorithm.

Data Set	Peak Matching Algorithm	COW Algorithm	
	Window Size in Data Points	Warp Size in Data Points	Segment Size in Data Points
Data Set Containing Burned then Spiked Samples	2, 3, 4, 5, 6, 7	1, 2, 3, 4, 5	55, 65, 75
Data Set Containing Simulated ILR Samples	2, 3, 4, 5, 6, 7	1, 2, 3, 4, 5	55, 65, 75

For the correlation optimized warping (COW) algorithm, all combinations of the warp sizes and the segment sizes in Table 4.2 were investigated. The aligned chromatograms were visually assessed to determine the parameters for optimal alignment. For the peak matching algorithm, each window size mentioned in Table 4.2 was investigated and visually assessed for misalignments. After retention time alignment, the data sets were normalized using maximum peak normalization followed by total area normalization, as described in Chapter 3 Section 2.4.

4.2.6 *Data Analysis*

Principal components analysis (PCA) was performed on the chromatograms of the mixed ignitable liquid standards and the burned carpet using MatLab (version 7.7.0.471, The Math Works, Natick, MA), following the procedure described in Chapter 3 Section 2.5.

Scores for the data set of the burned then spiked samples were then calculated in Microsoft Excel (version 12.0.6524.5003, Microsoft Corp., Redmond, WA) and projected onto the scores plot of the mixed ignitable liquid standards and the burned carpet, following procedures described in Chapter 3. The scores plot was used to assess differentiation of the burned then spiked samples in relation to the burned carpet and to the corresponding mixed liquid standards. This procedure was then repeated to calculate and project scores for the simulated ILR samples, which were then assessed in a similar manner.

Pearson product moment correlation (PPMC) coefficients were calculated for the aligned chromatograms using MatLab (The Math Works, Inc.) (Equation 2.1). The

PPMC coefficients were calculated among replicates of each mixed liquid to assess the precision of the extraction and analytical procedure. Correlation coefficients were then calculated for all pair-wise combinations of chromatograms for the data set of the burned then spiked samples to assess the correlation of the samples to the mixed liquid standard. The same procedure was repeated for the simulated ILR samples, and the correlations observed were assessed in a similar manner.

Using the scores calculated for each data set, HCA was performed in Pirouette (version 4.0, Infometrix, Inc., Bothwell, WA) in order to statistically evaluate the association and discrimination of the mixed liquids in the scores plot. The Euclidean distance (Equation 2.2) was first calculated among all pair-wise combinations of the PC scores. From the agglomerative method, each score was individually linked using the complete linkage method.

4.3 Results and Discussion

4.3.1 Optimization of Retention Time Alignment and Normalization

The retention time alignment and normalization were investigated separately for the data set of the burned then spiked samples and the data set of the simulated ILR samples. For both data sets, burned carpet and the mixed liquid standards were used to determine optimal parameters. It is noteworthy that the same optimal parameters were determined for both.

Window sizes of two to seven points were investigated for the peak matching algorithm (Table 4.2). Since major misalignments were observed for each window size,

the peak matching algorithm was excluded from further investigation.

Using the COW algorithm, major misalignments were observed for most combinations of warp sizes and segment sizes. Visual assessment of the chromatograms yielded a warp size of two points and a segment size of 75 points as the optimal alignment (Figure 4.1A and B). Hence, these parameters were used as the optimal alignment for both data sets.

After alignment, the chromatograms were normalized firstly with maximum peak normalization and then with total area normalization of the replicates to minimize differences in abundances (Figure 4.2A and B), as discussed in Chapter 3 Section 3.2.

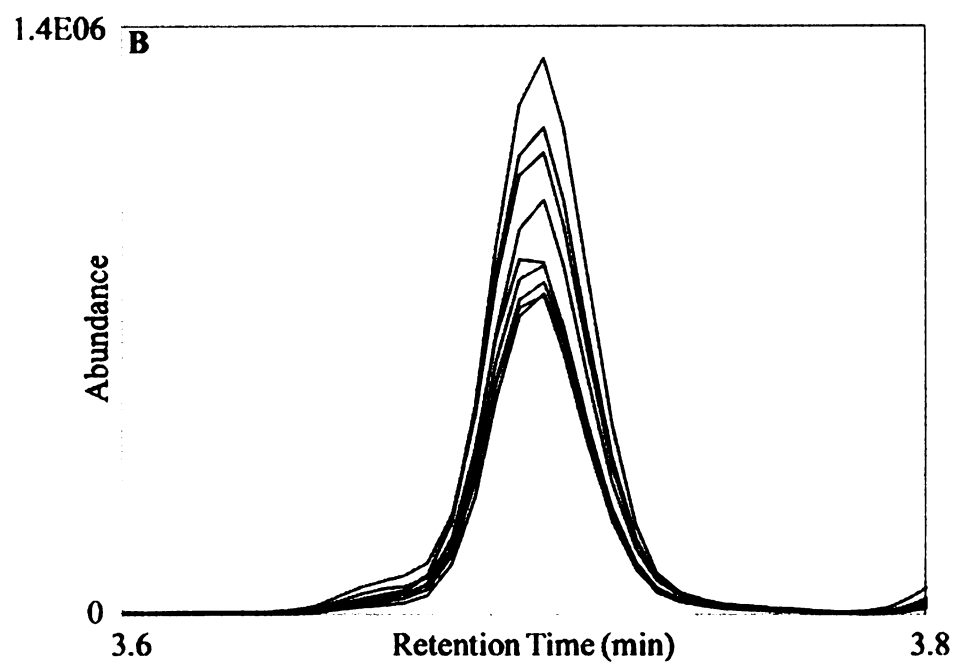
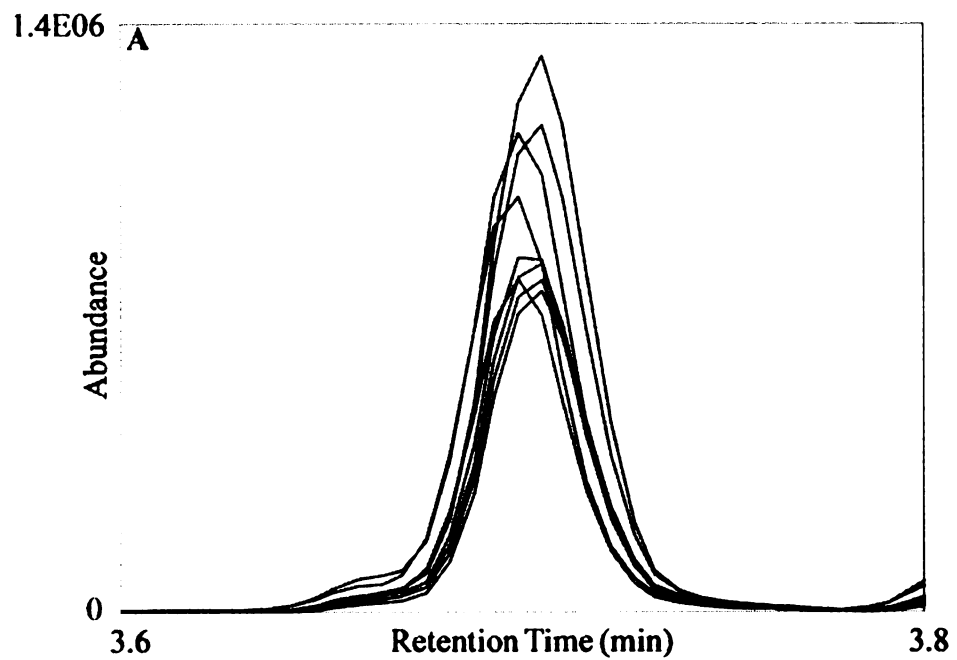


Figure 4.1: A) Unaligned toluene peak in the TIC of mixed liquids. B) Well aligned toluene peak in the TIC of mixed liquids with a warp size of two points and a segment size of 75 points.

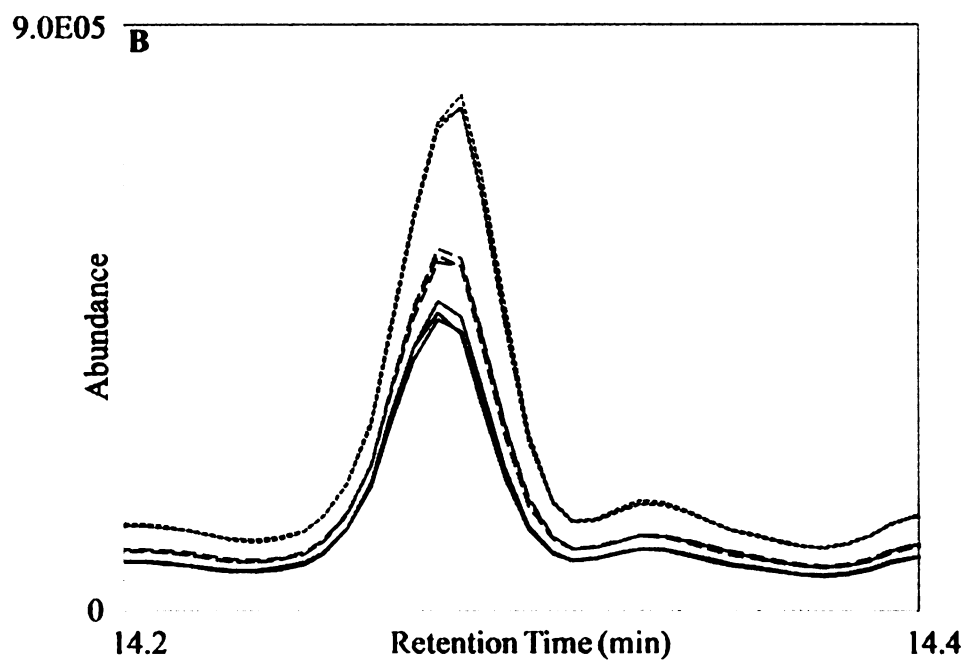
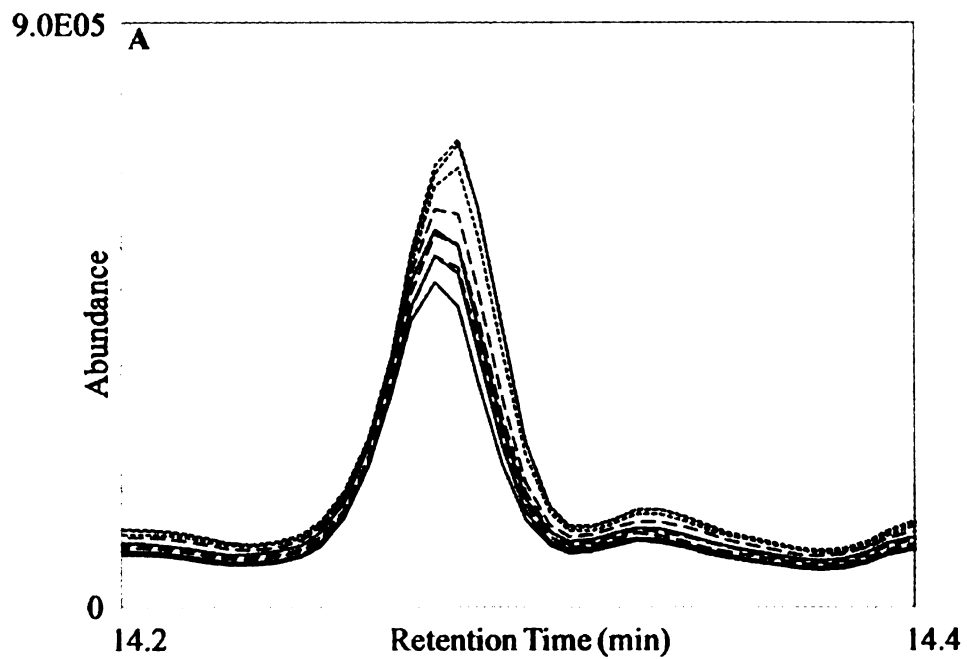


Figure 4.2: A) Unnormalized C_{14} normal alkane peak. B) Normalized C_{14} normal alkane peak. Neat Gasoline: Neat Kerosene Mixture (—), Neat Gasoline: 10% Evaporated Kerosene Mixture (---), Neat Gasoline: 50% Evaporated Kerosene Mixture (···).

4.3.2 Matrix Interferences

The TICs of burned carpet show matrix interferences such as 2,4-dimethyl-1-heptene, styrene, benzaldehyde, and acetophenone [1,2] (Figure 4.3A). These matrix interferences present are from the thermal degradation of the adhesive, the yarn, and the backing material in carpet [2]. The TICs of the mixed liquid standards (Appendix E, Figures E.1 to E.5) consist of the major compounds present in both gasoline and kerosene: toluene, the C₂- and C₃-alkylbenzenes, naphthalenes, and the C₁₁-C₁₇ normal alkanes (Figure 4.3B). Of the compounds that are common between chromatograms of the burned carpet and mixed liquid standards, only toluene is present in both. Thus, the use of toluene as an identifying peak for the gasoline in the mixed liquid is diminished.

From the burned then spiked samples, the effect of both matrix interferences and evaporation without combustion of the mixed liquid can be observed in the chromatograms (Figure 4.4A). The burned then spiked samples contain some of the more dominant compounds in the mixed liquids, such as toluene, the C₃-alkylbenzenes, cyclic alkanes, naphthalenes, and C₁₁-C₁₃ normal alkanes. The presence of these compounds is expected, since the mixed liquids have been spiked onto burned carpet and have not been subjected to the burning procedure. However, matrix interferences have complicated the identification of these compounds through visual assessment of the chromatogram. In the chromatograms, styrene (6.165 min) from the burned carpet coelutes with *p*-xylene (6.205 min) from the mixed liquid. Also, benzaldehyde (7.544 min) from the burned carpet coelutes with the *m*-ethyltoluene (7.556 min) in the mixed liquid. Even though

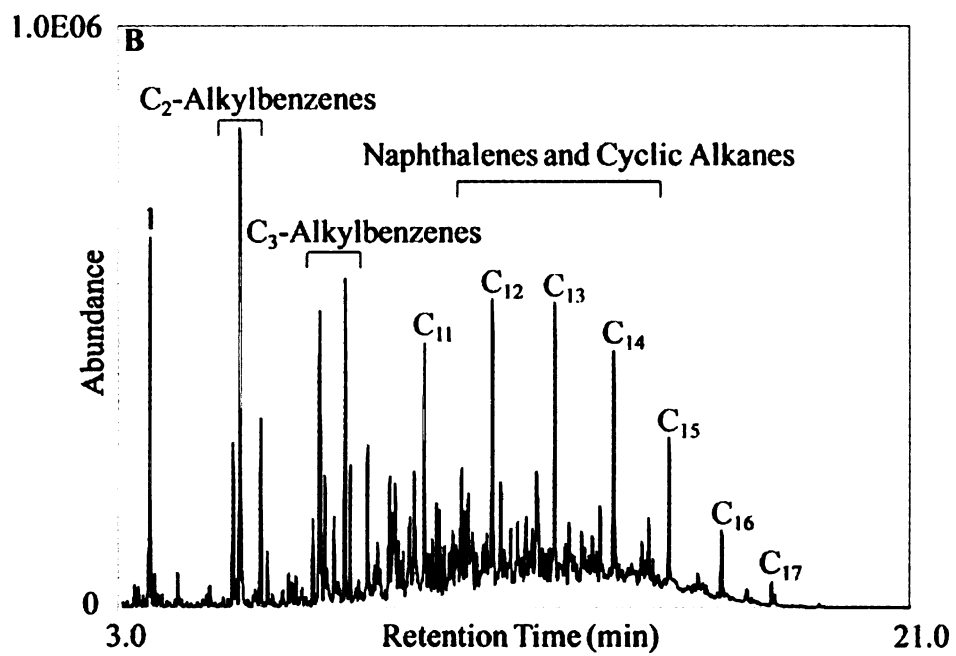
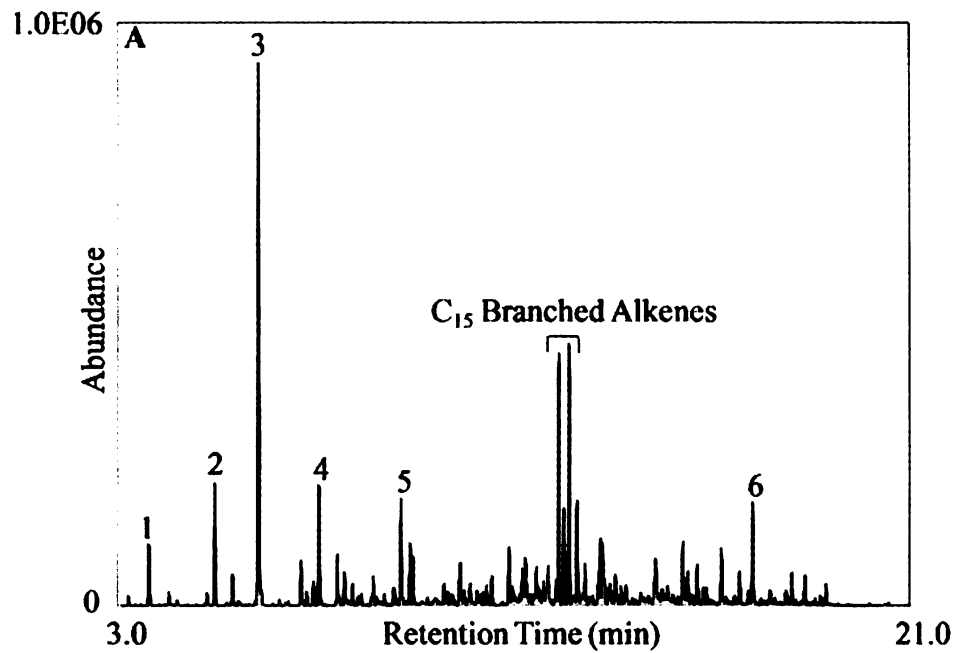


Figure 4.3: A) TIC of burned carpet. B) TIC of 10% evaporated gasoline: neat kerosene mixture. Major components are labeled: 1) toluene, 2) 2,4-dimethyl-1-heptene, 3) styrene, 4) benzaldehyde, 5) acetophenone, 6) 1,3-diphenylpropane

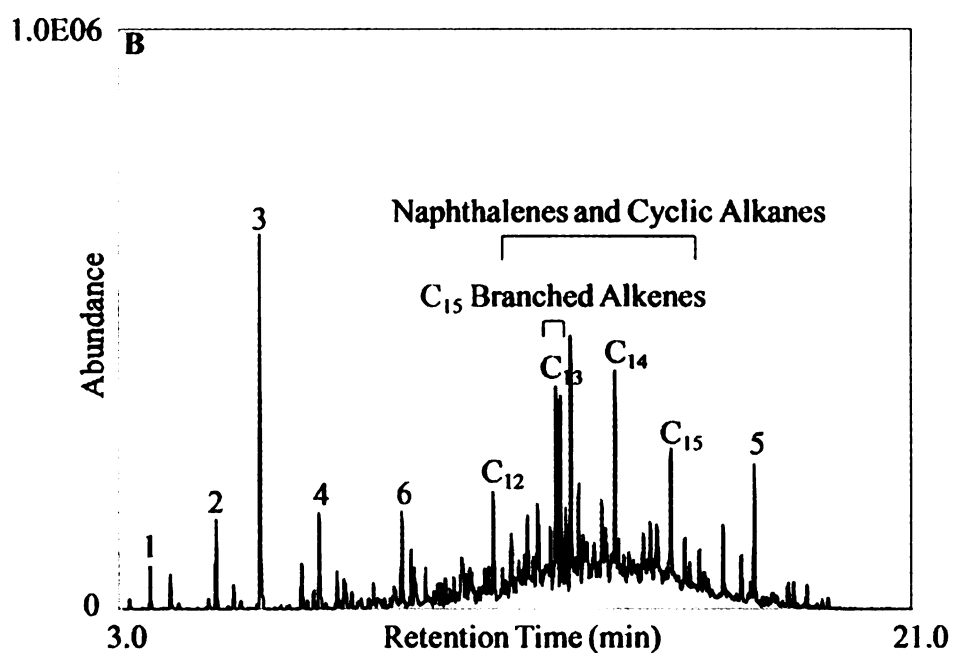
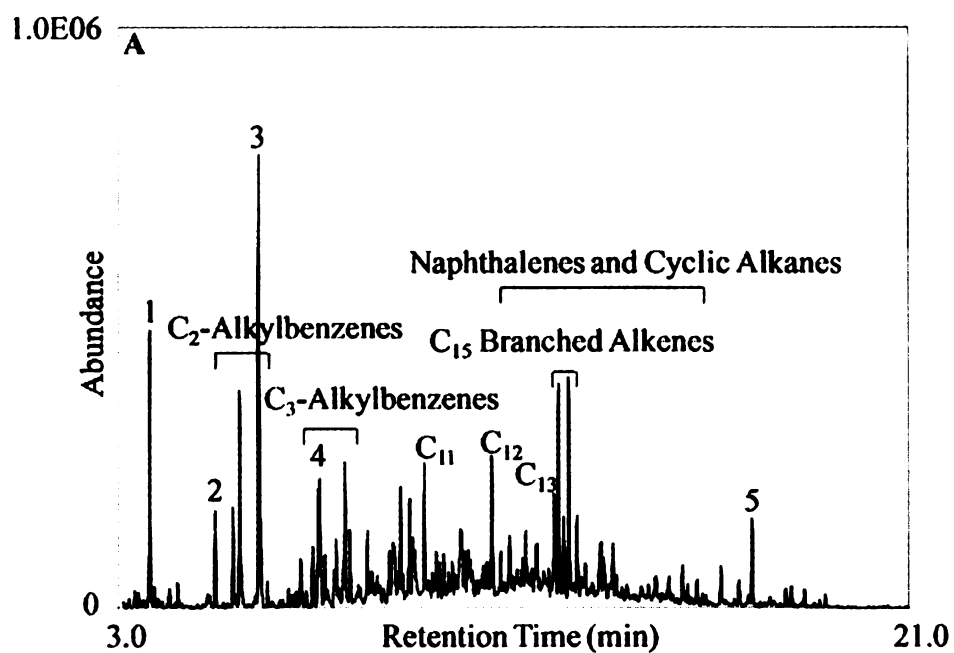


Figure 4.4: A) TIC of burned carpet spiked with 10% evaporated gasoline: neat kerosene mixture. B) TIC of 10% evaporated gasoline: neat kerosene simulated ILR sample. Major components are labeled: 1) toluene, 2) 2,4-dimethyl-1-heptene, 3) styrene, 4) benzaldehyde, 5) 1,3-diphenylpropane, 6) acetophenone.

some of the compounds from the burned carpet have eluted with some of the compounds in the mixed liquid, the relative peak heights of the C₂- and C₃-alkylbenzenes in the burned then spiked samples have not changed when compared to the mixed liquid standard. The relative peak heights for the normal alkanes in the burned then spiked sample when compared to the mixed liquid have decreased in abundance. Consequently, many of the later eluting normal alkanes are at a low abundance and not able to be identified in the chromatogram.

In addition, evaporation of the mixed liquid also complicates the subsequent identification. Since at least one of the liquids in each mixed liquid has been evaporated, some of the peaks in the burned then spiked samples have been lost due to evaporation. Although this is not highly problematic for burned carpet spiked with 10% evaporated gasoline: neat kerosene sample, evaporation complicates the burned carpet spiked with neat gasoline: 50% evaporated kerosene sample. The evaporated kerosene part of this burned then spiked sample has lost the early eluting alkanes. Thus, evaporation has increased the difficulty in identifying the mixed ignitable liquid as containing kerosene.

The difficulty in visual comparison of the simulated ILR samples (Figure 4.4B) to the mixed liquid standard has increased from that of the burned then spiked samples. Most of the compounds present at early retention times, such as the C₂- and C₃-alkylbenzenes, have been lost due to evaporation during the burning process. The C₁₂-C₁₅ normal alkanes along with cyclic alkanes and naphthalenes have been concentrated by evaporation during burning, but are still difficult to identify in the simulated ILR samples. The peak heights of the normal alkanes have also changed due to burning when

compared to the mixed liquid standard.

As observed in the chromatograms, the matrix interferences from the burned carpet coelute with or mask some of the compounds from the mixed liquids. The identification of the ignitable liquids from fire debris has become more difficult, making visual assessment even more complicated. Thus, an objective method is necessary to overcome the subjectivity introduced through visual assessment.

4.3.3 Association and Discrimination of Mixed Liquids in Presence of Matrix Interferences and Evaporation

Principal components analysis was used to develop an objective method. The scores plot of the first principal component (PC1) and the second principal component (PC2) accounts for 93.6% of the variance among the burned carpet and the mixed liquid standards (Figure 4.5). Very little spread is observed among the replicates of each of the mixed liquid standards, and each standard can be differentiated from each other. However, spread is observed among the burned carpet replicates.

The PPMC coefficients for replicates for the mixed liquid standards are greater than 0.99 indicating a precise analytical procedure (Table 4.3) (Appendix F, Table F.1). Although the average PPMC coefficient among the burned carpet replicates (0.9321 ± 0.0480) indicates strong correlation, a coefficient close to 1.0000 is expected for replicates. The greater spread in the replicates of the burned carpet is most likely due to the irreproducibility of burning as well as some variability in the extraction procedure.

The positioning of the burned carpet and mixed liquid standards on the scores plot can be explained with reference to the corresponding loadings plots (Figure 4.6).

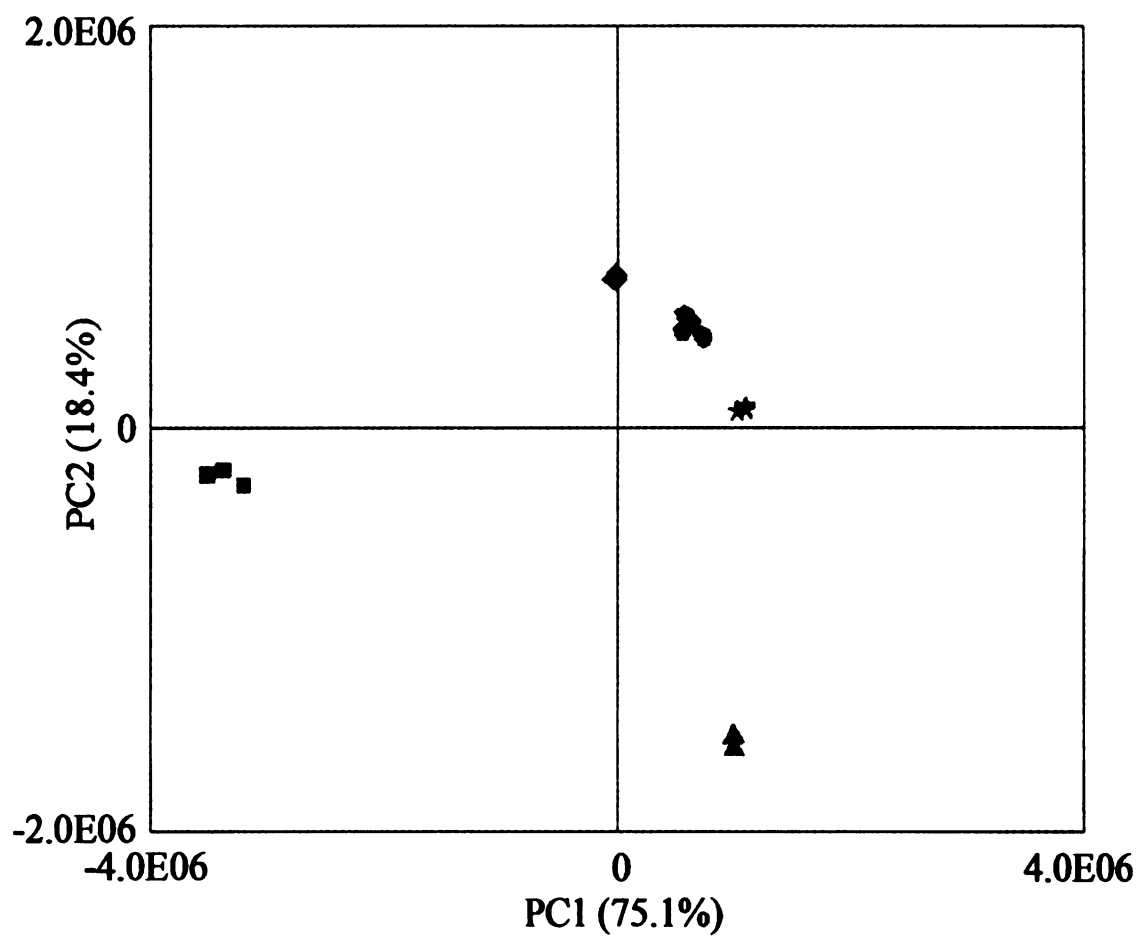


Figure 4.5: Scores plot of PC1 vs. PC2 based on the TIC for the burned carpet and the mixed liquid standards. Liquids were indicated by symbol. Burned Carpet (■), Neat Gasoline: Neat Kerosene Mixture (●), Neat Gasoline: 10% Evaporated Kerosene Mixture (★), Neat Gasoline: 50% Evaporated Kerosene Mixture (▲), 10% Evaporated Gasoline: Neat Kerosene Mixture (◆), and 50% Evaporated Gasoline: Neat Kerosene (◆).

Table 4.3: PPMC coefficients for replicates (n=3) for the mixed liquid standards and burned carpet based on the TIC.

Standards	Mean PPMC Coefficient ± Standard Deviation for Replicates
Neat Gasoline: Neat Kerosene	0.9969 ± 0.0022
Neat Gasoline: 10% Evaporated Kerosene	0.9972 ± 0.0022
Neat Gasoline: 50% Evaporated Kerosene	0.9994 ± 0.0003
10% Evaporated Kerosene: Neat Kerosene	0.9916 ± 0.0020
50% Evaporated Gasoline: Neat Kerosene	0.9944 ± 0.0025
Burned Carpet	0.9321 ± 0.0480

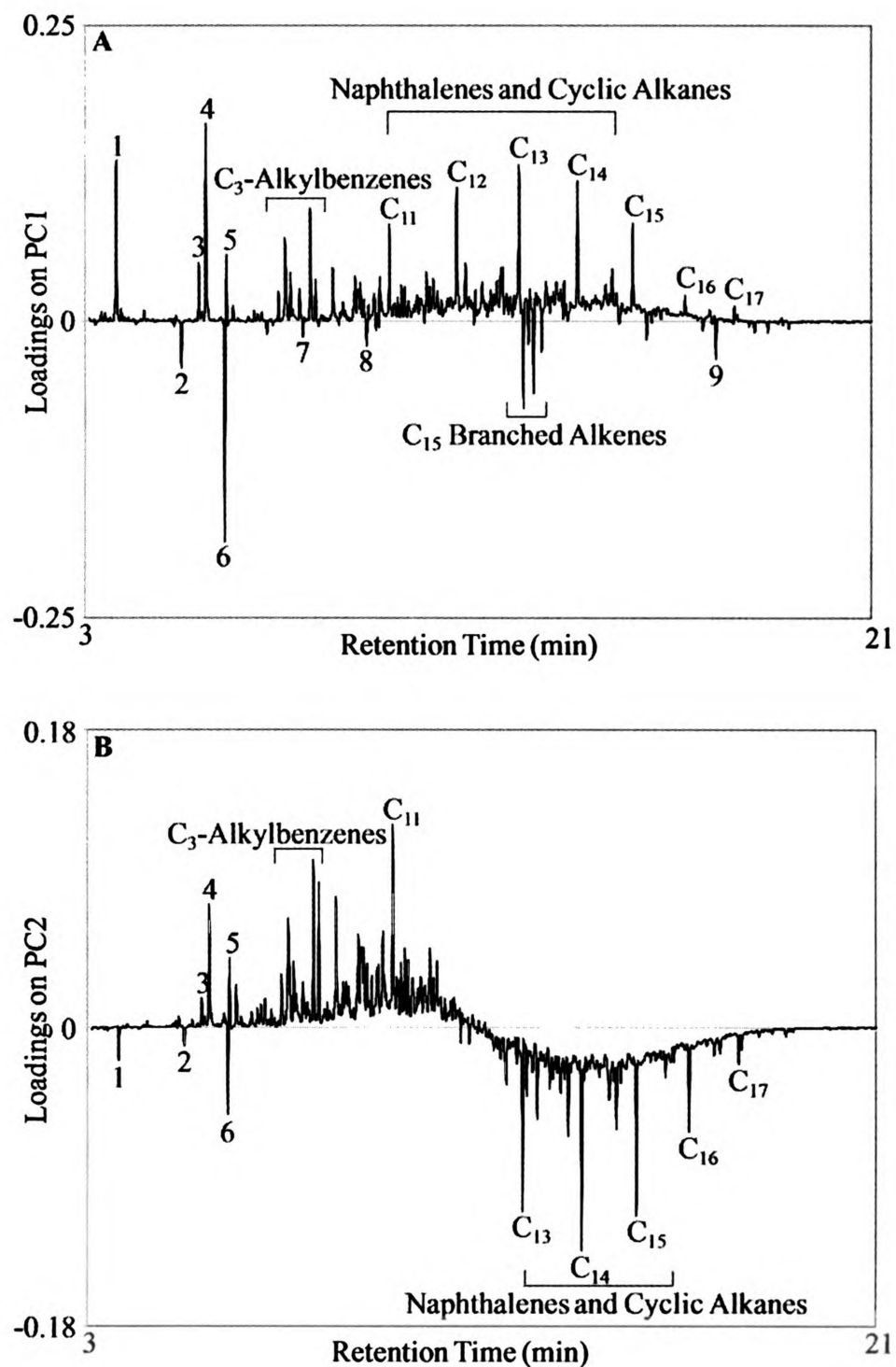


Figure 4.6: Loadings plots of (A) PC1 and (B) PC2 based on the TIC for burned carpet ad mixed liquid standards. Major components were labeled: 1) toluene, 2) 2,4-dimethyl-1-heptene 3) ethylbenzene, 4) *o*-xylene, 5) *p*-xylene, 6) styrene, 7) *α*-methylstyrene, 8) acetophenone, 9) 1,3-diphenylpropane.

The negative positioning of the burned carpet on PC1 is due to 2,4-dimethyl-1-heptene, styrene, benzaldehyde, acetophenone, and 1,3-diphenylpropane, which load negatively. The negative positioning of the burned carpet on PC2 is due to 2,4-dimethyl-1-heptene and styrene, which load negatively. The mixed liquids are positioned positively on PC1 due to toluene, the C₂- and C₃-alkylbenzenes, naphthalenes and C₁₁-C₁₇ normal alkanes. On PC2, the neat gasoline: 50% evaporated kerosene mixture is positioned negatively while the other mixed liquids are positioned positively. The neat gasoline: 50% evaporated kerosene mixture is positioned negatively due to the negative loading of the C₁₃-C₁₇ normal alkanes and naphthalenes, which are higher in abundance in this liquid. The other mixed liquids are positioned positively on PC2 due to the positively loading C₂- and C₃-alkylbenzenes, which are at a higher abundance in these mixed liquids.

When the burned then spiked samples are projected onto the scores plot, they are positioned negatively on PC1 between the burned carpet and the mixed liquid standards (Figure 4.7). The replicates of the burned then spiked samples are spread due to the irreproducibility of the burning process. For replicates of a sample, the PPMC coefficients are ideally expected to be 1.0000. Low correlation coefficients among replicates are observed for all of the burned then spiked samples, especially with the burned carpet spiked with 50% evaporated gasoline: neat kerosene mixture (0.8713 ± 0.1000) (Appendix F, Table F.2). Although a strong correlation is observed, the correlation coefficients are lower than expected for replicates of a sample.

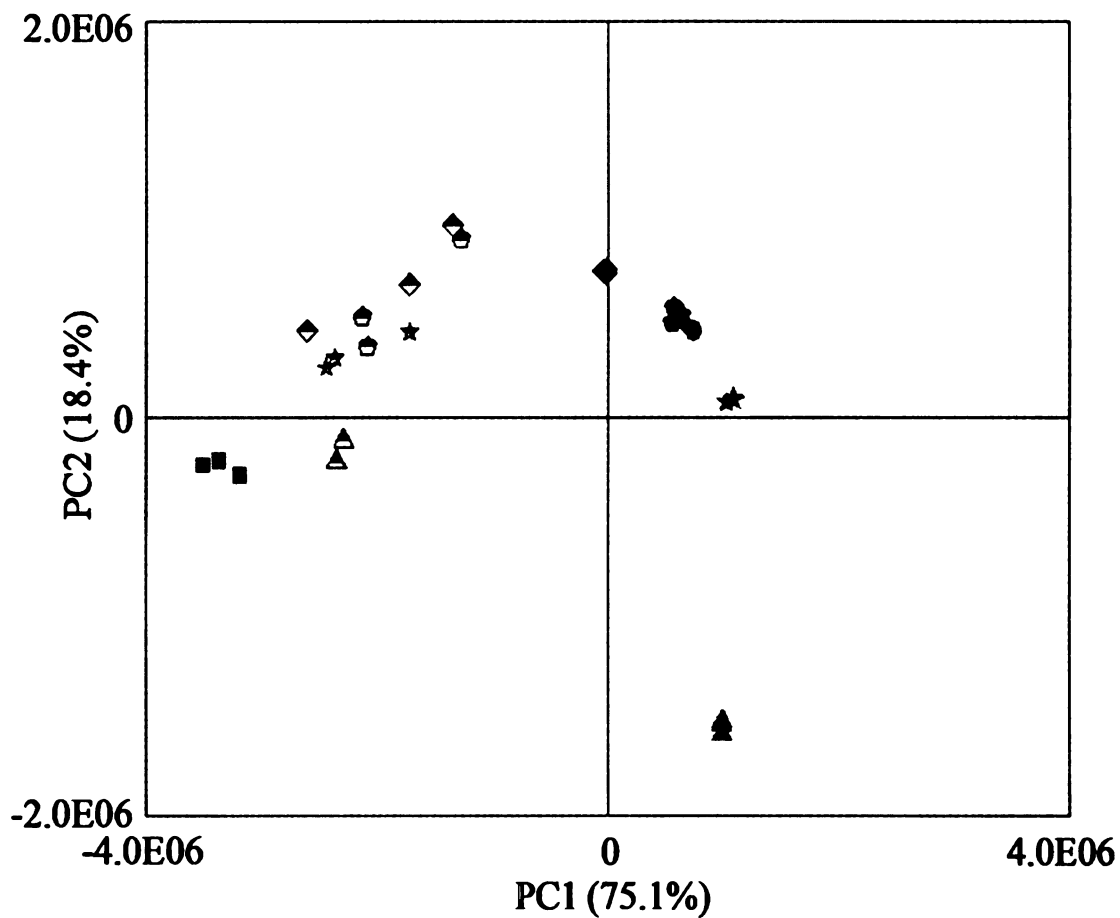


Figure 4.7: Scores plot of PC1 vs. PC2 based on the TIC for the burned carpet and mixed liquid standards. Liquids were indicated by symbol. Burned Carpet (■), Neat Gasoline: Neat Kerosene Mixture (●), Neat Gasoline: 10% Evaporated Kerosene Mixture (★), Neat Gasoline: 50% Evaporated Kerosene Mixture (▲), 10% Evaporated Gasoline: Neat Kerosene Mixture (◆), and 50% Evaporated Gasoline: Neat Kerosene (◆). The half fill indicates burned then spiked samples.

The burned carpet spiked with the neat gasoline: 50% evaporated kerosene mixture is positioned negatively on PC1 and slightly negatively on PC2 (Figure 4.7). When the positioning is visually compared to burned carpet and the corresponding mixed liquid standard, the burned then spiked sample is more closely positioned to the burned carpet on PC1 and PC2. When chromatograms of the burned carpet spiked with the neat gasoline: 50% evaporated kerosene mixture are assessed, the matrix interferences from the burned carpet are more abundant than the C₂- and C₃-alkylbenzenes and the C₁₃-C₁₇ normal alkanes from the mixed liquid. Because the matrix interferences present, such as 2,4-dimethyl-1-heptene, styrene, and acetophenone, are varying more than compounds from the mixed liquid, the burned then spiked sample is positioned negatively on PC1. Along with the matrix interferences, toluene and C₁₃-C₁₇ normal alkanes from the mixed liquid are loading negatively on PC2 and have positioned the liquid slightly negatively in the scores plot on that PC. Although the C₂- and C₃-alkylbenzenes are present in the liquid, they are less abundant than the matrix interferences and the C₁₃-C₁₇ normal alkanes, limiting their contribution to the positioning of the samples in the scores plot.

For PPMC coefficients, a moderate correlation is observed between the burned then spiked sample and the burned carpet (0.7515 ± 0.0478) (Table 4.4) (Appendix F, Tables F.3 to F.7). A moderate correlation is also observed between the burned then spiked sample and the corresponding mixed liquid standard (0.6462 ± 0.0162). Since moderate correlations are observed, the burned then spiked samples cannot be associated to the mixed liquids only using PPMC coefficients.

Table 4.4: PPMC coefficients between burned then spiked samples and corresponding mixed liquid standard (n=9) and burned then spiked samples and burned carpet (n=9) based on the TIC.

Burned then Spiked Samples	Mean PPMC Coefficient ± Standard Deviation Compared to Corresponding Mixed Liquid Standard	Mean PPMC Coefficient ± Standard Deviation Compared to Burned Carpet
Neat Gasoline: 10% Evaporated Kerosene	0.6869 ± 0.1228	0.7038 ± 0.1107
Neat Gasoline: 50% Evaporated Kerosene	0.6462 ± 0.0162	0.7515 ± 0.0478
10% Evaporated Gasoline: Neat Kerosene	0.7506 ± 0.0985	0.6532 ± 0.1381
50% Evaporated Gasoline: Neat Kerosene	0.7879 ± 0.1509	0.5520 ± 0.1827

When each burned then spiked sample is compared to the burned carpet and the corresponding mixed liquid standard using PPMC coefficients, moderate correlations are observed (Table 4.4). With HCA, the burned then spiked samples showed a higher similarity to the burned carpet (0.450) than their corresponding mixed liquid standards (Figure 4.8).

Through all of these data analysis procedures, the burned then spiked samples are differentiated from the burned carpet and the corresponding mixed liquid standard. As observed in the PCA scores plot, the burned then spiked samples are positioned between the burned carpet and the mixed liquid standards. The moderate PPMC coefficients indicate that the burned then spiked samples cannot be associated to either the burned carpet or the corresponding mixed liquid standard. Although the HCA dendrogram gives a higher similarity of the burned then spiked samples to the burned carpet than to the corresponding mixed liquid standard, the similarity observed does not confirm that the burned then spiked samples are positioned more closely to the burned carpet.

4.3.4 Association and Discrimination of Simulated ILR samples in the Presence of Matrix Interferences, Evaporation, and Combustion

The simulated ILR samples were used to assess the effects of matrix interferences and evaporative loss, as well as combustion due to burning. In order to assess the association and discrimination of the simulated ILR samples to the burned carpet and the mixed liquid standards, the simulated ILR samples were projected onto the scores plot (Figure 4.9).

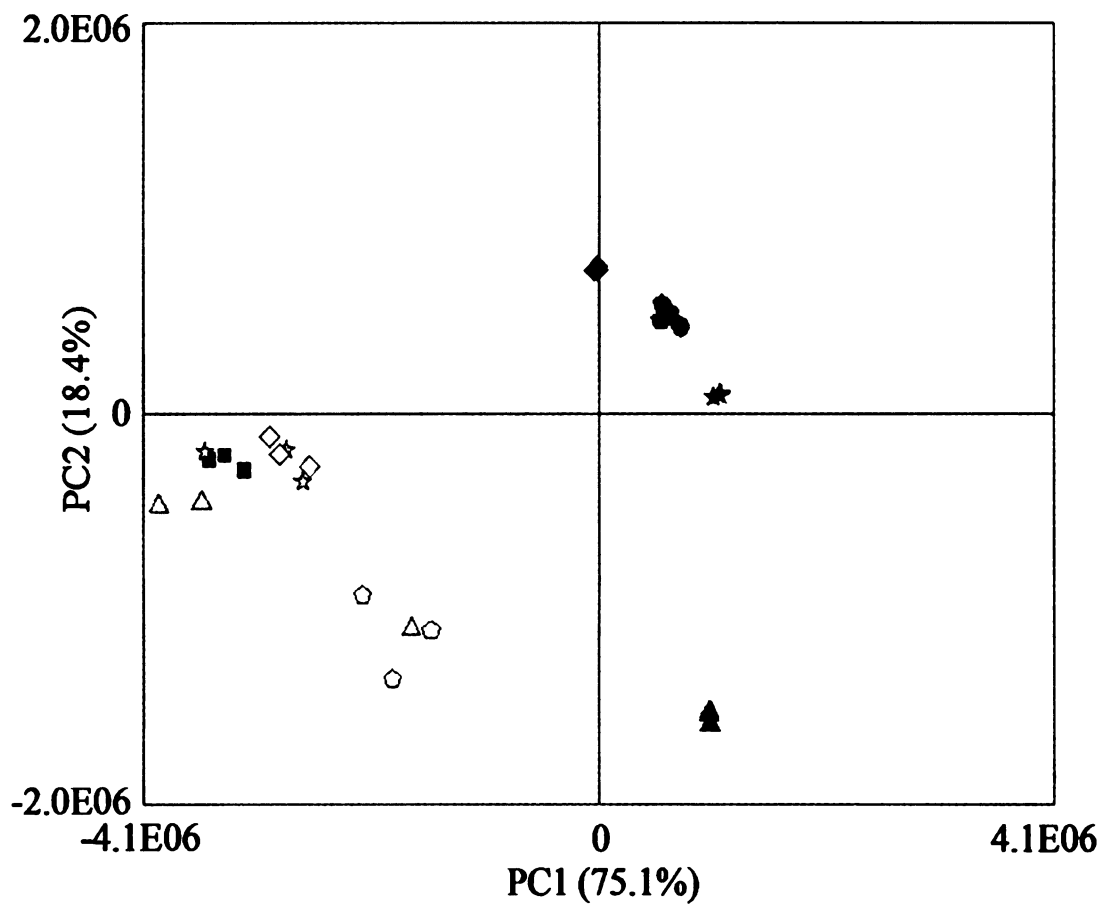


Figure 4.9: Scores plot of PC1 vs. PC2 based on the TIC for the burned carpet and the mixed liquid standards. Liquids were indicated by symbol. Burned Carpet (■), Neat Gasoline: Neat Kerosene Mixture(●), Neat Gasoline: 10% Evaporated Kerosene Mixture (★), Neat Gasoline: 50% Evaporated Kerosene Mixture (▲), 10% Evaporated Gasoline: Neat Kerosene Mixture (◆), and 50% Evaporated Gasoline: Neat Kerosene (◆). No fill indicates simulated ILR samples.

The simulated ILR samples, which are positioned negatively on both PC1 and PC2, are separated into two groups. One group containing most of the simulated ILR samples is positioned closely to the burned carpet. The other group, which contains the rest of the simulated ILR samples, is positioned between the burned carpet and the neat gasoline: 50% evaporated kerosene mixture. The spread observed among replicates is due to the irreproducibility of burning.

With replicates, PPMC coefficients of 1.0000 are ideally expected. Lower PPMC coefficients for replicates are observed for the simulated ILR samples, especially neat gasoline: 50% evaporated kerosene simulated ILR (0.6450 ± 0.2748) (Appendix G, Table G.1). Moderate to strong correlations of the simulated ILR samples are lower than expected for replicates.

The simulated ILR samples for 50% evaporated gasoline: neat kerosene mixture, neat gasoline: 10% evaporated kerosene mixture, and neat gasoline: 50% evaporated kerosene are associated with the burned carpet and differentiated from their corresponding mixed liquids in the scores plot. The other simulated ILR samples of 10% evaporated gasoline: neat kerosene mixture and one of the replicates of the neat gasoline: 50% evaporated kerosene mixture are differentiated from the burned carpet and the mixed liquid standards. Most of the compounds from mixed liquids have been lost due to burning, and matrix interferences are at a greater abundance.

All of the simulated ILR samples are negatively positioned on PC1 due to the matrix interferences from the burned carpet, such as 2,4-dimethyl-1-heptene and styrene. On PC2, the simulated ILR samples are separated due to the variability of burning. The simulated ILR samples of the 50% evaporated gasoline: neat kerosene mixture, neat

gasoline: 10% evaporated kerosene mixture, and neat gasoline: 50% evaporated kerosene are positioned slightly negatively on PC2. Their positioning is due to the matrix interferences from the burned carpet contributing to the positioning on that PC. The compounds from the mixed liquid are present in very low abundances and are not contributing the positioning of these simulated ILR samples. The simulated ILR samples of 10% evaporated gasoline: neat kerosene mixture and one replicate of the neat gasoline: 50% evaporated kerosene mixture are positioned negatively on PC2. Their negative positioning is due to the matrix interferences from the burned carpet along with the C₁₃-C₁₇ normal alkanes and the naphthalenes from the mixed liquids. All of these compounds are loading negatively on PC2.

When PPMC coefficients were calculated, a moderate to weak correlation was observed between the simulated ILR samples and the corresponding mixed liquid (Table 4.5) (Appendix G, G.2 to G.6). A moderate to strong correlation was observed between the simulated ILR samples and the burned carpet.

When the HCA dendrogram was assessed, the simulated ILR samples for the 50% evaporated gasoline: neat kerosene mixture, the neat gasoline: 10% evaporated kerosene mixture, and the neat gasoline: 50% evaporated kerosene liquids were grouped with the burned carpet at a similarity of 0.733 (Figure 4.10). The other simulated ILR samples are grouped with the burned carpet at a similarity of 0.503. All of the simulated ILR samples show a similarity of 0.000 to the corresponding mixed liquids.

Most simulated ILR samples are associated with the burned carpet and differentiated from the corresponding mixed liquid standard. This is confirmed in the PCA scores plot. The PPMC coefficients for the simulated ILR samples are moderate to

Table 4.5: PPMC coefficients between the simulated ILR sample and corresponding mixed liquid standard (n=9) and the simulated ILR sample and burned carpet (n=9) based on the TIC.

Simulated ILR Sample	Mean PPMC Coefficient ± Standard Deviation Compared to Corresponding Mixed Liquid Standard	Mean PPMC Coefficient ± Standard Deviation Compared to Burned Carpet
Neat Gasoline: 10% Evaporated Kerosene	0.3556 ± 0.1319	0.8485 ± 0.1107
Neat Gasoline: 50% Evaporated Kerosene	0.4068 ± 0.3016	0.7771 ± 0.2203
10% Evaporated Gasoline: Neat Kerosene	0.5365 ± 0.0588	0.7153 ± 0.0780
50% Evaporated Gasoline: Neat Kerosene	0.3502 ± 0.0496	0.8538 ± 0.0696

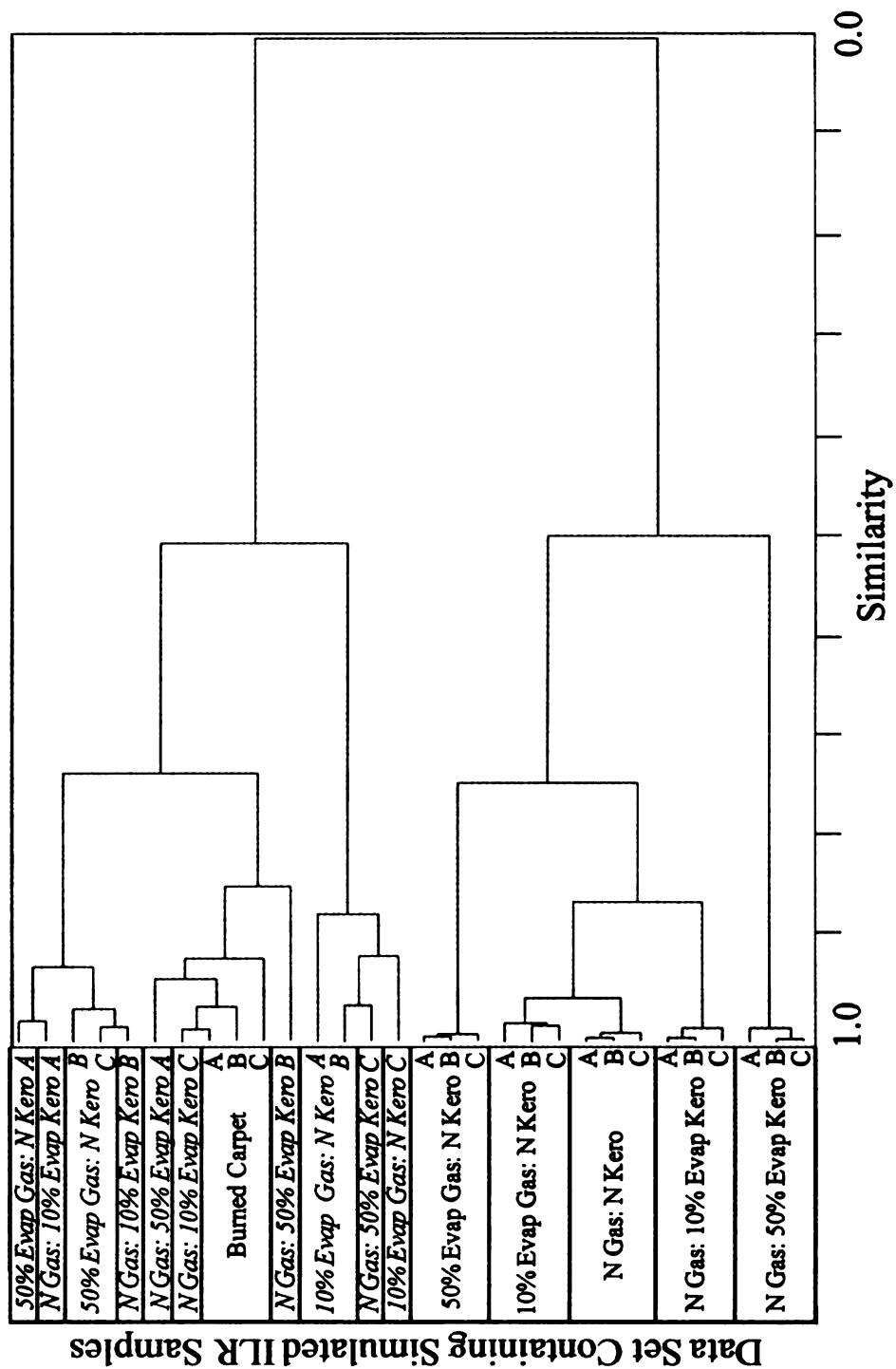


Figure 4.10: HCA Dendrogram of the scores of the data set containing the replicates (A, B, C) of the simulated ILR samples. The N is the neat part of the sample, and kero represents kerosene. The italicized labels indicate the simulated ILR samples.

strong when compared to the burned carpet, and weak correlations are observed when compared to the corresponding mixed liquid standard. With HCA, the simulated ILR samples are grouped with the burned carpet.

4.4 Conclusions

The burned then spiked samples were differentiated from both the burned carpet and the corresponding mixed liquids in the PCA scores plot. The PPMC coefficients indicated a moderate correlation between these samples and both the burned carpet and the corresponding mixed liquid. With HCA, the burned then spiked samples were more similar to the burned carpet than the mixed liquids, but the low similarity for the burned then spiked samples and the burned carpet cannot link these two groups.

The simulated ILR samples were more closely associated to the burned carpet than the corresponding mixed liquid. In the PCA scores plot, most of the simulated ILR samples were positioned closely to the burned carpet while the other simulated ILR samples were between the burned carpet and the mixed liquids. The PPMC coefficients showed moderate to strong correlations between the simulated ILR samples and the burned carpet and moderate to weak correlations between the simulated ILR samples and the corresponding mixed liquids. The HCA dendrogram grouped the simulated ILR samples with the burned carpet and showed no similarity to the mixed liquids. Thus, the simulated ILR samples are more correlated to the burned carpet than the corresponding mixed liquid.

Through PCA, PPMC coefficients, and HCA, the burned then spiked samples and the simulated ILR samples were not able to be associated with the corresponding mixed liquid. Furthermore, spread was observed between the replicates of the burned then spiked samples and the simulated ILR samples. Using these three chemometric procedures, the mixed ignitable liquid present in the samples was not able to be fully identified.

As a preliminary study on the identification of mixed ignitable liquids in the presence of matrix interferences, evaporation and combustion, only a small number of ignitable liquid mixtures at two evaporation levels was used. In future work, a larger data set of mixed ignitable liquids would be investigated. Also, other chemometric procedures along with extracted ion profiles of the total ion chromatograms used in this study could also be investigated to associate the mixed liquid samples to the corresponding mixed liquid standard.

4.5 References

1. Almirall JR, Furton KG. Characterization of background and pyrolysis products that may interfere with forensic analysis of fire debris. *J Anal Appl Pyrol* 2004; 71:51-67.
2. Stauffer E. Concept of pyrolysis for fire debris analysts. *Sci Justice* 2003; 43:29-40.

CHAPTER 5

Conclusions and Future Work

In this research, two major studies were undertaken in order to apply statistical and chemometric procedures to objectively identify the ignitable liquids despite evaporation, thermal degradation, and matrix interferences. The first study investigated the association of evaporated ignitable liquids to the corresponding neat liquid. In the second study, the association of mixed liquid samples to the corresponding mixed liquid standard was investigated in the presence of matrix interferences, evaporation, and thermal degradation.

5.1 Association of Evaporated Ignitable Liquids to Their Neat Counterparts Using Chemometric Procedures

The goal of this study was to associate the evaporated ignitable liquids to the corresponding neat liquid using statistical and chemometric procedures. With evaporation, early eluting compounds are lost from the liquids thus increasing the difficulty in identifying the ignitable liquid through visual assessment of chromatograms. Through principal components analysis (PCA), Pearson product moment correlation (PPMC) coefficients, and hierarchical cluster analysis (HCA), the association of the evaporated liquids to the corresponding neat liquid was assessed.

In this study, six ignitable liquids from different American Society for Testing and Materials (ASTM) classes were selected and evaporated. Each evaporated liquid, along with the corresponding neat liquid, was extracted using a passive headspace

procedure which is used in forensic laboratories, and analyzed by gas chromatography-mass spectrometry (GC-MS). The resulting chromatograms were subjected to data pretreatment procedures to reduce the non-chemical sources of variance introduced during analysis. The Savitzky-Golay algorithm was used to smooth the chromatograms. Retention time alignment of the chromatograms was optimized using the peak matching algorithm and the correlation optimized warping (COW) algorithm. A combination of maximum peak normalization followed by total area normalization of the replicates was then applied to the chromatograms.

Following data pretreatment, the chromatograms were subjected to the three data analysis procedures: PCA, PPMC coefficients, and HCA. Principal components analysis was used to discriminate the ignitable liquids, while associating the evaporated ignitable liquids to the corresponding neat liquid. Using PPMC coefficients, the precision of the extraction and analysis procedure was assessed. Furthermore, the correlation of the evaporated ignitable liquids to the corresponding neat liquid was assessed. With HCA, a statistical measure of the similarity among the scores of the evaporated liquid to the corresponding neat liquid in the PCA scores plot.

In this study, retention time alignment was investigated using the peak matching algorithm and the correlation optimized warping (COW) algorithm. Visual assessment of chromatograms along with PPMC coefficients was used in order to determine the best alignment. Using the peak matching algorithm, a window size of three showed the fewest misalignments. For the COW algorithm, the window size and segment size of 3 and 65 respectively were determined to contain the least misalignments. Of these two algorithms, the COW algorithm was determined to be the optimal alignment for the

chromatograms.

To reduce variation in abundance among chromatograms, two normalization procedures were used. The data set was first normalized using a maximum peak normalization followed by a total area normalization of the replicates. After the first normalization, some spread among replicates was still observed, and the second normalization was used to further minimize these differences.

Using the combination of these chemometric procedures, the evaporated ignitable liquids were able to be associated to the corresponding neat liquid. With PCA, the evaporated ignitable liquids were associated to the corresponding neat liquid in the scores plot with the exceptions of gasoline and lacquer thinner. While PC1 and PC2 only accounted for a certain percentage of the variance in the data set, PPMC coefficients assessed the correlation between each data point in a pair of chromatograms. Through PPMC coefficients, the evaporated ignitable liquids were observed to have a strong correlation to the corresponding neat ignitable liquids. Also, both neat and evaporated gasolines and lacquer thinners were able to be differentiated from one another with PPMC coefficients. From HCA, the evaporated liquids were grouped with the corresponding neat liquid. However, the neat and evaporated gasolines and lacquer thinners were not able to be differentiated from each other using HCA. The close positioning in the PCA scores plot and the high similarity in HCA is due to both liquids containing a dominant toluene peak.

This study has shown that chemometric procedures can be used to aid a fire debris analyst in identifying an ignitable liquid despite evaporation. With the combination of PCA, PPMC coefficients, and HCA, the evaporated liquids would most likely be

associated to the corresponding neat ignitable liquid even though some of the compounds have been lost due to evaporation. In this research, gasoline and lacquer thinner were not able to be distinguished using PCA and HCA. In order to implement this procedure in a forensic laboratory, more research is required on the association and discrimination of ignitable liquids using chemometric procedures.

5.2 Effect of Matrix Interferences, Thermal Degradation, and Evaporation on the Identification of Mixed Ignitable Liquids in Fire Debris using Chemometric Procedures

The goal of this study was to associate mixed ignitable liquid samples to the corresponding mixed ignitable liquid standard despite matrix interferences, thermal degradation and evaporative loss. In order to do so, an objective method using statistical and chemometric procedures was applied to the resulting chromatograms.

In this study, neat and evaporated gasoline and kerosene were combined in different combinations to form the mixed liquid standards. The mixed liquids were spiked onto burned carpet (burned then spiked samples) and spiked onto unburned carpet and burned to simulate an ILR. Carpet with no mixed liquid was also burned in order to assess matrix interferences.

All samples and standards were extracted using a passive headspace procedure and analyzed by GC-MS. The resulting chromatograms were separated into two data sets where one data set contained the burned then spiked samples and the other data set contained the simulated ILR samples. Each data set contained the burned carpet and the

mixed liquid standards. The data sets were separately smoothed, retention time aligned, and normalized. Then, PCA, PPMC coefficients, and HCA were applied to each data set.

Using chemometric procedures, the burned then spiked samples were not able to be associated to the corresponding mixed liquid standards. In the PCA scores plot, the burned then spiked samples were differentiated from both the burned carpet and the mixed liquid standards. Moderate correlation coefficients were observed when the burned then spiked samples were compared to the burned carpet and the corresponding mixed liquid standard. Within the HCA dendrogram, the burned then spiked samples were differentiated from both the burned carpet and the mixed liquid standards. Since the burned then spiked sample chromatograms contained both matrix interferences and compounds from the mixtures, the samples were differentiated from both the burned carpet and the mixed liquid standards.

The simulated ILR samples were not able to be associated to the corresponding mixed liquid standard. From PCA, most of the simulated ILR samples were positioned near the burned carpet, while the other simulated ILR samples were differentiated from the burned carpet and the mixed liquid standards. Moderate to strong correlations were observed between the simulated ILR samples and the burned carpet using PPMC coefficients. Also, moderate to weak correlation coefficients were observed between the simulated ILR samples and the corresponding mixed liquid standard. In the HCA dendrogram, all of the simulated ILR samples were grouped with the burned carpet and separated from the mixed liquid standards.

Through this study, the limitations of the application of these statistical and chemometric procedures to an arson case were visible. With evaporative loss, thermal

degradation, and matrix interferences, the mixed liquid samples were not associated to the corresponding mixed liquid standards. The matrix interferences present in the burned then spiked samples and the simulated ILR samples were more abundant than the mixed ignitable liquids, which led to the chemometric procedures not identifying the mixed ignitable liquid in the samples. This preliminary research has shown potential for the association and discrimination of ignitable liquids, but more work will be required in order to implement these procedures in a forensic laboratory.

5.3 Future Work

In order to further investigate the association of an ILR to the corresponding ignitable liquid using chemometric procedures, other studies must be done. At a suspected arson scene, other burned matrices besides carpet are present; a study should be pursued using other matrices. The matrix interferences from newspaper, wood, plastics, and other matrices should be investigated. Furthermore, both neat and evaporated ignitable liquids should be spiked onto each matrix and burned to simulate ILRs that would be present at an arson scene. Through the use of chemometric procedures, the association of the ignitable liquids to the neat ignitable liquid would be investigated.

The chemometric procedures in the mixed liquids study were unable to associate the mixed liquid samples to the corresponding standards. In future research, other chemometric procedures should be investigated in order to associate a sample with matrix interferences to the corresponding ignitable liquid standard. One of these chemometric procedures is the soft independent modeling of class analogy (SIMCA). With SIMCA, a

model in which to classify the samples is formed using the PCA results from the standards. The samples are then assigned to the standard that it best fits. Using SIMCA, the samples could be classified to the corresponding standards even in the presence of matrix interferences.

Further research of ignitable liquid mixtures should also be pursued. First, the data set of mixed ignitable liquids should be expanded to include more liquids from multiple ASTM classes. These mixtures should also be investigated in the presence of matrix interferences, thermal degradation, and evaporation in order to determine if a larger data set will increase association between the simulated ILR sample and the corresponding mixed liquid using chemometric procedures.

In order to implement these chemometric and statistical procedures in a forensic laboratory, more problems associated with the identification of an ignitable liquid in fire debris must be investigated. Presently, the objective method used is time consuming and difficult to implement. However, with future research, this proposed method will become more efficient at identifying the ignitable liquids present in an ILR and less time demanding. Only then will these chemometric procedures become a tool that will assist the fire debris analyst in his or her casework.

APPENDIX A

Total Ion Chromatograms of Neat Ignitable Liquids

In this appendix, representative total ion chromatograms (TIC) are shown for the neat ignitable liquids, lamp fuel, kerosene, marine fuel stabilizer, paint thinner, gasoline, and lacquer thinner. The experimental conditions are as described in Chapter 3, Section 3.2.3.

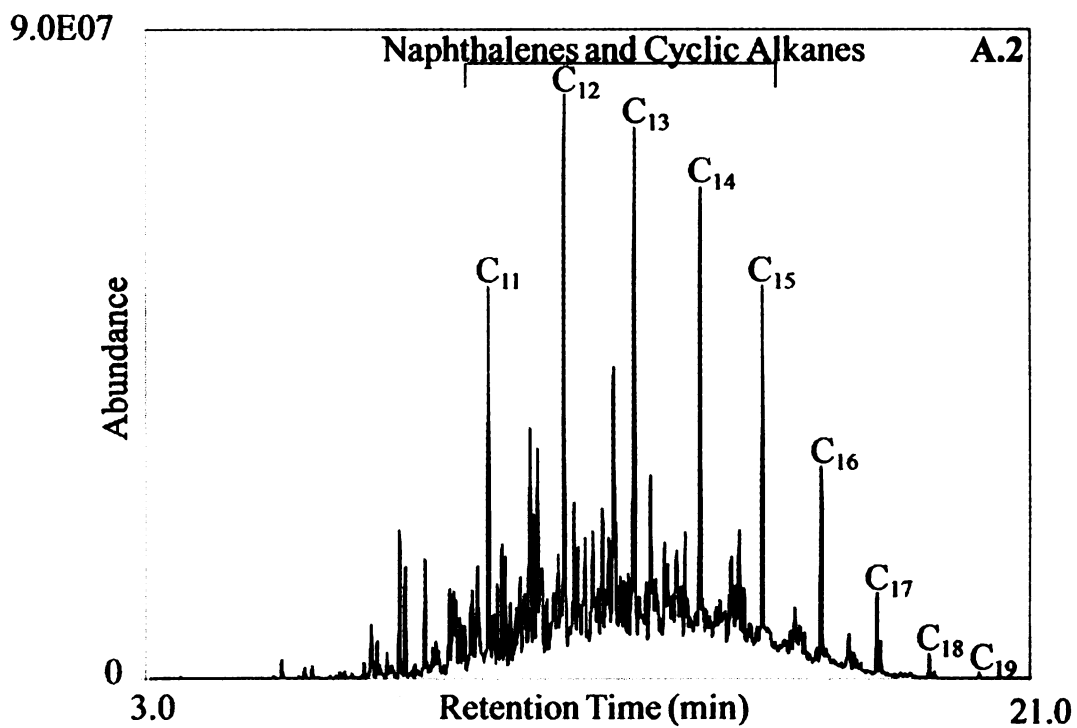
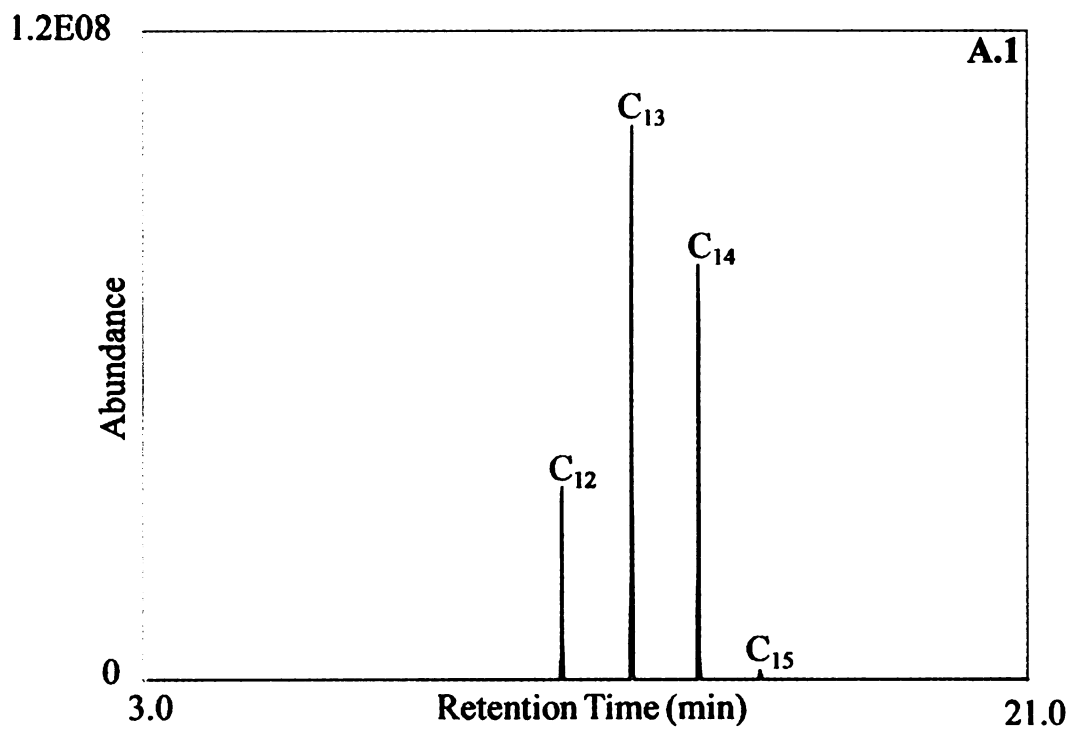


Figure A.1: Chromatogram of lamp fuel with major components labeled.
 Figure A.2: Chromatogram of kerosene with major components labeled.

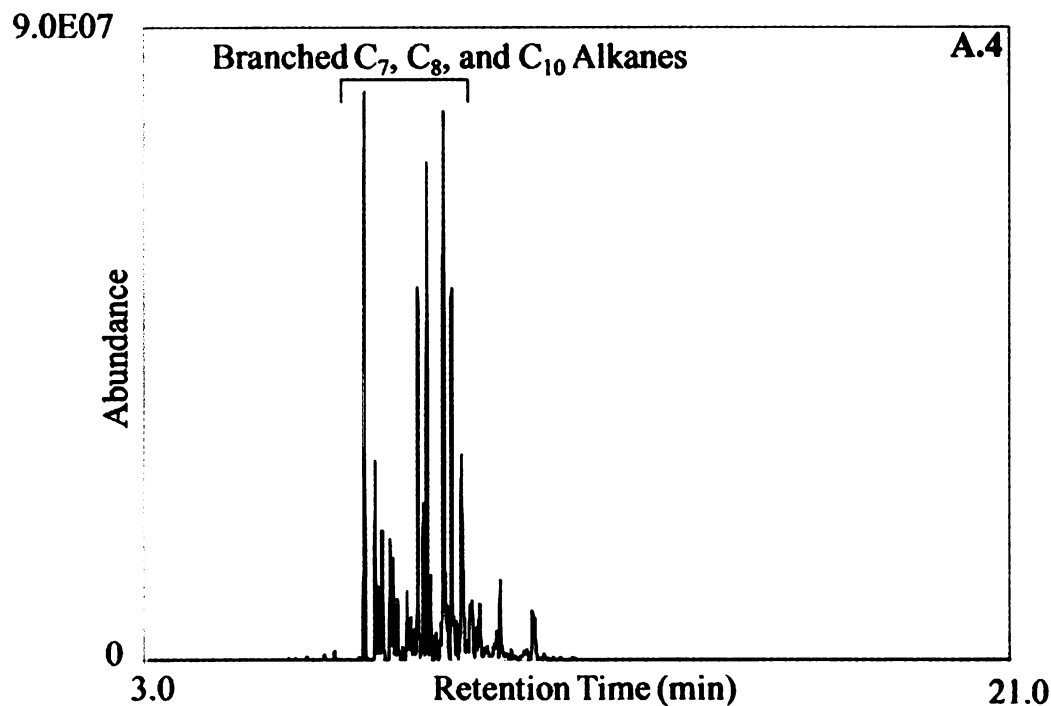
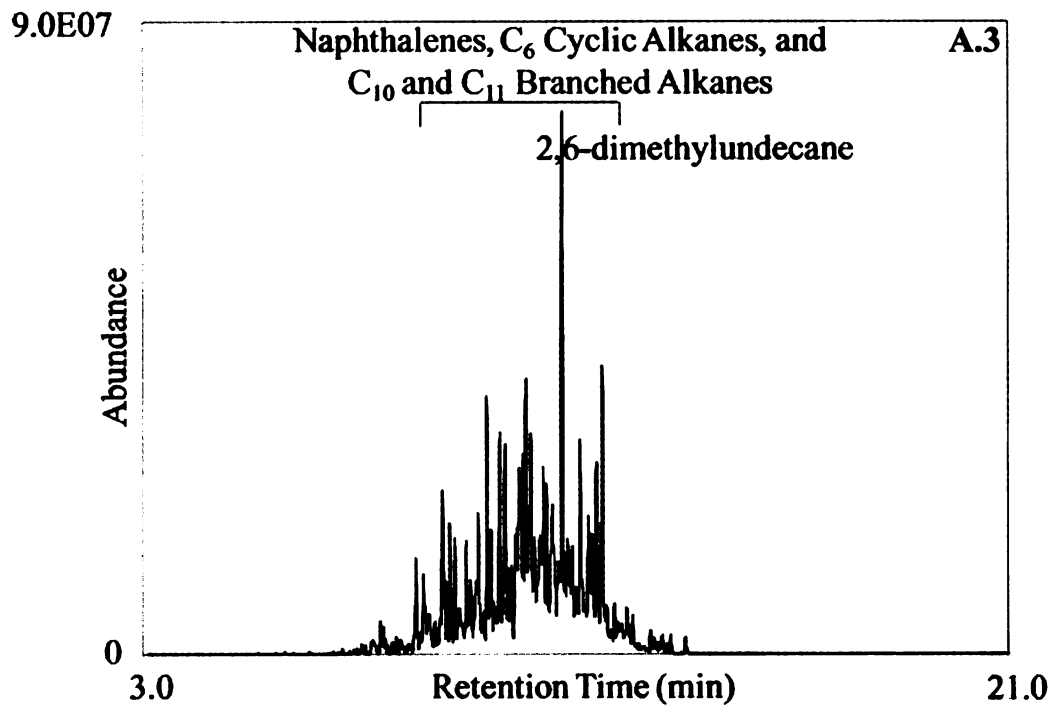


Figure A.3: Chromatogram of marine fuel stabilizer with major components labeled.
Figure A.4: Chromatogram of paint thinner with major components labeled.

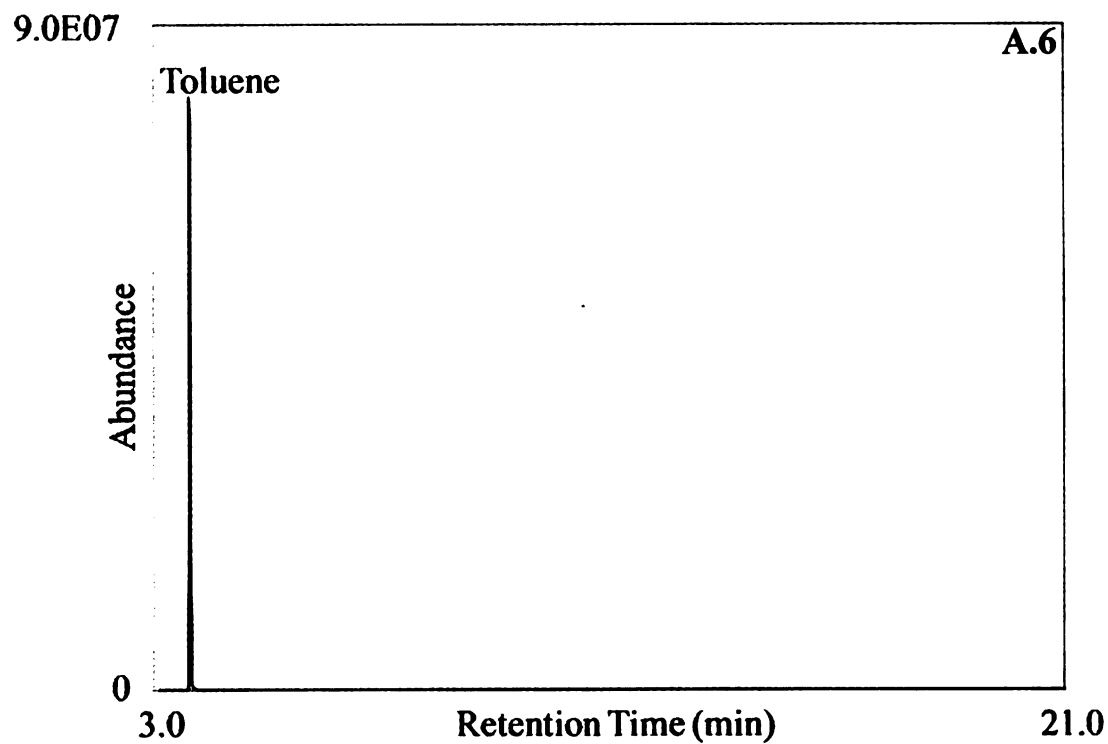
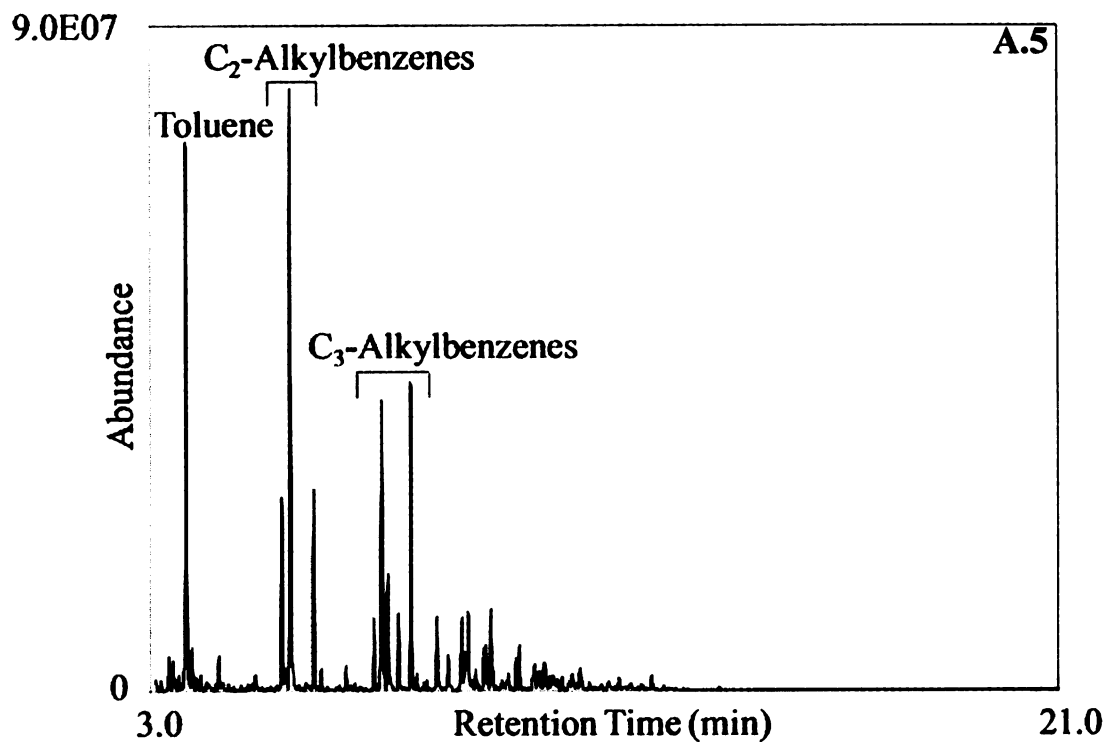


Figure A.5: Chromatogram of gasoline with major components labeled.
 Figure A.6: Chromatogram of lacquer thinner with major component labeled.

APPENDIX B
Total Ion Chromatograms of Evaporated Ignitable Liquids

In this appendix, representative total ion chromatograms (TIC) are shown for the evaporated ignitable liquids, lamp fuel, kerosene, marine fuel stabilizer, paint thinner, gasoline, and lacquer thinner, at each evaporation level (5%, 10% 20%, 50%). The experimental conditions are as described in Chapter 3, Section 3.2.3.

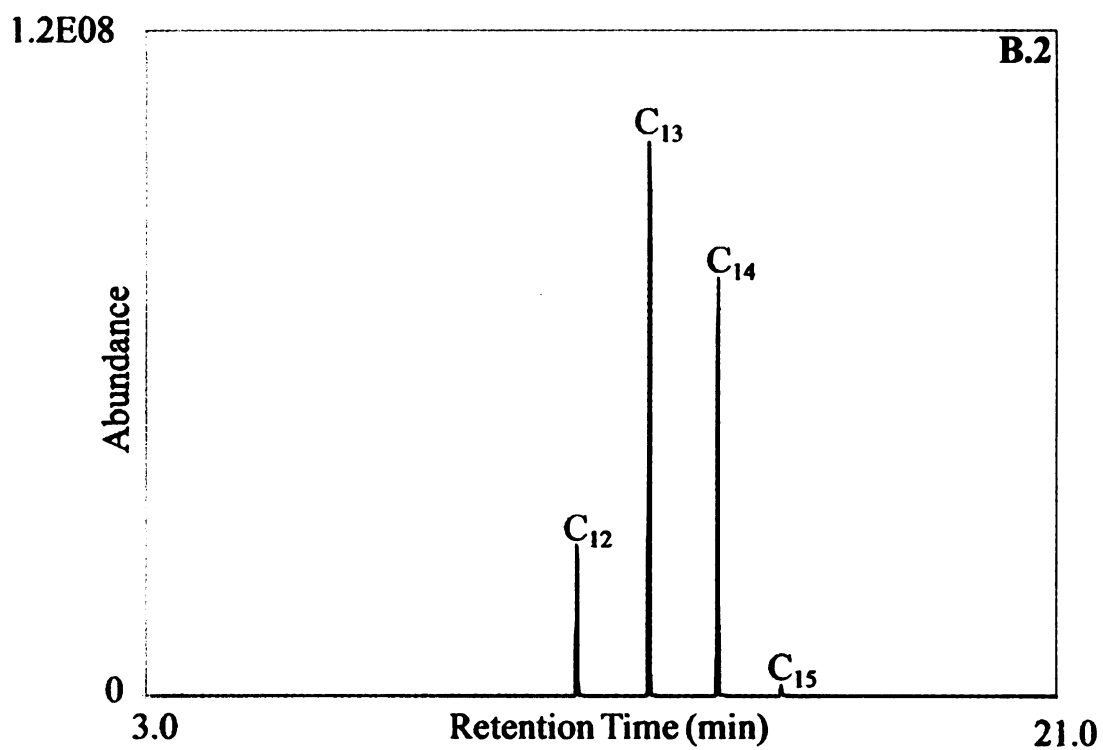
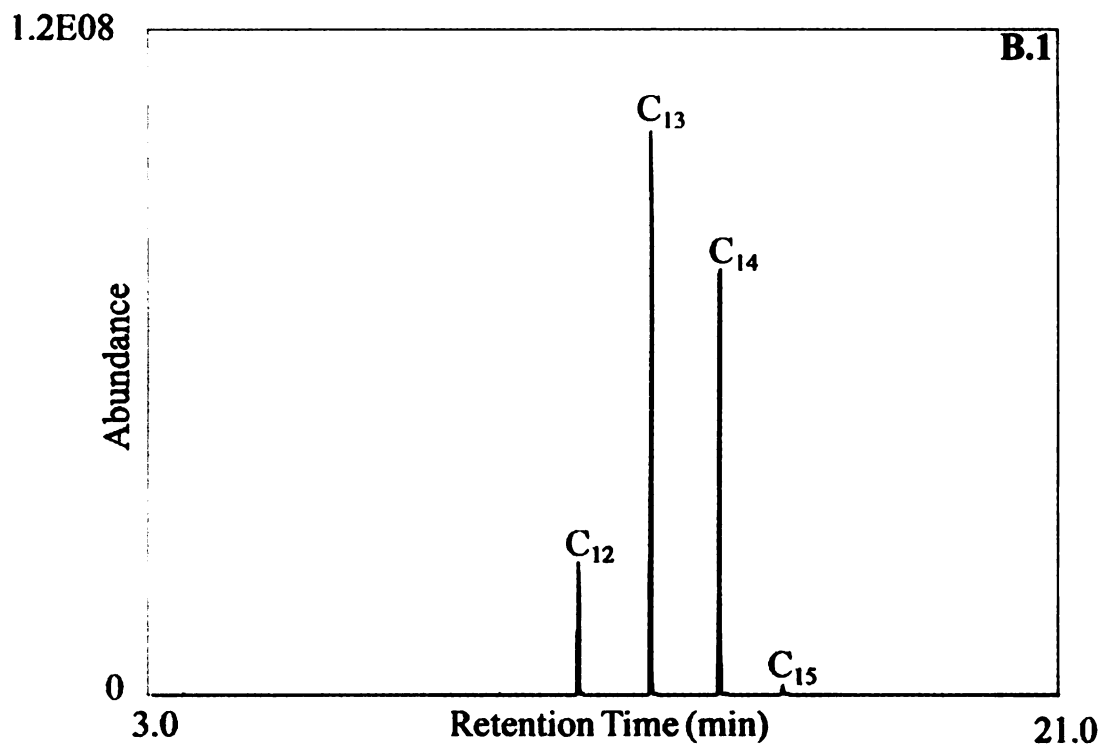


Figure B.1: Chromatogram of 5% evaporated lamp fuel with major components labeled.
Figure B.2: Chromatogram of 10% evaporated lamp fuel with major components labeled.

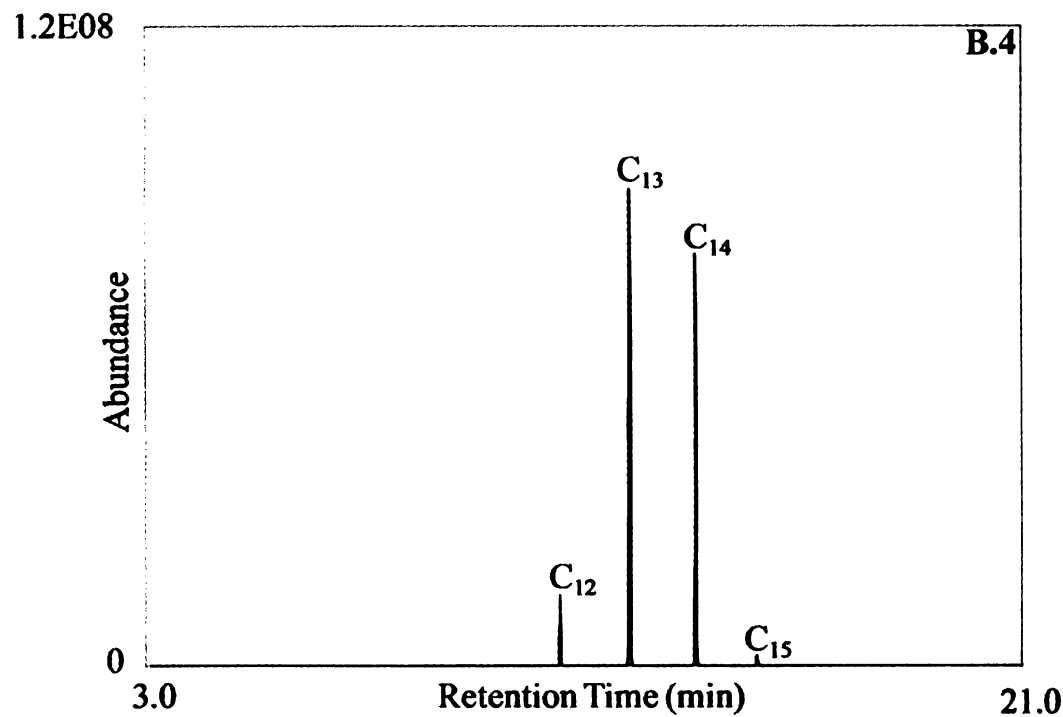
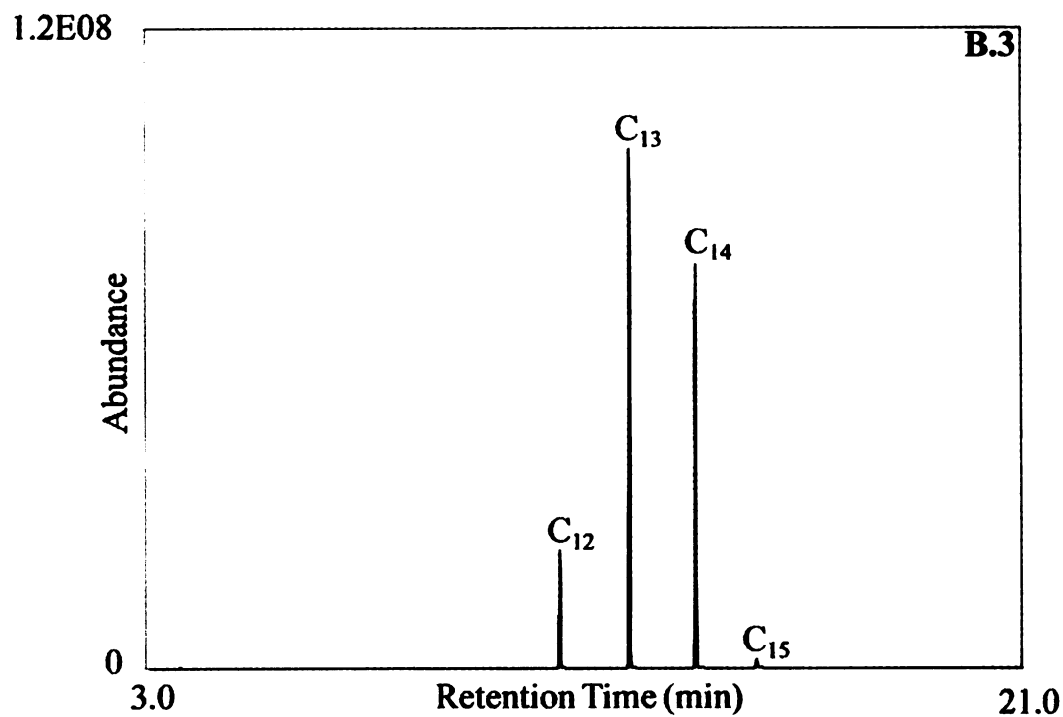


Figure B.3: Chromatogram of 20% evaporated lamp fuel with major components labeled.
Figure B.4: Chromatogram of 50% evaporated lamp fuel with major components labeled.

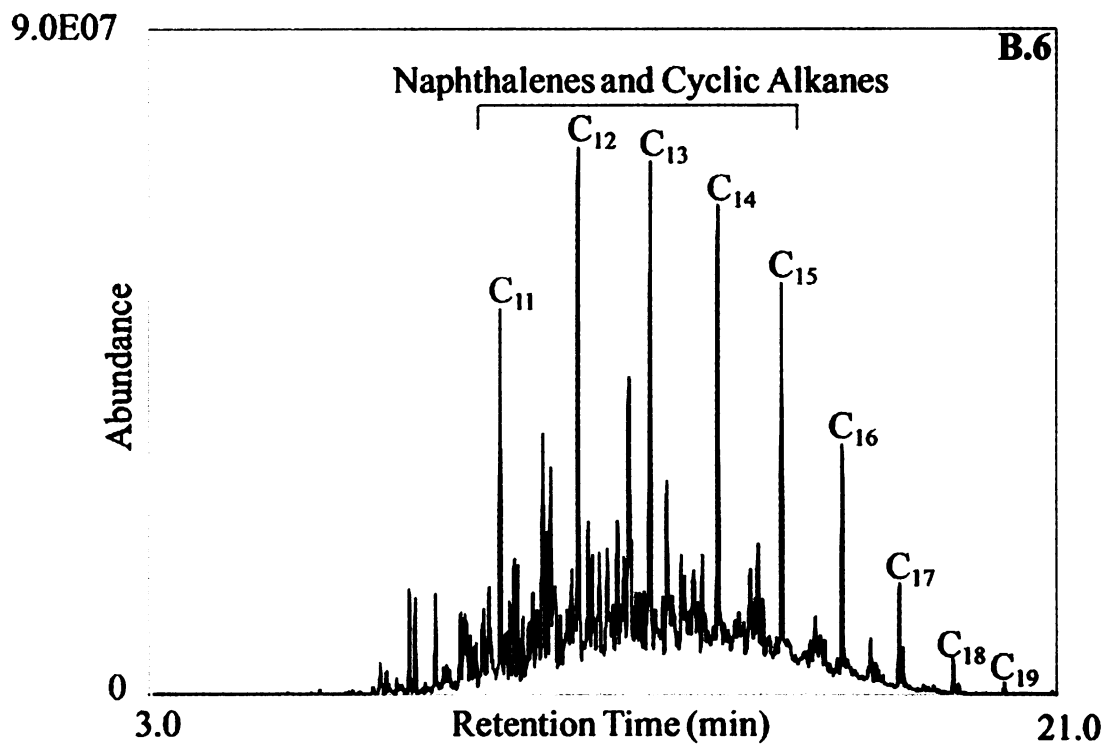
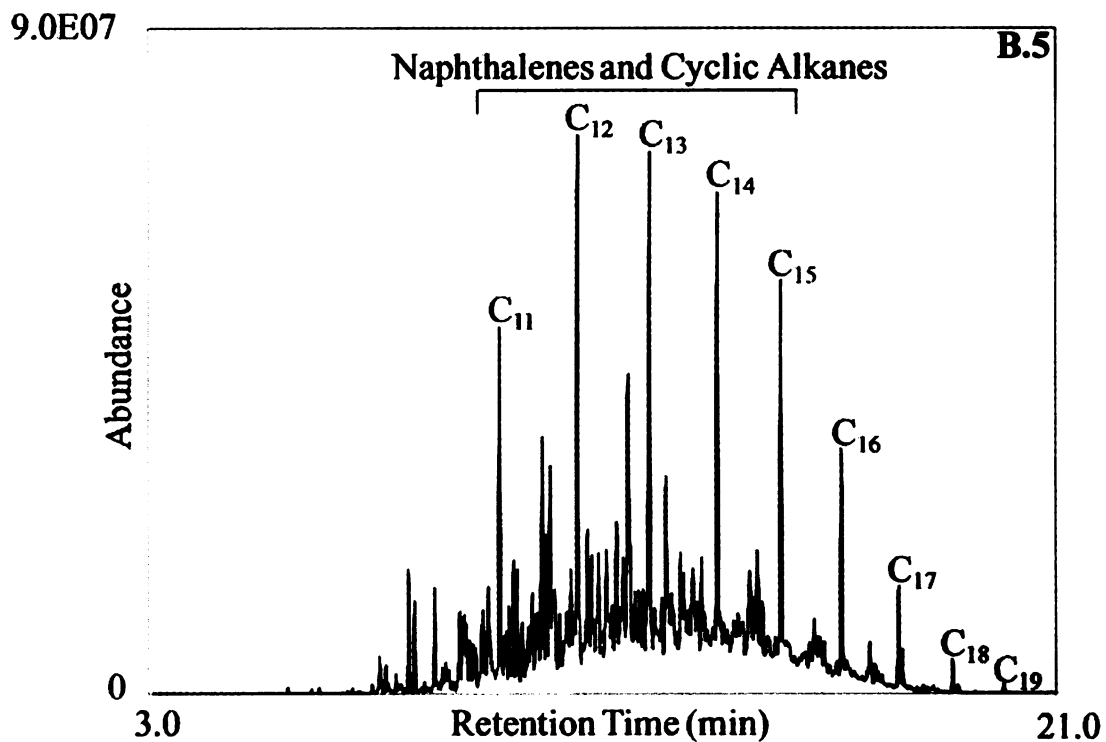


Figure B.5: Chromatogram of 5% evaporated kerosene with major components labeled.
 Figure B.6: Chromatogram of 10% evaporated kerosene with major components labeled.

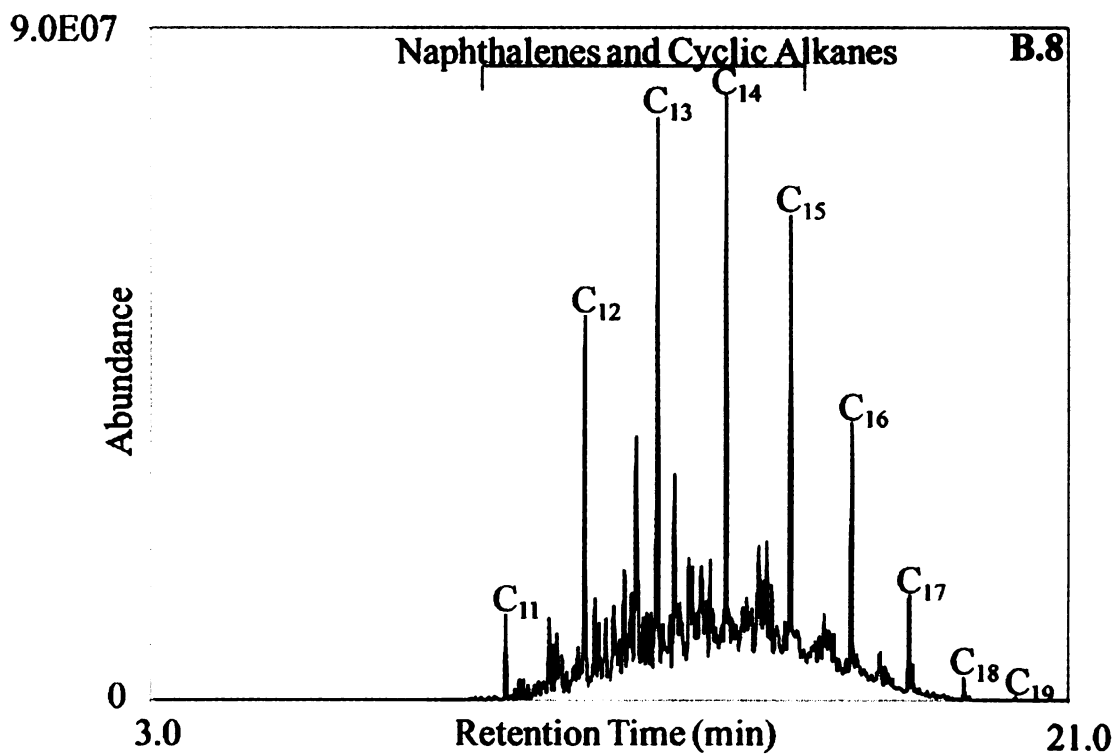
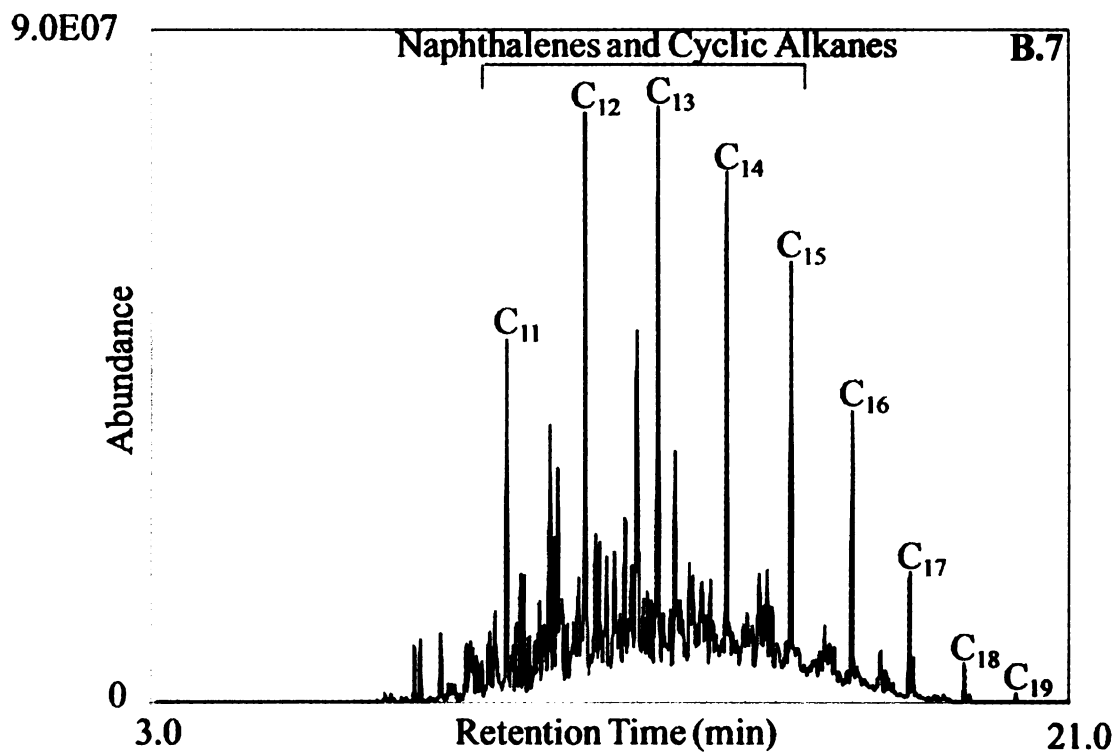


Figure B.7: Chromatogram of 20% evaporated kerosene with major components labeled.
 Figure B.8: Chromatogram of 50% evaporated kerosene with major components labeled.

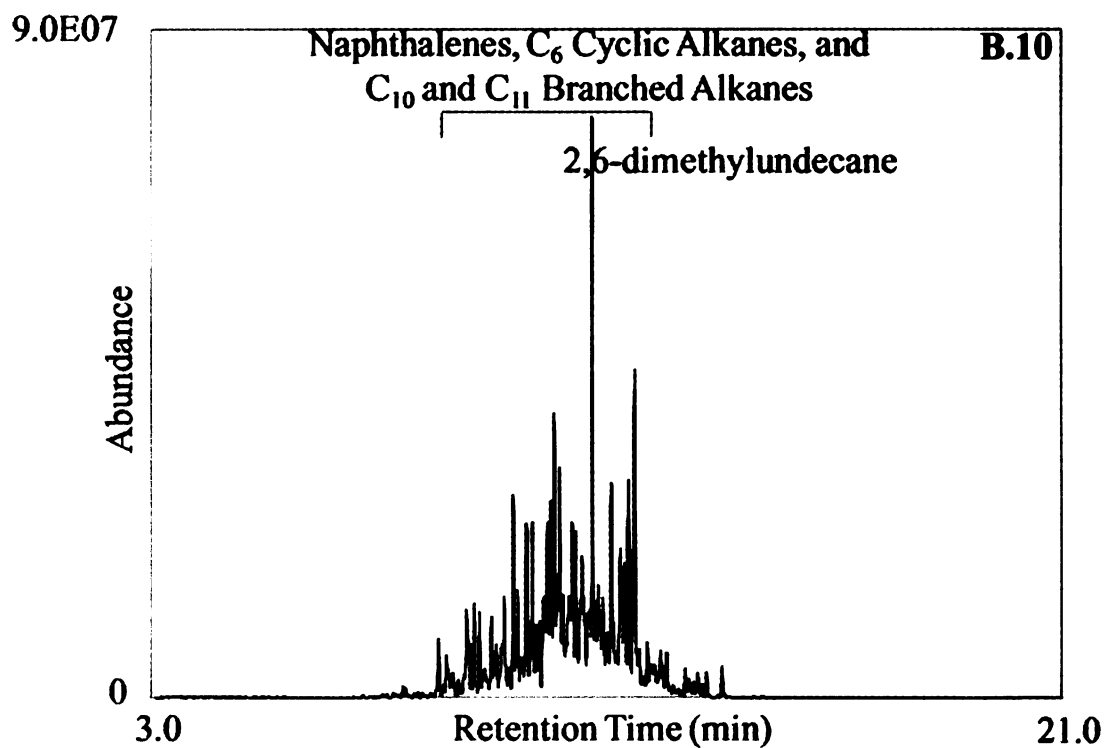
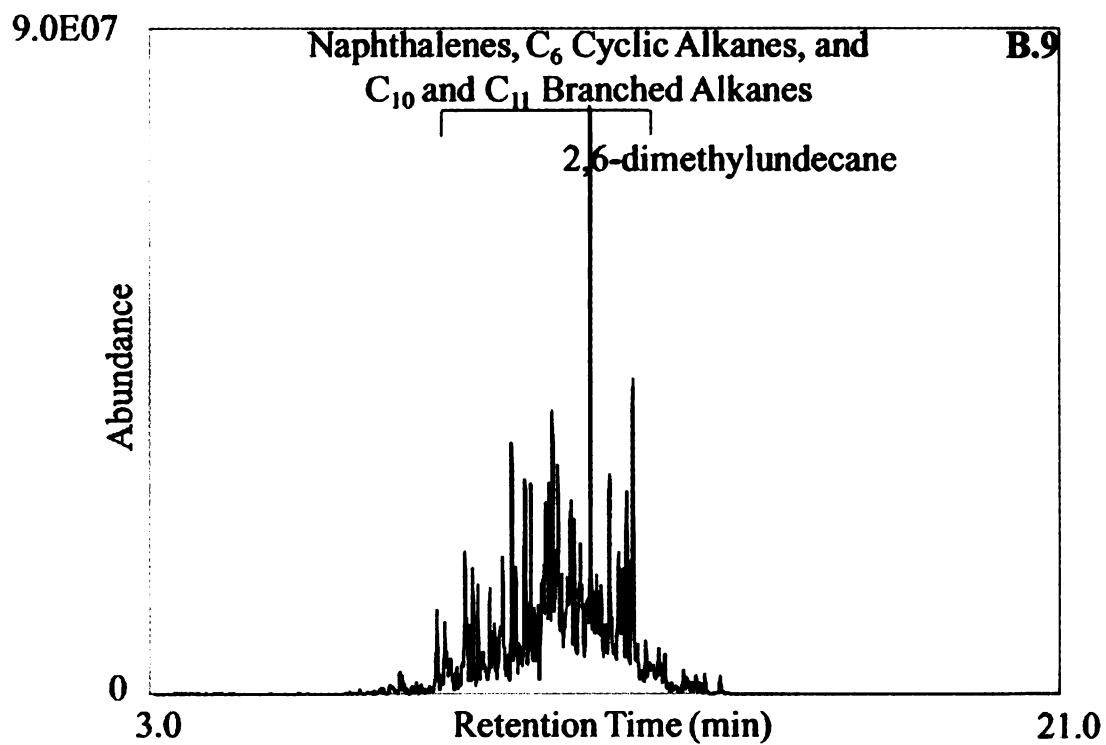


Figure B.9: Chromatogram of 5% evaporated marine fuel stabilizer with major components labeled.

Figure B.10: Chromatogram of 10% evaporated marine fuel stabilizer with major components labeled.

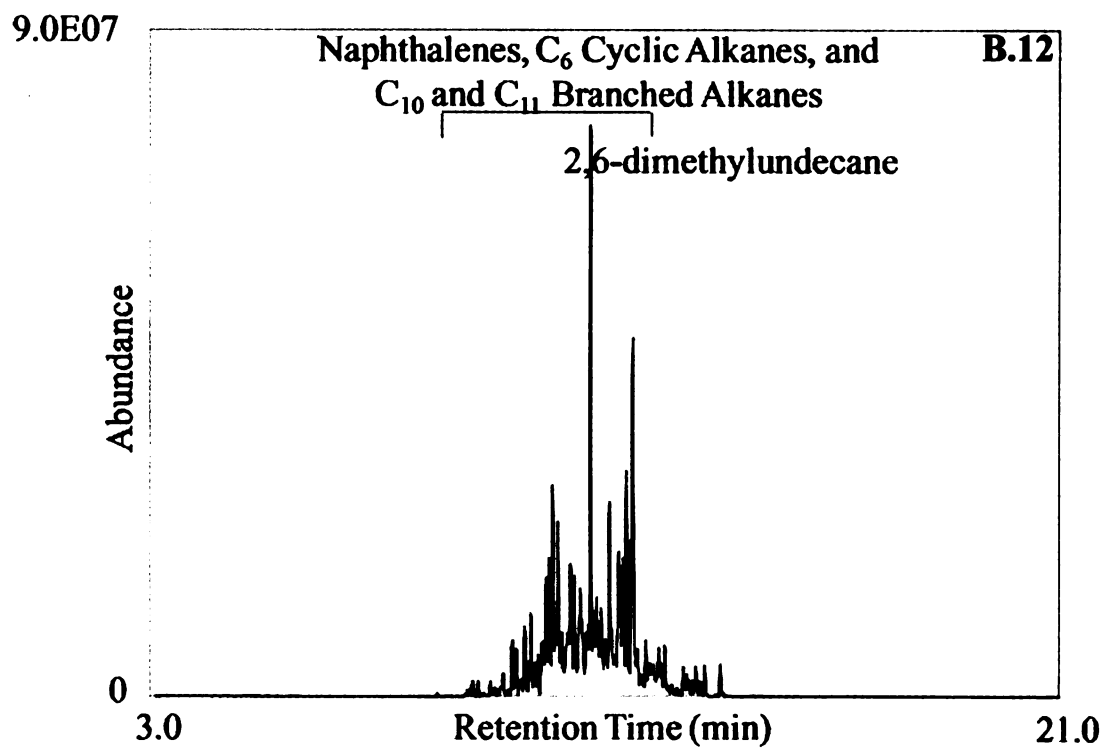
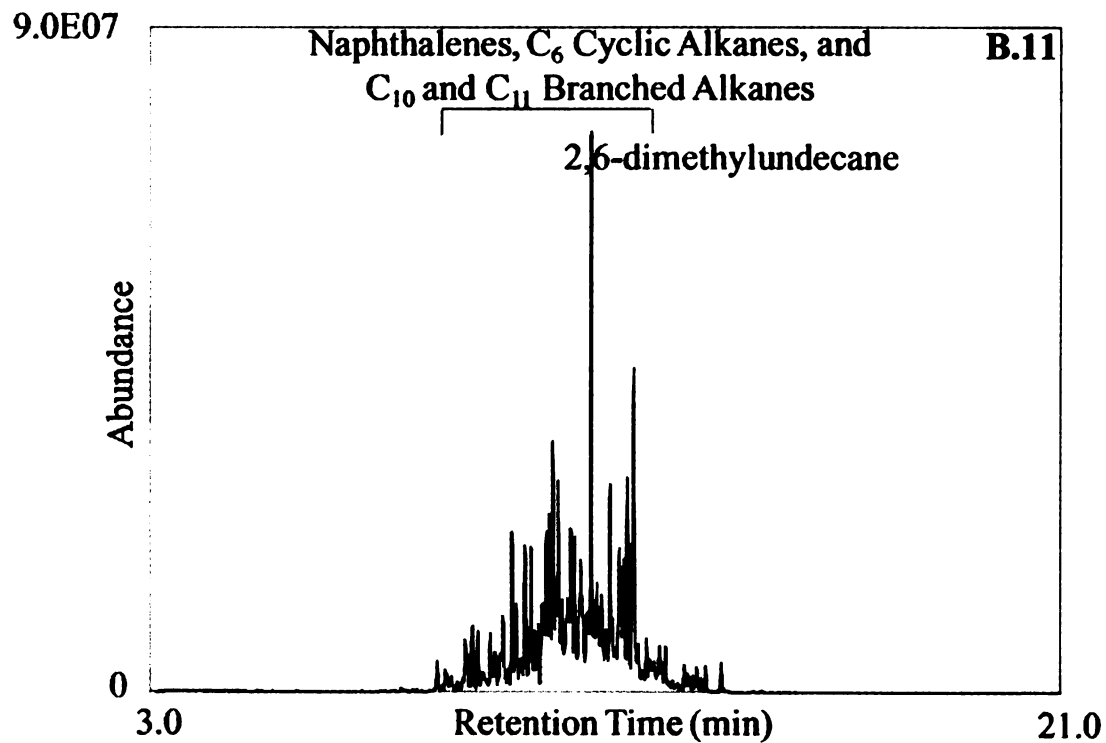


Figure B.11: Chromatogram of 20% evaporated marine fuel stabilizer with major components labeled.

Figure B.12: Chromatogram of 50% evaporated marine fuel stabilizer with major components labeled.

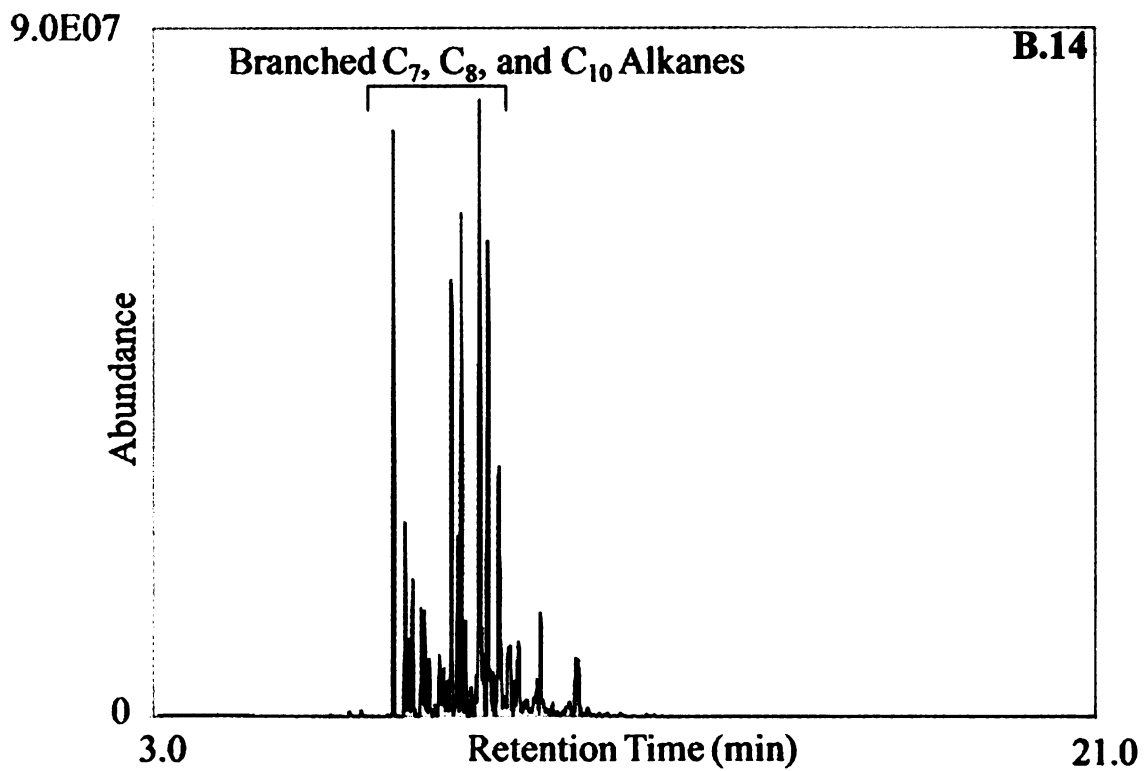
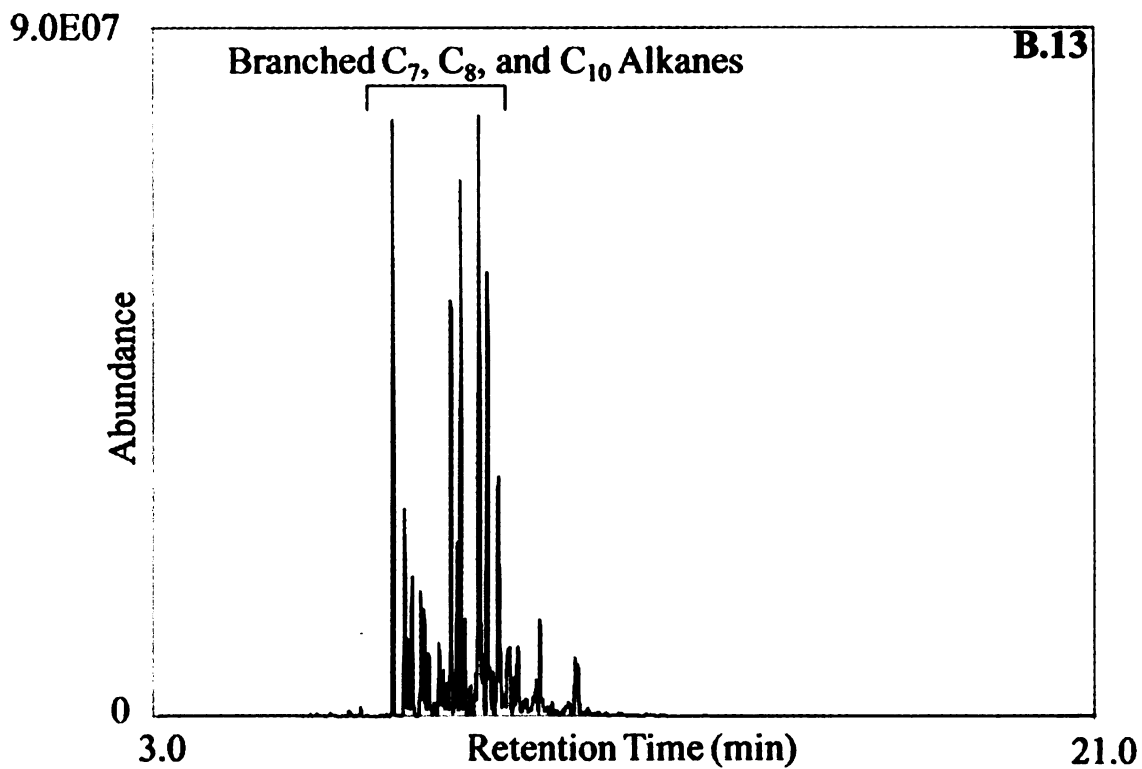


Figure B.13: Chromatogram of 5% evaporated paint thinner with major components labeled.

Figure B.14: Chromatogram of 10% evaporated paint thinner with major components labeled.

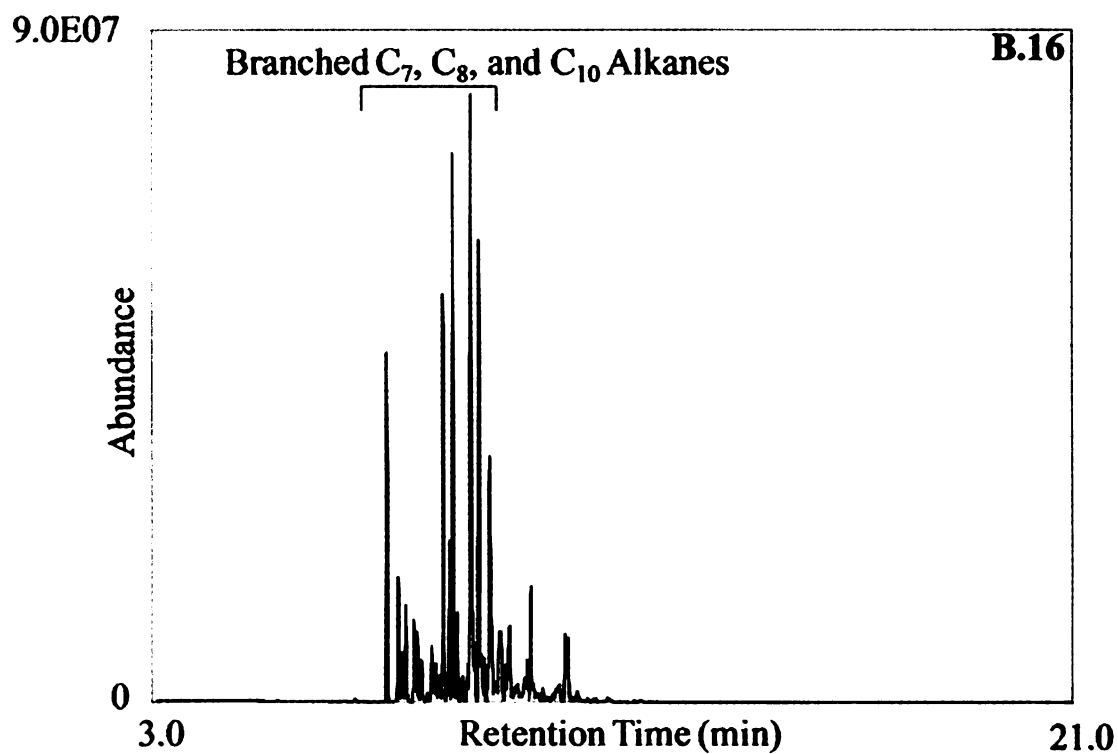
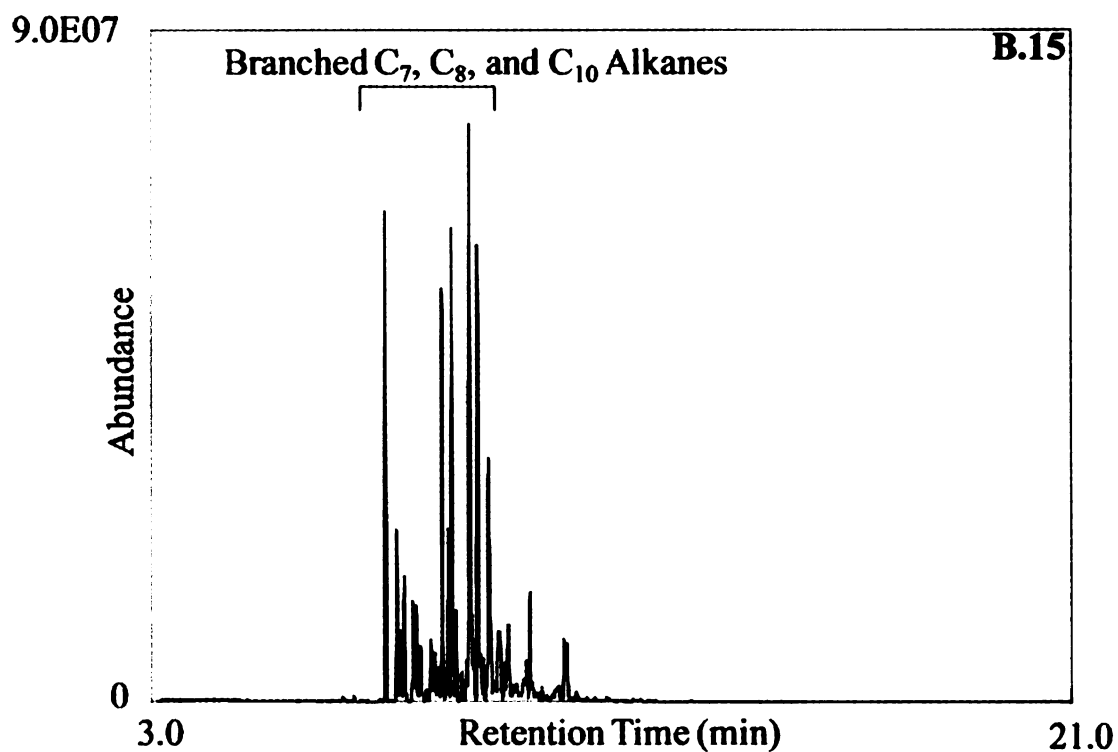


Figure B.15: Chromatogram of 20% evaporated paint thinner with major components labeled.

Figure B.16: Chromatogram of 50% evaporated paint thinner with major components labeled.

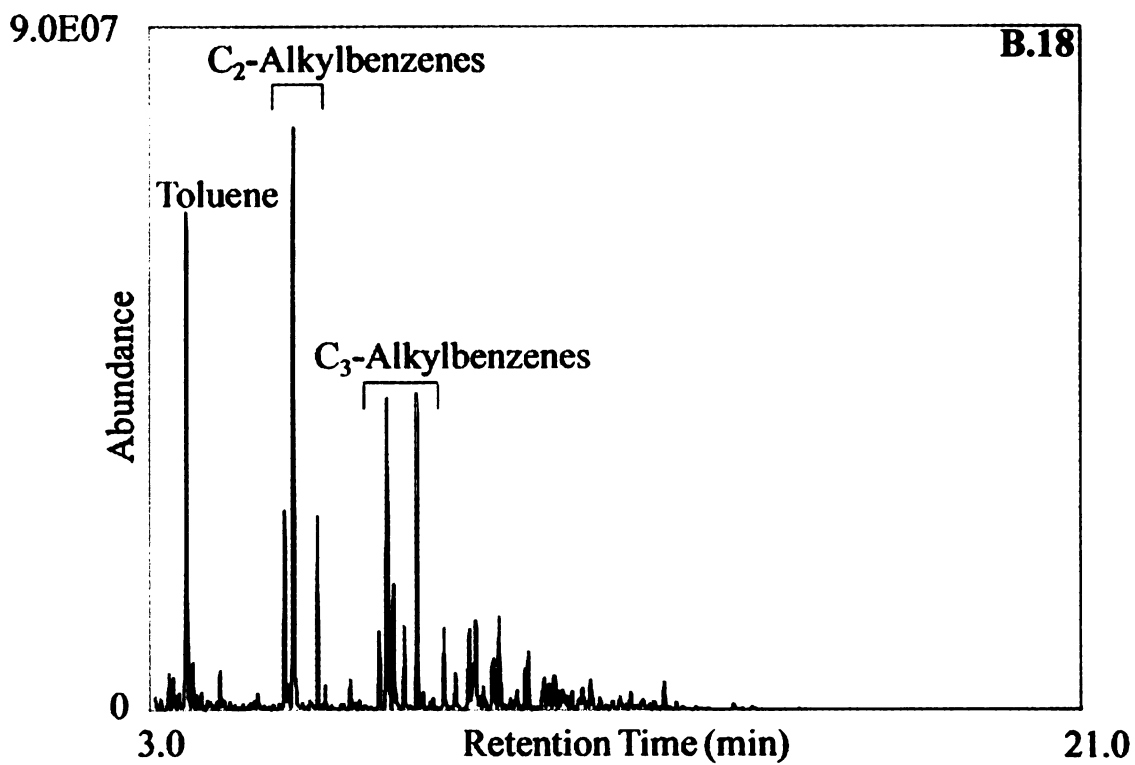
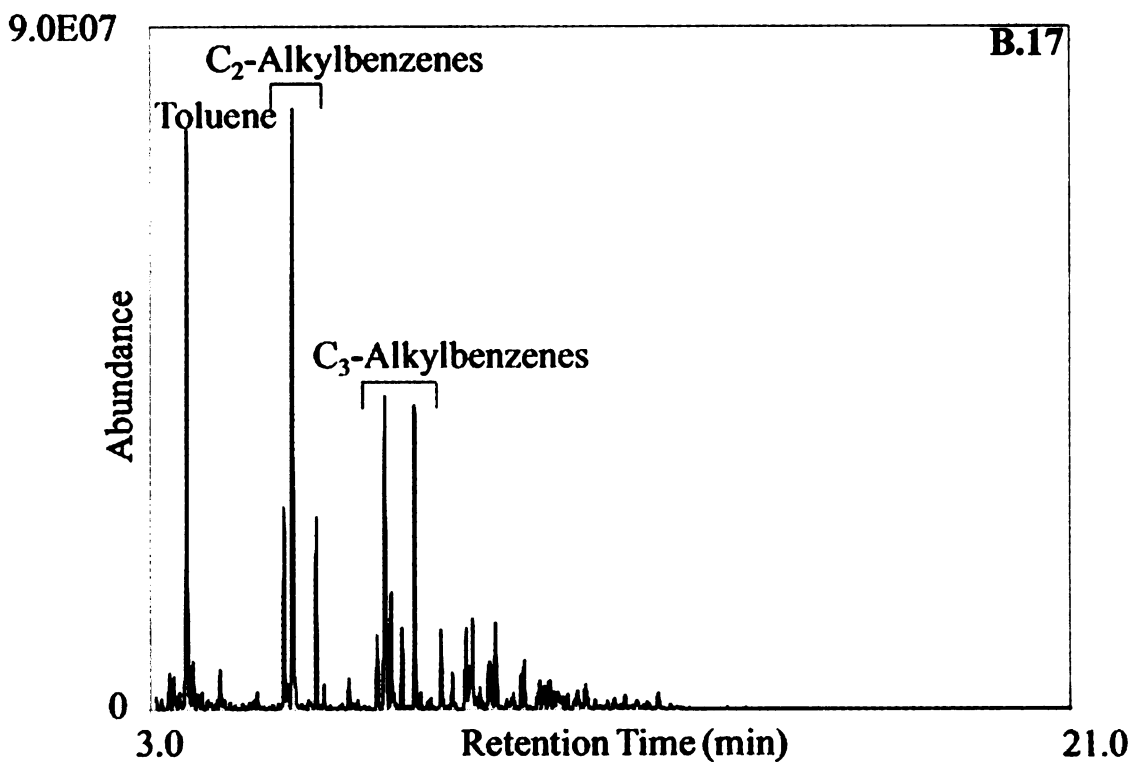


Figure B.17: Chromatogram of 5% evaporated gasoline with major components labeled.
Figure B.18: Chromatogram of 10% evaporated gasoline with major components labeled.

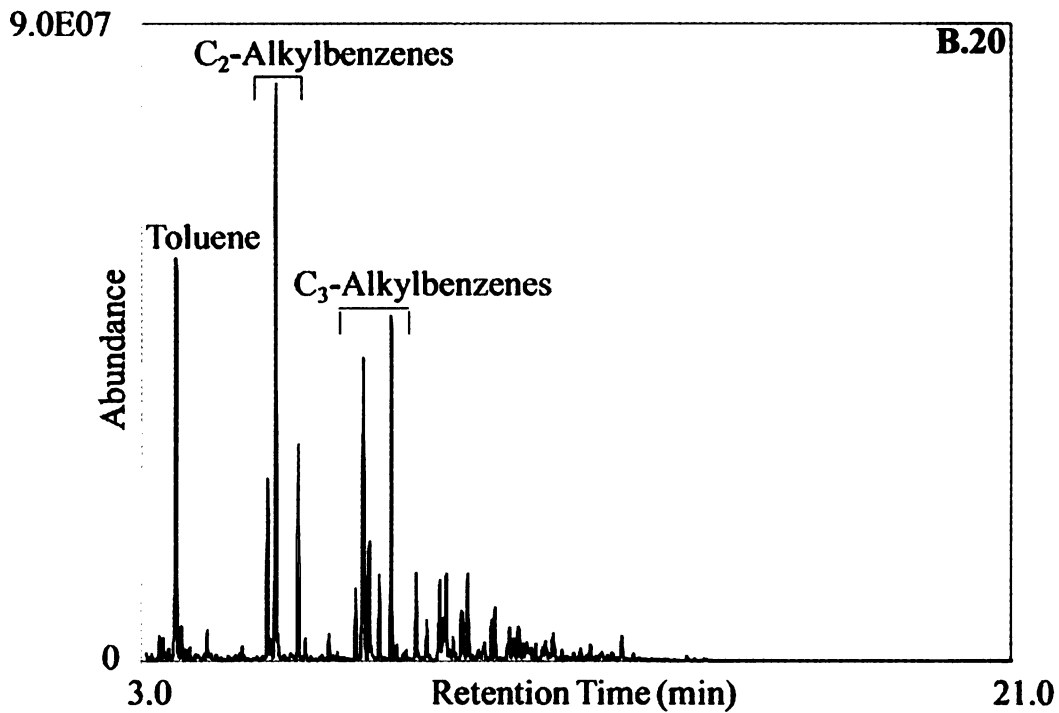
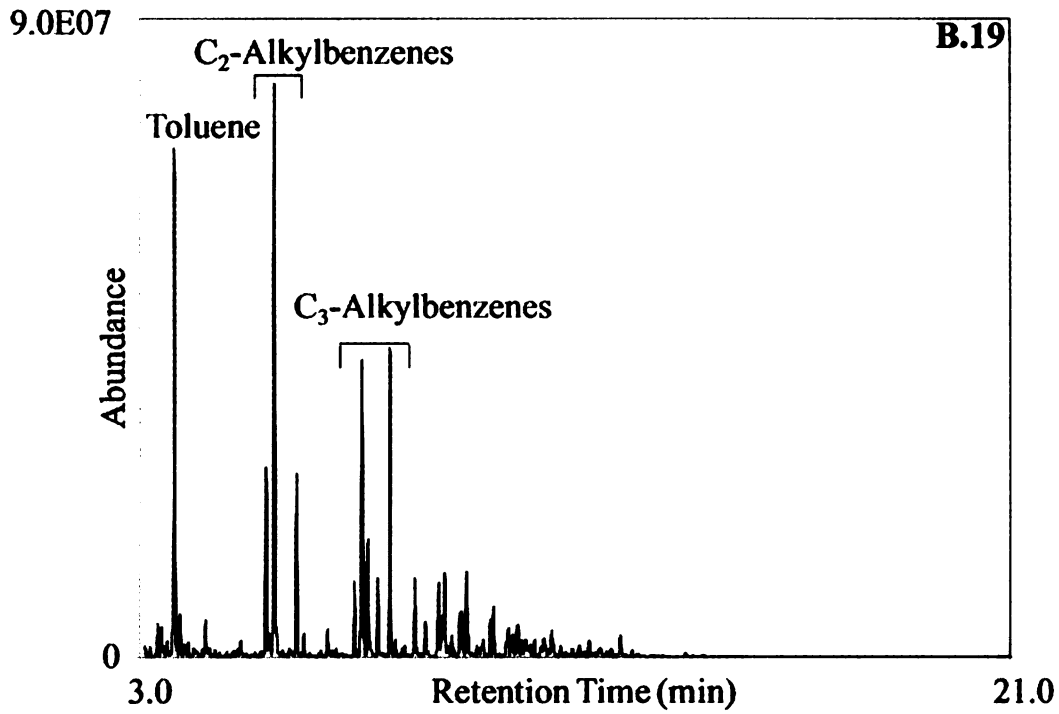


Figure B.19: Chromatogram of 20% evaporated gasoline with major components labeled.
 Figure B.20: Chromatogram of 50% evaporated gasoline with major components labeled.

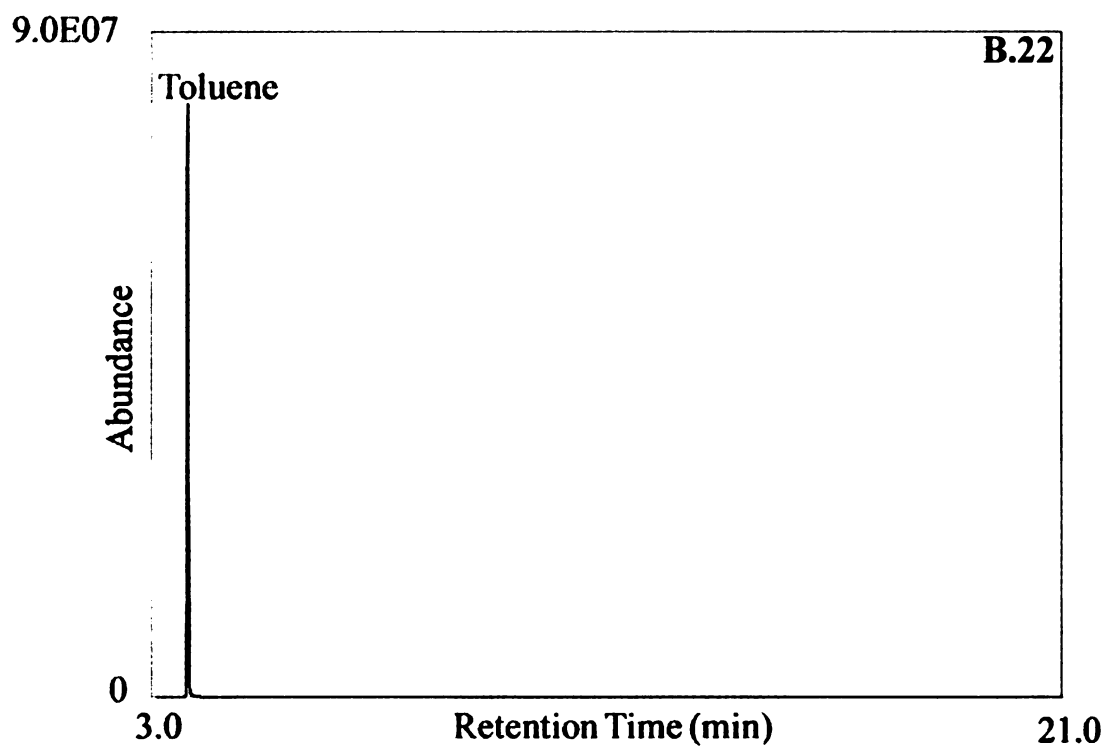
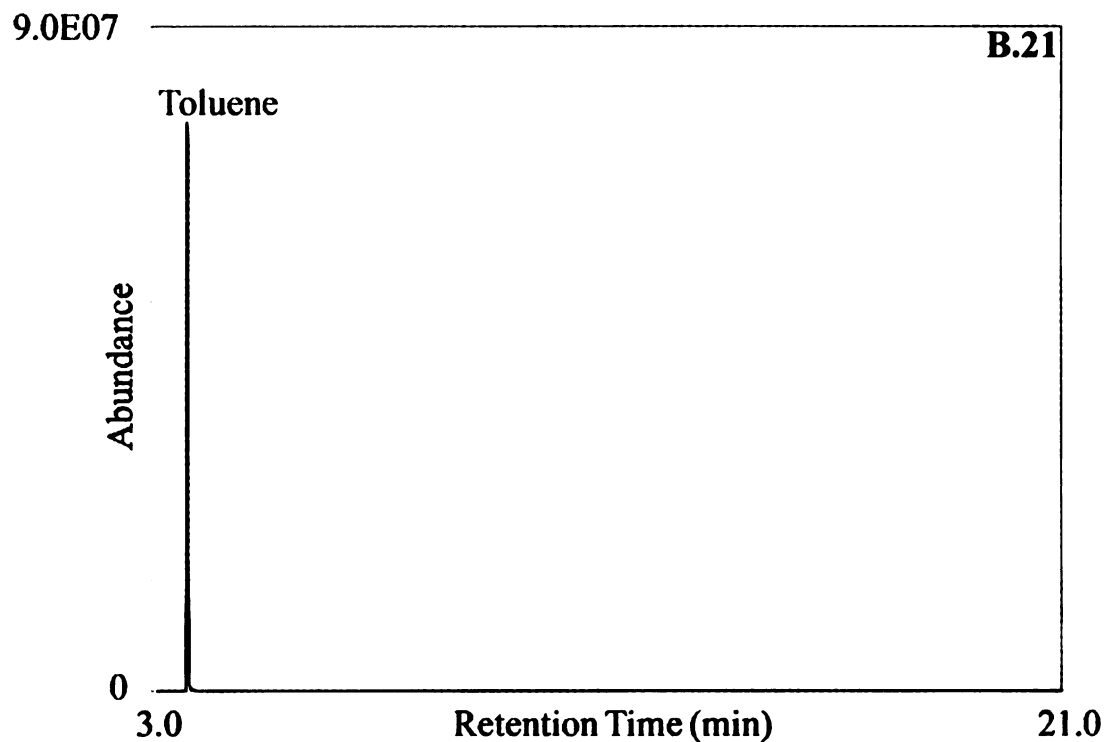


Figure B.21: Chromatogram of 5% evaporated lacquer thinner with major component labeled.

Figure B.22: Chromatogram of 10% evaporated lacquer thinner with major component labeled.

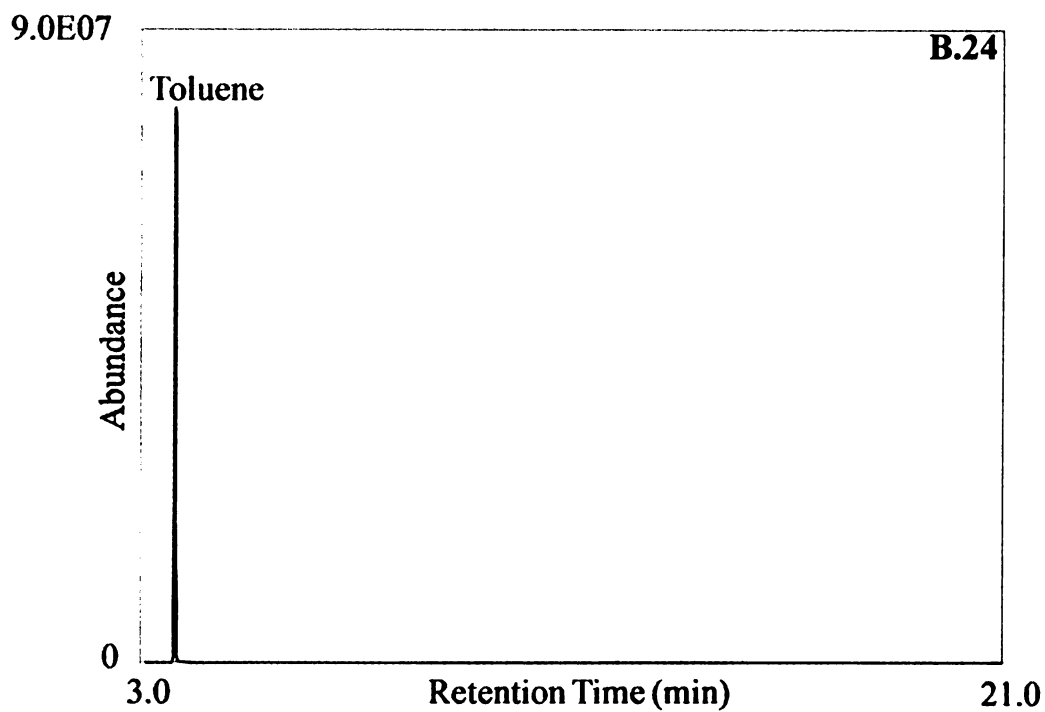
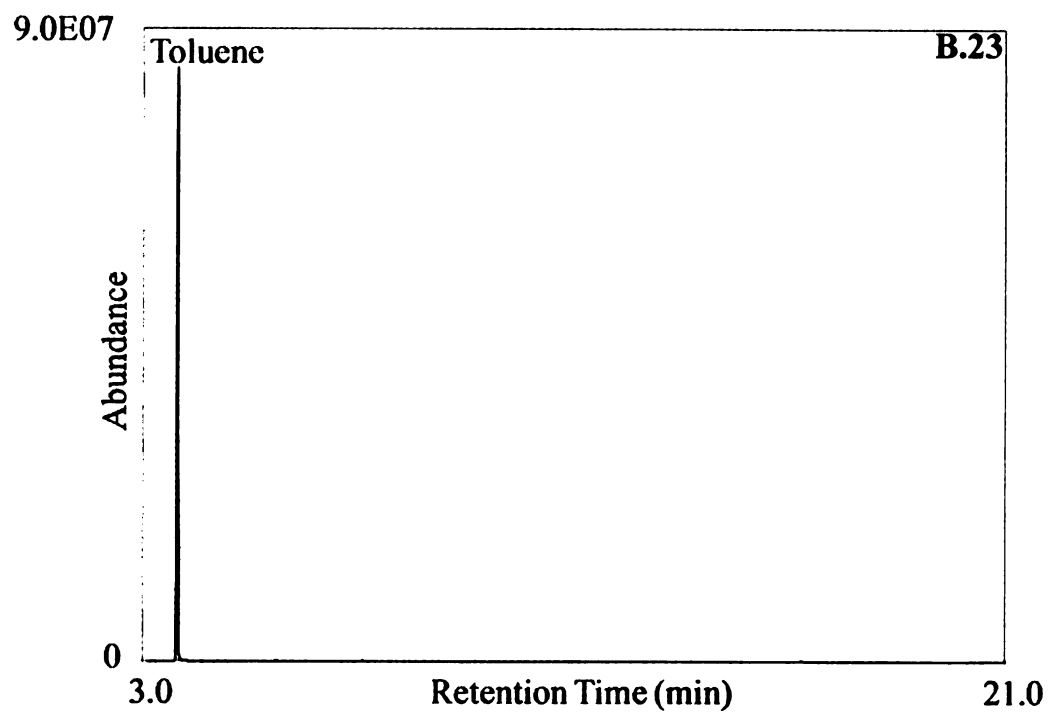


Figure B.23: Chromatogram of 20% evaporated lacquer thinner with major component labeled.

Figure B.24: Chromatogram of 50% evaporated gasoline with major component labeled.

APPENDIX C

Pearson Product Moment Correlation Coefficients for Total Ion Chromatograms of Neat and Evaporated Liquids by Ignitable Liquid Class

In this appendix, Pearson product moment correlation (PPMC) coefficients are shown for the neat and evaporated ignitable liquids, lamp fuel, kerosene, marine fuel stabilizer, paint thinner, gasoline, and lacquer thinner, by ignitable liquid class as summarized below:

Table C.1: PPMC Coefficients for Replicates (A, B, C) of Lamp Fuel at Neat (N), 5% Evaporated (5), 10% Evaporated (10), 20% Evaporated (20), 50% Evaporated (50)

Table C.2: PPMC Coefficients for Replicates (A, B, C) of Kerosene at Neat (N), 5% Evaporated (5), 10% Evaporated (10), 20% Evaporated (20), 50% Evaporated (50)

Table C.3: PPMC Coefficients for Replicates (A, B, C) of Marine Fuel Stabilizer at Neat (N), 5% Evaporated (5), 10% Evaporated (10), 20% Evaporated (20), 50% Evaporated (50)

Table C.4: PPMC Coefficients for Replicates (A, B, C) of Paint Thinner at Neat (N), 5% Evaporated (5), 10% Evaporated (10), 20% Evaporated (20), 50% Evaporated (50)

Table C.5: PPMC Coefficients for Replicates (A, B, C) of Lacquer Thinner at Neat (N), 5% Evaporated (5), 10% Evaporated (10), 20% Evaporated (20), 50% Evaporated (50)

Table C.6: PPMC Coefficients for Replicates (A, B, C) of Gasoline at Neat (N), 5% Evaporated (5), 10% Evaporated (10), 20% Evaporated (20), 50% Evaporated (50)

Table C.1 PPMC Coefficients of Neat and Evaporated Lamp Fuel (LF).

	LFNA	LFNB	LFNC	LF5A	LF5B	LF5C	LF10A	LF10B	LF10C	LF20A	LF20B	LF20C	LF50A	LF50B	LF50C
LFNA	1.0000	0.9933	0.9959	0.9915	0.9905	0.9888	0.9942	0.9923	0.9952	0.9913	0.9911	0.9851	0.9755	0.9722	0.9742
LFNB	0.9933	1.0000	0.9967	0.9896	0.9959	0.9880	0.9892	0.9934	0.9913	0.9943	0.9871	0.9835	0.9851	0.9716	0.9796
LFNC	0.9959	0.9967	1.0000	0.9964	0.9977	0.9951	0.9954	0.9987	0.9981	0.9987	0.9951	0.9938	0.9908	0.9851	0.9880
LF5A				1.0000	0.9973	0.9997	0.9890	0.9955	0.9936	0.9957	0.9902	0.9956	0.9903	0.9869	0.9837
LF5B				0.9973	1.0000	0.9970	0.9882	0.9963	0.9924	0.9976	0.9888	0.9923	0.9935	0.9829	0.9853
LF5C				0.9997	0.9970	1.0000	0.9867	0.9946	0.9918	0.9950	0.9885	0.9958	0.9914	0.9878	0.9839
LF10A							1.0000	0.9967	0.9988	0.9951	0.9992	0.9921	0.9846	0.9864	0.9897
LF10B							0.9967	1.0000	0.9984	0.9997	0.9978	0.9969	0.9946	0.9914	0.9941
LF10C							0.9988	0.9984	1.0000	0.9974	0.9988	0.9948	0.9881	0.9884	0.9903
LF20A										1.0000	0.9962	0.9962	0.9957	0.9902	0.9934
LF20B										0.9962	1.0000	0.9951	0.9888	0.9916	0.9939
LF20C										0.9962	0.9951	1.0000	0.9948	0.9974	0.9940
LF50A													1.0000	0.9932	0.9957
LF50B													0.9932	1.0000	0.9962
LF50C													0.9957	0.9962	1.0000

Table C.2 PPMC Coefficients of Neat and Evaporated Kerosene (Kero).

	Kero N A	Kero N B	Kero N C	Kero 5 A	Kero 5 B	Kero 5 C	Kero 10 A	Kero 10 B	Kero 10 C	Kero 20 A	Kero 20 B	Kero 20 C	Kero 50 A	Kero 50 B	Kero 50 C
Kero N A	1.0000	0.9948	0.9959	0.9947	0.9955	0.9952	0.9960	0.9962	0.9912	0.9851	0.9891	0.9867	0.8744	0.8755	0.8796
Kero N B	0.9948	1.0000	0.9956	0.9962	0.9971	0.9956	0.9950	0.9963	0.9933	0.9880	0.9894	0.9878	0.8772	0.8786	0.8835
Kero N C	0.9959	0.9956	1.0000	0.9960	0.9970	0.9992	0.9953	0.9968	0.9952	0.9894	0.9914	0.9926	0.8857	0.8869	0.8918
Kero 5 A	1.0000	0.9975	0.9967	1.0000	0.9975	0.9967	0.9966	0.9973	0.9956	0.9912	0.9964	0.9925	0.8946	0.8973	0.8999
Kero 5 B	0.9975	1.0000	0.9973	0.9975	1.0000	0.9973	0.9956	0.9989	0.9951	0.9903	0.9942	0.9932	0.8913	0.8924	0.8968
Kero 5 C	0.9967	0.9973	1.0000	0.9967	0.9973	1.0000	0.9965	0.9966	0.9975	0.9931	0.9936	0.9948	0.8921	0.8935	0.8985
Kero 10 A							1.0000	0.9960	0.9955	0.9919	0.9939	0.9924	0.8902	0.8924	0.8958
Kero 10 B							0.9960	1.0000	0.9937	0.9887	0.9944	0.9928	0.8852	0.8864	0.8904
Kero 10 C							0.9955	0.9937	1.0000	0.9980	0.9939	0.9950	0.9015	0.9033	0.9070
Kero 20 A										1.0000	0.9922	0.9941	0.9054	0.9084	0.9117
Kero 20 B										0.9922	1.0000	0.9959	0.9153	0.9179	0.9201
Kero 20 C										0.9941	0.9959	1.0000	0.9186	0.9200	0.9244
Kero 50 A													1.0000	0.9975	0.9985
Kero 50 B													0.9975	1.0000	0.9962
Kero 50 C													0.9985	0.9962	1.0000

Table C.3 PPMC Coefficients of Neat and Evaporated Marine Fuel Stabilizer (MFS).

	MFSNA	MFSNB	MFSNC	MFS5A	MFS5B	MFS5C	MFS10A	MFS10B	MFS10C	MFS20A	MFS20B	MFS20C	MFS50A	MFS50B	MFS50C
MFSNA	1.0000	0.9979	0.9974	0.9990	0.9979	0.9976	0.9859	0.9907	0.9889	0.9730	0.9744	0.9544	0.8700	0.8917	0.8906
MFSNB	0.9979	1.0000	0.9994	0.9981	0.9956	0.9982	0.9816	0.9880	0.9848	0.9676	0.9695	0.9500	0.8598	0.8850	0.8814
MFSNC	0.9974	0.9994	1.0000	0.9976	0.9942	0.9968	0.9791	0.9864	0.9824	0.9645	0.9671	0.9458	0.8535	0.8797	0.8759
MFS5A				1.0000	0.9984	0.9979	0.9876	0.9926	0.9901	0.9757	0.9779	0.9570	0.8734	0.8965	0.8950
MFS5B				0.9984	1.0000	0.9984	0.9935	0.9955	0.9955	0.9844	0.9852	0.9694	0.8947	0.9148	0.9138
MFS5C				0.9979	0.9984	1.0000	0.9895	0.9926	0.9920	0.9785	0.9791	0.9645	0.8830	0.9055	0.9024
MFS10A							1.0000	0.9970	0.9989	0.9971	0.9961	0.9886	0.9339	0.9499	0.9492
MFS10B							0.9970	1.0000	0.9967	0.9917	0.9925	0.9790	0.9146	0.9339	0.9328
MFS10C							0.9989	0.9967	1.0000	0.9955	0.9949	0.9858	0.9289	0.9451	0.9445
MFS20A										1.0000	0.9978	0.9944	0.9542	0.9679	0.9677
MFS20B										0.9978	1.0000	0.9926	0.9494	0.9640	0.9644
MFS20C										0.9944	0.9926	1.0000	0.9714	0.9812	0.9802
MFS50A													1.0000	0.9958	0.9976
MFS50B													0.9958	1.0000	0.9981
MFS50C													0.9976	0.9981	1.0000

Table C.4 PPMC Coefficients of Neat and Evaporated Paint Thinner (PT).

	PTNA	PTNB	PTNC	PT5A	PT5B	PT5C	PT10A	PT10B	PT10C	PT20A	PT20B	PT20C	PT50A	PT50B	PT50C
PTNA	1.0000	0.9909	0.9934	0.9917	0.9917	0.9864	0.9866	0.9823	0.9868	0.9845	0.9790	0.9717	0.9481	0.9248	0.9157
PTNB	0.9909	1.0000	0.9918	0.9979	0.9995	0.9980	0.9978	0.9965	0.9979	0.9955	0.9928	0.9888	0.9624	0.9462	0.9381
PTNC	0.9934	0.9918	1.0000	0.9955	0.9942	0.9882	0.9886	0.9855	0.9890	0.9868	0.9823	0.9746	0.9620	0.9327	0.9283
PT5A				1.0000	0.9987	0.9960	0.9978	0.9945	0.9962	0.9947	0.9936	0.9867	0.9678	0.9500	0.9415
PT5B				0.9987	1.0000	0.9981	0.9978	0.9968	0.9982	0.9964	0.9935	0.9894	0.9675	0.9495	0.9431
PT5C				0.9960	0.9981	1.0000	0.9984	0.9994	0.9998	0.9985	0.9970	0.9955	0.9723	0.9615	0.9551
PT10A							1.0000	0.9979	0.9984	0.9965	0.9973	0.9926	0.9693	0.9588	0.9494
PT10B							0.9979	1.0000	0.9993	0.9981	0.9974	0.9967	0.9757	0.9651	0.9598
PT10C							0.9984	0.9993	1.0000	0.9985	0.9971	0.9955	0.9738	0.9620	0.9556
PT20A										1.0000	0.9979	0.9968	0.9788	0.9706	0.9644
PT20B										0.9979	1.0000	0.9974	0.9804	0.9764	0.9676
PT20C										0.9968	0.9974	1.0000	0.9828	0.9810	0.9756
PT50A													1.0000	0.9843	0.9886
PT50B													0.9843	1.0000	0.9944
PT50C													0.9886	0.9944	1.0000

Table C.5 PPMC Coefficients of Neat and Evaporated Lacquer Thinner (LT).

	LTNA	LTNB	LTNC	LT5A	LT5B	LT5C	LT10A	LT10B	LT10C	LT20A	LT20B	LT20C	LT50A	LT50B	LT50C
LTNA	1.0000	0.9991	0.9969	1.0000	0.9989	0.9983	0.9717	0.9998	0.9978	0.9639	0.9953	0.9928	0.9994	0.9987	0.9905
LTNB	0.9991	1.0000	0.9991	0.9993	1.0000	0.9998	0.9806	0.9983	0.9997	0.9740	0.9982	0.9967	1.0000	0.9999	0.9953
LTNC	0.9969	0.9991	1.0000	0.9973	0.9991	0.9994	0.9865	0.9955	0.9996	0.9805	0.9985	0.9979	0.9988	0.9992	0.9980
LT5A				1.0000	0.9991	0.9986	0.9727	0.9998	0.9981	0.9651	0.9957	0.9933	0.9995	0.9989	0.9911
LT5B				0.9991	1.0000	0.9999	0.9814	0.9980	0.9997	0.9751	0.9987	0.9973	0.9999	1.0000	0.9955
LT5C				0.9986	0.9999	1.0000	0.9835	0.9972	0.9999	0.9775	0.9991	0.9980	0.9997	1.0000	0.9965
LT10A							1.0000	0.9676	0.9849	0.9993	0.9886	0.9920	0.9794	0.9823	0.9947
LT10B							0.9676	1.0000	0.9966	0.9593	0.9937	0.9908	0.9986	0.9977	0.9880
LT10C							0.9849	0.9966	1.0000	0.9789	0.9993	0.9983	0.9994	0.9998	0.9971
LT20A										1.0000	0.9840	0.9882	0.9728	0.9762	0.9907
LT20B										0.9840	1.0000	0.9997	0.9979	0.9989	0.9978
LT20C										0.9882	0.9997	1.0000	0.9962	0.9976	0.9987
LT50A													1.0000	0.9998	0.9946
LT50B													0.9998	1.0000	0.9959
LT50C													0.9946	0.9959	1.0000

Table C.6 PPMC Coefficients for the TIC of Neat and Evaporated Gasoline (Gas).

	Gas NA	Gas NB	Gas NC	Gas 5 A	Gas 5 B	Gas 5 C	Gas 10 A	Gas 10 B	Gas 10 C	Gas 20 A	Gas 20 B	Gas 20 C	Gas 50 A	Gas 50 B	Gas 50 C
Gas NA	1.0000	0.9950	0.9946	0.9948	0.9947	0.9946	0.9958	0.9967	0.9959	0.9962	0.9982	0.9926	0.9852	0.9863	0.9820
Gas NB	0.9950	1.0000	0.9936	0.9946	0.9945	0.9942	0.9965	0.9970	0.9979	0.9981	0.9961	0.9946	0.9847	0.9906	0.9821
Gas NC	0.9946	0.9936	1.0000	0.9970	0.9973	0.9972	0.9938	0.9937	0.9926	0.9935	0.9943	0.9985	0.9844	0.9868	0.9824
Gas 5 A				1.0000	0.9988	0.9994	0.9941	0.9938	0.9952	0.9960	0.9942	0.9975	0.9839	0.9904	0.9781
Gas 5 B				0.9988	1.0000	0.9989	0.9944	0.9942	0.9946	0.9953	0.9947	0.9972	0.9845	0.9891	0.9803
Gas 5 C				0.9994	0.9989	1.0000	0.9927	0.9927	0.9941	0.9953	0.9934	0.9972	0.9807	0.9879	0.9759
Gas 10 A							1.0000	0.9973	0.9972	0.9963	0.9979	0.9944	0.9927	0.9928	0.9888
Gas 10 B							0.9973	1.0000	0.9984	0.9976	0.9988	0.9932	0.9885	0.9873	0.9871
Gas 10 C							0.9972	0.9984	1.0000	0.9992	0.9983	0.9938	0.9864	0.9893	0.9825
Gas 20 A										1.0000	0.9976	0.9948	0.9826	0.9888	0.9782
Gas 20 B										0.9976	1.0000	0.9936	0.9886	0.9867	0.9863
Gas 20 C										0.9948	0.9936	1.0000	0.9842	0.9897	0.9814
Gas 50 A													1.0000	0.9902	0.9959
Gas 50 B													0.9902	1.0000	0.9819
Gas 50 C													0.9959	0.9819	1.0000

APPENDIX D

Pearson Product Moment Correlation Coefficients for Total Ion Chromatograms of Neat and Evaporated Liquids by Evaporation Level

In this appendix, Pearson product moment correlation (PPMC) coefficients are shown for the neat and evaporated ignitable liquids, lamp fuel, kerosene, marine fuel stabilizer, paint thinner, gasoline, and lacquer thinner, at each evaporation level (5%, 10%, 20%, 50%) as summarized below:

Table D.1: PPMC Coefficients for Replicates (A, B, C) of Neat Ignitable Liquids, Gasoline (Gas), Kerosene (Kero), Lacquer Thinner (LT), Lamp Fuel (LF), Marine Fuel Stabilizer (MFS), Paint Thinner (PT)

Table D.2: PPMC Coefficients for Replicates (A, B, C) of 5% Evaporated Ignitable Liquids, Gasoline (Gas), Kerosene (Kero), Lacquer Thinner (LT), Lamp Fuel (LF), Marine Fuel Stabilizer (MFS), Paint Thinner (PT)

Table D.3: PPMC Coefficients for Replicates (A, B, C) of 10% Evaporated Ignitable Liquids, Gasoline (Gas), Kerosene (Kero), Lacquer Thinner (LT), Lamp Fuel (LF), Marine Fuel Stabilizer (MFS), Paint Thinner (PT)

Table D.4: PPMC Coefficients for Replicates (A, B, C) of 20% Evaporated Ignitable Liquids, Gasoline (Gas), Kerosene (Kero), Lacquer Thinner (LT), Lamp Fuel (LF), Marine Fuel Stabilizer (MFS), Paint Thinner (PT)

Table D.5: PPMC Coefficients for Replicates (A, B, C) of 50% Evaporated Ignitable Liquids, Gasoline (Gas), Kerosene (Kero), Lacquer Thinner (LT), Lamp Fuel (LF), Marine Fuel Stabilizer (MFS), Paint Thinner (PT)

Table D.1 PPMC Coefficients for the TIC of Neat (N) Ignitable Liquids.

	GasNA	GasNB	GasNC	KeroNA	KeroNB	KeroNC	LTNA	LTNB	LTNC	LFNA	LFNB	LFNC	MFSNA	MFSNB	MFSNC	PTNA	PTNB	PTNC
GasNA	1.0000	0.9950	0.9946	0.0689	0.0744	0.0646	0.5435	0.5438	0.5426	0.0091	0.0081	0.0073	0.0511	0.0404	0.0492	0.2010	0.1966	0.2004
GasNB	0.9950	1.0000	0.9936	0.0799	0.0852	0.0752	0.5409	0.5389	0.5364	0.0164	0.0151	0.0141	0.0610	0.0498	0.0593	0.2065	0.2015	0.2058
GasNC	0.9946	0.9936	1.0000	0.0756	0.0807	0.0707	0.5455	0.5453	0.5438	0.0113	0.0102	0.0093	0.0584	0.0474	0.0566	0.2241	0.2188	0.2195
KeroNA				1.0000	0.9948	0.9959	-0.0188	-0.0189	-0.0201	0.4999	0.4910	0.4814	0.5283	0.5263	0.5383	0.0787	0.0794	0.0790
KeroNB				0.9948	1.0000	0.9956	-0.0188	-0.0189	-0.0201	0.4959	0.4899	0.4810	0.5152	0.5132	0.5252	0.0834	0.0839	0.0835
KeroNC				0.9959	0.9956	1.0000	-0.0187	-0.0187	-0.0199	0.5212	0.5127	0.5044	0.5131	0.5108	0.5227	0.0723	0.0730	0.0726
LTNA							1.0000	0.9991	0.9969	-0.0023	-0.0025	-0.0025	-0.0085	-0.0144	-0.0126	-0.0061	-0.0058	-0.0063
LTNB							0.9991	1.0000	0.9991	-0.0023	-0.0025	-0.0025	-0.0086	-0.0144	-0.0127	-0.0061	-0.0058	-0.0063
LTNC							0.9969	0.9991	1.0000	-0.0025	-0.0027	-0.0026	-0.0095	-0.0153	-0.0136	-0.0065	-0.0062	-0.0067
LFNA										1.0000	0.9933	0.9959	0.0540	0.0481	0.0585	-0.0096	-0.0097	-0.0096
LFNB										0.9933	1.0000	0.9967	0.0514	0.0453	0.0559	-0.0097	-0.0098	-0.0097
LFNC										0.9959	0.9967	1.0000	0.0455	0.0395	0.0497	-0.0096	-0.0097	-0.0096
MFSNA													1.0000	0.9979	0.9974	0.1871	0.1906	0.1905
MFSNB													0.9979	1.0000	0.9994	0.1872	0.1910	0.1907
MFSNC													0.9974	0.9994	1.0000	0.1954	0.1991	0.1988
PTNA																1.0000	0.9909	0.9934
PTNB																0.9909	1.0000	0.9918
PTNC																0.9934	0.9918	1.0000

Table D.2 PPMC Coefficients for the TIC of 5% Evaporated (5) Ignitable Liquids.

	Gas 5 A	Gas 5 B	Gas 5 C	Kero 5 A	Kero 5 B	Kero 5 C	LT 5 A	LT 5 B	LT 5 C	LF 5 A	LF 5 B	LF 5 C	MFS 5 A	MFS 5 B	MFS 5 C	PT 5 A	PT 5 B	PT 5 C
Gas 5 A	1.0000	0.9988	0.9994	0.0509	0.0552	0.0512	0.5570	0.5538	0.5552	0.0082	0.0084	0.0078	0.0395	0.0391	0.0379	0.2152	0.2169	0.2113
Gas 5 B	0.9988	1.0000	0.9989	0.0667	0.0709	0.0670	0.5521	0.5511	0.5507	0.0165	0.0168	0.0160	0.0516	0.0508	0.0497	0.2123	0.2141	0.2086
Gas 5 C	0.9994	0.9989	1.0000	0.0487	0.0529	0.0489	0.5692	0.5682	0.5677	0.0081	0.0084	0.0078	0.0372	0.0368	0.0356	0.2074	0.2090	0.2036
Kero 5 A				1.0000	0.9975	0.9967	-0.0204	-0.0200	-0.0202	0.4950	0.4948	0.4922	0.5158	0.5081	0.5026	0.0646	0.0643	0.0669
Kero 5 B				0.9975	1.0000	0.9973	-0.0199	-0.0195	-0.0197	0.5069	0.5043	0.5038	0.5133	0.5055	0.5000	0.0689	0.0686	0.0712
Kero 5 C				0.9967	0.9973	1.0000	-0.0200	-0.0196	-0.0198	0.4979	0.4960	0.4948	0.5155	0.5080	0.5019	0.0631	0.0630	0.0656
LT 5 A							1.0000	0.9991	0.9986	-0.0025	-0.0025	-0.0026	-0.0146	-0.0128	-0.0139	-0.0061	-0.0059	-0.0054
LT 5 B							0.9991	1.0000	0.9999	-0.0025	-0.0025	-0.0025	-0.0143	-0.0126	-0.0136	-0.0060	-0.0058	-0.0053
LT 5 C							0.9986	0.9999	1.0000	-0.0025	-0.0025	-0.0025	-0.0145	-0.0127	-0.0138	-0.0061	-0.0059	-0.0053
LF 5 A										1.0000	0.9973	0.9997	0.0418	0.0398	0.0343	-0.0096	-0.0096	-0.0096
LF 5 B										0.9973	1.0000	0.9970	0.0431	0.0410	0.0355	-0.0096	-0.0096	-0.0096
LF 5 C										0.9997	0.9970	1.0000	0.0399	0.0379	0.0324	-0.0096	-0.0096	-0.0096
MFS 5 A													1.0000	0.9984	0.9979	0.1755	0.1771	0.1833
MFS 5 B													0.9984	1.0000	0.9984	0.1574	0.1589	0.1647
MFS 5 C													0.9979	0.9984	1.0000	0.1677	0.1693	0.1755
PT 5 A																1.0000	0.9987	0.9960
PT 5 B																0.9987	1.0000	0.9981
PT 5 C																0.9960	0.9981	1.0000

Table D.3 PPMC Coefficients for the TIC of 10% Evaporated (10) Ignitable Liquids.

	Gas 10 A	Gas 10 B	Gas 10 C	Kero 10 A	Kero 10 B	Kero 10 C	LT 10 A	LT 10 B	LT 10 C	LF 10 A	LF 10 B	LF 10 C	MFS 10 A	MFS 10 B	MFS 10 C	PT 10 A	PT 10 B	PT 10 C
Gas 10 A	1.0000	0.9973	0.9972	0.0632	0.0693	0.0589	0.4827	0.4988	0.4972	0.0208	0.0197	0.0204	0.0415	0.0474	0.0429	0.2170	0.2122	0.2128
Gas 10 B	0.9973	1.0000	0.9984	0.0514	0.0573	0.0471	0.4922	0.5160	0.5120	0.0136	0.0126	0.0132	0.0338	0.0396	0.0352	0.2073	0.2027	0.2031
Gas 10 C	0.9972	0.9984	1.0000	0.0520	0.0578	0.0476	0.5069	0.5329	0.5283	0.0126	0.0116	0.0122	0.0347	0.0405	0.0362	0.2091	0.2046	0.2050
Kero 10 A				1.0000	0.9960	0.9955	-0.0207	-0.0206	-0.0205	0.4627	0.4600	0.4631	0.5206	0.5311	0.5215	0.0640	0.0648	0.0660
Kero 10 B				0.9960	1.0000	0.9937	-0.0202	-0.0201	-0.0200	0.4947	0.4910	0.4947	0.5184	0.5292	0.5200	0.0695	0.0702	0.0715
Kero 10 C				0.9955	0.9937	1.0000	-0.0195	-0.0194	-0.0194	0.4940	0.4930	0.4953	0.4976	0.5070	0.4979	0.0492	0.0498	0.0511
LT 10 A							1.0000	0.9676	0.9849	-0.0025	-0.0026	-0.0025	-0.0130	-0.0135	-0.0130	-0.0048	-0.0049	-0.0048
LT 10 B							0.9676	1.0000	0.9966	-0.0025	-0.0026	-0.0025	-0.0130	-0.0134	-0.0130	-0.0048	-0.0048	-0.0048
LT 10 C							0.9849	0.9966	1.0000	-0.0025	-0.0026	-0.0025	-0.0130	-0.0134	-0.0130	-0.0048	-0.0048	-0.0048
LF 10 A										1.0000	0.9967	0.9988	0.0511	0.0506	0.0502	-0.0098	-0.0099	-0.0073
LF 10 B										0.9967	1.0000	0.9984	0.0471	0.0468	0.0465	-0.0097	-0.0098	-0.0073
LF 10 C										0.9988	0.9984	1.0000	0.0496	0.0491	0.0488	-0.0097	-0.0098	-0.0072
MFS 10 A													1.0000	0.9970	0.9989	0.1085	0.1121	0.1117
MFS 10 B													0.9970	1.0000	0.9967	0.1290	0.1330	0.1326
MFS 10 C													0.9989	0.9967	1.0000	0.1205	0.1242	0.1237
PT 10 A																1.0000	0.9979	0.9984
PT 10 B																0.9979	1.0000	0.9993
PT 10 C																0.9984	0.9993	1.0000

Table D.4 PPMC Coefficients for the TIC of 20% Evaporated (20) Ignitable Liquids.

	Gas 20 A	Gas 20 B	Gas 20 C	Kero 20 A	Kero 20 B	Kero 20 C	LT20 A	LT20 B	LT20 C	LF 20 A	LF 20 B	LF 20 C	MFS 20 A	MFS 20 B	MFS 20 C	PT 20 A	PT 20 B	PT 20 C
Gas 20 A	1.0000	0.9976	0.9948	0.0330	0.0293	0.0278	0.5215	0.5451	0.5429	0.0202	0.0203	0.0190	0.0294	0.0306	0.0265	0.1919	0.1916	0.1835
Gas 20 B	0.9976	1.0000	0.9936	0.0342	0.0304	0.0289	0.4978	0.5160	0.5145	0.0145	0.0146	0.0133	0.0323	0.0336	0.0293	0.1929	0.1927	0.1843
Gas 20 C	0.9948	0.9936	1.0000	0.0427	0.0389	0.0373	0.5187	0.5373	0.5358	0.0233	0.0234	0.0220	0.0373	0.0388	0.0340	0.2058	0.2050	0.1968
Kero 20 A				1.0000	0.9922	0.9941	-0.0187	-0.0192	-0.0190	0.4898	0.4837	0.4790	0.4957	0.5098	0.4821	0.0364	0.0348	0.0335
Kero 20 B				0.9922	1.0000	0.9959	-0.0195	-0.0200	-0.0198	0.5003	0.4978	0.4933	0.5031	0.5168	0.4890	0.0407	0.0390	0.0378
Kero 20 C				0.9941	0.9959	1.0000	-0.0192	-0.0198	-0.0195	0.4997	0.4986	0.4937	0.4928	0.5070	0.4801	0.0336	0.0319	0.0307
LT20 A							1.0000	0.9840	0.9882	-0.0025	-0.0025	-0.0024	-0.0122	-0.0127	-0.0107	-0.0057	-0.0047	-0.0037
LT20 B							0.9840	1.0000	0.9997	-0.0025	-0.0026	-0.0024	-0.0125	-0.0130	-0.0109	-0.0058	-0.0050	-0.0039
LT20 C							0.9882	0.9997	1.0000	-0.0025	-0.0025	-0.0024	-0.0124	-0.0128	-0.0108	-0.0058	-0.0049	-0.0038
LF 20 A										1.0000	0.9962	0.9962	0.0472	0.0555	0.0491	-0.0099	-0.0098	-0.0099
LF 20 B										0.9962	1.0000	0.9951	0.0479	0.0559	0.0496	-0.0099	-0.0099	-0.0100
LF 20 C										0.9962	0.9951	1.0000	0.0425	0.0511	0.0448	-0.0099	-0.0098	-0.0098
MFS 20 A													1.0000	0.9978	0.9944	0.0883	0.0835	0.0852
MFS 20 B													0.9978	1.0000	0.9926	0.0984	0.0937	0.0954
MFS 20 C													0.9944	0.9926	1.0000	0.0674	0.0627	0.0644
PT 20 A																1.0000	0.9979	0.9968
PT 20 B																0.9979	1.0000	0.9974
PT 20 C																0.9968	0.9974	1.0000

Table D.5 PPMC Coefficients for the TIC of 50% Evaporated (50) Ignitable Liquids.

	Gas 50 A	Gas 50 B	Gas 50 C	Kero 50 A	Kero 50 B	Kero 50 C	LT 50 A	LT 50 B	LT 50 C	LF 50 A	LF 50 B	LF 50 C	MFS 50 A	MFS 50 B	MFS 50 C	PT 50 A	PT 50 B	PT 50 C
Gas 50 A	1.0000	0.9902	0.9959	-0.0236	-0.0253	-0.0217	0.4230	0.4228	0.4194	0.0152	0.0145	0.0150	0.0191	0.0206	0.0207	0.1795	0.1582	0.1606
Gas 50 B	0.9902	1.0000	0.9819	-0.0159	-0.0176	-0.0138	0.4984	0.4982	0.4943	0.0233	0.0222	0.0229	0.0267	0.0285	0.0284	0.1741	0.1545	0.1561
Gas 50 C	0.9959	0.9819	1.0000	-0.0225	-0.0241	-0.0206	0.4072	0.4068	0.4029	0.0152	0.0142	0.0148	0.0195	0.0209	0.0211	0.1782	0.1552	0.1588
Kero 50 A				1.0000	0.9975	0.9985	-0.0169	-0.0171	-0.0172	0.5479	0.5501	0.5438	0.2892	0.3079	0.2986	-0.0531	-0.0514	-0.0519
Kero 50 B				0.9975	1.0000	0.9962	-0.0174	-0.0176	-0.0177	0.5404	0.5381	0.5344	0.2991	0.3179	0.3088	-0.0542	-0.0525	-0.0529
Kero 50 C				0.9985	0.9962	1.0000	-0.0167	-0.0168	-0.0169	0.5495	0.5514	0.5452	0.2929	0.3120	0.3026	-0.0514	-0.0496	-0.0501
LT 50 A							1.0000	0.9998	0.9946	-0.0023	-0.0022	-0.0023	-0.0088	-0.0096	-0.0096	-0.0049	-0.0047	-0.0035
LT 50 B							0.9998	1.0000	0.9959	-0.0024	-0.0023	-0.0024	-0.0088	-0.0097	-0.0096	-0.0049	-0.0047	-0.0036
LT 50 C							0.9946	0.9959	1.0000	-0.0025	-0.0023	-0.0025	-0.0089	-0.0097	-0.0097	-0.0049	-0.0047	-0.0036
LF 50 A										1.0000	0.9932	0.9957	0.0407	0.0563	0.0451	-0.0095	-0.0097	-0.0098
LF 50 B										0.9932	1.0000	0.9962	0.0385	0.0537	0.0430	-0.0096	-0.0099	-0.0099
LF 50 C										0.9957	0.9962	1.0000	0.0401	0.0553	0.0446	-0.0097	-0.0099	-0.0099
MFS 50 A													1.0000	0.9958	0.9976	0.0041	0.0120	0.0138
MFS 50 B													0.9958	1.0000	0.9981	0.0099	0.0190	0.0210
MFS 50 C													0.9976	0.9981	1.0000	0.0103	0.0194	0.0214
PT 50 A																1.0000	0.9843	0.9886
PT 50 B																0.9843	1.0000	0.9944
PT 50 C																0.9886	0.9944	1.0000

APPENDIX E

Total Ion Chromatograms of Mixed Ignitable Liquid Standards

In this appendix, representative total ion chromatograms (TIC) are shown for the mixed ignitable liquid standards, neat gasoline: neat kerosene, neat gasoline: 10% evaporated kerosene, neat gasoline: 50% evaporated kerosene, 10% evaporated gasoline: neat kerosene, 50% evaporated gasoline: neat kerosene. The experimental conditions are as described in Chapter 4, Section 4.2.2.

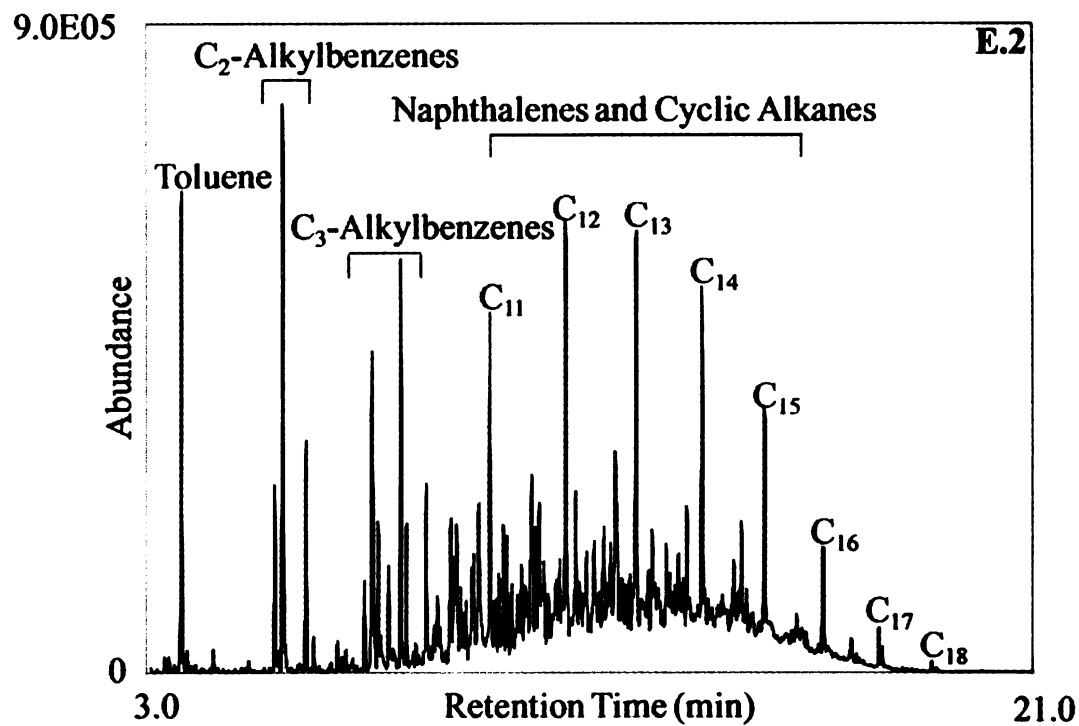
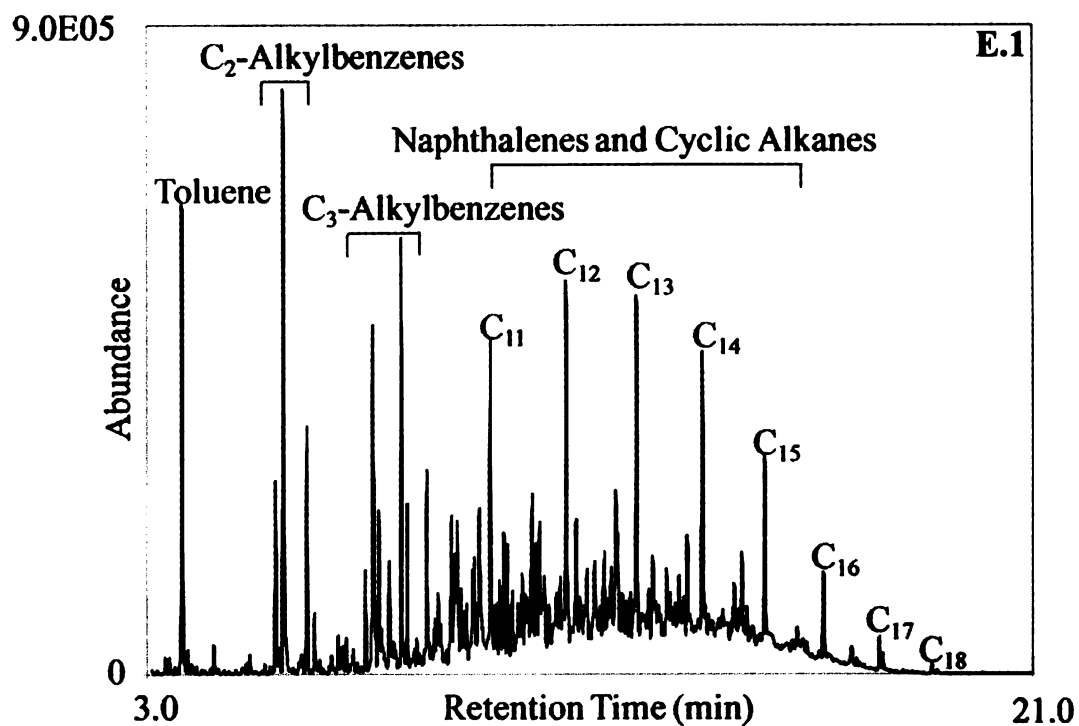


Figure E.1: Chromatogram of neat gasoline: neat kerosene mixture with major components labeled.

Figure E.2: Chromatogram of neat gasoline: 10% evaporated kerosene mixture with major components labeled.

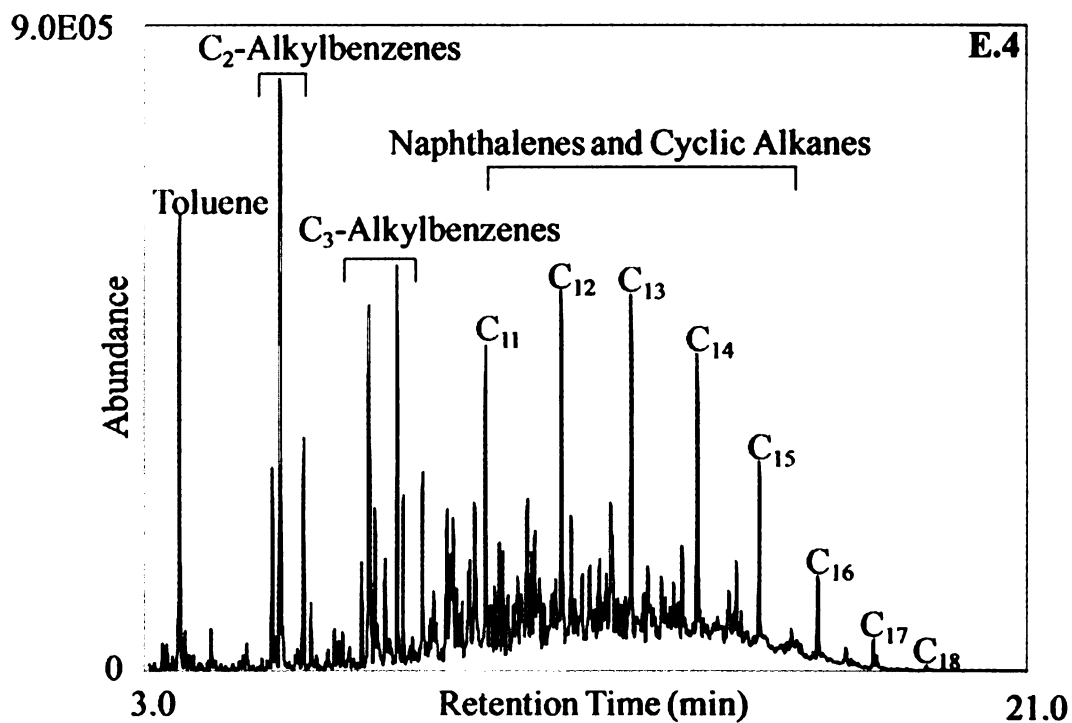
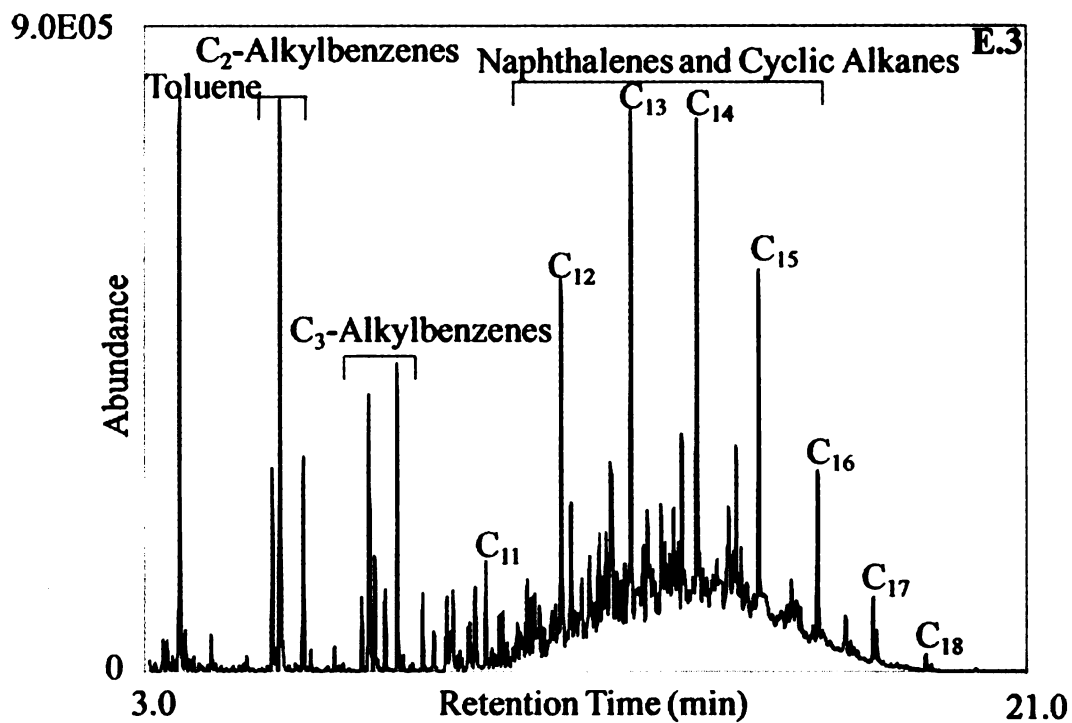


Figure E.3: Chromatogram of neat gasoline: 50% evaporated kerosene mixture with major components labeled.

Figure E.4: Chromatogram of 10% evaporated gasoline: neat kerosene mixture with major components labeled.

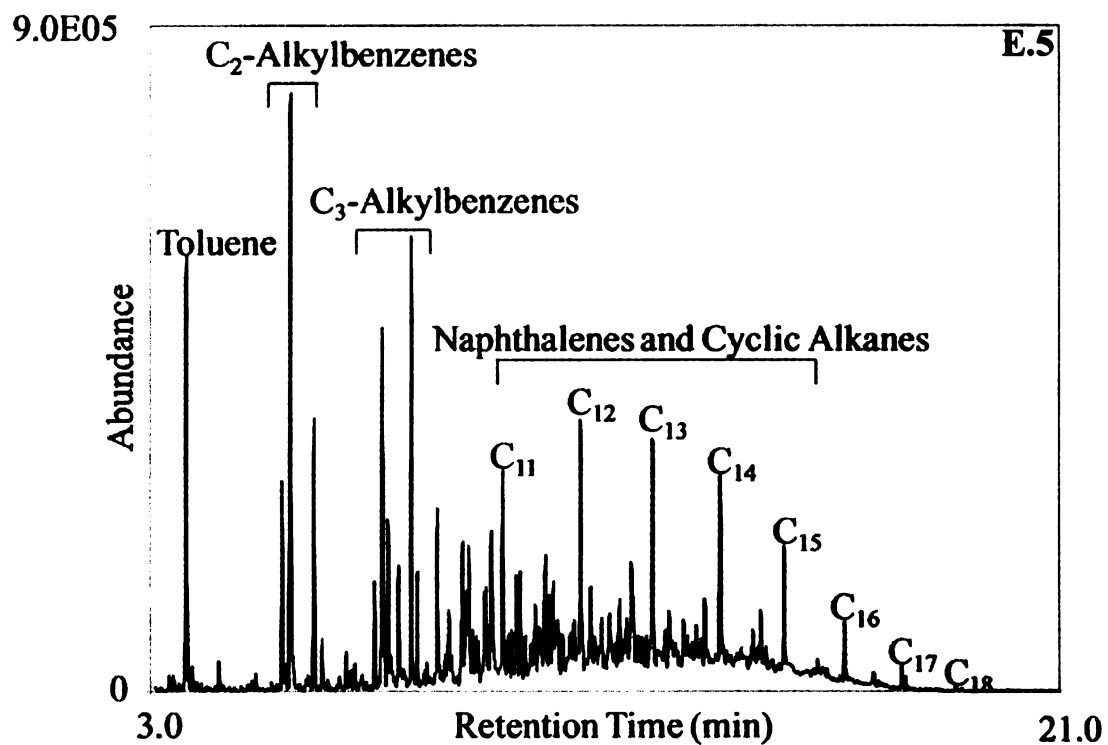


Figure E.5: Chromatogram of 50% evaporated gasoline: neat kerosene mixture with major components labeled.

APPENDIX F

Pearson Product Moment Correlation Coefficients for Total Ion Chromatograms of Burned Carpet, Mixed Liquid Standards, and Burned then Spiked Samples

In this appendix, Pearson product moment correlation (PPMC) coefficients are shown for the burned carpet, the mixed liquids, and the burned then spiked samples, which are burned pieces of carpet spiked with the mixed liquid, as summarized below:

Table F.1: PPMC Coefficients for Replicates (A, B, C) of Burned Carpet (BC) and Mixed Liquid Standards, Neat gasoline: Neat Kerosene (NG:NK), Neat Gasoline: 10% Evaporated Kerosene (NG:10K), Neat Gasoline: 50% Evaporated Kerosene (NG:50K), 10% Evaporated Gasoline: Neat Kerosene (10G:NK). 50% Evaporated Gasoline: Neat Kerosene (50G:NK)

Table F.2: PPMC Coefficients for Replicates (A, B, C) of Burned then Spiked Samples, Neat gasoline: Neat Kerosene Sample (BNG:NK), Neat Gasoline: 10% Evaporated Kerosene Sample (BNG:10K), Neat Gasoline: 50% Evaporated Kerosene Sample (BNG:50K), 10% Evaporated Gasoline: Neat Kerosene Sample (B10G:NK). 50% Evaporated Gasoline: Neat Kerosene Sample (B50G:NK)

Table F.3: PPMC Coefficients for Replicates (A, B, C) of Burned Carpet (BC) and Burned then Spiked Samples, Neat gasoline: Neat Kerosene Sample (BNG:NK), Neat Gasoline: 10% Evaporated Kerosene Sample (BNG:10K), Neat Gasoline: 50% Evaporated Kerosene Sample (BNG:50K), 10% Evaporated Gasoline: Neat Kerosene Sample (B10G:NK). 50% Evaporated Gasoline: Neat Kerosene Sample (B50G:NK)

Table F.4: PPMC Coefficients for Replicates (A, B, C) of Neat Gasoline: 10% Evaporated Kerosene Mixture (NG:10K) and Corresponding Burned then Spiked Samples (BNG:10K)

Table F.5: PPMC Coefficients for Replicates (A, B, C) of Neat Gasoline: 50% Evaporated Kerosene Mixture (NG:50K) and Corresponding Burned then Spiked Samples (BNG:50K)

Table F.6: PPMC Coefficients for Replicates (A, B, C) of 10% Evaporated Gasoline: Neat Kerosene Mixture (10G:NK) and Corresponding Burned then Spiked Samples (B10G:NK)

Table F.7: PPMC Coefficients for Replicates (A, B, C) of 50% Evaporated Gasoline: Neat Kerosene Mixture (50G:NK) and Corresponding Burned then Spiked Samples (B50G:NK)

Table F.1: PPMC Coefficients for Burned Carpet and Mixed Liquid Standards.

	BCA	BCB	BCC	NG:NKA	NG:NKB	NG:NKC	NG:10KA	NG:10KB	NG:10KC	NG:50KA	NG:50KB	NG:50KC	10G:NKA	10G:NKB	10G:NKC	50G:NKA	50G:NKB	50G:NKC
BCA	1.0000	0.9787	0.9347	0.2097	0.2088	0.2108	0.2178	0.2141	0.2126	0.2191	0.2182	0.2163	0.2046	0.2034	0.2003	0.1996	0.2017	0.1993
BCB	0.9787	1.0000	0.8829	0.1801	0.1820	0.1829	0.1898	0.1868	0.1864	0.1863	0.1857	0.1834	0.1749	0.1745	0.1695	0.1694	0.1711	0.1704
BCC	0.9347	0.8829	1.0000	0.2343	0.2288	0.2328	0.2524	0.2456	0.2423	0.2726	0.2710	0.2700	0.2230	0.2216	0.2191	0.2104	0.2118	0.2049
NG:NKA	1.0000	0.9944	0.9975	1.0000	0.9944	0.9975	0.9907	0.9910	0.9892	0.8759	0.8740	0.8698	0.9930	0.9909	0.9899	0.9730	0.9690	0.9651
NG:NKB	0.9944	1.0000	0.9987	0.9944	1.0000	0.9987	0.9844	0.9902	0.9924	0.8762	0.8762	0.8703	0.9908	0.9955	0.9857	0.9693	0.9659	0.9705
NG:NKC	0.9975	0.9987	1.0000	0.9975	0.9987	1.0000	0.9893	0.9928	0.9930	0.8799	0.8791	0.8741	0.9931	0.9949	0.9902	0.9702	0.9668	0.9673
NG:10KA	1.0000	0.9980	0.9948	1.0000	0.9980	0.9948	1.0000	0.9980	0.9948	0.9096	0.9079	0.9049	0.9788	0.9775	0.9768	0.9454	0.9426	0.9338
NG:10KB	0.9980	1.0000	0.9989	0.9980	1.0000	0.9989	0.9980	1.0000	0.9989	0.9106	0.9101	0.9068	0.9807	0.9840	0.9785	0.9457	0.9426	0.9394
NG:10KC	0.9948	0.9989	1.0000	0.9948	0.9989	1.0000	0.9948	0.9989	1.0000	0.9086	0.9089	0.9048	0.9796	0.9863	0.9764	0.9446	0.9411	0.9426
NG:50KA	1.0000	0.9997	0.9991	1.0000	0.9997	0.9991	1.0000	0.9997	0.9991	1.0000	0.9997	0.9991	0.8629	0.8680	0.8634	0.8240	0.8197	0.8175
NG:50KB	0.9997	1.0000	0.9993	0.9997	1.0000	0.9993	0.9997	1.0000	0.9993	0.9997	1.0000	0.9993	0.8614	0.8680	0.8617	0.8206	0.8164	0.8162
NG:50KC	0.9991	0.9993	1.0000	0.9991	0.9993	1.0000	0.9991	0.9993	1.0000	0.9991	0.9993	1.0000	0.8558	0.8630	0.8585	0.8113	0.8065	0.8050
10G:NKA	1.0000	0.9902	0.9938	1.0000	0.9902	0.9938	1.0000	0.9902	0.9938	1.0000	0.9902	0.9938	1.0000	0.9902	0.9938	0.9794	0.9769	0.9742
10G:NKB	0.9902	1.0000	0.9907	0.9902	1.0000	0.9907	0.9902	1.0000	0.9907	0.9902	1.0000	0.9907	0.9902	1.0000	0.9907	0.9640	0.9583	0.9660
10G:NKC	0.9938	0.9907	1.0000	0.9938	0.9907	1.0000	0.9938	0.9907	1.0000	0.9938	0.9907	1.0000	0.9938	0.9907	1.0000	0.9657	0.9598	0.9576
50G:NKA	1.0000	0.9973	0.9933	1.0000	0.9973	0.9933	1.0000	0.9973	0.9933	1.0000	0.9973	0.9933	1.0000	0.9973	0.9933	1.0000	0.9973	0.9933
50G:NKB	0.9973	1.0000	0.9926	0.9973	1.0000	0.9926	0.9973	1.0000	0.9926	0.9973	1.0000	0.9926	0.9973	1.0000	0.9926	0.9973	1.0000	0.9926
50G:NKC	0.9933	0.9926	1.0000	0.9933	0.9926	1.0000	0.9933	0.9926	1.0000	0.9933	0.9926	1.0000	0.9933	0.9926	1.0000	0.9933	0.9926	1.0000

Table F.2: PPMC Coefficients of Burned then Spiked Samples.

	BNG:10KA	BNG:10KBB	BNG:10KC	BNG:50KA	BNG:50KBB	BNG:50KC	B10G:NKA	B10G:NKB	B10G:NKC	B50G:NKA	B50G:NKB	B50G:NKC
BNG:10KA	1.0000	0.9180	0.9824	0.9580	0.9680	0.9615	0.9737	0.9921	0.8658	0.8602	0.7714	0.9701
BNG:10KB	0.9180	1.0000	0.8624	0.9151	0.9099	0.8985	0.9588	0.9267	0.9771	0.9432	0.9211	0.8610
BNG:10KC	0.9824	0.8624	1.0000	0.9321	0.9553	0.9526	0.9314	0.9810	0.8116	0.8117	0.7188	0.9699
BNG:50KA				1.0000	0.9883	0.9862	0.9536	0.9450	0.8417	0.8636	0.7723	0.9273
BNG:50KB				0.9883	1.0000	0.9907	0.9432	0.9616	0.8496	0.8758	0.7883	0.9525
BNG:50KC				0.9862	0.9907	1.0000	0.9397	0.9497	0.8231	0.8413	0.7499	0.9369
B10G:NKA							1.0000	0.9735	0.9152	0.9063	0.8342	0.9368
B10G:NKB							0.9735	1.0000	0.8932	0.8892	0.8123	0.9774
B10G:NKC							0.9152	0.8932	1.0000	0.9536	0.9585	0.8223
B50G:NKA										1.0000	0.9718	0.8703
B50G:NKB										0.9718	1.0000	0.7719
B50G:NKC										0.8703	0.7719	1.0000

Table F.4: PPMC Coefficients of Neat Gasoline: 10% Evaporated Kerosene Mixture and Corresponding Burned then Spiked Samples.

	NG:10K A	NG:10K B	NG:10K C	BNG:10KA	BNG:10KB	BNG:10KC
NG:10K A	1.0000	0.9980	0.9948	0.6258	0.8409	0.5763
NG:10K B	0.9980	1.0000	0.9989	0.6311	0.8486	0.5821
NG:10K C	0.9948	0.9989	1.0000	0.6361	0.8546	0.5869
BNG:10KA				1.0000	0.9180	0.9824
BNG:10KB				0.9180	1.0000	0.8624
BNG:10KC				0.9824	0.8624	1.0000

Table F.5: PPMC Coefficients of Neat Gasoline: 50% Evaporated Kerosene Mixture and Corresponding Burned then Spiked Samples.

	NG:50K A	NG:50K B	NG:50K C	BNG:50KA	BNG:50KB	BNG:50KC
NG:50K A	1.0000	0.9997	0.9991	0.6672	0.6307	0.6448
NG:50K B	0.9997	1.0000	0.9993	0.6679	0.6322	0.6458
NG:50K C	0.9991	0.9993	1.0000	0.6618	0.6245	0.6406
BNG:50KA				1.0000	0.9883	0.9862
BNG:50KB				0.9883	1.0000	0.9907
BNG:50KC				0.9862	0.9907	1.0000

Table F.6: PPMC Coefficients of 10% Evaporated Gasoline: Neat Kerosene Mixture and Corresponding Burned Then Spiked Samples.

	10G:NK A	10G:NK B	10G:NK C	B10G:NK A	B10G:NK B	B10G:NK C
10G:NK A	1.0000	0.9902	0.9938	0.7125	0.6653	0.8803
10G:NK B	0.9902	1.0000	0.9907	0.7157	0.6708	0.8879
10G:NK C	0.9938	0.9907	1.0000	0.7012	0.6536	0.8677
B10G:NK A				1.0000	0.9735	0.9152
B10G:NK B				0.9735	1.0000	0.8932
B10G:NK C				0.9152	0.8932	1.0000

Table F.7: PPMC Coefficients of 50% Evaporated Gasoline: Neat Kerosene Mixture and Corresponding Burned Then Spiked Samples.

	50G:NK A	50G:NK B	50G:NK C	B50G:NK A	B50G:NK B	B50G:NK C
50G:NK A	1.0000	0.9973	0.9933	0.8466	0.9131	0.5854
50G:NK B	0.9973	1.0000	0.9926	0.8445	0.9101	0.5852
50G:NK C	0.9933	0.9926	1.0000	0.8695	0.9346	0.6021
B50G:NK A				1.0000	0.9718	0.8703
B50G:NK B				0.9718	1.0000	0.7719
B50G:NK C				0.8703	0.7719	1.0000

APPENDIX G

Pearson Product Moment Correlation Coefficients for Total Ion Chromatograms of Burned Carpet, Mixed Liquid Standards, and Simulated Ignitable Liquid Residue Samples

In this appendix, Pearson product moment correlation (PPMC) coefficients are shown for the burned carpet, the mixed liquids, and the simulated ignitable liquid residue (ILR) samples, as summarized below:

Table G.1: PPMC Coefficients for Replicates (A, B, C) of Simulated ILR Samples, Neat gasoline: Neat Kerosene ILR Sample (SNG:NK), Neat Gasoline: 10% Evaporated Kerosene ILR Sample (SNG:10K), Neat Gasoline: 50% Evaporated Kerosene ILR Sample (SNG:50K), 10% Evaporated Gasoline: Neat Kerosene ILR Sample (S10G:NK), 50% Evaporated Gasoline: Neat Kerosene ILR Sample (S50G:NK)

Table G.2: PPMC Coefficients for Replicates (A, B, C) of Burned Carpet (BC) and Simulated ILR Samples, Neat gasoline: Neat Kerosene ILR Sample (SNG:NK), Neat Gasoline: 10% Evaporated Kerosene ILR Sample (SNG:10K), Neat Gasoline: 50% Evaporated Kerosene ILR Sample (SNG:50K), 10% Evaporated Gasoline: Neat Kerosene ILR Sample (S10G:NK). 50% Evaporated Gasoline: Neat Kerosene ILR Sample (S50G:NK)

Table G.3: PPMC Coefficients for Replicates (A, B, C) of Neat Gasoline: 10% Evaporated Kerosene Mixture (NG:10K) and Corresponding Simulated ILR Samples (SNG:10K)

Table G.4: PPMC Coefficients for Replicates (A, B, C) of Neat Gasoline: 50% Evaporated Kerosene Mixture (NG:50K) and Corresponding Simulated ILR Samples (SNG:50K)

Table G.5: PPMC Coefficients for Replicates (A, B, C) of 10% Evaporated Gasoline: Neat Kerosene Mixture (10G:NK) and Corresponding Simulated ILR Samples (S10G:NK)

Table G.6: PPMC Coefficients for Replicates (A, B, C) of 50% Evaporated Gasoline: Neat Kerosene Mixture (50G:NK) and Corresponding Simulated ILR Samples (S50G:NK)

Table G.1: PPMC Coefficients of Simulated ILR Samples.

	SNG:10KA	SNG:10KB	SNG:10KC	SNG:50KA	SNG:50KB	SNG:50KC	S10G:NKA	S10G:NKB	S10G:NKC	S50G:NKA	S50G:NKB	S50G:NKC
SNG:10KA	1.0000	0.9128	0.8129	0.8582	0.9050	0.7582	0.9027	0.8413	0.9160	0.9101	0.8809	0.9238
SNG:10KB	0.9128	1.0000	0.9225	0.9082	0.8952	0.6913	0.8450	0.8136	0.9616	0.9836	0.9758	0.9673
SNG:10KC	0.8129	0.9225	1.0000	0.9262	0.9086	0.4632	0.6738	0.5853	0.8107	0.9169	0.9233	0.8545
SNG:50KA				1.0000	0.9619	0.4729	0.6761	0.6127	0.8336	0.9348	0.9456	0.8659
SNG:50KB				0.9619	1.0000	0.5002	0.7117	0.6204	0.8162	0.9035	0.9012	0.8585
SNG:50KC				0.4729	0.5002	1.0000	0.9240	0.9601	0.8321	0.6776	0.6244	0.7963
S10G:NKA							1.0000	0.9582	0.9178	0.8197	0.7879	0.8912
S10G:NKB							0.9582	1.0000	0.9290	0.7988	0.7614	0.8827
S10G:NKC							0.9178	0.9290	1.0000	0.9569	0.9374	0.9767
S50G:NKA										1.0000	0.9865	0.9740
S50G:NKB										0.9865	1.0000	0.9452
S50G:NKC										0.9740	0.9452	1.0000

Table G.2: PPMC Coefficients of Burned Carpet and Simulated ILR Samples.

	BCA	BCB	BCC	SNG:10KA	SNG:10KB	SNG:10KC	SNG:50KA	SNG:50KB	SNG:50KC	SIOG:NKA	SIOG:NKB	SIOG:NKC	SSOG:NKA	SSOG:NKB	SSOG:NKC
BCA	1.0000	0.9787	0.9347	0.8638	0.8780	0.8781	0.9661	0.9467	0.4873	0.7051	0.6304	0.8193	0.8954	0.9115	0.8303
BCB	0.9787	1.0000	0.8829	0.8493	0.9016	0.9097	0.9849	0.9444	0.4793	0.6958	0.6256	0.8346	0.9255	0.9390	0.8556
BC C	0.9347	0.8829	1.0000	0.8214	0.7865	0.7477	0.8432	0.8341	0.5079	0.7252	0.6400	0.7614	0.7836	0.8062	0.7375
SNG:10KA				1.0000	0.9128	0.8129	0.8582	0.9050	0.7582	0.9027	0.8413	0.9160	0.9101	0.8809	0.9238
SNG:10KB				0.9128	1.0000	0.9225	0.9082	0.8952	0.6913	0.8450	0.8136	0.9616	0.9836	0.9758	0.9673
SNG:10KC				0.8129	0.9225	1.0000	0.9262	0.9086	0.4632	0.6738	0.5853	0.8107	0.9169	0.9233	0.8545
SNG:50KA							1.0000	0.9619	0.4729	0.6761	0.6127	0.8336	0.9348	0.9456	0.8659
SNG:50KB							0.9619	1.0000	0.5002	0.7117	0.6204	0.8162	0.9035	0.9012	0.8585
SNG:50KC							0.4729	0.5002	1.0000	0.9240	0.9601	0.8321	0.6776	0.6244	0.7963
SIOG:NKA										1.0000	0.9582	0.9178	0.8197	0.7879	0.8912
SIOG:NKB										0.9582	1.0000	0.9290	0.7988	0.7614	0.8827
SIOG:NKC										0.9178	0.9290	1.0000	0.9569	0.9374	0.9767
SSOG:NKA													1.0000	0.9865	0.9740
SSOG:NKB													0.9865	1.0000	0.9452
SSOG:NKC													0.9740	0.9452	1.0000

Table G.3: PPMC Coefficients of Neat Gasoline: 10% Evaporated Kerosene Mixture and Corresponding Simulated ILR Samples.

	NG:10K A	NG:10K B	NG:10K C	SNG:10KA	SNG:10KB	SNG:10KC
NG:10K A	1.0000	0.9980	0.9948	0.4757	0.4210	0.1832
NG:10K B	0.9980	1.0000	0.9989	0.4682	0.4151	0.1824
NG:10K C	0.9948	0.9989	1.0000	0.4619	0.4109	0.1818
SNG:10KA				1.0000	0.9128	0.8129
SNG:10KB				0.9128	1.0000	0.9225
SNG:10KC				0.8129	0.9225	1.0000

Table G.4: PPMC Coefficients of Neat Gasoline: 50% Evaporated Kerosene Mixture and Corresponding Simulated ILR Samples.

	NG:50K A	NG:50K B	NG:50K C	SNG:50KA	SNG:50KB	SNG:50KC
NG:50K A	1.0000	0.9997	0.9991	0.1800	0.2348	0.8051
NG:50K B	0.9997	1.0000	0.9993	0.1792	0.2342	0.8037
NG:50K C	0.9991	0.9993	1.0000	0.1772	0.2328	0.8141
SNG:50KA				1.0000	0.9619	0.4729
SNG:50KB				0.9619	1.0000	0.5002
SNG:50KC				0.4729	0.5002	1.0000

Table G.5: PPMC Coefficients of 10% Evaporated Gasoline: Neat Kerosene Mixture and Corresponding Simulated ILR Samples.

	10G:NK A	10G:NK B	10G:NK C	S10G:NKA	S10G:NKB	S10G:NKC
10G:NK A	1.0000	0.9902	0.9938	0.5028	0.6099	0.4871
10G:NK B	0.9902	1.0000	0.9907	0.5055	0.6137	0.4904
10G:NK C	0.9938	0.9907	1.0000	0.5104	0.6189	0.4901
S10G:NKA				1.0000	0.9582	0.9178
S10G:NKB				0.9582	1.0000	0.9290
S10G:NKC				0.9178	0.9290	1.0000

Table G.5: PPMC Coefficients of 50% Evaporated Gasoline: Neat Kerosene Mixture and Corresponding Simulated ILR Samples.

	50G:NK A	50G:NK B	50G:NK C	S50G:NKA	S50G:NKB	S50G:NKC
50G:NK A	1.0000	0.9973	0.9933	0.3282	0.3105	0.4191
50G:NK B	0.9973	1.0000	0.9926	0.3297	0.3117	0.4203
50G:NK C	0.9933	0.9926	1.0000	0.3218	0.3043	0.4061
S50G:NKA				1.0000	0.9865	0.9740
S50G:NKB				0.9865	1.0000	0.9452
S50G:NKC				0.9740	0.9452	1.0000

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