Investigation of Water Effect on Ignitable Liquid Residue Analysis by Coupling Solid-Phase Microextraction with Direct Analysis in Real Time Mass Spectrometry

by

Tori Bascou

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Thesis Committee:

Dr. Mengliang Zhang, Thesis Director

Dr. Ngee Sing Chong, Second Reader

Dr. Amy Phelps, Thesis Committee Chair

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APPROVED:

Dr. Mengliang Zhang, Thesis Director
[Associate Professor, Chemistry Department]

Dr. Ngee Sing Chong, Second Reader
[Professor, Chemistry Department]

Dr. Amy Phelps, Thesis Committee Chair
[Professor and Interim Chair, Chemistry Department]

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Abstract

Arson investigation and explosive analysis is a subfield of forensic science that focuses on examining the physical evidence that is collected from a scene in which a fire occurred. Accelerants and ignitable liquids (ILs) are often used in arson fires to maximize the damage that the fire creates. Common ILs include lighter fluid and gasoline, with gasoline being one of the most volatile compounds. Direct analysis in real time-mass spectrometry (DART-MS) is known for its ability to analyze volatile weather-exposed compounds and to demonstrate sensitive detection of explosives. In recent research, the DART-MS was coupled with an extraction method called Solid Phase Microextraction (SPME) to aid in the analysis of IL residue on substrates (i.e., wood floor, paper). This study hypothesizes that water could interfere with gasoline residue analysis by DART-MS which is dependent on the gasoline to water ratios and the type of substrates. The objective is to conduct a comprehensive evaluation of the water effect in gasoline residue detection by DART-MS method to provide results that will aid in a better understanding of water and substrates factors in the IL detection method.

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List of Terms

Direct Analysis in Real Time Mass-Spectroscopy (DART-MS): An analytical instrument capable of measuring molecules based on their mass-to-charge ratio (*m/z*).

Ignitable Liquid: Any liquid that can easily be ignited and has a flashpoint at or above 37.8 °C.

Ignitable Liquid Residue (ILR): The unburned portion of the ignitable liquid remaining on a substrate or piece of evidence.

Mass Spectrum: A plot showing the *m/z* ratios of the ions present in a sample against their relative intensities.

Polydimethylsiloxane (PDMS): The coating used on SPME fiber designed for extracting analytes of volatile compounds.

Signal of Interest: The signal that has a specified significance to the analysis.

Solid-Phase Microextraction (SPME): A sample preparation technique and extraction method involving a fiber coated in an extraction phase, which can extract analytes from various types of media.

Thermal Desorption: A technique that utilizes heat to increase the volatility of contaminants so that the contaminants can be evaporated and desorbed.

Total Ion Chromatogram (TIC): A chromatogram that represents the sum of intensities across the range of masses detected at every point in an analysis.

I: INTRODUCTION

Forensic science is a discipline within the criminal justice system that aids in the reconstruction and understanding of crimes, their scenes, timeline of events, and the investigations that occur in order to interpret the events of the crime so that correct measures can be taken for proper prosecution.[10] Forensic science holds an imperative role in the legal system as the evidence and results produced by forensic scientists often are presented in the court of law in order to aid in the prosecution of a perpetrator and the resolution of the crime itself. Collecting, analyzing, and examining evidence is a common practice that forensic scientists use to develop objective findings resulting from the information found at crime scenes. Within forensic science, many subfields exist in the laboratory with focuses on specific disciplines such as blood spatter analysis, DNA analysis, handwriting analysis, toxicology, trace evidence examination (e.g., fibers, paints, glass, and hairs), latent fingerprint examination, etc. Each category has its own team of specialized agents or scientists who are trained in identifying and researching these materials. One of the subfields is arson investigation and explosive analysis. Forensic cases that involve arson are just as prevalent as cases involving murder, rape, robbery, aggravated assault, burglary, and motor vehicle theft, and oftentimes the arson cases include one or more of these other felony crimes.

David Berkowitz, more commonly known as “Son of Sam”, is one of the most notorious serial killers known to this day, with his nickname striking fear in individuals to this day and various films/TV series being created featuring his story. What is less known about Berkowitz is that his life of crime started with setting fire to buildings across New York City. It was one of his fires that caused his reign of terror and killings to come to an end. New York City law enforcement was focused on identifying “Son of Sam” and paid no attention to these fires that were being set by Berkowitz himself until one day he set a fire that was intended to ignite .22 caliber bullets set out in front of his neighbor, Craig Glassman’s door, but the fire was not hot enough to do so. Glassman was suspicious of Berkowitz and gave his name to the police along with threatening notes he had received from him. Police were able to arrest David Berkowitz and from there he confessed to six murders he had committed. The fires that were set by Berkowitz led to the capture of this well-known serial killer and showed the importance of arson investigations in forensic science.

Arson (and fire) investigations focus on examining the physical evidence that is collected from a scene in which a fire occurred. [3,5] The physical evidence collected from the scene can aid in determining if the fire was deliberate or not, which can suggest criminal activity. Arson investigations also pay close attention to determining the fire’s point of origin,[6] discerning the cause of the fire, observing specific burn patterns, and identifying the presence of accelerants. Accelerants and ignitable liquids are often used in arson fires to maximize the damage that the fire creates and to ensure that the fire will completely burn through materials. Ignitable liquids are also used in cases where the materials to be set on fire are highly resistant to being burned quickly, and the liquid is treated as the accelerant to aid in the spread of the fire. Common ignitable liquids include lighter fluid, kerosene, acetone, and gasoline. [9] Gasoline is the most commonly used accelerant because of its accessibility and its property of being extremely flammable.

One of the key components of investigating a fire scene is determining if the scene was caused by accident or arson (deliberately executed with a specific purpose in mind), as well as collecting evidence to be examined. Evidence can include debris samples, burned materials, items doused in ignitable liquids, and various other substances. Gas chromatography-mass spectrometry (GC-MS) is the primary analytical technique used to analyze evidence from a fire or arson scene. GC-MS is favored when analyzing volatile substances and has proven efficiency when doing so. On the other hand, direct analysis in real time-mass spectrometry (DART-MS) is able to analyze less volatile compounds that have been exposed to weather conditions, which is useful in many arson cases where evidence has been exposed to various factors that can lead to the residue compounds being less volatile.[7] DART-MS is also known for demonstrating the sensitive detection of explosives.[4] In previous experiments, DART-MS with the QuickStrip sample introduction approach was used to investigate and identify ignitable liquids, however, this method is designed to analyze liquid samples and cannot be applied to the detection of ignitable liquids on substrates.

In recent research, the DART-MS was coupled with an extraction method called Solid Phase Microextraction (SPME), a common technique used in sample preparation that utilizes a fiber coated with a liquid polymer or solid sorbent that can extract analytes from various media[9], in order to aid in the analysis of ignitable liquid residue (ILR) on substrates (i.e., wood floor, textile fabric, paper, sand, or their debris). However, water, one of the most common fire-extinguishing agents, could interfere with the analysis; its impact on ILR detection is largely unknown. In this study, water was added to gasoline residues in various ratios to simulate the potential of water interference with the gasoline signals produced from the collected DART-MS data. Specifically in this study, the DART-MS was coupled with the SPME method for the analysis of the gasoline-water samples (Figure 1 on page 8) so that there would be a heightened sensitivity to the gasoline-related signals.

Data produced from these methods of analysis included a total ion chromatogram (TIC) and mass spectra for each sample analyzed. The TIC displays signal versus time for the analysis of the gasoline-water samples and is useful for viewing peaks produced from the insertion of the polydimethylsiloxane (PDMS) fiber into the helium gas stream. The mass spectra are useful in detailing all ions present in a sample, with the relative abundance of each ion being displayed as well. The mass spectra are key in signaling out a signal of interest with its relative intensity. Figures 2 and 3 on page 9 detail examples of TIC and mass spectra to show the generalized format of the produced data from these methods. A heat map, such as the one presented in Figure 4 on page 10, is another way to view the relative intensities of ions present in a sample.

Previous research found that specific ions are representative signals of gasoline. These signals are at *m/z* 474, *m/z* 530, and *m/z* 586, which were determined to correspond to the polyisobutylene succinimide (PIBS), commonly used as fuel additives in gasoline. The most prevalent and consistent signal is the *m/z* 474 signal, which was the signal of interest for this research. This study proposes that DART-MS coupled with SPME would provide effective, consistent, and optimal results for the analysis of ignitable liquids on substrates or fire debris samples. The study focused on the gasoline-water ratios, investigating the water effect on the intensity of the gasoline signals present. The research was expected to provide results that would aid in differentiating and identifying ignitable liquids depending on their exposed conditions to other interference liquids.

II: METHODS

Materials

Previous research in Zhang's group has shown the effectiveness of DART-MS for the detection of ILR with and without substrates, therefore some of the experimental parameters will be adopted from this literature.[1,2,8] In this study, gasoline samples from Shell gas station will be used. A SPME device with a 7 μm PDMS fiber was used to extract gasoline samples, with a SPME holder, printed from the 3-D printer specifically designed to assist in creating a reproducible environment for the SPME desorption in the DART-MS instrument. The DART-MS utilized a helium gas source to aid in the SPME desorption. Tap water from a sink in the lab was used for all water samples added to gasoline. Gasoline-water ratios were measured using pipettes and then transported into 40 mL glass vials. The glass vials were enclosed with tan silicone septa, which were secured with black phenolic screw caps. A 28 mm heating block was used to heat the samples to allow for better fiber absorption, and samples were mixed while being heated using a rotating feature on the heating block. A T-junction tube was used to direct helium gas stream during analysis of samples.

Methods

Gasoline samples were tested in various ratios of gasoline and water. The gasoline remained in 100 μL amounts throughout the experimental process, with the addition of water being added in varying amounts. Ratios of gasoline to water are as follows: 0, 0.1, 0.2, 0.3, 0.5, 0.75, 1, 5, 7.5, 10, 50, 99. Gasoline:water mixtures were pipetted into clean glass vials and closed via septa and screw cap. The septa secured onto the glass vial was carefully pierced with a needle and the SPME device was inserted into the vial to extract gasoline residues, utilizing predetermined parameters for SPME optimization.[1,2,8] The 7 μm PDMS coating fiber remained within the SPME needle until the tool was pierced through the septum to prevent breaking or damaging the fiber. Once inside the vial, the fiber was exposed to the vaporized analytes from the gasoline sample within the vial and extracted compounds in the gas phase onto the fiber (Figure 1A on page 8). After the extraction, the SPME was placed into the 3-D printed SPME holder and the fiber was exposed to the helium gas stream from DART for desorption. As a result, the desorbed molecules were ionized and detected by DART-MS (Figure 1B on page 8).

During the extraction period, the samples were heated and mixed by rotation on a heating block for 20 minutes at 150°C. The optimized temperature for analysis using the DART-MS is 300°C, and this temperature was used for all extracted samples analyzed on the DART-MS in order to aid in thermal desorption. For the extraction, the SPME needle was inserted into the glass vial through a small hole created in the septum and the PDMS fiber was extended to be exposed to analytes within the vial. Extension of the fiber is vital for the extraction process as analytes were absorbed into the fiber for later analysis. The fiber was extended each time (for both extraction and analysis) at a length halfway between non-extended and fully extended in order to maintain consistency. Extension of the fiber is a sensitive process that requires attention to detail as the PDMS fiber is extremely fragile and prone to breaking/becoming contaminated. After the extraction, the SPME fiber was exposed to the heated ion source from the DART 300°C (Figure 1B on page 8) for 1.5 minutes, and then removed. Figure 1C on page 8 shows a real image of the setup for DART-MS analysis, including the 3D-printed SPME holder and the T-junction tube. Data collected by DART-MS was analyzed in search of the *m/z* 474 signal of interest to identify the possible presence of the gasoline residues. TIC and mass spectra produced from DART-MS were collected for each analysis and evaluated, with the mass range being *m/z* 50-1000. Data from each sample was compared to identify the characteristic properties of gasoline that can help to differentiate between gasoline and other ignitable liquids. Duplicates of each experiment were performed to maintain the integrity of the data.

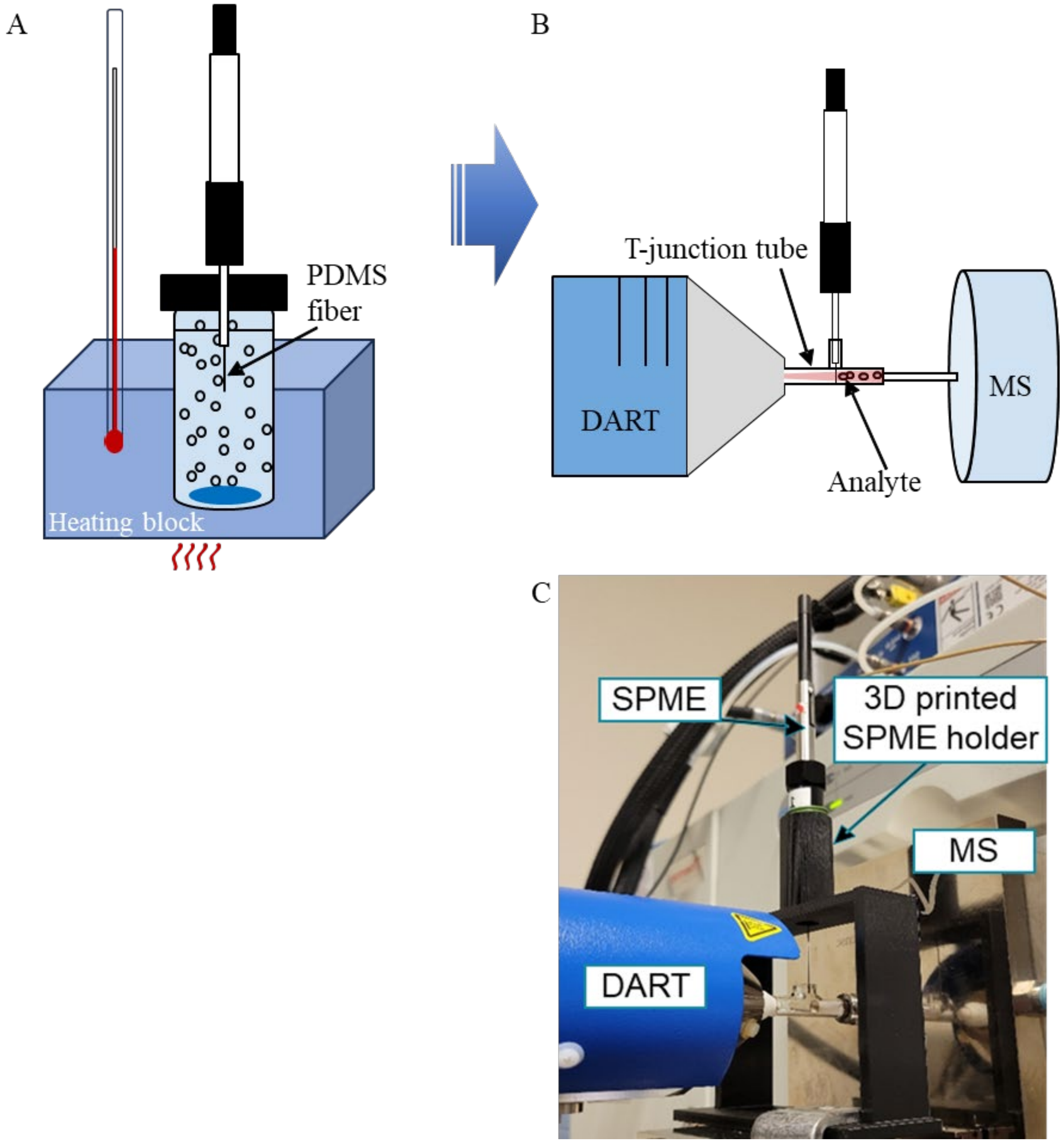

Figure 1: Diagram of SPME extraction with gasoline-water ratio (A), DART-MS analysis (B), and real-life image of analysis with SPME holder and T-junction tube (C)

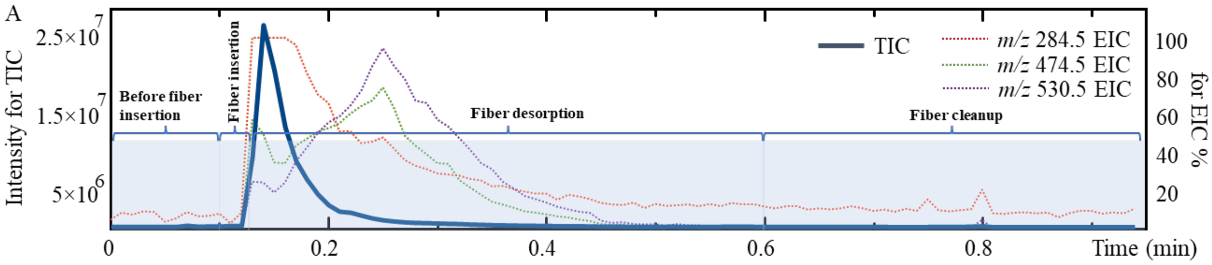

Figure 2: A total ion chromatogram (TIC) and extracted ion chromatograms (EIC) of characteristic ions for a gasoline sample.

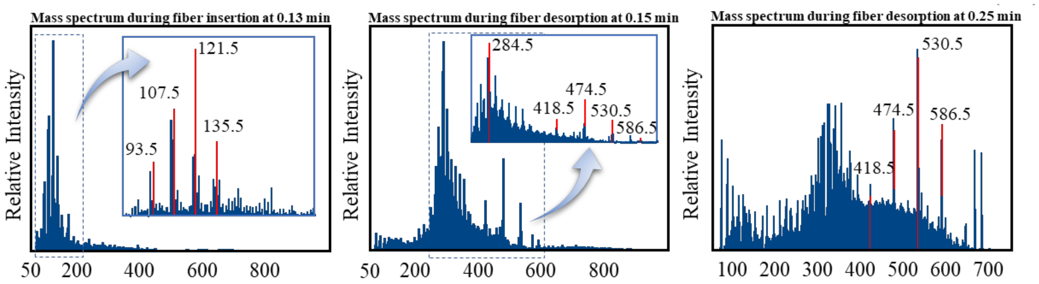

Figure 3: Representative mass spectra during the SPME fiber insertion and desorption process.

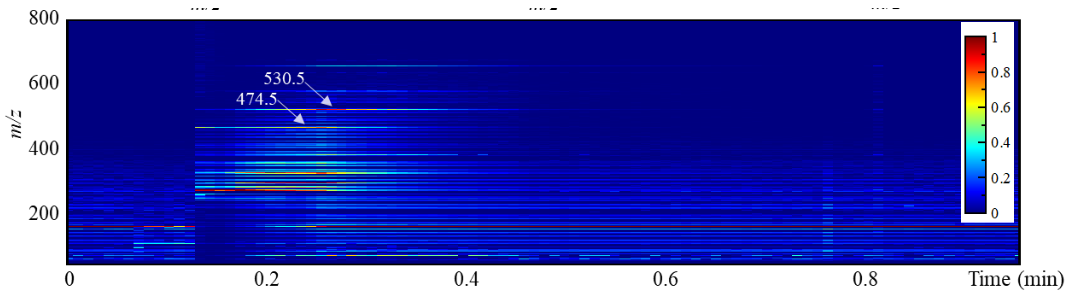

Figure 4: A display of raw data in a heat map with ion intensity normalized to maximum intensity.

III: RESULTS

Data collected from each analyzed sample via the DART-MS produced a series of mass spectra with the ions measured from the desorption of the SPME fiber over time. The area of peak interest was identified to be *m/z* 474 due to that signal's dominant pattern, seen in previous research. [1,2,8] TIC and mass spectra from each analysis were collected and analyzed in search of this signal of interest. The exact mass and intensity of the signals from each sample were exported, and the relative intensity of the *m/z* 474 signals was identified. Each intensity was noted, as well as the intensity of the *m/z* 663 background signal. These two signals were compared, and their ratios were calculated. A representative graph of the amount of gasoline (%) versus the average intensity of the signal ratios was created, showing that the water did have an overall effect on the intensity of the gasoline signals (Figure 5 on page 11).

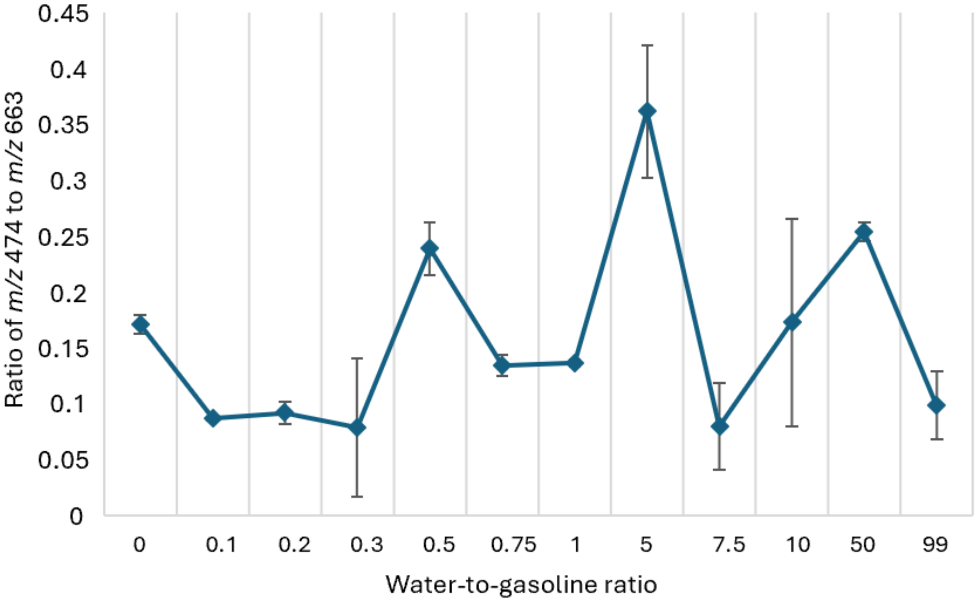

Figure 5: Graph of water-to-gasoline ratio versus ratio of intensities.

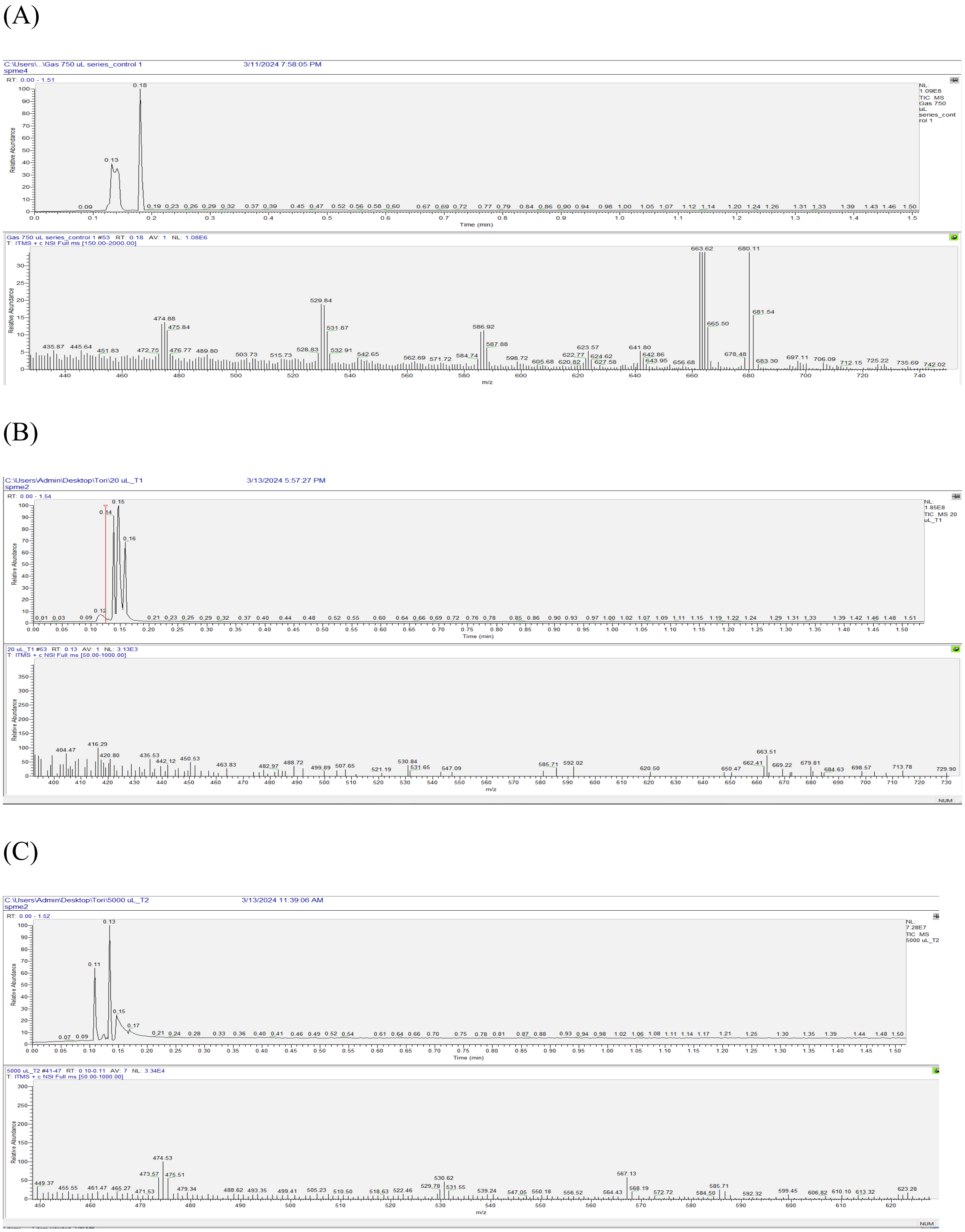

Figure 6: Representative mass spectra under different gasoline-water ratio conditions; 100 µL gasoline and 0 µL water (A), 100 µL gasoline and 20 µL water (B), and 100 µL gasoline and 5500 µL water (C).

IV: DISCUSSION

The data from this research concluded that the addition of water in varying ratios with gasoline does have an effect on the relative intensity of signals produced from DART-MS analysis. Figure 6 on page 12 details the TIC and mass spectra produced as a result of the analysis of the following samples: a control sample with 100 μL gasoline and 0 μL water (A), 100 μL gasoline and 20 μL water (B), and 100 μL gasoline and 5500 μL water (C). The TIC produced from each analysis shows multiple large peaks at the time of fiber insertion, and a decreased intensity of peaks is seen as thermal desorption of the fiber occurs. The mass spectra details every peak signal present during the analysis duration with the relative intensity of peaks being seen.

The spectra from each sample analysis consistently produced the *m/z* 474 signal, showing that this is most likely the dominant gasoline signal. There were a couple of incidents where the *m/z* 473 signal was present and had a more significant intensity compared to the *m/z* 474 signal. This is potentially a result of the water changing the dominant *m/z* 474 signal's intensity greatly, making the *m/z* 473 signal shown on the spectra have a more significant intensity overall. The *m/z* 663 signal was present in every spectrum produced; the signal always had an intensity at least 3 times greater than the intensity of the *m/z* 474 signal from the same spectra. This *m/z* 663 signal was determined to most likely be a background signal as a result of the SPME fiber itself, as the signal is consistent in its large intensity and presence. The ratios of the signals determined by dividing the *m/z* 474 signal by the *m/z* 663 created an overall average of the ratios from the duplicate runs of the gasoline:water samples. These averages were plotted on an Excel graph (Figure 5 on page 11).

Results were expected to show some effect on the intensity of the ratios of the gasoline signals, and the results showed the expected effect. The water affected the gasoline signals by decreasing their overall intensity. In some instances, the *m/z* 473 signal (which is another, less dominant gasoline signal) had an intensity that was much larger than the *m/z* 474 signal. One possible reason for this is that the NH_2 compound present in gasoline may determine the solubility characteristics of the gasoline. The potential of having more water may make the *m/z* 474 signal more soluble and, therefore, more difficult to extract, resulting in the intensity of this signal being less than the *m/z* 473 signal which could be less soluble in water. This research proves the relevance of water's presence combined with gasoline.

This experiment was a qualitative method that was meant to either prove or disprove the general idea that water has an effect on gasoline signals. The method was intended to show what effect was seen on the gasoline signal intensities, but the intent was not to quantify the effect produced. This research process experienced some issues, as some runs of the analysis produced spectra that did not exhibit any gasoline signals. The lack of gasoline signals on some spectra suggested that there was an error in the extraction itself. The results could be improved after more familiarization. Additionally, the transfer of the SPME device to the DART-MS instrument is not ideal, as it creates the potential for the analytes to be contaminated before they reach the DART-MS. Other errors occurred because other signals, *m/z* 530 and *m/z* 586, were not as consistent as the *m/z* 474 signal, and so the data from those signals were not helpful during this analysis.

Additionally, the ranging intensities seen between the same signals are interesting, as the gasoline was obtained from one sample throughout the duration of the experiment. Therefore, the gasoline signals should not vary in intensity greatly unless some other factor affects it.

Specific training is required in the research involved with the SPME. As previously mentioned, the PDMS fiber is extremely sensitive and requires extreme care in its handling/usage. Many discrepancies found in the data have been sourced from issues with the extraction process and attributed to the PDMS fiber. The fiber has a lifespan that is relatively short, and the fiber often becomes clogged with analytes, which produces a cluttered spectrum with various background signals and inconsistent peaks. The SPME fiber needs to be handled with care, as the fiber's highly sensitive nature caused issues with its ability to extract analytes consistently. The extraction period duration is also a factor that could have negatively affected the extraction process. The extraction period proved to be long enough for the extraction of ratios that totaled under 500 μL, as the samples were able to produce enough condensation for the analytes to be extracted. However, a longer extraction period would most likely prove to be beneficial for samples larger than 500 μL to ensure that sufficient vaporization takes place.

In sample preparation, the gasoline was pipetted into the vials first, with the water following, and so rotating/mixing the solutions during extraction helped to disperse the gasoline fully into the water. The rotation of the vials on the heating block could also influence the vaporization of the ratios, as the liquids would most likely transform into their gaseous state while in a resting position. However, the rotation of the gasoline-water ratios is necessary as it aids in the creation of a fully mixed solution which helps in the reproducibility of the analysis. Additionally, while all samples were rotated within their vials and heated at the same temperature for the same duration of time on the heating block, the vaporization of the ratios varied significantly, which could have contributed to the discrepancies within the data. Observation of the vials during the extraction process showed that the more water that was added to the gasoline mixture, less condensation was produced from the heating. This feature also seems to have played a role in the extraction process, as there was less condensation produced leading to varying amounts of thermal desorption of the fiber and fewer analytes being extracted by the PDMS fiber.

In future research, continuing the pattern of analysis seen from this experiment would be optimal. Analyzing other ignitable liquids, such as kerosene and lighter fluid would help to broaden the range of the application of these results. Continuing to enhance the method of analysis would be optimal in lessening any potential effects on the extraction or analysis itself, as well as the reproducibility of the results. Performing more analysis on samples, as well as other ratios, may be ideal to cover the broader range of possibilities seen in this analysis. Utilizing other interference liquids/materials such as blood or fire extinguisher foam/powder would be helpful in proving that this method is applicable not only to water but also to other substances. Analyzing gasoline's interaction with other interference liquids would help to include other commonly used ignitable liquids found with evidence at crime scenes, as gasoline is not the only ignitable liquid used. Lastly, spiking different substrates such as carpet, wood, or cotton fiber would aid in creating a sample that is most similar to what would be found at a real crime scene – with the ignitable liquid being soaked into a substrate rather than being present in a clear sample. Testing with the parameters outlined in this research combined with these other factors would help to create an experiment that is highly realistic and applicable to what is analyzed in crime labs.

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