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Aisha Tamara Barnes

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Master of Science degree in Forensic Science

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COMPARISON OF GASOLINES USING GAS CHROMATOGRAPHY/MASS SPECTROMETRY AND TARGET ION RESPONSE

By

Aisha Tamara Barnes

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ABSTRACT

COMPARISON OF GASOLINES USING GAS CHROMATOGRAPHY/MASS SPECTROMETRY AND TARGET ION RESPONSE

By

Aisha Tamara Barnes

Gas chromatography/mass spectrometry was used to compare gasoline samples obtained from different sources based on the difference in response of the ion detector to the target ions of certain components found in gasoline. Many suspected arson cases involve comparing an accelerant extracted from fire debris to an ignitable liquid found in a suspect's possession to determine if it could have been used in the fire. These types of comparisons are currently based on pattern recognition and component identification and do not take into account the variation that exists in some commonly used accelerants such as gasoline. Fifty and seventy-five percent-evaporated gasoline samples were both found to contain similar ratios of certain components when compared to the same source gasoline unevaporated. This research proposes ratios to be used to determine if an unevaporated gasoline sample could have originated from the same source as an evaporated gasoline extract from fire debris. The results of the comparisons in this study demonstrate that for cases involving gasoline as the accelerant, that has been evaporated up to 50% and extracted from pine, it is possible to eliminate comparison samples as originating from the same source. The results of the 75% comparisons suggest it may be possible to apply the same type of comparison to cases involving 75% evaporated gasoline.

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Chapter One: Introduction

In many suspected arson cases, the presence of an ignitable liquid may be detected in fire debris. Often times a comparison ignitable liquid, possibly found in a suspect's possession, is submitted to the testing laboratory to determine if it is of the same type as that found in the fire debris. The strongest associations fire debris chemists can make regarding the debris and ignitable liquid are based on pattern recognition and component identification through use of gas chromatography coupled to a mass spectrometer (GC/MS).

Since gasoline is the accelerant in a large percentage of arson cases, more definitive methods of determining whether a suspected gasoline possibly originated from the same source as that found in the fire are necessary. It is widely known that different gasoline companies add patented performance markers to their gasoline that distinguish it from other gasoline, but that information is proprietary and the markers are present in only minute concentrations.[1] However, there are many other measurable ways in which gasoline produced by oil refineries can differ as a result of chemical conversion methods, treatment and reformulation processes, blending, and storage. Moreover, once a new shipment is sent out to a gasoline station, the newly refined gasoline is mixed with the residual gasoline still in the pumps, further lending to the possibility of distinguishing gasoline from different sources.

Nevertheless, comparing gasoline found in debris to unevaporated gasoline is more complicated than analyzing gasoline alone. Fire debris does not contain an uncontaminated ignitable liquid, but rather many compounds that can contribute to (or interfere with) the chromatogram and make comparison to the same gasoline unevaporated very difficult. Materials such as synthetic carpets, found in debris from residential fires, produce pyrolysis products of the same type as some components normally found in the chromatogram of gasoline alone, such as ethylbenzene, m- and p-xylenes, and isopropylbenzene. Wood products such as pine are also commonly found in residential fires[2], yet their pyrolysis products have retention times that do not interfere with those of gasoline, leaving many components of gasoline unadulterated and useful for comparison purposes.

Research demonstrates that gasoline from different sources will vary in the abundance of its components when injected into the gas chromatograph (GC).[3-4] Furthermore, by calculating ratios of sequential peak components in gasoline, differences can be detected. This study proposes a method of differentiating gasoline by comparing the ratios of certain components present in the headspace of unevaporated and evaporated gasoline to gasoline from different sources. The results of this study demonstrate it is possible to eliminate gasoline samples as originating from the same source and should not be used to suggest with certainty that two gasoline samples originated from the same source. In addition, the results indicate it is feasible to include a sample as a possible source of an evaporated gasoline sample.

Background Information

Previous work by Dale Mann demonstrated that by using capillary GC, the peak ratios and chromatograms obtained from the C5 to C8 region of gasoline vary among different sources.[4] In his first paper he compared eight corresponding peak ratios by first overlaying relevant peaks to see if they were superimposable. Next, he did a quantitative comparison on non-superimposable peaks by dividing the peak area of the peaks of interest by reference compounds to get ratios such that gasoline from the same source yielded similar ratios.

His second paper looked at difficulties in applying his comparison methods to cases involving gasoline headspace.[5] He used his method to compare the headspace of unevaporated gasoline to that of gasoline up to 40% evaporated, using heated headspace as his sampling method. He noted that samples involving gasoline evaporated more than 40% resulted in a lack of enough usable peaks in the C5-C8 region of the chromatogram from GC. He also found that certain materials yielded pyrolysis products in the region of interest when a sample of fire debris headspace was injected, interfering with making gasoline headspace to fire debris headspace comparisons. Nevertheless, he established that comparing sequential peak ratios of the components in gasoline using GC is useful in discriminating gasoline samples through application of his method to case studies.

Although fundamental to the comparison of gasoline, Mann's methods had many limitations. Mann had not incorporated a mass spectrometer into his gasoline analysis scheme. With GC/MS, not only is the gasoline separated into its individual components, but the mass spectrometer allows for the examiner to identify and classify the individual hydrocarbons present in gasoline, moving away from simple pattern recognition and retention time as an indication of where individual components elute. Also, Mann did his ratio calculations by hand, which was very time consuming and increased the likelihood of human error. Therefore, he could not analyze a wider range of possible ratios available from the gasoline components.

Many of these limitations were evaluated in the research done by Julia Dolan and Christopher Ritacco.[6] They compared liquid gasoline from different sources using

GC/MS with an autosampler and computer software to calculate sequential peak ratios based on target compound response. Using a Target Compound Program available from Hewlett Packard, peaks of interest and the relative abundance of their target ions were input based on parameters identified from a liquid gasoline standard. The relative abundance data was then imported into Microsoft Excel, which was set up to compute sequential peak ratios, standard deviation, and percent standard deviation of replicate runs of the same gasoline.

They originally started out with 87 possible ratios and narrowed the scope by eliminating ratios that remained similar among different gasolines, ratios that were not reproducible among replicate runs of the same gasoline, and ratios that did not reproducibly integrate or resolve among replicate runs. With this data, they were able to narrow their focus to 20 peak ratios that yielded distinguishable ratios among gasoline from different sources, yet remained similar among gasoline of the same source when compared to unevaporated, 25%, and 50% evaporated gasoline from the same source. The research of Dolan and Ritacco established that ratios used in the comparison of gasoline could be generated using components throughout the chromatogram of gasoline, not limited to the C5 to C8 region as proposed by Mann. This research is an ongoing project, and thus far they have been able to discriminate 44 different gasolines from various states in the U.S. through liquid-to-liquid comparisons (straight injections) evaporated up to 50%. This method has been validated and used by the Bureau of Alcohol, Tobacco, and Firearms (BATF) in cases involving liquid-to-liquid gasoline comparisons.

The Problem to be Studied

Regardless of the ability to differentiate liquid gasoline samples, some arson cases will involve the comparison of collected debris in a sealed paint can to an ignitable liquid believed to have been used in the fire. Currently, the most common way to analyze fire debris involves extracting a sample of the volatile material onto an adsorbent surface, which can be concentrated with a solvent and analyzed using GC/MS.[7] This chromatogram is then compared to an injection of a comparison ignitable liquid (when available) or to the laboratory's standards of ignitable liquids. If the debris is found to contain gasoline through pattern and component recognition and the comparison liquid is determined to be gasoline, a relationship can be established between the two regardless of the possibility of different origins. These current methods do not take into account the variation that exists among gasoline.

In this study, using GC/MS and the sequential peak ratio method developed by Dolan and Ritacco, the headspace of evaporated gasoline extracted from fire debris will be associated with the headspace of the same unevaporated gasoline. Higher evaporated gasoline (not extracted from debris) will be compared to unevaporated gasoline from the same source to test out the possibility of using these methods on highly evaporated gasoline. If these ratios are statistically similar, then they can be compared to different gasoline sets of unevaporated and evaporated samples such that gasoline from varying sources can be discriminated. Therefore, the research questions proposed are: does the headspace of gasoline from the same source unevaporated and 50% evaporated on debris contain statistically similar ratios of its components, and are these ratios different when the gasoline is from a different source? The same questions will be addressed using 75%

evaporated gasoline without debris addition. In researching this question, the presence of the wood substrate will be analyzed to see if it complicates the association. Lastly, the comparison methods will be utilized to possibly exclude unevaporated gasoline samples as originating from the same source as an evaporated extract from fire debris (50% evaporated gasoline) or clean substrate (75% evaporated gasoline).

Considering that there are four major methods of headspace sampling carried out by fire debris chemists before injection into GC/MS, a decision of which method yields the most reproducible data must first be established. In this study, headspace and static adsorption/elution methods are shown to be appropriate methods whereby adequate representation of the components in gasoline can be obtained for comparison using GC/MS.

In order to answer the research questions, optimal sample size and operating conditions must be established to be able to analyze gasoline headspace using GC/MS. Furthermore, the sampling methods used must demonstrate highly reproducible ratios of the same components during replicate runs. Enough replicate runs must be run to display can to can variation of the same sample, sampling error, and reproducibility as a result of the method chosen. It is also necessary to deduce the best way to simulate fire debris. Moreover, a suitable substrate on which to put unevaporated gasoline that will not interfere in its analysis must be chosen.

Subsequently, it must also be established that even with pyrolysis products present in the chromatogram, the ratios of the useful components in gasoline from the same source must remain similar. Therefore, a material commonly found in arson cases that does not interfere with the comparison of useful components in gasoline headspace must be used. Moreover, the useful components in gasoline headspace must be determined and a mathematical analysis performed that demonstrates their utility for comparison purposes. All optimization parameters will be demonstrated on 50% evaporated gasoline. Upon confirmation that 50% evaporated gasoline can be associated to its unevaporated counterpart, 75% evaporated gasoline will be correlated to gasoline of the same source unevaporated and compared among different sources without the introduction of fire debris. This last step serves to exhibit the possibility that highly evaporated gasoline contains enough components that a useful comparison can be done.

Purpose of the Study

As mentioned, the ability to discriminate among gasoline sources even though evaporated and present in fire debris would be highly beneficial in cases where a comparison gasoline sample has been obtained. It can serve to rule out samples as originating from the same source as the gasoline found in the debris, or include a gasoline sample as a possible source.

This research will prove very advantageous to the investigation of arson. Since this research was performed in conjunction with the BATF, it could result in the implementation of a new protocol in the analysis of arson evidence and possibly explosion cases. Lastly, this study offers instrument parameters, sampling methods, and a simple mathematical approach that can be successfully utilized to determine whether a sample of evaporated and unevaporated gasoline could have or could not have originated from the same source.

Hypothesis

Upon development of suitable sampling methods to use for 50% and 75% evaporated gasoline that yield reproducible results, it is expected that correlating 50% evaporated gasoline extracted from debris to the same source gasoline unevaporated is possible. Mann's work demonstrated that such an association is possible using the headspace of gasoline up to 40% evaporated extracted from debris.[4-5] Since he only looked at a limited part of the gasoline chromatogram, the 50% comparisons using peaks throughout the chromatogram should also work. Also, the debris type chosen for this study has been found not to interfere with components normally found in gasoline. Secondly, the research done by Dolan and Ritacco using liquid injections of gasoline demonstrated that liquid gasoline up to 50% evaporated could correctly be associated with the same source unevaporated gasoline, further lending confidence that the same association between such gasoline's headspace is possible.[6]

None of the previous research was able to correctly relate gasoline evaporated up to 75% to the same unevaporated gasoline, and thus the decisions on the result of such tests are based upon the reproducibility of the sampling method. It is expected that the sampling method used on 50% evaporated gasoline will not work efficiently on 75% evaporated gasoline because there will be greater evaporative loss of the highly volatile components for higher evaporated gasoline. Therefore, using a method that is reproducible but still yields a sufficient amount of peaks for comparison purposes should result in an association between same source gasolines, especially considering that in this study, the 75% evaporated gasoline will not be extracted from debris (no interference). It is also expected that the peaks used for comparison purposes of the 50% evaporated gasoline will not all be the same peaks useful in linking 75% evaporated gasoline to unevaporated gasoline from the same source. This is because the chromatogram of 75% evaporated gasoline will have a higher concentration of hydrocarbons in the later eluting region and thus will be shifted to the right in comparison to that of 50% evaporated gasoline (see Appendix III).

Limitations

The burning process used to simulate fire debris was performed under a hood until each piece appeared charred. Since the burning took place under a hood, it was understood that some pyrolysis products would constantly be lost between burning and sealing the can the debris were placed in.

This study uses gasoline undergoing controlled environmental evaporation up to 75% to represent evaporated gasoline in fires. This does not take into account the evaporative nature of gasoline if present in a real fire, which burns in an uncontrolled nature. Also, in a real fire, gasoline is evaporated mostly by burning and can be evaporated more than 90%.[8]

Another limitation is the available knowledge about the background of the gasoline used in the study. It is known from what station and city the gasoline was purchased, but the terminal from where the gasoline was picked up before it was deposited to particular stations is unknown. Consequently, it is not known whether a comparison is being attempted between gasoline that has come from the same production batch, refinery, or terminal.

The substrate choice for the simulation of debris is another limitation in that the information from this study is only applicable to cases involving pine in the debris, or other softwoods that yield the same pyrolysis products. There are many other common debris types found in residential and commercial fires in addition to pine, which are not addressed in this study.

Refining Gasoline from Crude Oil

The ability to differentiate gasoline has its basis in the process that produces gasoline—the refinery of crude oil. Gasoline, a product derived from crude oil, is a mixture of volatile hydrocarbons composed of paraffins (alkanes), naphthenes (cycloalkanes), olefins (alkenes), and aromatics. Crude oil is naturally made material found in the ground that contains a mixture of oxygen, carbon, hydrogen, nitrogen, sulfur, metals, and salts. Since no two crude oils are exactly identical in composition and nature, variation exists between batches of gasoline produced from different crude oil. Furthermore, the refinery process varies among refineries, adding more variation to the final products that result from their processes.[1]

Gasoline is produced in refineries and sent via pipeline or barge to various terminals in cities throughout the U.S. depending on where that particular refinery sends their gasoline. The gasoline used in this study was obtained from various cities in the state of Maryland along with a sample from Virginia and Pennsylvania (see Table 1.1). The refineries responsible for supplying gasoline to these states are located in Delaware, Pennsylvania, New Jersey, and Texas.[9]

Table 1.1 Gasoline Information for 50% Comparisons (Left) and 75% (Right)

Gasoline #	Station Name and Octane Number	Obtained From	Gasoline #	Station Name and Octane Number	Obtained From
1	Citgo 89	Randallstown, MD	1	Citgo 87	Wheaton, MD
2	Amoco 89	Wheaton, MD	2	Exxon 87	Rockville, MD
3	Sunoco 89	Wheaton, MD	3	Sunoco 89	Wheaton, MD
4	Citgo 87	Glenwood, MD	4	Citgo 87	Manassas Park, VA
5	Exxon 89	Randallstown, MD	5	Exxtra Mart 87	Upper Marlboro, MD
6	Exxon 87	Rockville, MD	6	Mobil 87	Glenmont, MD
7	Exxtra Mart 87	Upper Marlboro, MD	7	Amoco 87	Randallstown, MD
8	Exxon 93	Gaithersburg, MD	8	Exxon 89	Randallstown, MD
9	Exxon 87	Bethesda, MD	9	Exxon 87	Gaithersburg, MD
10	Citgo 87	Manassas Park, VA	10	Exxon 93	Gaithersburg, MD
11	Amoco 87	Owings Mills, MD			
12	Amoco 93	Harrisburg, PA			
13	Exxon 87	Baltimore, MD			
14	Mobil 87	Glenmont, MD			
15	Amoco 87	Randallstown, MD			
15	Amoco 87	Randallstown, MD			
16	Exxon 87	Gaithersburg, MD			

The first process involved in refining crude oil into gasoline is a separation process in which crude oil is heated, vaporized, and partitioned according to boiling point.[10] Through such processes as distillation (separation based on boiling point), crystallization (separation based on melting point and solubility), solvent extraction (aromatic compounds removed), adsorption (removal of heavier hydrocarbons), and absorption (purifies lighter hydrocarbons), the crude oil will separate into light, medium, and heavy fractions and be sent to different areas of the refinery for further processing. Because these separation processes vary among refineries, variation can be seen in products like gasoline that result from a blending of these materials. Moreover, because the materials at this step are highly volatile, the low molecular weight components of gasoline will contain majority of the differences when compared to gasoline produced by a different refinery.

The next step involves a chemical conversion of the components. There are three major processes involved: cracking, polymerization/alkylation, and reforming.[11] Cracking breaks large hydrocarbons into lighter ones and can involve the use of catalysts, hydrogen, and pressure to aid the breakdown process. For example, fluid catalytic cracking uses high temperature (up to 538° Celsius), low pressure, and a powdered catalyst to produce gasoline. Hydrocracking uses lower temperatures, higher pressure, hydrogen, and a catalyst to convert medium to heavy gas oils into gasoline and jet fuel.[12]

Polymerization and alkylation involve taking the byproducts of the cracking process and combining them to make gasoline. Polymerization refers to the combination of molecules to form higher molecular weight molecules. Alkylation results in production of high-octane hydrocarbons that are blended with gasoline to improve octane rating (reduce knocking) and involves combining olefins and paraffins. Octane rating refers to how much gasoline can be compressed before it causes knocking, gasoline ignited due to compression.[13]

Reforming refers to the process of forming higher-octane hydrocarbons (mostly aromatics) by rearranging molecular structures. The higher octane number is a result of using higher reforming temperatures to convert paraffins to olefins. Dehydrocyclization, dehydrogenation, hydrocracking, and isomerization (all with the aid of hydrogenation-dehydrogenation catalysts) are the chemical processes occurring during reforming. Dehydrocyclization involves the removal of hydrogen (dehydrogenation) from straight-chain paraffins to form rings in the hydrocarbon structure. Hydrocracking involves using high pressure and temperature to break long chain paraffins into smaller chains in the presence of hydrogen. Isomerization is the conversion of straight-chain paraffins to branched chain paraffins. Isomerization is utilized to produce some of the hydrocarbons used in the alkylation process. Isomerization also forms products that can be heated under high pressure to form products with a boiling point in the gasoline range.[1]

The next step involves treating the chemically processed fractions to remove impurities such as oxygen, nitrogen, sulfur, water, dissolved metals, some alkenes, and inorganic salts. The use of drying agents removes water from the processed fractions. Sulfuric acid is used to remove alkenes, nitro and oxygenated compounds, tars, and asphalt if present. Most of the contaminating sulfur compounds are converted to hydrogen sulfide and mercaptans (R-SH) during the processing of crude oil to assist in their removal. There are numerous methods available to remove sulfur compounds and can involve the use of chemicals, catalysts, or adsorption onto materials.[1,12]

The next step involves blending the fractions to form different grades of gasoline. What to blend is based on specifications such as octane level, where the gas will be used, the season the gas is used (i.e. summer versus winter), vapor pressure ratings, and other specifications as determined by the government. Lastly, performance additives and dyes are added, which can be used to distinguish the different types of gasoline from those of other gasoline stations.[1]

Chapter Two: Instrumentation

Capillary Gas Chromatography

Gas chromatography (GC) is used to separate complex mixtures into their individual components. The method relies on the principle of partition chromatography, which refers to the competition between the mobile phase and stationary phase for the substance to be separated, the analyte. In GC, the mobile phase is a gas and the stationary phase is a liquid adsorbed onto an inert solid inside a column. The separation takes place because the analyte partitions between the mobile and stationary phase to varying degrees such that constituents of the analyte that are weakly retained in the stationary phase will move quickly through the column.[14] The difference in mobility throughout the column results in a difference in times of the components of the analyte leaving the column and being detected. The time it takes for each component of the analyte to reach the detector upon the analyte being injected into the GC is called its retention time. The output of a GC is a chromatogram. It contains peaks, which represent the components of the analyte, their abundance, and their retention time.

The instrument's main components include an injection port, column, and detector. The sample is introduced to the GC at the injection port, where it must be vaporized because, as mentioned previously, the mobile phase is a gas, and the analyte must also be a gas also to be carried through the column. The mobile phase therefore is a carrier gas and thus must be chemically inactive so it does not react with the substance to be separated. In this study, helium was used as the mobile phase. Because the analyte is vaporized in the injection port, it must be set to a temperature slightly higher than the boiling point of the least volatile component in the sample to ensure everything becomes volatile before entering the column.

Depending on how much sample is necessary to be carried through the column and reach the detector, the injector port can be operated in split or splitless mode. In this study, split mode was used to avoid flooding the column. Split mode only allows a portion of the analyte injected to enter the column while the rest is removed via a valve in the injection port. This mode is designated by a ratio input by the user. The splitless method allows all of the analyte to enter the column.

The term *capillary* GC refers to the type of column used in the GC. Capillary columns have a small diameter and can have their walls covered with liquid stationary phase or a layer of support material and then stationary phase. Capillary columns are normally found wound into coils in the GC. The column sits in an oven which can be programmed to increase in temperature over time. This is useful for instances in which the analyte is composed of components with a wide boiling point range, such as gasoline. Smaller components will vaporize at a lower temperature and consequently move through the column quicker compared to heavier components.

Electron Ionization Mass Spectrometry

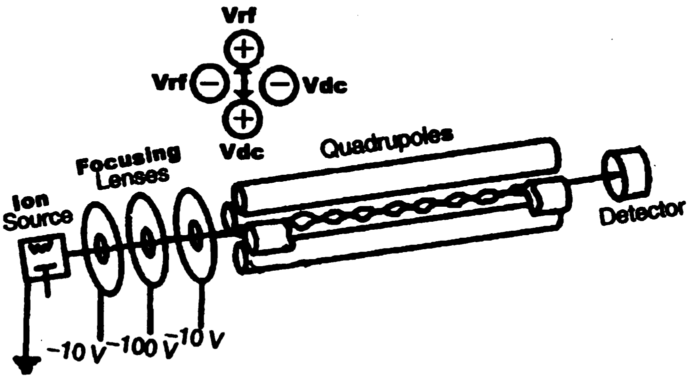
The mass spectrometer (MS) is used as a detector for the GC. The components of the analyte that have been separated by GC will each pass into the MS to be detected and a mass spectrum will be generated for each component. The mass spectrum is a series of peaks representing the ionized molecule (in some cases) and fragmentations of it, plotted as relative abundance (y-axis) versus mass-to-charge ratio (x-axis).

The mass spectrometer is composed of an ionization source, mass analyzer, ion detector, and a computer to process the data. The ionization source, mass analyzer, and ion detector all must be housed in a low pressure environment to prevent the ionized fragments that are formed from colliding with other gas phase molecules on the way to the ion detector.

In order for the analyte, that has been separated in the GC, to be detected, it must first be ionized (acquire a net electric charge). The ionization source in electron ionization is electrons coming from a heated filament, which are accelerated in a direction perpendicular to the inlet of the gas phase analyte. These high-energy electrons can pass close enough to the gaseous analyte molecules that they impart some of their energy, causing the gaseous analyte to become ionized. There is usually enough energy remaining from the interaction with the electrons that the ionized analyte molecule can lose more electrons or undergo fragmentation, which causes numerous peaks in the mass spectrum that can be interpreted to give structural information about the original molecule.[15]

The ionized analyte molecule and its fragments are then sorted on the basis of their mass-to-charge ratio by a quadrupole mass analyzer. The quadrupole mass analyzer is comprised of four parallel rods and focusing lenses which aim the ions toward the rods.

Figure 2.1 Quadrupole Mass Spectrometer: Ion Source, Mass Analyzer, and Detector.[15]



There is frequency modulated current (V_{rf}) and a voltage of direct current (V_{dc}) being passed through the poles such that the two poles in the z-axis have a V_{rf} and V_{dc} signal that is 180° out of phase with the V_{rf} and V_{dc} signal in the x-axis.[15] The potential at any point inside the quadrupole is constantly changing such that an ion within a desired mass range undergoes stable oscillations as it moves through the poles. When the voltages change between the quadrupoles, only ions with a mass that falls within the stability region can pass through the poles. Those ions outside the selected mass range will undergo unstable oscillations as a result of an increased force on the molecule, causing them to hit the quadrupoles as they attempt to pass through to the detector. Therefore, by changing the voltages passing through the rods, selected masses are allowed to pass through the quadrupoles and be detected.

Once the ions pass through the poles they reach the ion detector. There are various types of detectors available, but in general, their goal is to transform the sorted ions into a usable signal. The detector used in this study was an electron multiplier. The electron multiplier works by first emitting secondary particles as a result of ions hitting a curved plate known as a dynode. There are several dynodes in the electron multiplier and the secondary particles hit another dynode with enough energy causing electrons to be released. The electrons then hit a series of dynodes causing more and more electrons to be discharged. The amplification factor can reach up to 10^7 electrons produced each time a dynode is struck.[15] In the end, numerous electrons are created, resulting in a computable current, whose signal is a representation of the ions leaving the quadrupole mass analyzer. An analog-to-digital converter changes the analog voltages into digital voltages that can be read by the computer and transformed into usable output. The computer will display a mass spectrum for each component that has entered the MS and usually contains a library of spectra to which to compare it for identification purposes.

Chapter Three: Forensic Methods of Accelerant Separation and Concentration from Fire Debris

The detection of an ignitable liquid at a fire scene is a strong indicator for arson when the liquid is not normally found at the fire scene. If an accelerant was used, it is often highly evaporated by the time fire debris evidence is collected and must be extracted out of the debris for analysis. There are several methods available to fire debris chemists to separate and concentrate ignitable liquid residues from fire debris such as steam distillation, headspace sampling, solvent extraction, and static adsorption/elution. Each varies in preparation time, extraction efficiency for certain petroleum distillates, and use in the field. Therefore, extraction and separation methods must be dependent upon the type of accelerant suspected.

One of the most common extraction techniques used on a variety of petroleum distillates due to its high sensitivity is the static adsorption/elution technique.[7] Other techniques utilized by fire debris chemists that are less sensitive to a wide hydrocarbon range include headspace sampling and solvent extraction. Headspace sampling, solvent extraction, and static adsorption/elution are discussed below and were chosen for the study because they are commonly used techniques by the BATF.

Headspace Sampling

Headspace analysis requires that fire debris be contained within a sealed vessel for a sufficient amount of time such that a representative sampling of what is contained within the debris is in the vapor above the debris. Once this equilibrium is established, a sample of the headspace is removed and analyzed. This method tends to favor the low molecular weight, highly volatile components in the debris because they have a high vapor pressure and vaporize readily. The high molecular weight components have a lower vapor pressure due to an increased strength of the intermolecular forces between the molecules comprising them and do not vaporize as easily.[16] Headspace sampling is ideal in situations where a highly volatile accelerant, such as gasoline, is present and a high concentration of the low molecular weight components is sought.

To look at some of the less volatile components of an accelerant in a fire debris sample, the vessel can be heated. Vapor pressure increases with temperature, so by heating the container the less volatile molecules become more energetic and can escape into the vapor phase easier. Nevertheless, both headspace and heated headspace methods show a higher concentration of the low molecular weight, highly volatile components in the debris headspace, and thus should only be used when accelerants with a generally high vapor pressure are suspected. Moreover, both methods are non-destructive, allow for repeat analysis, have fairly reproducible results, and are commonly used screening techniques.

Solvent Extraction

Since all vapor concentration methods tend to under represent the less volatile, heavier components, solvent extraction is a useful technique when heavier petroleum ignitable liquids are involved. Solvent extraction is primarily used in instances when a nonporous sample has been collected to determine the presence of an accelerant. In solvent extraction, the debris is washed with a solvent such as pentane or carbon disulfide, and the solvent extract concentrated by evaporating to a small volume and analyzed by a chromatographic technique. Since solvent extraction can be destructive, the sample may not be useful for further analysis. Therefore, this method should be done last in an analysis scheme and some of the original material should be preserved for other analytical techniques.

A problem with solvent extraction is that other contaminants can also be extracted, interfering with pattern recognition of an ignitable liquid. Also, during the extract concentration step, some ignitable liquid can also evaporate. Nevertheless, solvent extraction extracts heavy and light components with the same efficiency so it is useful to differentiate between heavy petroleum distillates.[17]

Static Adsorption/Elution

Static adsorption/elution using activated charcoal is one of the most widely used separation techniques due to its increased sensitivity over the other methods, non-destructive nature, and ease of preparation. Activated charcoal is created by grinding up charcoal, washing it with carbon disulfide, and drying and activating (at 50° and 120° C) the charcoal under vacuum.[7] Static adsorption/elution is a technique in which fire debris is sealed in an airtight container with an activated charcoal strip suspended from the lid. The container is then heated in an oven for a sufficient amount of time (from 4-24 hours). It is important not to overheat the container because the less volatile components tend to displace the more volatile components from the charcoal strip over time. The strip is then removed and washed with a solvent, usually carbon disulfide, and the solvent extract injected into the GC/MS. The typical chromatogram generated by this method will be shifted to the right compared to headspace sampling chromatograms due to more complete recovery of the heavy components. During incubation, replacement of high volatiles occurs by heavier, less volatile components over time, so incubation time can be varied depending on the results expected.[17]

Chapter Four: Development of Experiment Parameters

Instrumental Conditions

All analyses were performed on an Agilent 6890 GC coupled to a 5973 MS operated at 20/1 split ratio. The GC/MS was equipped with a 60m DB-1 column with a .25mm internal diameter and 1µm film thickness. The oven temperature was programmed from 35°C for 2 minutes, followed by a temperature ramp of 5°C/minute to 110°C, then to 250°C at 12° C/minute. The scanning mode for the MS was 29 to 200 amu's.

The instrument also had an autosampler that could be used to automatically inject liquid samples. This was useful for solvent extraction and static adsorption/elution techniques in which solvent extracts needed to be analyzed.

Software Considerations

Once the instrument parameters were designed, software had to be employed that could identify components in gasoline so that ratios of components could be analyzed in the comparison. Hewlett Packard's Chemstation Target Compound Program came with the GC/MS and was useful for this study. Since this project was performed in conjunction with the BATF, the software had already been designed to pick the following components that elute in the five to twenty-nine minute region of a typical gasoline chromatogram run on a 60m column.

Table 4.1 Components Chosen by Software

Peak #	Retention Time (min)	Compound Name
1	5.10	isobutane
2	5.50	n-butane
3	5.62	butene
4	6.37	2-pentene
5	6.70	isopentane
6	6.98	1-pentene
7	7.27	n-pentane
8	7.62	(Z)-2-pentene

Peak #	Retention Time (min)	Compound Name
9	7.78	2-methyl-butene
10	8.23	2,2-dimethylbutane
11	8.77	cyclopentene
12	9.04	MTBE
13	9.23	2-methylpentane
14	9.72	3-methylpentane
15	9.91	a methylpentene
16	10.33	n-hexane
17	10.47	2-hexene
18	10.51	a methylpentene
19	10.67	a methylpentene
20	10.78	hexene
21	11.00	3-methyl-2-pentene
22	11.38	methylcyclopentene
23	12.19	methylcyclopentene
24	12.69	cyclohexane
25	12.86	2-methylhexane
26	13.25	3-methylhexane
27	13.62	1,3-dimethylcyclopentane
28	13.81	isooctane
29	14.03	3-heptene
30	14.17	n-heptane
31	14.69	dimethylcyclopentene
32	15.19	dimethylcyclopentane
33	15.26	methylcyclohexane
34	15.50	2,5-dimethylhexane
35	15.62	2,4-dimethylhexane
36	15.98	a trimethylcyclopentane
37	16.37	2,3,4-trimethylpentane
38	16.58	toluene
39	16.84	2-methylheptane
40	16.92	4-methylheptane
41	16.99	methylcyclohexene
42	17.12	dimethylhexane
43	17.21	3-methylheptane
44	17.24	3-ethylhexane
45	17.38	a trimethylcyclopentane
46	17.53	dimethylcyclohexane
47	17.65	2,2,5-trimethylhexane
48	17.88	1-ethyl-3-methylcyclopentane
49	17.93	a dimethylcyclohexane
50	17.99	a dimethylcyclohexane
51	18.13	ethylbenzene
52	18.32	a dimethylcyclohexane
53	18.53	a dimethylcyclohexane

Peak #	Retention Time (min)	Compound Name
54	20.01	ethylbenzene
55	20.27	m & p-xylenes
56	21.82	isopropylbenzene
57	22.55	n-propylbenzene
58	22.70	ethyltoluene
59	25.39	methylindane
60	25.86	1,2,4,5-tetramethylbenzene
61	25.92	1,2,3,5-tetramethylbenzene
62	26.30	methylindane
63	26.49	methylindane
64	27.08	naphthalene
65	27.98	dimethylindane
66	28.68	2-methylnaphthalene
67	28.93	1-methylnaphthalene

To set up the software to pick these compounds, their name, retention time, and target ions were entered to be used for selection criteria. The target ions were the base peak for each component, and their abundance in the mass spectrum was normalized to 100 percent. In instances where more than one component in gasoline had the same base peak, the abundance data of other distinguishing peaks in the mass spectrum was entered into the program. With this information, as each sample was run through the program, data was generated containing the compound name, retention time of the compound, and the target response of the base peak. The target response refers to a number representative of the response generated by how many target ions are detected by the ion detector.

It was found that a few changes had to be made to the program such as updating the retention times and entering in qualifier ions (other MS peaks in addition to the base peak) to ensure the correct peaks were chosen for purposes of this study. With the mass spectral information, the mass spectrum of each compound chosen was checked against a library of known mass spectra to ensure the peak chosen by the program was the correct gasoline component. Once this was established, the target ion responses were imported into a Microsoft Excel® spreadsheet that was designed to compute ratios of sequential components for three runs, average them, and determine standard deviation and percent standard deviation. This data was used to analyze replicate runs to ensure good reproducibility within a sample.

Selection of an Extraction/Concentration Method

Before any gasoline comparisons could be done, four common extraction methods used by the BATF were tested to determine which yielded the best reproducibility: headspace, heated headspace, solvent extraction, and static adsorption/elution. To do this, a sample of 89-octane gasoline from Citgo located in Randallstown, MD was used.

First, an appropriate injection volume had to be established that would yield sufficient information for the headspace methods. Using a sample containing three drops of unevaporated gasoline on a Kimwipe and sealed in an airtight, quart-sized paint can, it was found that 2ml of headspace was an appropriate injection volume.

Next, it had to be decided if the same syringe could be used for replicate runs of the same sample for manual headspace injections. Following a headspace injection of unevaporated gasoline, another injection consisting only of air was made using the same syringe. The resulting chromatogram displayed carryover, so a different syringe was used for every injection, except when a blank was performed; the same syringe used for a blank was then used for the first injection following it and then discarded.

To evaluate the headspace technique, 50µl of unevaporated gasoline was placed on a Kimwipe inside a quart-sized paint can and immediately sealed. This was done three times such that there were three sealed cans containing 50µl each of the same gasoline. A can containing only a Kimwipe was also sealed to see if the Kimwipe contributed any chromatographic peaks. The cans were allowed to sit undisturbed for approximately 24 hours. After 24 hours, a hole was placed in the lid of the first can, covered with Scotch® tape, and three (2ml) headspace draws were injected into the GC. This was repeated for the other two cans such that a total of nine injections (3 per can) had been done upon completion. One injection was made from the can that contained only a Kimwipe and it was found that the Kimwipe alone did not contribute to the chromatogram.

The next method evaluated was heated headspace. The cans were prepared in the same manner as for the headspace at room temperature, but were placed in a 65° C oven for fifteen minutes prior to injection and the hole was placed in the lid and covered with tape prior to heating. For both headspace methods, blanks of room air were injected between triplicates.

For solvent extraction, 50μl of gasoline was placed on a Kimwipe and sealed in a can as mentioned above, but after 24hrs, the Kimwipe was rinsed with 5ml of pentane in the can and the solution poured into a vial. A pentane blank consisting of pentane in a vial was included in the experiment to make sure the pentane was not contaminated. Also, a control involving pentane rinsed in a can and then poured into a vial was included to make sure the method itself was yielding accurate results. The sample vials, the blank, and the control were allowed to evaporate under the hood to approximately 1ml and were then run using the autosampler which was set up to make three injections per vial and one for the blank.

Lastly, static adsorption/elution was performed using 25μl of gasoline on a Kimwipe sealed in a can and allowed to sit overnight. A system blank of just a Kimwipe sealed in a can was included in the analysis. The following day, the lids from the four cans (3 samples, 1 blank) were removed and a paper clip containing a 1cm long charcoal strip (Abrayco Lab Inc.) was suspended from each lid using a magnet placed on the outside of the lid. The cans containing the suspended charcoal strips were then placed in a 65° C oven for 16 hours. After 16 hours, the charcoal strips were removed and each placed in separate vials to which 250µl of carbon disulfide was added. The solvent extracts were then run in triplicate (except for the system blank) using the autosampler.

The percent standard deviation of the ratios (nine runs) generated from each method was used to assess reproducibility. This was done by calculating the standard deviation and percent standard deviation of sequential ratios generated using only compounds eluting in the nine to twenty-nine minute region for each method with triplicate runs. This time region was chosen because it was found by the BATF to contain ratios of components that were reproducible and useful in liquid-to-liquid gasoline comparisons. Headspace and heated headspace had similar reproducibility and displayed all the peaks of interest based on the peak selection method (from 3-methylpentane to the methylnaphthalenes). Static adsorption/elution also had good reproducibility but lacked the first three peaks for which the program looks: 3-methylpentane, 2methyl-1-pentene, and n-hexane (present in 50% evaporated gasoline). Solvent extraction was found not to be useful because twenty of the thirty-four components being evaluated were absent from the chromatogram because they had presumably evaporated during the concentration step of the technique.

Headspace and static adsorption/elution were further compared by introducing 50% evaporated gasoline spiked on debris to see if the presence of the wood substrate would interfere with reproducibility of the method. Gasoline 50% evaporated (50µl) was placed on a piece of charred pine and sealed in a can and allowed to sit for 24 hours. Then headspace and static adsorption/elution techniques were used to extract the gasoline and the data was run through the Target Compound Program and ratios generated using the Excel worksheet. This was repeated using the same source gasoline unevaporated. The averages of the ratios from the unevaporated gasoline were compared to the 50% evaporated gasoline extract ratio averages using standard deviation and percent standard deviation. The headspace technique had lower percent standard deviations between the evaporated and unevaporated ratios compared to static adsorption/elution. Since static adsorption/elution yields a chromatogram shifted to the right compared to the headspace technique, it was found that for static adsorption/elution many of the early eluting components in gasoline were not reproducibly present. Therefore, for the 50% comparison part of the study, headspace was chosen because it picked up the early eluting components in the chromatogram and was the most reproducible regardless if the wood substrate was present.

A similar comparison was done using 50µl of 75% evaporated and unevaporated gasoline from the same source placed on a Kimwipe and sealed in separate cans. The ratio averages obtained from both cans were compared using the headspace and static adsorption/elution methods. Since the chromatogram for 75% evaporated gasoline is shifted to the right compared to unevaporated gasoline (see Appendix III), static adsorption/elution was an ideal method. Headspace was not useful for looking at components in 75% evaporated gasoline because the target response for the heavier components was very low to nonexistent. Moreover, 75% evaporated gasoline contains an abundance of the heavier compounds compared to 50% evaporated gasoline, so static adsorption/elution was chosen for the 75% comparisons.

Selection of Substrates

Two substrate types were selected to compare for the simulation of fire debris: pine and nylon carpet. Both are common substrates found in fire scenes that ignitable liquids can be extracted from. The carpet used was obtained from a local carpet store and was cut into a 6cm x 6cm square. The pine was purchased from Home Depot in Rockville, MD and was cut into the same dimensions as the carpet. To simulate fire debris, both materials were burned on all sides under a hood with a 14.1L propane torch and then allowed to catch flame and dropped in a quart-sized paint can. After the substrates appeared charred, the lids were placed on the cans and sealed. After approximately 2 hours, a 2ml sample of each material's headspace was run on GC/MS and the results evaluated with the Target Compound software. This process was repeated several times to see if the pyrolysis products were consistent from run to run.

The pine was selected to be used in the debris experiments because its pyrolysis products did not interfere with the detection of gasoline (see Appendix IV) and were fairly consistent among each run.

Determination of Amount of Gasoline to Use

Once the instrument parameters were established, the extraction methods and substrate types evaluated, and comparison software optimized, a determination of an appropriate amount of gasoline to use for each part of the study had to be ascertained. Since 50µl of gasoline on Kimwipes gave decent abundance values in the determination of an extraction method, that amount was used for all samples consisting of unevaporated gasoline on a Kimwipe for the 50% comparisons. For the 50% evaporated gasoline that was going to be placed on charred pine, 50μl and 100μl amounts were compared by placing each on the charred pine in a can and sealing for 24 hours. After 24 hours, a sample of the headspace of each can was run and the abundance values compared. Both 50μl and 100μl gave strong abundances, but the can with 100μl placed on the pine gave stronger abundance values and was the amount chosen to use on all simulated debris.

The comparison of the headspace of 75% evaporated gasoline on a Kimwipe to the headspace of unevaporated gasoline on a Kimwipe required a smaller amount of gasoline because static adsorption/elution is a more sensitive extraction technique. Amounts of 5μl, 10μl, and 20μl for both the 75% evaporated and unevaporated gasoline were evaluated. Using 10μl of evaporated and unevaporated gasoline gave sufficient abundance data such that a comparison could be made, and this volume was used for this part of the study.

Experimental Setup

The gasoline used for the experiment was collected from the pump of several gasoline stations and stored in Quorpack® 4oz bottles with Teflon®-lined lids to prevent evaporation. For each sample of gasoline collected, an aliquot was removed for the unevaporated samples and the rest was evaporated by 50% and 75% of the original volume underneath a hood. Gasoline from the same source refers to gasoline collected from the same station and derived from the same bottle for the study. Sixteen gasoline samples were used for the 50% comparisons and 10 gasoline samples were used for the 75% comparisons.

A. 50% Comparisons

Three cans were set up for each gasoline sample so that nine runs total, three from each can, would be made for both the evaporated and unevaporated gasoline (six cans total per gasoline). This number of replicates was chosen so reproducibility and variation from can to can could be assessed and to provide enough replicate information such that outlying data could be discarded if necessary. To represent simulated fire debris where gasoline was used as an accelerant, first a 6x6cm piece of pine was charred and sealed in a paint can. Thirty minutes later, 100µl of 50% evaporated gasoline was injected through a hole (.64cm in diameter) in the lid and covered with tape. This was repeated with the two other cans, and all three cans were allowed to sit for 24 hours before headspace samples were run on GC/MS. Before any samples were injected and between each can, a blank (2ml of air) was run.

Next, three cans containing one Kimwipe each were spiked with 50µl of unevaporated gasoline from the same source as the 50% evaporated gasoline and immediately sealed. These cans were also allowed to sit 24 hours before any headspace samples were run on GC/MS.

B. 75% Comparisons

For this part of the study, only six runs per sample were done (four cans total per gasoline sample). The 50% comparisons demonstrated that two cans per sample were just as effective as three cans, so 10µl of 75% evaporated gasoline was placed on Kimwipes and sealed in two separate cans. This was repeated using 10µl of unevaporated gasoline from the same source. The four cans were allowed to sit for 24 hours and then a 1cm long charcoal strip was attached to a paper clip and suspended from the inside of the lids using a magnet on the outside. All cans were then placed in a 65° C oven for 16 hours. A system blank containing a kimwipe and charcoal strip, but no gasoline, was included anytime cans were placed in the oven. The system blank demonstrated that, if properly sealed, no cross-contamination occurred between cans in the oven.

After all cans were removed from the oven, they were allowed to cool for 30-45 minutes before the charcoal strips were removed and placed into separate glass autosampler vials using tweezers that were rinsed in carbon disulfide before touching each charcoal strip. To each vial, 250µl of carbon disulfide was added and the vials were run (three injections per vial) using the autosampler.

Comparison Mechanics

For each run, the data was run through the target compound program, which identified the peaks of interest, and provided retention time and the target response for all the compounds listed in Table 4.1. The target response information was copied into the Excel templates which were already set up to calculate sequential ratios, average them, and determine standard deviation. The process resulted in triplicate values for ratios, averages, and standard deviations per can for the 50% and 75% data.

In selecting valuable ratios for comparison, the ratio must remain similar when gasoline is compared to gasoline from the same source but evaporated. In the 50% comparisons, unevaporated gasoline ratios were compared to the ratios obtained from the 50% evaporated gasoline extracted from charred pine. This was done for sixteen different gasoline sets. The same was done for the 75% evaporated gasoline and unevaporated gasoline from the same source using ten different gasoline samples. However, the 75% evaporated gasoline was not extracted from pine. To clarify, for each gasoline sample there were two values: an average (from all runs) of each ratios' values for evaporated and an average for the unevaporated gasoline ratio values. The average was of all the values obtained for a particular ratio after nine runs for the 50% comparisons and after six runs for the 75% comparisons. The standard deviation and percent standard deviation were calculated for each ratio and used to compare the unevaporated gasoline to the evaporated gasoline. Percent standard deviations less than five percent were considered similar.

Table 4.2 Example of How Similar Ratios Were Determined

Ratio	**Gasoline 1-75% evaporated**	**Gasoline 1 unevaporated**	**Average**	**Standard Deviation**	**Percent Standard Deviation**	**Ratios Similar?**
A	0.639	0.630	0.635	0.006	0.997	Yes
B	0.133	0.136	0.134	0.003	1.881	Yes

For all the ratios that had a less than five percent standard deviation when unevaporated gasoline averages were compared to evaporated averages, their reproducibility among the three runs per can was assessed. Random error is evident in every scientific measurement because there is some error in the reproducibility of the instrument used. Reproducibility was determined by how close the values for all runs of a sample were (see Appendix VIII). If, for a particular ratio, the values remained under five percent standard deviation when evaporated and unevaporated gasoline from the same source were compared and the ratio was reproducible within a sample, it was considered a useful ratio.

Since a goal of the study was to be able to eliminate unevaporated gasolines as possible sources of a sample of evaporated gasoline, another comparison was performed. For all the ratios that were found to be reproducible and remain similar between unevaporated and evaporated gasoline from the same source, the evaporated ratio averages from one gasoline were compared to all other unevaporated gasoline's same ratio averages. The purpose of this comparison was to see if the standard deviations of the ratios considered useful were greater when the comparison involved a different source gasoline (see Appendix Table 1.2). If they were, the ratios were useful to discriminate among different gasolines.

In this study, pattern recognition based on chromatograms was not used to compare the gasoline samples.

Chapter Five: Results and Conclusions, Discussion, and Further Research

Results and Conclusions

A. 50% Comparisons

The sixteen gasolines used in the 50% comparisons were readily distinguished using the six ratios outlined in Appendix Figure 5.1. Ratio one corresponds to the target response of the target ion in methylcyclohexane: dimethylcyclopentane, ratio two to 2,4-dimethylhexane: 2,5-dimethylhexane, ratio three to 1,2,4-trimethylcyclopentane: 2,4-dimethylhexane, ratio four to 2,3,4-trimethylpentane: 1,2,4-trimethylcyclopentane, ratio five to dimethylcyclohexane: 1,2,4-trimethylcyclopentane, and ratio six to 1,4 dimethylcyclohexane: 1,2-dimethylcyclohexane.

Furthermore, the headspace of unevaporated gasoline and 50% evaporated gasoline (extracted from debris) from the same source contain similar ratios of their components and these six ratios differ among gasoline from different sources. Appendix VI shows multiple comparisons of all sixteen gasolines for each of the six ratios and they clearly are different from one another when all six ratios are taken into account. It must be noted though that in order to have an effective comparison, all six ratios must be used. For example, gasolines #1 and #2 are very similar for all ratios except ratio four based upon the comparison graphs, which is very interesting considering they are from stations over 50 miles away from each other. Nevertheless, by comparing gasoline #1, 50% evaporated extract, to gasoline #2's values for all ratios (Appendix Table 1.2), the percent standard deviations are all higher than a comparison of only gasoline #1's values. For the comparison of gasoline #1, 50% evaporated to the same unevaporated gasoline, the values for ratios four and five were the highest standard deviations of all the ratios, but still were under the five percent cut-off. It must also be noted that there are instances, where for one of the six ratios, two samples with different sources have a lower standard deviation than five percent when compared to two samples from the same source. However, most ratios will be significantly higher than five percent compared to two samples from the same source and thus all ratios must be considered when determining whether a sample can be eliminated as originating from the same source.

Appendix Figures 6.7-6.12 demonstrate that when using the data from an evaporated gasoline sample and comparing it to all other gasolines unevaporated, only one unevaporated sample remains similar when compared among all ratios. This demonstrates that it is possible to rule out unevaporated samples as originating from the same source as a 50% evaporated sample.

Pine was chosen for the substrate because the pyrolysis products produced (see Appendix IV) do not interfere with the compounds used in the comparison ratios. However, once the gasoline was added, it was not known whether the pine would absorb some of the gasoline, interfering with the reproducibility of the comparisons. Nevertheless, the data demonstrates the presence of the wood substrate does not interfere in the comparisons. The sources of five samples selected from the sixteen gasoline samples were correctly identified in a blind study.

B. 75% Comparisons

The ten gasolines used in this study were distinguished using the four ratios outlined in Appendix Figure 5.2. Ratio one corresponds to the target response of the target ion in 2,4-dimethylhexane: 2,5-dimethylhexane, ratio two to 1,2,4-trimethylcyclopentane: 2,4-dimethylhexane, ratio three to methylindane: 1,2,3,5-

tetramethylbenzene, and ratio four to 1-methylnaphthalene: 2-methylnaphthalene. Ratios one and two correspond to ratios two and three of the 50% comparisons, indicating it may be possible to use those two ratios for cases involving gasoline up to 75% evaporated.

In this study, 75% evaporated gasoline was found to contain similar values to the same unevaporated gasoline using the four ratios mentioned above and clean substrates (see Appendix VII). Appendix Figure 7.5 clearly demonstrates that all ten gasolines are different using the data obtained from the unevaporated gasoline samples for the four ratios. Addition of the data obtained using the 75% evaporated gasoline made it easy to eliminate unevaporated samples as originating from the same source as the 75% evaporated sample. Appendix Figures 7.6-7.9 compare 75% evaporated gasoline to all ten unevaporated gasolines for each ratio, and only gasoline from the same source show consistently similar data for all ratios. As mentioned previously, the comparison is only valid when all four ratios are used because as Appendix Tables 2.2-2.5 demonstrate, there are instances where, for a particular ratio, a sample from a different source may have a percent standard deviation under five percent. However, inspection of the percent standard deviation information for a comparison of unevaporated and 75% evaporated gasoline from the same source shows it will be the only comparison in which all ratios have a percent standard deviation under five percent. The sources of three samples selected from the ten gasoline samples were correctly identified in a blind study.

Discussion and Further Research

The reproducibility for the 75% values was very good as evidenced by the example of reproducibility shown in Appendix VIII. This is probably due to using the autosampler versus manual injections, which were used in the 50% comparisons. Using an autosampler automates the process and removes inherent human error present when making manual injections. Also, because clean substrates were used in the 75% comparisons, addition of a complex substrate like wood may interfere with how good the reproducibility of the data is or the ability to do the comparisons at all. The 75% evaporated gasoline was not extracted from debris because it was only an attempt to see if such comparisons could be done on highly evaporated gasoline. Further research can examine what happens when 75% evaporated gasoline is extracted from debris. The method looks most promising for cases involving softwoods such as pine because its presence in debris does not interfere with the four ratios found to be useful for such a comparison. Also, because ratio three and four of the 75% comparisons involve compounds eluting in the late region of the chromatogram, attempts to do such a comparison using higher than 75% evaporated gasoline may prove feasible.

The results of the comparisons in this study demonstrate that for cases involving gasoline as an accelerant that has been evaporated up to 50% and extracted from pine, it is possible to eliminate gasoline comparisons as originating from the same source. The results of the 75% comparisons suggest it may be possible to apply the same type of comparison to cases involving 75% evaporated gasoline. Because there were two ratios that were applicable to both comparisons, it may be possible to use them in cases involving gasoline evaporated up to 75% and extracted from pine.

The ability to carry out the comparisons using gasoline from a small distribution area is very beneficial. The samples used in this study were obtained from places that could possibly have received gasoline from the same refinery and/or production batch, or terminal. Because they were distinguished from one another, doing larger scale comparisons involving gasoline from outside the distribution area of one another should result in even more levels of comparison and the ability to possibly classify gasoline.

It was not known at the beginning of this research if this would be an attempt to distinguish gasolines that are not technically from different sources because specific distribution information was not available. Nevertheless, the fact that the gasoline samples were distinguished from one another suggests that even without such information, a comparison can still be made, lending more credibility to evidence of this type. Not knowing the distribution information may be the reason why only a few ratios were useful in the comparison, but the combination of new shipments of gasoline, storage conditions of the gasoline, and the gasoline residue still in the tank add to detecting the types of differences found in this study.

In this study, all gasoline samples were collected in the summer and thus do not have as many light end components because they cause vapor lock in car engines. Future research should attempt to incorporate samples from winter as well, because winter gasoline has more light end compounds, and see how such changes affect the ratios useful for gasoline comparisons.

Before application of this method to actual arson cases, a 'controlled' arson scenario should be carried out where a certain amount of gasoline is added to the pine and then burned until the desired evaporation state is obtained. The evaporation amount of the gasoline should then be determined and the components remaining identified to see if they change under combustion or what effect combustion has at all on using the specified ratios. If the comparison method is still found to be useful, it should then be applied to actual arson cases.

Appendix I: Data for 50% Comparisons

Table 1.1 Values Obtained for Ratios 1-6 for Gasolines #1-16 (Neat=Unevaporated)

	Gasoline 1 neat	**Gasoline 1 50% evap.**		**Gasoline 2 neat**	**Gasoline 2 50% evap.**		**Gasoline 3 neat**	**Gasoline 3 50% evap.**
Ratio 1	3.904	4.047		4.665	4.785		7.756	7.818
Ratio 2	0.764	0.762		0.713	0.706		0.948	0.926
Ratio 3	0.307	0.304		0.282	0.286		0.336	0.329
Ratio 4	11.596	12.335		14.787	14.829		9.742	9.92
Ratio 5	2.458	2.606		2.779	2.888		5.339	5.256
Ratio 6	2.332	2.325		2.417	2.361		0.719	0.699
	Gasoline 4 neat	**Gasoline 4 50% evap.**		**Gasoline 5 neat**	**Gasoline 5 50% evap.**		**Gasoline 6 neat**	**Gasoline 6 50% evap.**
Ratio 1	11.313	11.212		6.475	6.426		5.083	5.196
Ratio 2	0.78	0.772		0.76	0.761		0.673	0.672
Ratio 3	0.389	0.389		0.336	0.331		0.481	0.477
Ratio 4	9.7	9.825		11.703	11.673		8.987	9.42
Ratio 5	6.538	6.584		4.292	4.236		3.213	3.311
Ratio 6	0.773	0.765		1.088	1.068		2.039	2.086
	Gasoline 7 neat	**Gasoline 7 50% evap.**		**Gasoline 8 neat**	**Gasoline 8 50% evap.**		**Gasoline 9 neat**	**Gasoline 9 50% evap.**
Ratio 1	5.369	5.375		3.842	3.93		5.702	5.694
Ratio 2	0.968	0.96		0.634	0.634		0.653	0.655
Ratio 3	0.733	0.72		0.135	0.136		0.329	0.318
Ratio 4	2.126	2.172		36.262	34.647		14.245	14.756
Ratio 5	2.435	2.422		2.557	2.605		3.851	3.838
Ratio 6	2.253	2.18		2.747	2.692		1.867	1.842

	Gasoline 10 neat	Gasoline 10 50% evap.		Gasoline 11 neat	Gasoline 11 50% evap.		Gasoline 12 neat	Gasoline 12 50% evap.
Ratio 1	3.714	3.74		8.461	8.462		2.896	3
Ratio 2	0.79	0.786		1.021	0.994		1.048	1.041
Ratio 3	0.489	0.485		0.871	0.865		0.228	0.229
Ratio 4	6.136	6.15		2.482	2.506		11.705	12.001
Ratio 5	2.359	2.312		6.295	6.23		3.994	4.114
Ratio 6	2.572	2.556		0.689	0.674		3.9	3.834
	Gasoline 13 neat	**Gasoline 13 50% evap.**		**Gasoline 14 neat**	**Gasoline 14 50% evap.**		**Gasoline 15 neat**	**Gasoline 15 50% evap.**
Ratio 1	4.392	4.417		4.114	4.153		5.91	5.876
Ratio 2	0.953	0.941		0.838	0.835		0.899	0.893
Ratio 3	0.927	0.913		0.388	0.382		0.502	0.483
Ratio 4	1.217	1.253		6.882	6.981		5.545	5.592
Ratio 5	2.712	2.657		2.521	2.526		3.459	3.295
Ratio 6	1.593	1.579		2.209	2.126		1.545	1.483
	Gasoline 16 neat	**Gasoline 16 50% evap.**						
Ratio 1	3.959	4.042						
Ratio 2	0.670	0.668						
Ratio 3	0.389	0.381						
Ratio 4	11.983	12.542						
Ratio 5	2.782	2.9145						
Ratio 6	2.989	3.116						

Table 1.1 Continued: Values Obtained for Ratios 1-6 for Gasolines #1-16 (Neat=Unevaporated)

Table 1.2 Comparison of 50% Evaporated Gasoline #1 (Debris Extract) to Gasolines #1-16 Neat; Gas=Abbreviation for Gasoline

	Gas 1 50%	**Gas 1 neat**	Average	Standard deviation	%std dev = (stdev/avg)*100
Ratio 1	4.047	3.904	3.976	0.101	2.543
Ratio 2	0.762	0.764	0.763	0.001	0.185
Ratio 3	0.304	0.307	0.306	0.002	0.694
Ratio 4	12.335	11.596	11.966	0.523	4.367
Ratio 5	2.606	2.458	2.532	0.105	4.133
Ratio 6	2.325	2.332	2.329	0.005	0.213
	Gas 1 50%	**Gas 2 neat**	Average	Standard deviation	%std dev
Ratio 1	4.047	4.665	4.356	0.437	10.032
Ratio 2	0.762	0.713	0.738	0.035	4.698
Ratio 3	0.304	0.282	0.293	0.016	5.309
Ratio 4	12.335	14.787	13.561	1.734	12.785
Ratio 5	2.606	2.779	2.693	0.122	4.543
Ratio 6	2.325	2.417	2.371	0.065	2.744
	Gas 1 50%	**Gas 3 neat**	Average	Standard deviation	%std dev
Ratio 1	4.047	7.756	5.902	2.623	44.441
Ratio 2	0.762	0.948	0.855	0.132	15.383
Ratio 3	0.304	0.336	0.320	0.023	7.071
Ratio 4	12.335	9.742	11.039	1.834	16.610
Ratio 5	2.606	5.339	3.973	1.933	48.648
Ratio 6	2.325	0.719	1.522	1.136	74.613
	Gas 1 50%	**Gas 4 neat**	Average	Standard deviation	%std dev
Ratio 1	4.047	11.313	7.680	5.138	66.899
Ratio 2	0.762	0.780	0.771	0.013	1.651
Ratio 3	0.304	0.389	0.347	0.060	17.346
Ratio 4	12.335	9.700	11.018	1.863	16.912
Ratio 5	2.606	6.538	4.572	2.780	60.812
Ratio 6	2.325	0.773	1.549	1.097	70.848
	Gas 1 50%	**Gas 5 neat**	Average	Standard deviation	%std dev
Ratio 1	4.047	6.475	5.261	1.717	32.634
Ratio 2	0.762	0.760	0.761	0.001	0.186
Ratio 3	0.304	0.336	0.320	0.023	7.071
Ratio 4	12.335	11.703	12.019	0.447	3.718
Ratio 5	2.606	4.292	3.449	1.192	34.566
Ratio 6	2.325	1.088	1.707	0.875	51.256

Table 1.2 Continued: Comparison of 50% Evaporated Gasoline #1 (Debris Extract) to Gasolines #1-16 Neat

	Gas 1 50%	**Gas 6 neat**	Average	Standard deviation	%std dev
Ratio 1	4.047	5.083	4.565	0.733	16.047
Ratio 2	0.762	0.673	0.718	0.063	8.771
Ratio 3	0.304	0.481	0.393	0.125	31.887
Ratio 4	12.335	8.987	10.661	2.367	22.206
Ratio 5	2.606	3.213	2.910	0.429	14.752
Ratio 6	2.325	2.039	2.182	0.202	9.268
	Gas 1 50%	**Gas 7 neat**	Average	Standard deviation	%std dev
Ratio 1	4.047	5.369	4.708	0.935	19.855
Ratio 2	0.762	0.968	0.865	0.146	16.840
Ratio 3	0.304	0.733	0.519	0.303	58.505
Ratio 4	12.335	2.126	7.231	7.219	99.839
Ratio 5	2.606	2.435	2.521	0.121	4.797
Ratio 6	2.325	2.253	2.289	0.051	2.224
	Gas 1 50%	**Gas 8 neat**	Average	Standard deviation	%std dev
Ratio 1	4.047	3.842	3.945	0.145	3.675
Ratio 2	0.762	0.634	0.698	0.091	12.967
Ratio 3	0.304	0.135	0.220	0.120	54.442
Ratio 4	12.335	36.262	24.299	16.919	69.630
Ratio 5	2.606	2.557	2.582	0.035	1.342
Ratio 6	2.325	2.747	2.536	0.298	11.767
	Gas 1 50%	**Gas 9 neat**	Average	Standard deviation	%std dev
Ratio 1	4.047	5.702	4.875	1.170	24.008
Ratio 2	0.762	0.653	0.708	0.077	10.894
Ratio 3	0.304	0.329	0.317	0.018	5.585
Ratio 4	12.335	14.245	13.290	1.351	10.162
Ratio 5	2.606	3.851	3.229	0.880	27.268
Ratio 6	2.325	1.867	2.096	0.324	15.451
	Gas 1 50%	**Gas 10 neat**	Average	Standard deviation	%std dev
Ratio 1	4.047	3.714	3.881	0.235	6.068
Ratio 2	0.762	0.790	0.776	0.020	2.551
Ratio 3	0.304	0.489	0.397	0.131	32.992
Ratio 4	12.335	6.136	9.236	4.383	47.462
Ratio 5	2.606	2.359	2.483	0.175	7.035
Ratio 6	2.325	2.572	2.449	0.175	7.133

Table 1.2 Continued: Comparison of 50% Evaporated Gasoline #1 (Debris Extract) to Gasolines #1-16 Neat

	Gas 1 50%	**Gas 11 neat**	Average	Standard deviation	%std dev
Ratio 1	4.047	8.461	6.254	3.121	49.907
Ratio 2	0.762	1.021	0.892	0.183	20.543
Ratio 3	0.304	0.871	0.588	0.401	68.243
Ratio 4	12.335	2.482	7.409	6.967	94.042
Ratio 5	2.606	6.295	4.451	2.609	58.612
Ratio 6	2.325	0.689	1.507	1.157	76.764
	Gas 1 50%	**Gas 12 neat**	Average	Standard deviation	%std dev
Ratio 1	4.047	2.896	3.472	0.814	23.445
Ratio 2	0.762	1.048	0.905	0.202	22.346
Ratio 3	0.304	0.228	0.266	0.054	20.203
Ratio 4	12.335	11.705	12.020	0.445	3.706
Ratio 5	2.606	3.994	3.300	0.981	29.741
Ratio 6	2.325	3.900	3.113	1.114	35.781
	Gas 1 50%	**Gas 13 neat**	Average	Standard deviation	%std dev
Ratio 1	4.047	4.392	4.220	0.244	5.782
Ratio 2	0.762	0.953	0.858	0.135	15.750
Ratio 3	0.304	0.927	0.616	0.441	71.572
Ratio 4	12.335	1.217	6.776	7.862	116.021
Ratio 5	2.606	2.712	2.659	0.075	2.819
Ratio 6	2.325	1.593	1.959	0.518	26.422
	Gas 1 50%	**Gas 14 neat**	Average	Standard deviation	%std dev
Ratio 1	4.047	4.114	4.081	0.047	1.161
Ratio 2	0.762	0.838	0.800	0.054	6.718
Ratio 3	0.304	0.388	0.346	0.059	17.167
Ratio 4	12.335	6.882	9.609	3.856	40.130
Ratio 5	2.606	2.521	2.564	0.060	2.345
Ratio 6	2.325	2.209	2.267	0.082	3.618
	Gas 1 50%	**Gas 15 neat**	Average	Standard deviation	%std dev
Ratio 1	4.047	5.910	4.979	1.317	26.461
Ratio 2	0.762	0.899	0.831	0.097	11.664
Ratio 3	0.304	0.502	0.403	0.140	34.741
Ratio 4	12.335	5.545	8.940	4.801	53.705
Ratio 5	2.606	3.459	3.033	0.603	19.890
Ratio 6	2.325	1.545	1.935	0.552	28.504

Table 1.2 Continued: Comparison of 50% Evaporated Gasoline #1 (Debris Extract) to Gasolines #1-16 Neat

	Gas 1 50%	**Gas 16 neat**	Average	Standard deviation	%std dev
Ratio 1	4.047	3.959	4.003	0.062	1.554
Ratio 2	0.762	0.670	0.716	0.065	9.086
Ratio 3	0.304	0.389	0.347	0.060	17.346
Ratio 4	12.335	11.983	12.159	0.249	2.047
Ratio 5	2.606	2.782	2.694	0.124	4.620
Ratio 6	2.325	2.989	2.657	0.470	17.671

Table 1.3 Comparison of 50% Evaporated Gasoline #2 (Debris Extract) to Gasolines #1-16 Neat

	Gas 2 50%	**Gas 1 neat**	Average	Standard deviation	%std dev
Ratio 1	4.785	3.904	4.345	0.623	14.339
Ratio 2	0.706	0.764	0.735	0.041	5.580
Ratio 3	0.286	0.307	0.297	0.015	5.008
Ratio 4	14.829	11.596	13.213	2.286	17.302
Ratio 5	2.888	2.458	2.673	0.304	11.375
Ratio 6	2.361	2.332	2.347	0.021	0.874
	Gas 2 50%	**Gas 2 neat**	Average	Standard deviation	%std dev
Ratio 1	4.785	4.665	4.725	0.085	1.796
Ratio 2	0.706	0.713	0.710	0.005	0.698
Ratio 3	0.286	0.282	0.284	0.003	0.996
Ratio 4	14.829	14.787	14.808	0.030	0.201
Ratio 5	2.888	2.779	2.834	0.077	2.720
Ratio 6	2.361	2.417	2.389	0.040	1.658
	Gas 2 50%	**Gas 3 neat**	Average	Standard deviation	%std dev
Ratio 1	4.785	7.756	6.271	2.101	33.503
Ratio 2	0.706	0.948	0.827	0.171	20.692
Ratio 3	0.286	0.336	0.311	0.035	11.368
Ratio 4	14.829	9.742	12.286	3.597	29.279
Ratio 5	2.888	5.339	4.114	1.733	42.132
Ratio 6	2.361	0.719	1.540	1.161	75.394
	Gas 2 50%	**Gas 4 neat**	Average	Standard deviation	%std dev
Ratio 1	4.785	11.313	8.049	4.616	57.349
Ratio 2	0.706	0.780	0.743	0.052	7.043
Ratio 3	0.286	0.389	0.338	0.073	21.580
Ratio 4	14.829	9.700	12.265	3.627	29.571
Ratio 5	2.888	6.538	4.713	2.581	54.762
Ratio 6	2.361	0.773	1.567	1.123	71.658

Table 1.3 Continued: Comparison of 50% Evaporated Gasoline #2 (Debris Extract) to Gasolines #1-16 Neat

	Gas 2 50%	**Gas 5 neat**	Average	Standard deviation	%std dev
Ratio 1	4.785	6.475	5.630	1.195	21.226
Ratio 2	0.706	0.760	0.733	0.038	5.209
Ratio 3	0.286	0.336	0.311	0.035	11.368
Ratio 4	14.829	11.703	13.266	2.210	16.662
Ratio 5	2.888	4.292	3.590	0.993	27.654
Ratio 6	2.361	1.088	1.725	0.900	52.198
	Gas 2 50%	**Gas 6 neat**	Average	Standard deviation	%std dev
Ratio 1	4.785	5.083	4.934	0.211	4.271
Ratio 2	0.706	0.673	0.690	0.023	3.384
Ratio 3	0.286	0.481	0.384	0.138	35.955
Ratio 4	14.829	8.987	11.908	4.131	34.690
Ratio 5	2.888	3.213	3.051	0.230	7.534
Ratio 6	2.361	2.039	2.200	0.228	10.349
	Gas 2 50%	**Gas 7 neat**	Average	Standard deviation	%std dev
Ratio 1	4.785	5.369	5.077	0.413	8.134
Ratio 2	0.706	0.968	0.837	0.185	22.134
Ratio 3	0.286	0.733	0.510	0.316	62.037
Ratio 4	14.829	2.126	8.478	8.982	105.955
Ratio 5	2.888	2.435	2.662	0.320	12.035
Ratio 6	2.361	2.253	2.307	0.076	3.310
	Gas 2 50%	**Gas 8 neat**	Average	Standard deviation	%std dev
Ratio 1	4.785	3.842	4.314	0.667	15.458
Ratio 2	0.706	0.634	0.670	0.051	7.599
Ratio 3	0.286	0.135	0.211	0.107	50.724
Ratio 4	14.829	36.262	25.546	15.155	59.327
Ratio 5	2.888	2.557	2.723	0.234	8.597
Ratio 6	2.361	2.747	2.554	0.273	10.687
	Gas 2 50%	**Gas 9 neat**	Average	Standard deviation	%std dev
Ratio 1	4.785	5.702	5.244	0.648	12.366
Ratio 2	0.706	0.653	0.680	0.037	5.515
Ratio 3	0.286	0.329	0.308	0.030	9.888
Ratio 4	14.829	14.245	14.537	0.413	2.841
Ratio 5	2.888	3.851	3.370	0.681	20.209
Ratio 6	2.361	1.867	2.114	0.349	16.524

Table 1.3 Continued: Comparison of 50% Evaporated Gasoline #2 (Debris Extract) to Gasolines #1-16 Neat

	Gas 2 50%	**Gas 10 neat**	Average	Standard deviation	%std dev
Ratio 1	4.785	3.714	4.250	0.757	17.821
Ratio 2	0.706	0.790	0.748	0.059	7.941
Ratio 3	0.286	0.489	0.388	0.144	37.043
Ratio 4	14.829	6.136	10.483	6.147	58.639
Ratio 5	2.888	2.359	2.624	0.374	14.258
Ratio 6	2.361	2.572	2.467	0.149	6.049
	Gas 2 50%	**Gas 11 neat**	Average	Standard deviation	%std dev
Ratio 1	4.785	8.461	6.623	2.599	39.247
Ratio 2	0.706	1.021	0.864	0.223	25.795
Ratio 3	0.286	0.871	0.579	0.414	71.505
Ratio 4	14.829	2.482	8.656	8.731	100.868
Ratio 5	2.888	6.295	4.592	2.409	52.469
Ratio 6	2.361	0.689	1.525	1.182	77.527
	Gas 2 50%	**Gas 12 neat**	Average	Standard deviation	%std dev
Ratio 1	4.785	2.896	3.841	1.336	34.780
Ratio 2	0.706	1.048	0.877	0.242	27.575
Ratio 3	0.286	0.228	0.257	0.041	15.958
Ratio 4	14.829	11.705	13.267	2.209	16.650
Ratio 5	2.888	3.994	3.441	0.782	22.728
Ratio 6	2.361	3.900	3.131	1.088	34.762
	Gas 2 50%	**Gas 13 neat**	Average	Standard deviation	%std dev
Ratio 1	4.785	4.392	4.589	0.278	6.056
Ratio 2	0.706	0.953	0.830	0.175	21.056
Ratio 3	0.286	0.927	0.607	0.453	74.733
Ratio 4	14.829	1.217	8.023	9.625	119.969
Ratio 5	2.888	2.712	2.800	0.124	4.445
Ratio 6	2.361	1.593	1.977	0.543	27.469
	Gas 2 50%	**Gas 14 neat**	Average	Standard deviation	%std dev
Ratio 1	4.785	4.114	4.450	0.474	10.663
Ratio 2	0.706	0.838	0.772	0.093	12.090
Ratio 3	0.286	0.388	0.337	0.072	21.402
Ratio 4	14.829	6.882	10.856	5.619	51.765
Ratio 5	2.888	2.521	2.705	0.260	9.595
Ratio 6	2.361	2.209	2.285	0.107	4.704

Table 1.3 Continued: Comparison of 50% Evaporated Gasoline #2 (Debris Extract) to Gasolines #1-16 Neat

	Gas 2 50%	**Gas 15 neat**	Average	Standard deviation	%std dev
Ratio 1	4.785	5.910	5.348	0.795	14.876
Ratio 2	0.706	0.899	0.803	0.136	17.006
Ratio 3	0.286	0.502	0.394	0.153	38.765
Ratio 4	14.829	5.545	10.187	6.565	64.443
Ratio 5	2.888	3.459	3.174	0.404	12.723
Ratio 6	2.361	1.545	1.953	0.577	29.544
	Gas 2 50%	**Gas 16 neat**	Average	Standard deviation	%std dev
Ratio 1	4.785	3.959	4.372	0.584	13.359
Ratio 2	0.706	0.670	0.688	0.025	3.700
Ratio 3	0.286	0.389	0.338	0.073	21.580
Ratio 4	14.829	11.983	13.406	2.012	15.011
Ratio 5	2.888	2.782	2.835	0.075	2.644
Ratio 6	2.361	2.989	2.675	0.444	16.600

Table 1.4 Comparison of 50% Evaporated Gasoline #3 (Debris Extract) to Gasolines #1-16 Neat

	Gas 3 50%	**Gas 1 neat**	Average	Standard deviation	%std dev
Ratio 1	7.818	3.904	5.861	2.768	47.221
Ratio 2	0.926	0.764	0.845	0.115	13.556
Ratio 3	0.329	0.307	0.318	0.016	4.892
Ratio 4	9.920	11.596	10.758	1.185	11.016
Ratio 5	5.256	2.458	3.857	1.978	51.296
Ratio 6	0.699	2.332	1.516	1.155	76.193
	Gas 3 50%	**Gas 2 neat**	Average	Standard deviation	%std dev
Ratio 1	7.818	4.665	6.242	2.230	35.721
Ratio 2	0.926	0.713	0.820	0.151	18.379
Ratio 3	0.329	0.282	0.306	0.033	10.879
Ratio 4	9.920	14.787	12.354	3.441	27.858
Ratio 5	5.256	2.779	4.018	1.752	43.597
Ratio 6	0.699	2.417	1.558	1.215	77.972
	Gas 3 50%	**Gas 3 neat**	Average	Standard deviation	%std dev
Ratio 1	7.818	7.756	7.787	0.044	0.563
Ratio 2	0.926	0.948	0.937	0.016	1.660
Ratio 3	0.329	0.336	0.333	0.005	1.489
Ratio 4	9.920	9.742	9.831	0.126	1.280
Ratio 5	5.256	5.339	5.298	0.059	1.108
Ratio 6	0.699	0.719	0.709	0.014	1.995

Table 1.4 Continued: Comparison of 50% Evaporated Gasoline #3 (Debris Extract) to Gasolines #1-16 Neat

	Gas 3 50%	**Gas 4 neat**	Average	Standard deviation	%std dev
Ratio 1	7.818	11.313	9.566	2.471	25.836
Ratio 2	0.926	0.780	0.853	0.103	12.103
Ratio 3	0.329	0.389	0.359	0.042	11.818
Ratio 4	9.920	9.700	9.810	0.156	1.586
Ratio 5	5.256	6.538	5.897	0.907	15.372
Ratio 6	0.699	0.773	0.736	0.052	7.109
	Gas 3 50%	**Gas 5 neat**	Average	Standard deviation	%std dev
Ratio 1	7.818	6.475	7.147	0.950	13.288
Ratio 2	0.926	0.760	0.843	0.117	13.924
Ratio 3	0.329	0.336	0.333	0.005	1.489
Ratio 4	9.920	11.703	10.812	1.261	11.661
Ratio 5	5.256	4.292	4.774	0.682	14.278
Ratio 6	0.699	1.088	0.894	0.275	30.785
	Gas 3 50%	**Gas 6 neat**	Average	Standard deviation	%std dev
Ratio 1	7.818	5.083	6.451	1.934	29.981
Ratio 2	0.926	0.673	0.800	0.179	22.376
Ratio 3	0.329	0.481	0.405	0.107	26.538
Ratio 4	9.920	8.987	9.454	0.660	6.979
Ratio 5	5.256	3.213	4.235	1.445	34.115
Ratio 6	0.699	2.039	1.369	0.948	69.213
	Gas 3 50%	**Gas 7 neat**	Average	Standard deviation	%std dev
Ratio 1	7.818	5.369	6.594	1.732	26.264
Ratio 2	0.926	0.968	0.947	0.030	3.136
Ratio 3	0.329	0.733	0.531	0.286	53.799
Ratio 4	9.920	2.126	6.023	5.511	91.502
Ratio 5	5.256	2.435	3.846	1.995	51.872
Ratio 6	0.699	2.253	1.476	1.099	74.447
	Gas 3 50%	**Gas 8 neat**	Average	Standard deviation	%std dev
Ratio 1	7.818	3.842	5.830	2.811	48.224
Ratio 2	0.926	0.634	0.780	0.206	26.471
Ratio 3	0.329	0.135	0.232	0.137	59.129
Ratio 4	9.920	36.262	23.091	18.627	80.666
Ratio 5	5.256	2.557	3.907	1.908	48.854
Ratio 6	0.699	2.747	1.723	1.448	84.048

Table 1.4 Continued: Comparison of 50% Evaporated Gasoline #3 (Debris Extract) to Gasolines #1-16 Neat

	Gas 3 50%	**Gas 9 neat**	Average	Standard deviation	%std dev
Ratio 1	7.818	5.702	6.760	1.496	22.134
Ratio 2	0.926	0.653	0.790	0.193	24.451
Ratio 3	0.329	0.329	0.329	0.000	0.000
Ratio 4	9.920	14.245	12.083	3.058	25.311
Ratio 5	5.256	3.851	4.554	0.993	21.818
Ratio 6	0.699	1.867	1.283	0.826	64.373
	Gas 3 50%	**Gas 10 neat**	Average	Standard deviation	%std dev
Ratio 1	7.818	3.714	5.766	2.902	50.329
Ratio 2	0.926	0.790	0.858	0.096	11.208
Ratio 3	0.329	0.489	0.409	0.113	27.662
Ratio 4	9.920	6.136	8.028	2.676	33.329
Ratio 5	5.256	2.359	3.808	2.048	53.801
Ratio 6	0.699	2.572	1.636	1.324	80.979
	Gas 3 50%	**Gas 11 neat**	Average	Standard deviation	%std dev
Ratio 1	7.818	8.461	8.140	0.455	5.586
Ratio 2	0.926	1.021	0.974	0.067	6.900
Ratio 3	0.329	0.871	0.600	0.383	63.875
Ratio 4	9.920	2.482	6.201	5.259	84.816
Ratio 5	5.256	6.295	5.776	0.735	12.721
Ratio 6	0.699	0.689	0.694	0.007	1.019
	Gas 3 50%	**Gas 12 neat**	Average	Standard deviation	%std dev
Ratio 1	7.818	2.896	5.357	3.480	64.969
Ratio 2	0.926	1.048	0.987	0.086	8.740
Ratio 3	0.329	0.228	0.279	0.071	25.644
Ratio 4	9.920	11.705	10.813	1.262	11.673
Ratio 5	5.256	3.994	4.625	0.892	19.294
Ratio 6	0.699	3.900	2.300	2.263	98.432
	Gas 3 50%	**Gas 13 neat**	Average	Standard deviation	%std dev
Ratio 1	7.818	4.392	6.105	2.423	39.681
Ratio 2	0.926	0.953	0.940	0.019	2.032
Ratio 3	0.329	0.927	0.628	0.423	67.333
Ratio 4	9.920	1.217	5.569	6.154	110.514
Ratio 5	5.256	2.712	3.984	1.799	45.153
Ratio 6	0.699	1.593	1.146	0.632	55.162

Table 1.4 Continued: Comparison of 50% Evaporated Gasoline #3 (Debris Extract) to Gasolines #1-16 Neat

	Gas 3 50%	**Gas 14 neat**	Average	Standard deviation	%std dev
Ratio 1	7.818	4.114	5.966	2.619	43.901
Ratio 2	0.926	0.838	0.882	0.062	7.055
Ratio 3	0.329	0.388	0.359	0.042	11.637
Ratio 4	9.920	6.882	8.401	2.148	25.571
Ratio 5	5.256	2.521	3.889	1.934	49.735
Ratio 6	0.699	2.209	1.454	1.068	73.434
	Gas 3 50%	**Gas 15 neat**	Average	Standard deviation	%std dev
Ratio 1	7.818	5.910	6.864	1.349	19.656
Ratio 2	0.926	0.899	0.913	0.019	2.092
Ratio 3	0.329	0.502	0.416	0.122	29.442
Ratio 4	9.920	5.545	7.733	3.094	40.008
Ratio 5	5.256	3.459	4.358	1.271	29.161
Ratio 6	0.699	1.545	1.122	0.598	53.317
	Gas 3 50%	**Gas 16 neat**	Average	Standard deviation	%std dev
Ratio 1	7.818	3.959	5.889	2.729	46.340
Ratio 2	0.926	0.670	0.798	0.181	22.684
Ratio 3	0.329	0.389	0.359	0.042	11.818
Ratio 4	9.920	11.983	10.952	1.459	13.320
Ratio 5	5.256	2.782	4.019	1.749	43.528
Ratio 6	0.699	2.989	1.844	1.619	87.813

Table 1.5 Comparison of 50% Evaporated Gasoline #4 (Debris Extract) to Gasolines #1-16 Neat

	Gas 4 50%	**Gas 1 neat**	Average	Standard deviation	%std dev
Ratio 1	11.212	3.904	7.558	5.168	68.372
Ratio 2	0.772	0.764	0.768	0.006	0.737
Ratio 3	0.389	0.307	0.348	0.058	16.662
Ratio 4	9.825	11.596	10.711	1.252	11.692
Ratio 5	6.584	2.458	4.521	2.918	64.533
Ratio 6	0.765	2.332	1.549	1.108	71.555
	Gas 4 50%	**Gas 2 neat**	Average	Standard deviation	%std dev
Ratio 1	11.212	4.665	7.939	4.629	58.316
Ratio 2	0.772	0.713	0.743	0.042	5.619
Ratio 3	0.389	0.282	0.336	0.076	22.552
Ratio 4	9.825	14.787	12.306	3.509	28.512
Ratio 5	6.584	2.779	4.682	2.691	57.472
Ratio 6	0.765	2.417	1.591	1.168	73.422

Table 1.5 Continued: Comparison of 50% Evaporated Gasoline #4 (Debris Extract) to Gasolines #1-16 Neat

	Gas 4 50%	**Gas 3 neat**	Average	Standard deviation	%std dev
Ratio 1	11.212	7.756	9.484	2.444	25.767
Ratio 2	0.772	0.948	0.860	0.124	14.471
Ratio 3	0.389	0.336	0.363	0.037	10.338
Ratio 4	9.825	9.742	9.784	0.059	0.600
Ratio 5	6.584	5.339	5.962	0.880	14.767
Ratio 6	0.765	0.719	0.742	0.033	4.384
	Gas 4 50%	**Gas 4 neat**	Average	Standard deviation	%std dev
Ratio 1	11.212	11.313	11.263	0.071	0.634
Ratio 2	0.772	0.780	0.776	0.006	0.729
Ratio 3	0.389	0.389	0.389	0.000	0.000
Ratio 4	9.825	9.700	9.763	0.088	0.905
Ratio 5	6.584	6.538	6.561	0.033	0.496
Ratio 6	0.765	0.773	0.769	0.006	0.736
	Gas 4 50%	**Gas 5 neat**	Average	Standard deviation	%std dev
Ratio 1	11.212	6.475	8.844	3.350	37.876
Ratio 2	0.772	0.760	0.766	0.008	1.108
Ratio 3	0.389	0.336	0.363	0.037	10.338
Ratio 4	9.825	11.703	10.764	1.328	12.337
Ratio 5	6.584	4.292	5.438	1.621	29.803
Ratio 6	0.765	1.088	0.927	0.228	24.651
	Gas 4 50%	**Gas 6 neat**	Average	Standard deviation	%std dev
Ratio 1	11.212	5.083	8.148	4.334	53.192
Ratio 2	0.772	0.673	0.723	0.070	9.689
Ratio 3	0.389	0.481	0.435	0.065	14.955
Ratio 4	9.825	8.987	9.406	0.593	6.300
Ratio 5	6.584	3.213	4.899	2.384	48.661
Ratio 6	0.765	2.039	1.402	0.901	64.255
	Gas 4 50%	**Gas 7 neat**	Average	Standard deviation	%std dev
Ratio 1	11.212	5.369	8.291	4.132	49.836
Ratio 2	0.772	0.968	0.870	0.139	15.930
Ratio 3	0.389	0.733	0.561	0.243	43.359
Ratio 4	9.825	2.126	5.976	5.444	91.106
Ratio 5	6.584	2.435	4.510	2.934	65.058
Ratio 6	0.765	2.253	1.509	1.052	69.727

Table 1.5 Continued: Comparison of 50% Evaporated Gasoline #4 (Debris Extract) to Gasolines #1-16 Neat

	Gas 4 50%	**Gas 8 neat**	Average	Standard deviation	%std dev
Ratio 1	11.212	3.842	7.527	5.211	69.236
Ratio 2	0.772	0.634	0.703	0.098	13.881
Ratio 3	0.389	0.135	0.262	0.180	68.552
Ratio 4	9.825	36.262	23.044	18.694	81.124
Ratio 5	6.584	2.557	4.571	2.848	62.302
Ratio 6	0.765	2.747	1.756	1.401	79.811
	Gas 4 50%	**Gas 9 neat**	Average	Standard deviation	%std dev
Ratio 1	11.212	5.702	8.457	3.896	46.070
Ratio 2	0.772	0.653	0.713	0.084	11.810
Ratio 3	0.389	0.329	0.359	0.042	11.818
Ratio 4	9.825	14.245	12.035	3.125	25.969
Ratio 5	6.584	3.851	5.218	1.933	37.039
Ratio 6	0.765	1.867	1.316	0.779	59.212
	Gas 4 50%	**Gas 10 neat**	Average	Standard deviation	%std dev
Ratio 1	11.212	3.714	7.463	5.302	71.042
Ratio 2	0.772	0.790	0.781	0.013	1.630
Ratio 3	0.389	0.489	0.439	0.071	16.107
Ratio 4	9.825	6.136	7.981	2.609	32.686
Ratio 5	6.584	2.359	4.472	2.988	66.813
Ratio 6	0.765	2.572	1.669	1.278	76.580
	Gas 4 50%	**Gas 11 neat**	Average	Standard deviation	%std dev
Ratio 1	11.212	8.461	9.837	1.945	19.776
Ratio 2	0.772	1.021	0.897	0.176	19.640
Ratio 3	0.389	0.871	0.630	0.341	54.099
Ratio 4	9.825	2.482	6.154	5.192	84.379
Ratio 5	6.584	6.295	6.440	0.204	3.173
Ratio 6	0.765	0.689	0.727	0.054	7.392
	Gas 4 50%	**Gas 12 neat**	Average	Standard deviation	%std dev
Ratio 1	11.212	2.896	7.054	5.880	83.361
Ratio 2	0.772	1.048	0.910	0.195	21.446
Ratio 3	0.389	0.228	0.309	0.114	36.902
Ratio 4	9.825	11.705	10.765	1.329	12.349
Ratio 5	6.584	3.994	5.289	1.831	34.627
Ratio 6	0.765	3.900	2.333	2.217	95.039

Table 1.5 Continued: Comparison of 50% Evaporated Gasoline #4 (Debris Extract) to Gasolines #1-16 Neat

	Gas 4 50%	**Gas 13 neat**	Average	Standard deviation	%std dev
Ratio 1	11.212	4.392	7.802	4.822	61.811
Ratio 2	0.772	0.953	0.863	0.128	14.839
Ratio 3	0.389	0.927	0.658	0.380	57.815
Ratio 4	9.825	1.217	5.521	6.087	110.248
Ratio 5	6.584	2.712	4.648	2.738	58.905
Ratio 6	0.765	1.593	1.179	0.585	49.659
	Gas 4 50%	**Gas 14 neat**	Average	Standard deviation	%std dev
Ratio 1	11.212	4.114	7.663	5.019	65.497
Ratio 2	0.772	0.838	0.805	0.047	5.797
Ratio 3	0.389	0.388	0.389	0.001	0.182
Ratio 4	9.825	6.882	8.354	2.081	24.912
Ratio 5	6.584	2.521	4.553	2.873	63.108
Ratio 6	0.765	2.209	1.487	1.021	68.666
	Gas 4 50%	**Gas 15 neat**	Average	Standard deviation	%std dev
Ratio 1	11.212	5.910	8.561	3.749	43.793
Ratio 2	0.772	0.899	0.836	0.090	10.748
Ratio 3	0.389	0.502	0.446	0.080	17.936
Ratio 4	9.825	5.545	7.685	3.026	39.381
Ratio 5	6.584	3.459	5.022	2.210	44.005
Ratio 6	0.765	1.545	1.155	0.552	47.753
	Gas 4 50%	**Gas 16 neat**	Average	Standard deviation	%std dev
Ratio 1	11.212	3.959	7.586	5.129	67.611
Ratio 2	0.772	0.670	0.721	0.072	10.003
Ratio 3	0.389	0.389	0.389	0.000	0.000
Ratio 4	9.825	11.983	10.904	1.526	13.994
Ratio 5	6.584	2.782	4.683	2.688	57.408
Ratio 6	0.765	2.989	1.877	1.573	83.783

Table 1.6 Comparison of 50% Evaporated Gasoline #5 (Debris Extract) to Gasolines #1-16 Neat

	Gas 5 50%	**Gas 1 neat**	Average	Standard deviation	%std dev
Ratio 1	6.426	3.904	5.165	1.783	34.527
Ratio 2	0.761	0.764	0.763	0.002	0.278
Ratio 3	0.331	0.307	0.319	0.017	5.320
Ratio 4	11.673	11.596	11.635	0.054	0.468
Ratio 5	4.236	2.458	3.347	1.257	37.563
Ratio 6	1.068	2.332	1.700	0.894	52.575

Table 1.6 Continued: Comparison of 50% Evaporated Gasoline #5 (Debris Extract) to Gasolines #1-16 Neat

	Gas 5 50%	**Gas 2 neat**	Average	Standard deviation	%std dev
Ratio 1	6.426	4.665	5.546	1.245	22.455
Ratio 2	0.761	0.713	0.737	0.034	4.605
Ratio 3	0.331	0.282	0.307	0.035	11.304
Ratio 4	11.673	14.787	13.230	2.202	16.643
Ratio 5	4.236	2.779	3.508	1.030	29.373
Ratio 6	1.068	2.417	1.743	0.954	54.742
	Gas 5 50%	**Gas 3 neat**	Average	Standard deviation	%std dev
Ratio 1	6.426	7.756	7.091	0.940	13.263
Ratio 2	0.761	0.948	0.855	0.132	15.474
Ratio 3	0.331	0.336	0.334	0.004	1.060
Ratio 4	11.673	9.742	10.708	1.365	12.752
Ratio 5	4.236	5.339	4.788	0.780	16.291
Ratio 6	1.068	0.719	0.894	0.247	27.620
	Gas 5 50%	**Gas 4 neat**	Average	Standard deviation	%std dev
Ratio 1	6.426	11.313	8.870	3.456	38.961
Ratio 2	0.761	0.780	0.771	0.013	1.744
Ratio 3	0.331	0.389	0.360	0.041	11.392
Ratio 4	11.673	9.700	10.687	1.395	13.055
Ratio 5	4.236	6.538	5.387	1.628	30.216
Ratio 6	1.068	0.773	0.921	0.209	22.661
	Gas 5 50%	**Gas 5 neat**	Average	Standard deviation	%std dev
Ratio 1	6.426	6.475	6.451	0.035	0.537
Ratio 2	0.761	0.760	0.761	0.001	0.093
Ratio 3	0.331	0.336	0.334	0.004	1.060
Ratio 4	11.673	11.703	11.688	0.021	0.181
Ratio 5	4.236	4.292	4.264	0.040	0.929
Ratio 6	1.068	1.088	1.078	0.014	1.312
	Gas 5 50%	**Gas 6 neat**	Average	Standard deviation	%std dev
Ratio 1	6.426	5.083	5.755	0.950	16.503
Ratio 2	0.761	0.673	0.717	0.062	8.679
Ratio 3	0.331	0.481	0.406	0.106	26.125
Ratio 4	11.673	8.987	10.330	1.899	18.386
Ratio 5	4.236	3.213	3.725	0.723	19.422
Ratio 6	1.068	2.039	1.554	0.687	44.197

Table 1.6 Continued: Comparison of 50% Evaporated Gasoline #5 (Debris Extract) to Gasolines #1-16 Neat

	Gas 5 50%	**Gas 7 neat**	Average	Standard deviation	%std dev
Ratio 1	6.426	5.369	5.898	0.747	12.673
Ratio 2	0.761	0.968	0.865	0.146	16.931
Ratio 3	0.331	0.733	0.532	0.284	53.432
Ratio 4	11.673	2.126	6.900	6.751	97.844
Ratio 5	4.236	2.435	3.336	1.273	38.180
Ratio 6	1.068	2.253	1.661	0.838	50.462
	Gas 5 50%	**Gas 8 neat**	Average	Standard deviation	%std dev
Ratio 1	6.426	3.842	5.134	1.827	35.589
Ratio 2	0.761	0.634	0.698	0.090	12.875
Ratio 3	0.331	0.135	0.233	0.139	59.482
Ratio 4	11.673	36.262	23.968	17.387	72.544
Ratio 5	4.236	2.557	3.397	1.187	34.955
Ratio 6	1.068	2.747	1.908	1.187	62.240
	Gas 5 50%	**Gas 9 neat**	Average	Standard deviation	%std dev
Ratio 1	6.426	5.702	6.064	0.512	8.442
Ratio 2	0.761	0.653	0.707	0.076	10.802
Ratio 3	0.331	0.329	0.330	0.001	0.429
Ratio 4	11.673	14.245	12.959	1.819	14.034
Ratio 5	4.236	3.851	4.044	0.272	6.733
Ratio 6	1.068	1.867	1.468	0.565	38.499
	Gas 5 50%	**Gas 10 neat**	Average	Standard deviation	%std dev
Ratio 1	6.426	3.714	5.070	1.918	37.824
Ratio 2	0.761	0.790	0.776	0.021	2.644
Ratio 3	0.331	0.489	0.410	0.112	27.249
Ratio 4	11.673	6.136	8.905	3.915	43.969
Ratio 5	4.236	2.359	3.298	1.327	40.250
Ratio 6	1.068	2.572	1.820	1.063	58.433
	Gas 5 50%	**Gas 11 neat**	Average	Standard deviation	%std dev
Ratio 1	6.426	8.461	7.444	1.439	19.332
Ratio 2	0.761	1.021	0.891	0.184	20.634
Ratio 3	0.331	0.871	0.601	0.382	63.534
Ratio 4	11.673	2.482	7.078	6.499	91.826
Ratio 5	4.236	6.295	5.266	1.456	27.650
Ratio 6	1.068	0.689	0.879	0.268	30.506

Table 1.6 Continued: Comparison of 50% Evaporated Gasoline #5 (Debris Extract) to Gasolines #1-16 Neat

	Gas 5 50%	**Gas 12 neat**	Average	Standard deviation	%std dev
Ratio 1	6.426	2.896	4.661	2.496	53.553
Ratio 2	0.761	1.048	0.905	0.203	22.437
Ratio 3	0.331	0.228	0.280	0.073	26.058
Ratio 4	11.673	11.705	11.689	0.023	0.194
Ratio 5	4.236	3.994	4.115	0.171	4.158
Ratio 6	1.068	3.900	2.484	2.003	80.617
	Gas 5 50%	**Gas 13 neat**	Average	Standard deviation	%std dev
Ratio 1	6.426	4.392	5.409	1.438	26.590
Ratio 2	0.761	0.953	0.857	0.136	15.842
Ratio 3	0.331	0.927	0.629	0.421	67.001
Ratio 4	11.673	1.217	6.445	7.394	114.717
Ratio 5	4.236	2.712	3.474	1.078	31.020
Ratio 6	1.068	1.593	1.331	0.371	27.902
	Gas 5 50%	**Gas 14 neat**	Average	Standard deviation	%std dev
Ratio 1	6.426	4.114	5.270	1.635	31.021
Ratio 2	0.761	0.838	0.800	0.054	6.810
Ratio 3	0.331	0.388	0.360	0.040	11.211
Ratio 4	11.673	6.882	9.278	3.388	36.516
Ratio 5	4.236	2.521	3.379	1.213	35.894
Ratio 6	1.068	2.209	1.639	0.807	49.241
	Gas 5 50%	**Gas 15 neat**	Average	Standard deviation	%std dev
Ratio 1	6.426	5.910	6.168	0.365	5.915
Ratio 2	0.761	0.899	0.830	0.098	11.757
Ratio 3	0.331	0.502	0.417	0.121	29.031
Ratio 4	11.673	5.545	8.609	4.333	50.333
Ratio 5	4.236	3.459	3.848	0.549	14.280
Ratio 6	1.068	1.545	1.307	0.337	25.816
	Gas 5 50%	**Gas 16 neat**	Average	Standard deviation	%std dev
Ratio 1	6.426	3.959	5.193	1.744	33.595
Ratio 2	0.761	0.670	0.716	0.064	8.993
Ratio 3	0.331	0.389	0.360	0.041	11.392
Ratio 4	11.673	11.983	11.828	0.219	1.853
Ratio 5	4.236	2.782	3.509	1.028	29.300
Ratio 6	1.068	2.989	2.029	1.358	66.963

Appendix II: Data for 75% Comparisons

Table 2.1 Value Obtained for Ratios 1-4 for Gasolines #01-10 (Neat=Unevaporated)

Ratio #	**Gasoline 01 neat**	**Gasoline 01 75% evap.**		**Gasoline 02 neat**	**Gasoline 02 75% evap.**		**Gasoline 03 neat**	**Gasoline 03 75% evap.**
1	0.774	0.782		0.669	0.687		0.930	0.947
2	0.398	0.382		0.497	0.478		0.357	0.343
3	0.546	0.557		0.858	0.845		0.421	0.421
4	0.434	0.436		0.293	0.293		0.429	0.418
Ratio #	**Gasoline 04 neat**	**Gasoline 04 75% evap.**		**Gasoline 05 neat**	**Gasoline 05 75% evap.**		**Gasoline 06 neat**	**Gasoline 06 75% evap.**
1	0.794	0.800		0.964	0.946		0.837	0.842
2	0.490	0.482		0.737	0.716		0.387	0.382
3	0.675	0.685		1.257	1.257		0.706	0.701
4	0.400	0.393		0.489	0.493		0.449	0.444
Ratio #	**Gasoline 07 neat**	**Gasoline 07 75% evap.**		**Gasoline 08 neat**	**Gasoline 08 75% evap.**		**Gasoline 09 neat**	**Gasoline 09 75% evap.**
1	0.900	0.909		0.760	0.769		0.667	0.669
2	0.491	0.486		0.341	0.326		0.405	0.387
3	0.488	0.482		0.444	0.443		0.908	0.902
4	0.486	0.492		0.443	0.444		0.256	0.253
Ratio #	**Gasoline 10 neat**	**Gasoline 10 75% evap.**						
1	0.630	0.639						
2	0.136	0.133						
3	0.576	0.588						
4	0.418	0.413						

Table 2.2 Comparison of 75% Evaporated Gasoline #01 to Gasolines #01-10 Neat

Ratio #	**Gas 01 75% evap.**	**Gas 01 neat**	Average	Standard deviation	%std dev=(stdev/avg.)*100
1	0.782	0.774	0.778	0.005	0.682
2	0.382	0.398	0.390	0.011	2.922
3	0.557	0.546	0.551	0.007	1.347
4	0.436	0.434	0.435	0.001	0.244
Ratio #	**Gas 01 75% evap.**	**Gas 02 neat**	Average	Standard deviation	%std dev
1	0.774	0.669	0.721	0.074	10.298
2	0.398	0.497	0.447	0.070	15.731
3	0.546	0.858	0.702	0.221	31.489
4	0.434	0.293	0.363	0.100	27.545
Ratio #	**Gas 01 75% evap.**	**Gas 03 neat**	Average	Standard deviation	%std dev
1	0.774	0.930	0.852	0.110	12.955
2	0.398	0.357	0.377	0.029	7.690
3	0.546	0.421	0.483	0.088	18.217
4	0.434	0.429	0.431	0.004	0.902
Ratio #	**Gas 01 75% evap.**	**Gas 04 neat**	Average	Standard deviation	%std dev
1	0.774	0.794	0.784	0.014	1.805
2	0.398	0.490	0.444	0.065	14.668
3	0.546	0.675	0.610	0.092	15.005
4	0.434	0.400	0.417	0.024	5.854
Ratio #	**Gas 01 75% evap.**	**Gas 05 neat**	Average	Standard deviation	%std dev
1	0.774	0.964	0.869	0.135	15.505
2	0.398	0.737	0.567	0.240	42.320
3	0.546	1.257	0.901	0.503	55.823
4	0.434	0.489	0.462	0.039	8.427
Ratio #	**Gas 01 75% evap.**	**Gas 06 neat**	Average	Standard deviation	%std dev
1	0.774	0.837	0.805	0.045	5.534
2	0.398	0.387	0.392	0.008	1.984
3	0.546	0.706	0.626	0.113	18.087
4	0.434	0.449	0.442	0.011	2.402
Ratio #	**Gas 01 75% evap.**	**Gas 07 neat**	Average	Standard deviation	%std dev
1	0.774	0.900	0.837	0.089	10.665
2	0.398	0.491	0.444	0.066	14.876
3	0.546	0.488	0.517	0.040	7.802
4	0.434	0.486	0.460	0.036	7.921

Table 2.2 Continued: Comparison of 75% Evaporated Gasoline #01 to Gasolines #01-10 Neat

Ratio #	**Gas 01 75% evap.**	**Gas 08 neat**	Average	Standard deviation	%std dev
1	0.774	0.760	0.767	0.010	1.243
2	0.398	0.341	0.369	0.040	10.844
3	0.546	0.444	0.495	0.072	14.491
4	0.434	0.443	0.438	0.006	1.403
Ratio #	**Gas 01 75% evap.**	**Gas 09 neat**	Average	Standard deviation	%std dev
1	0.774	0.667	0.720	0.075	10.464
2	0.398	0.405	0.401	0.005	1.271
3	0.546	0.908	0.727	0.257	35.293
4	0.434	0.256	0.345	0.126	36.555
Ratio #	**Gas 01 75% evap.**	**Gas 10 neat**	Average	Standard deviation	%std dev
1	0.774	0.630	0.702	0.101	14.447
2	0.398	0.136	0.267	0.185	69.211
3	0.546	0.576	0.561	0.022	3.863
4	0.434	0.418	0.426	0.012	2.730

Table 2.3 Comparison of 75% Evaporated Gasoline #02 to Gasolines #01-10 Neat

Ratio #	**Gas 02 75% evap.**	**Gas 01 neat**	Average	Standard deviation	%std dev
1	0.687	0.774	0.731	0.062	8.421
2	0.478	0.398	0.438	0.057	12.986
3	0.845	0.546	0.696	0.211	30.399
4	0.293	0.434	0.364	0.100	27.428
Ratio #	**Gas 02 75% evap.**	**Gas 02 neat**	Average	Standard deviation	%std dev
1	0.687	0.669	0.678	0.013	1.930
2	0.478	0.497	0.488	0.013	2.756
3	0.845	0.858	0.852	0.009	1.080
4	0.293	0.293	0.293	0.000	0.121
Ratio #	**Gas 02 75% evap.**	**Gas 03 neat**	Average	Standard deviation	%std dev
1	0.687	0.930	0.808	0.171	21.215
2	0.478	0.357	0.417	0.086	20.590
3	0.845	0.421	0.633	0.300	47.364
4	0.293	0.429	0.361	0.096	26.559
Ratio #	**Gas 02 75% evap.**	**Gas 04 neat**	Average	Standard deviation	%std dev
1	0.687	0.794	0.740	0.075	10.173
2	0.478	0.490	0.484	0.008	1.681
3	0.845	0.675	0.760	0.120	15.817
4	0.293	0.400	0.346	0.075	21.749

Table 2.3 Continued: Comparison of 75% Evaporated Gasoline #02 to Gasolines #01-10 Neat

Ratio #	**Gas 02 75% evap.**	**Gas 05 neat**	Average	Standard deviation	%std dev
1	0.687	0.964	0.826	0.196	23.727
2	0.478	0.737	0.608	0.183	30.147
3	0.845	1.257	1.051	0.291	27.719
4	0.293	0.489	0.391	0.139	35.446
Ratio #	**Gas 02 75% evap.**	**Gas 06 neat**	Average	Standard deviation	%std dev
1	0.687	0.837	0.762	0.106	13.878
2	0.478	0.387	0.432	0.065	14.968
3	0.845	0.706	0.775	0.099	12.724
4	0.293	0.449	0.371	0.110	29.733
Ratio #	**Gas 02 75% evap.**	**Gas 07 neat**	Average	Standard deviation	%std dev
1	0.687	0.900	0.793	0.150	18.956
2	0.478	0.491	0.484	0.009	1.891
3	0.845	0.488	0.667	0.252	37.814
4	0.293	0.486	0.389	0.136	34.970
Ratio #	**Gas 02 75% evap.**	**Gas 08 neat**	Average	Standard deviation	%std dev
1	0.687	0.760	0.724	0.052	7.137
2	0.478	0.341	0.409	0.097	23.681
3	0.845	0.444	0.645	0.283	43.981
4	0.293	0.443	0.368	0.106	28.776
Ratio #	**Gas 02 75% evap.**	**Gas 09 neat**	Average	Standard deviation	%std dev
1	0.687	0.667	0.677	0.014	2.097
2	0.478	0.405	0.441	0.052	11.742
3	0.845	0.908	0.877	0.045	5.106
4	0.293	0.256	0.274	0.026	9.608
Ratio #	**Gas 02 75% evap.**	**Gas 10 neat**	Average	Standard deviation	%std dev
1	0.687	0.630	0.659	0.040	6.108
2	0.478	0.136	0.307	0.242	78.674
3	0.845	0.576	0.711	0.190	26.755
4	0.293	0.418	0.355	0.088	24.791

Table 2.4 Comparison of 75% Evaporated Gasoline #03 to Gasolines #01-10 Neat

Ratio #	**Gas 03 75% evap.**	**Gas 01 neat**	Average	Standard deviation	%std dev
1	0.947	0.774	0.861	0.122	14.216
2	0.343	0.398	0.370	0.039	10.529
3	0.421	0.546	0.484	0.088	18.281
4	0.418	0.434	0.426	0.011	2.656
Ratio #	**Gas 03 75% evap.**	**Gas 02 neat**	Average	Standard deviation	%std dev
1	0.947	0.669	0.808	0.197	24.380
2	0.343	0.497	0.420	0.109	26.027
3	0.421	0.858	0.640	0.309	48.320
4	0.418	0.293	0.355	0.089	24.980
Ratio #	**Gas 03 75% evap.**	**Gas 03 neat**	Average	Standard deviation	%std dev
1	0.947	0.930	0.938	0.012	1.319
2	0.343	0.357	0.350	0.010	2.832
3	0.421	0.421	0.421	0.000	0.000
4	0.418	0.429	0.423	0.007	1.754
Ratio #	**Gas 03 75% evap.**	**Gas 04 neat**	Average	Standard deviation	%std dev
1	0.947	0.794	0.870	0.109	12.472
2	0.343	0.490	0.416	0.104	24.987
3	0.421	0.675	0.548	0.180	32.775
4	0.418	0.400	0.409	0.013	3.200
Ratio #	**Gas 03 75% evap.**	**Gas 05 neat**	Average	Standard deviation	%std dev
1	0.947	0.964	0.956	0.012	1.258
2	0.343	0.737	0.540	0.279	51.682
3	0.421	1.257	0.839	0.591	70.458
4	0.418	0.489	0.454	0.050	11.070
Ratio #	**Gas 03 75% evap.**	**Gas 06 neat**	Average	Standard deviation	%std dev
1	0.947	0.837	0.892	0.078	8.762
2	0.343	0.387	0.365	0.031	8.536
3	0.421	0.706	0.563	0.201	35.716
4	0.418	0.449	0.434	0.022	5.057
Ratio #	**Gas 03 75% evap.**	**Gas 07 neat**	Average	Standard deviation	%std dev
1	0.947	0.900	0.923	0.033	3.624
2	0.343	0.491	0.417	0.105	25.190
3	0.421	0.488	0.455	0.048	10.489
4	0.418	0.486	0.452	0.048	10.566

Table 2.4 Continued: Comparison of 75% Evaporated Gasoline #03 to Gasolines #01-10 Neat

Ratio #	**Gas 03 75% evap.**	**Gas 08 neat**	Average	Standard deviation	%std dev
1	0.947	0.760	0.854	0.132	15.490
2	0.343	0.341	0.342	0.001	0.335
3	0.421	0.444	0.433	0.016	3.776
4	0.418	0.443	0.430	0.017	4.058

Ratio #	**Gas 03 75% evap.**	**Gas 09 neat**	Average	Standard deviation	%std dev
1	0.947	0.667	0.807	0.198	24.542
2	0.343	0.405	0.374	0.044	11.774
3	0.421	0.908	0.665	0.345	51.843
4	0.418	0.256	0.337	0.115	34.065

Ratio #	**Gas 03 75% evap.**	**Gas 10 neat**	Average	Standard deviation	%std dev
1	0.947	0.630	0.789	0.224	28.415
2	0.343	0.136	0.239	0.146	60.915
3	0.421	0.576	0.499	0.110	22.003
4	0.418	0.418	0.418	0.000	0.074

Table 2.5 Comparison of 75% Evaporated Gasoline #04 to Gasolines #01-10 Neat

Ratio #	**Gas 04 75% evap.**	**Gas 01 neat**	Average	Standard deviation	%std dev
1	0.800	0.774	0.787	0.018	2.336
2	0.482	0.398	0.440	0.059	13.497
3	0.685	0.546	0.616	0.098	15.969
4	0.393	0.434	0.413	0.029	7.101

Ratio #	**Gas 04 75% evap.**	**Gas 02 neat**	Average	Standard deviation	%std dev
1	0.800	0.669	0.734	0.093	12.664
2	0.482	0.497	0.489	0.011	2.240
3	0.685	0.858	0.772	0.122	15.856
4	0.393	0.293	0.343	0.071	20.645

Ratio #	**Gas 04 75% evap.**	**Gas 03 neat**	Average	Standard deviation	%std dev
1	0.800	0.930	0.865	0.092	10.589
2	0.482	0.357	0.419	0.088	21.095
3	0.685	0.421	0.553	0.187	33.757
4	0.393	0.429	0.411	0.025	6.201

Table 2.5 Continued: Comparison of 75% Evaporated Gasoline #04 to Gasolines #01-10 Neat

Ratio #	**Gas 04 75% evap.**	**Gas 04 neat**	Average	Standard deviation	%std dev
1	0.800	0.794	0.797	0.005	0.577
2	0.482	0.490	0.486	0.006	1.165
3	0.685	0.675	0.680	0.007	1.040
4	0.393	0.400	0.396	0.005	1.250
Ratio #	**Gas 04 75% evap.**	**Gas 05 neat**	Average	Standard deviation	%std dev
1	0.800	0.964	0.882	0.116	13.148
2	0.482	0.737	0.609	0.181	29.654
3	0.685	1.257	0.971	0.404	41.654
4	0.393	0.489	0.441	0.068	15.482
Ratio #	**Gas 04 75% evap.**	**Gas 06 neat**	Average	Standard deviation	%std dev
1	0.800	0.837	0.818	0.026	3.154
2	0.482	0.387	0.434	0.067	15.478
3	0.685	0.706	0.695	0.014	2.085
4	0.393	0.449	0.421	0.040	9.495
Ratio #	**Gas 04 75% evap.**	**Gas 07 neat**	Average	Standard deviation	%std dev
1	0.800	0.900	0.850	0.070	8.293
2	0.482	0.491	0.486	0.007	1.375
3	0.685	0.488	0.587	0.139	23.687
4	0.393	0.486	0.439	0.066	14.980
Ratio #	**Gas 04 75% evap.**	**Gas 08 neat**	Average	Standard deviation	%std dev
1	0.800	0.760	0.780	0.028	3.624
2	0.482	0.341	0.411	0.099	24.182
3	0.685	0.444	0.565	0.170	30.173
4	0.393	0.443	0.418	0.035	8.500
Ratio #	**Gas 04 75% evap.**	**Gas 09 neat**	Average	Standard deviation	%std dev
1	0.800	0.667	0.733	0.094	12.830
2	0.482	0.405	0.443	0.054	12.254
3	0.685	0.908	0.797	0.158	19.821
4	0.393	0.256	0.324	0.097	29.841
Ratio #	**Gas 04 75% evap.**	**Gas 10 neat**	Average	Standard deviation	%std dev
1	0.800	0.630	0.715	0.120	16.799
2	0.482	0.136	0.309	0.244	79.029
3	0.685	0.576	0.631	0.077	12.207
4	0.393	0.418	0.405	0.018	4.375

Appendix III: Demonstration of Comparison Ratios and Where They Lie on a Typical Chromatogram

Figure 3.1 Ratios Used in 50% Comparisons

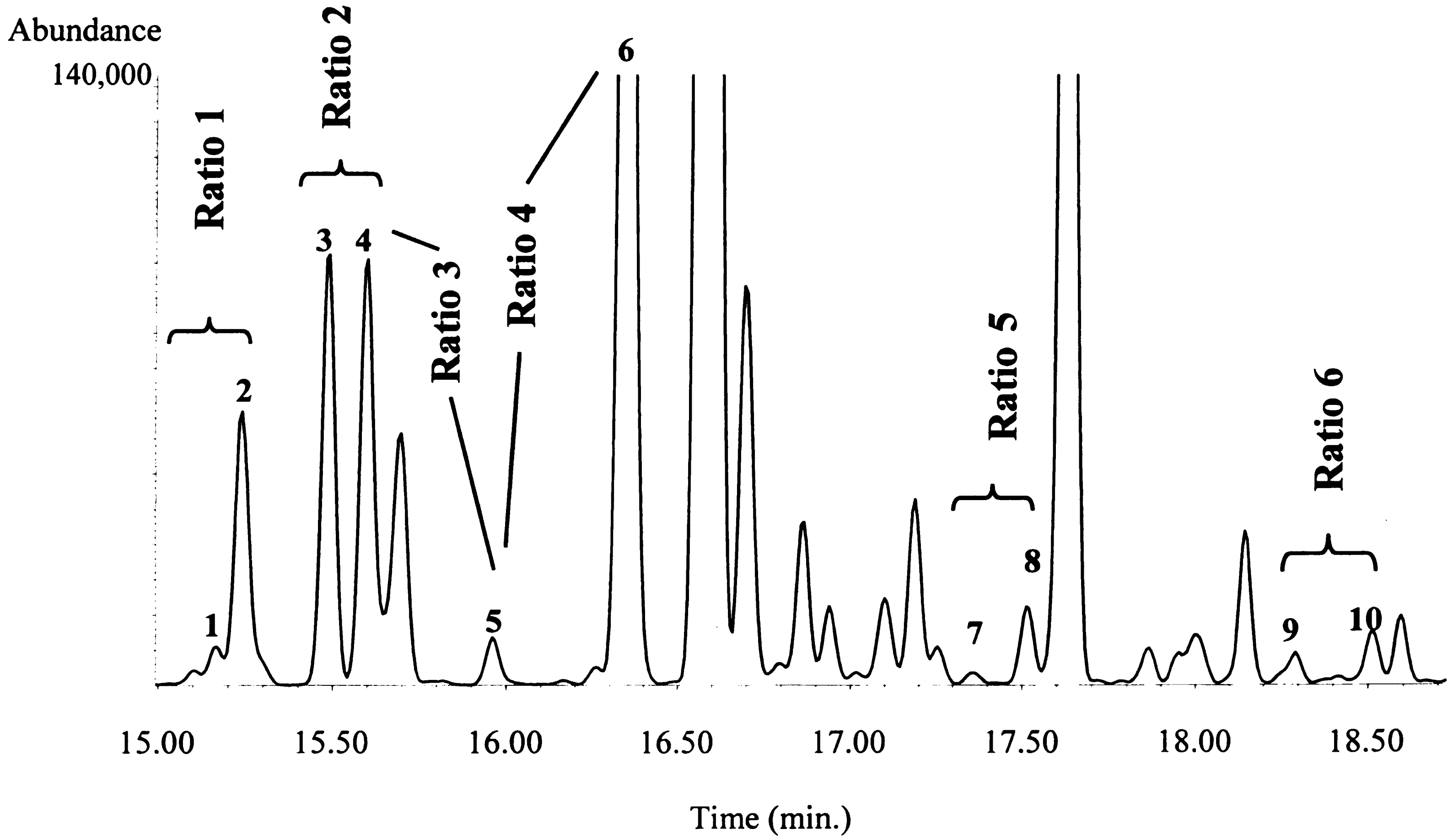
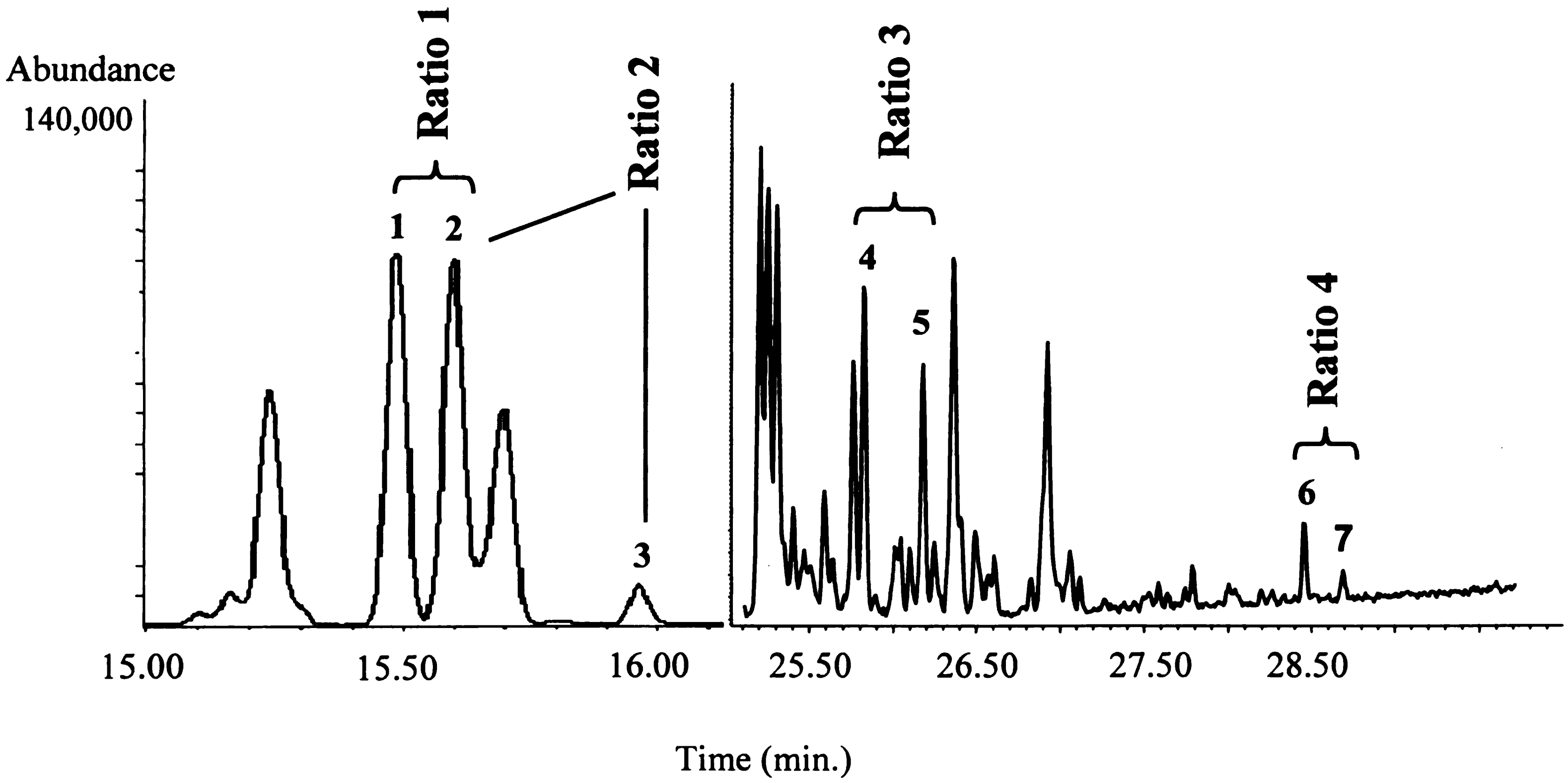


Figure 3.2 Ratios Used in 75% Comparisons



Notes

Chapter One: Introduction

[1] Speight, J.G. 1999. *The Chemistry and Technology of Petroleum, 4th ed.* New York: Marcel Dekker, Inc.

[2] Trimpe, M.A. 1991. Turpentine in Arson Analysis. *Journal of Forensic Sciences.* 36(4): 1059-1073.

[3] Friedman, A.J. 2002 Hydrocarbon Pattern Analyses: Elucidating Deeper Truths or Just Finding the Pope in the Pizza? Or the Sorcerers...And Their Apprentices. Presentation from the American Academy of Forensic Sciences Meeting in Atlanta, GA.

[4] Mann, D.C. 1987. Comparison of Automotive Gasolines Using Capillary Gas Chromatography I: Comparison Methodology. *Journal of Forensic Sciences* 32(3): 606-615.

[5] Mann, D.C. 1987. Comparison of Automotive Gasolines Using Capillary Gas Chromatography II: Limitations of Automotive Gasoline Comparisons in Casework. *Journal of Forensic Sciences* 32(3): 616-628.

[6] Dolan, J.A. and C. Ritacco. 2002. Gasoline Comparison by Gas Chromatography-Mass Spectrometry Utilizing an Automated Approach to Data Analysis. Presentation from the American Academy of Forensic Sciences Meeting in Atlanta, GA.

[7] Smith, C.B. and J. Macy. 1991. Methods of Fire Debris Preparation for Detection of Accelerants. *Forensic Science Review.* 3: 57-68.

[8] Kuk, R. Fire Debris Chemist, Bureau of Alcohol, Tobacco, and Firearms. Personal Communications.

[9] Klontz, Bill. Petroleum Products Supervisor, Exxon-Mobil. Personal Communications.

[10] Thornton, J.I. and B. Fukayama. The Implications of Refining Operations to the Characterization and Analysis of Arson Accelerants: Part I Physical Separation. *Arson Analysis Newsletter* 3(3): 1-16.

[11] Thornton, J.I. and B. Fukayama. The Implications of Refining Operations to the Characterization and Analysis of Arson Accelerants: Part II Chemical Conversions, Treating Processes, and Subsidiary Processes. *Arson Analysis Newsletter* 3(3): 1-16.

[12] San Joaquin Geological Society. 2002. What is a Refinery? A Lesson in How to Make Gasoline. www.sjgs.com/refinery.html

[13] Freudenrich, C. 1998. How Oil Refining Works. http://www.howstuffworks.com/oil-refining5.htm.

Chapter Two: Instrumentation

[14] Skoog, D., F.J. Holler, and T. Nieman. 1998. *Principles of Instrumental Analysis, 5th ed.* Florida: Harcourt Brace & Co.

[15] Hoffman, E. and V. Stroobant. 2002. *Mass Spectrometry: Principles and Applications, 2nd ed.* England: John Wiley & Sons.

Chapter Three: Forensic Methods of Accelerant Separation and Concentration from Fire Debris

[16] Atkins, P.W. 1989. *General Chemistry*. New York: Oxford University Press.

[17] American Society for Testing and Materials (ASTM). 2002. Standard test methods E 1386 and E 1412: West Conshohocken, PA.

BIBLIOGRAPHY

American Society for Testing and Materials (ASTM). 2002. Standard test methods E 1386 and E 1412: West Conshohocken, PA.

Atkins, P.W. 1989. *General Chemistry.* New York: Oxford University Press.

Dolan, J.A. and C. Ritacco. 2002. Gasoline Comparison by Gas Chromatography-Mass Spectrometry Utilizing an Automated Approach to Data Analysis. Presentation from the American Academy of Forensic Sciences Meeting in Atlanta, GA.

Freudenrich, C. 1998. How Oil Refining Works. http://www.howstuffworks.com/oil-refining5.htm.

Friedman, A.J. 2002 Hydrocarbon Pattern Analyses: Elucidating Deeper Truths or Just Finding the Pope in the Pizza? Or the Sorcerers...And Their Apprentices. Presentation from the American Academy of Forensic Sciences Meeting in Atlanta, GA.

Hoffman, E. and V. Stroobant. 2002. *Mass Spectrometry: Principles and Applications, 2nd ed.* England: John Wiley & Sons.

Klontz, Bill. Oil Chemist, Exxon-Mobil. Personal Communications.

Kuk, R. Arson Chemist, Bureau of Alcohol, Tobacco, and Firearms. Personal Communications.

Mann, D.C. 1987. Comparison of Automotive Gasolines Using Capillary Gas Chromatography I: Comparison Methodology. *Journal of Forensic Sciences* 32(3): 606-615.

Mann, D.C. 1987. Comparison of Automotive Gasolines Using Capillary Gas Chromatography II: Limitations of Automotive Gasoline Comparisons in Casework. *Journal of Forensic Sciences* 32(3): 616-628.

San Joaquin Geological Society. 2002. What is a Refinery? A Lesson in How to Make Gasoline. www.sjgs.com/refinery.html

Skoog, D., F.J. Holler, and T. Nieman. 1998. *Principles of Instrumental Analysis, 5th ed.* Florida: Harcourt Brace & Co.

Smith, C.B. and J. Macy. 1991. Methods of Fire Debris Preparation for Detection of Accelerants. *Forensic Science Review.* 3: 57-68.

Speight, J.G. 1999. *The Chemistry and Technology of Petroleum, 4th ed.* New York: Marcel Dekker, Inc.

Thornton, J.I. and B. Fukayama. 1979. The Implications of Refining Operations to the Characterization and Analysis of Arson Accelerants: Part I Physical Separation. *Arson Analysis Newsletter* 3(2): 1-16.

Thornton, J.I. and B. Fukayama. The Implications of Refining Operations to the Characterization and Analysis of Arson Accelerants: Part II Chemical Conversions, Treating Processes, and Subsidiary Processes. *Arson Analysis Newsletter* 3(3):1-16.

Trimpe, M.A. 1991. Turpentine in Arson Analysis. *Journal of Forensic Sciences.* 36(4): 1059-1073.

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