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An Investigation into Air Sample Testing using a Miniature Atmospheric Chamber and Gas

Chromatography-Mass Spectrometry

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I.   Abstract

Atmospheric chambers have been used in various fields of chemical study in conjunction with Gas Chromatography-Mass Spectrometry (GC/MS) for a myriad of purposes. Many of these studies have dealt with the application of atmospheric chambers in environmental chemistry. This study seeks to verify the efficacy of a custom-made, low-cost atmospheric chamber in analyzing gas-phase samples using GC/MS. The focus of the chamber testing revolves around a mixture of air and pure acetylene. Chamber assembly and preparation was conducted through a series of leak-tests and input/output design alterations. Additionally, a GC/MS method for the analysis of acetylene was derived from an existing ethanol headspace analysis method. Finally, the chamber was tested for the ability to introduce a sample mixture into the chamber and successfully analyze the sample using East Texas Baptist University's GC/MS. Results of the chamber evaluation are promising and warrant further development and research.

II. Introduction

Background

Various types of mass spectrometry have been used in several fields of chemical inquiry. These studies have encompassed the measurement of volatile organic compounds (VOCs) in marine chemistry using GC/MS,[1] the analysis of hydroxyl free radicals with proton-transfer mass spectrometry,[2] as well as the analysis of the oxidation effects of acetaldehyde when it is exposed to radicals at night using Fourier transform infrared spectrometry.[3] Each of these studies uses a particular method of mass spectrometry to analyze a chemical sample in such a way that each compound can be accounted for and measured not only on a qualitative level (determining which compounds are present) but also on a quantitative level (determining the concentrations in which those chemicals are present). GC/MS is not restricted to testing gas-phase samples only; it can be used for any number of other applications.[4–7] Still, this methodology is particularly useful in the analysis of gas-phase samples of unknown composition and concentration. Of specific interest is the pairing of gas chromatography and mass spectrometry. The combination of chromatography and spectrometry gives a more thorough analysis of the composition of a given sample than either method alone could provide because of the specific ability of GC/MS to separate the analyte (the substance being analyzed) from the rest of the sample.[8]

Despite its efficacy in testing, GC/MS must be paired with some sort of collection method in order to be of any significant use. In particular, the application of atmospheric chambers in gas-phase testing provides an opportunity to simulate a variety of environmental conditions in a more controlled manner than what would be otherwise possible.[9] This technique has been the foundation of both small-scale experiments as well as the basis for larger simulations.[3,10,11] For both large and

small-scale experiments, the purpose is to simulate reactions in order to understand or forecast the overall behavior of the earth's atmosphere more thoroughly.[3,10,12,13] The understanding gained through these studies can be used for the management of various atmospheric effects.

Beyond sample collection and analysis, reaction modeling through the use of computational chemistry becomes a valuable supplement in analyzing reactions. The application of Density Functional Theory (DFT) in computing the ground-state energies of certain smaller-scale molecules provides another method of analysis useful to studies of atmospheric conditions.[14] The combination of this technique with GC/MS can be especially useful in the study of environmental issues such as pollution or atmospheric forecasting. Many studies have been done in order to map atmospheric conditions and pollutants using a variety of methods both for sample collection as well as analysis.[3,12,13,15]

Whether atmospheric conditions were simulated or observed *in situ* (at the location of the natural reaction being analyzed), the purpose of many atmospheric studies is to understand the causes and environmental effects of chemical reactions. Those results can then be applied to any efforts to reduce atmospheric pollution or can be used in further research of those same issues. The environmental applications of this sort of study are of particular importance to the region of East Texas as well as the entire state because of the unique environmental concerns affecting both.[16–25]

Atmospheric Chambers

As stated previously, atmospheric chambers are important collection and simulation methods in many experimental studies in environmental and atmospheric chemistry.[3,9,10] However, any consideration of an atmospheric chamber must first include the specific variety of atmospheric chamber being used. Commonly, atmospheric chambers are referred to as either environmental chambers[2,9,15,26,27] or smog chambers.[28–30]

Both varieties range in size from smaller, portable apparatuses[10] to chambers that take up entire buildings.[9,26] Despite these differences, several characteristics are shared among the majority of these chambers. A key component of each is the main chamber itself, which contains the primary sample being tested. These are typically lined with a non-bonding coating such as Teflon or fluorinated ethylene propylene (FEP).[31] These linings hinder the gas-phase samples' tendency to chemically bond with the walls of the chamber. The bonding of these compounds to the side-walls of an atmospheric chamber is part of what are collectively referred to as chamber effects. Beyond the main chamber, the schematics of each chamber vary significantly; however, most chambers also contain a reactor for the purpose of actually simulating the reaction being studied. Reactors may be of variable size and pressure in order to keep the reaction matrix as consistent as possible throughout the course of the experiment.[9] Generally, these reactors are smaller in size than the containment chamber of the apparatus; however, they are the central component of a large number of these systems.[9,27,30,31] Many chamber designs also include a light source for the analysis of photochemical reactions normally associated with environmental systems.[3,9,31–33] Beyond these elements, the actual assembly of the chamber depends upon the parameters of the specific tests being run.

Atmospheric chambers of all varieties are most often used for the express purpose of analyzing and simulating gas-phase reactions in order to compare them to reactions naturally occurring in the atmosphere.[12,13,15,34] For many of these chambers, they are used in conjunction with some form of analytical instrumentation so the reactions taking place can be properly studied. Many chambers are used to study the reactions of aerosols (colloidal suspensions of solid particles in a gaseous solution) in order to more accurately model their presence and effects on the atmosphere as a whole.[29,31,32,35–37] However, not all studies are centered on the understanding of

aerosol compounds.[28,38,39] No matter the specific compounds being analyzed, the focus of experiments using these chambers is that of simulation. The simulations generated in these chambers can subsequently be used in conjunction with mathematical modeling techniques to predict and model chemical reactions and systems in the atmosphere as a whole.[10,11,34,40] Once collected, the data can be used to formulate strategies that will aid in mitigating a variety of atmospheric concerns.

Gas Chromatography-Mass Spectrometry

Despite the utility of atmospheric chambers, they can only be effectively used if they are paired with an appropriate analytical technique. For many studies, the most effective analysis comes through the usage of advanced quantitative instruments known as mass spectrometers. There are many types of mass spectrometers, ranging from simpler time-of-flight mass spectrometers to more complex proton-transfer mass spectrometers.[2,32,41,42] For the sake of this study, only a quadrupole mass spectrometer coupled with a gas chromatograph will be discussed in detail.

Before the specific instrument being used can be fully discussed, the operating theory behind GC/MS must first be understood on a practical level. The GC/MS instrument itself is comprised of two parts—a gas chromatograph and a mass spectrometer. In order to understand the theory of these two instruments working in conjunction each must be understood individually, beginning with gas chromatography.

Gas Chromatography is primarily a separation method, meaning that it is used to separate chemical species out of solution in order to determine the solution's chemical makeup. This is particularly useful in understanding the composition of more complex solutions. Gas chromatography, like all other forms of chromatography, consists of a mobile-phase sample that

is forced through an immiscible, stationary-phase partition. In basic chromatography, the chemical species that are greatly hindered by the partition travel slowly, whereas the species less hindered by the partition travel quickly. The simplest forms of chromatography can use only a piece of paper, ink, and a liquid. The liquid travels up the paper, carrying the components of the ink various distances. This process generates bands that aid in the identification of the specific compounds in the solution.[43] Gas chromatography operates under the same general principle. However, both the instrumentation and analysis are both far more complex. In gas chromatography, the analyte is vaporized and suspended between a mobile gas phase and an immobilized liquid phase. After this suspension, the analyte travels through a chromatographic column within the instrument and produces thin bands in a spectrum. The spectra are subsequently analyzed to reveal the components of the solution.

The purpose of gas chromatography is to separate the analyte from the reaction matrix; however, separation alone is not sufficient to fully analyze the solution. Therefore, another analysis method must be coupled with the chromatography. In many cases, the second analytical process will be some form of mass spectrometry. For this study, the specific type of mass spectrometer is a quadrupole mass spectrometer. The operation of these spectrometers depends on the central idea of the quadrupole. In quadrupole mass spectrometers, four metal rods are spaced equidistant from each other to create a channel through which the ions from the sample solution can travel. A magnetic field is generated within the quadrupole and ions of specific masses are selected through the variation of power from a direct current (DC) source as well as variable radio frequency (RF) with an alternating current source. This variation allows for the selection of specific ions according to their mass through adjusting both the DC potentials and RF alternating current potentials. The voltage applied via the RF potentials causes the quadrupole to act as an ion channel, allowing any

ion to pass through the length of the quadrupole itself. However, the voltage from the DC potentials restricts certain ions from being selected according to their mass and their charge. The combination of these potentials, and the alternation of both, gives the ability to produce spectra according to the mass and charge of the ions in the solution by selecting certain ions throughout the analysis.[44] When coupled with gas chromatography, the two become particularly useful in analyzing the ionic compounds found within complex solutions. Although a gas chromatograph can separate most compounds from each other, certain compounds elute at very similar rates. Therefore, a mass spectrometer is used to further separate the compounds from each other and analyze them according to their respective masses. This analysis is accomplished through the production of spectra, which are comprised of peaks of various intensities and sizes to indicate the concentration and presence of the compounds in the solution being analyzed.

The operation of the GC/MS depends largely on the specific instrument being used; however, the fundamentals of the process remain the same. For the specific GC/MS at ETBU, the instrument consists of a gas chromatograph, a vacuum pump, a vacuum gauge, ion sources (both electron impact and electron energy/current variation), a quadrupole mass filter, and an electron multiplier detector.[45] Each piece of the instrument works in conjunction with the other elements to separate and analyze the chemical species upon which the experiment is focused. To test a gas-phase sample using the GC/MS, the sample is first pulled into the gas chromatograph by the vacuum pump. Once the sample has entered the chromatograph column, the solution is separated into its component parts within the column. Next, the sample is drawn through the quadrupole according to selected masses and accelerated toward the detector at the other end of the mass spectrometer. The data collected from the detector is then compiled into spectra, and the result is analyzed to determine the presence and concentration of the analyte. This is accomplished by

looking for specific peaks and measuring the area of each peak.

Although GC/MS can be used either for liquid-phase or gas-phase sample testing, this research will be solely concerned with the gas-phase testing applications of GC/MS. The particular usefulness of this analytical method in the context of gas-phase samples is that of matrix separation. The specific ability of GC/MS to effectively separate the components of a chemical solution and analyze each part individually lends accuracy to gas-phase testing that is useful in a wide variety of applications.[1,4-7,8] This means that the use of GC/MS in studies of this nature is of significant importance and greatly increases the capacity for accurate analysis.

Additional Concerns

In addition to GC/MS and atmospheric chambers, another source of interest in this research comes from the field of computational chemistry. Primarily, computational chemistry deals with simulating chemical reactions through advanced computer models based on quantum physics. This is achieved through the application of Density Functional Theory (DFT), a concept that originated in quantum mechanics.[14] The foundation of DFT is Erwin Schrödinger's equation for wave-function, which establishes a relationship between ground-state energy, intramolecular interactions, and time. The bulk of computational chemistry deals with the ground-state energy of the atoms taking part in the reaction. Ground-state energy is the lowest energy of an atom or molecule before it is excited by any outside forces or reactions. This is then used to approximate the location of subatomic particles in a reaction system. Once the approximations have been made, the information is then used to predict the energy inherent to the reaction system.

The primary applications of computational chemistry come through modeling chemical reactions in various situations. The utility of this modeling comes primarily through the ability to more accurately understand what takes place during the course of the reaction being studied. This

application is useful to many aspects of chemistry because of its accuracy in revealing the nature of different chemical systems by estimating the charges and potentials of the particles involved in the reaction itself. Applications of DFT in computational chemistry can be found in many aspects of chemical research, since every chemical reaction has the potential to be analyzed on a simulated level. This makes computations a viable supplement to any number of studies, including those in atmospheric chemistry.

In addition to computational chemistry, another concern affecting this research is environmental in nature. For the state of Texas, multiple atmospheric factors have effected significant changes in the chemical make-up of the environment. Because of the industrial, commercial, and natural sources of pollution in Texas, there have been many noticeable side-effects for the inhabitants of Texas.[16] An example of these side effects that has been noticed in recent years is that the air conditions in Texas have adversely affected the birth weight and neural development of children born in the state.[20,24] Many of these results were gained through the application of environmental testing through gas-phase analysis of air samples.[19,22,24,25] Because of this tangible application, research into the air quality within the state is of great relevance to the scientific community as well as the general populace.

III.   Experimental

Chamber Design

Chamber assembly began at the beginning of the spring 2015 semester. The chamber itself was supported by a polyvinyl chloride (PVC) pipe cage, the schematic for which is shown in Figure 1 below.

Figure 1: Dimensions and structure of PVC pipe cage.

The pipe cage was constructed using two 2-foot segments, three 3-foot segments, and four 0.75-foot segments of 1/2-inch PVC piping. At junctions A-F in Fig. 1, the pipe segments were joined using 1/2-inch corner pieces, and were joined by 1/2-inch T-junctions at points G and H. The chamber itself was suspended by the top crossbar between junctions A and B using a series of clamps tied around the top of the cage. Holes were drilled in the vertical supports to allow input and output lines leading into and out of the chamber to be supported structurally.

The chamber consisted of a Teflon/fluorinated ethylene propylene (FEP) bag measuring 2.5 feet by 1.5 feet. A structural diagram of the chamber is shown in Figure 2.
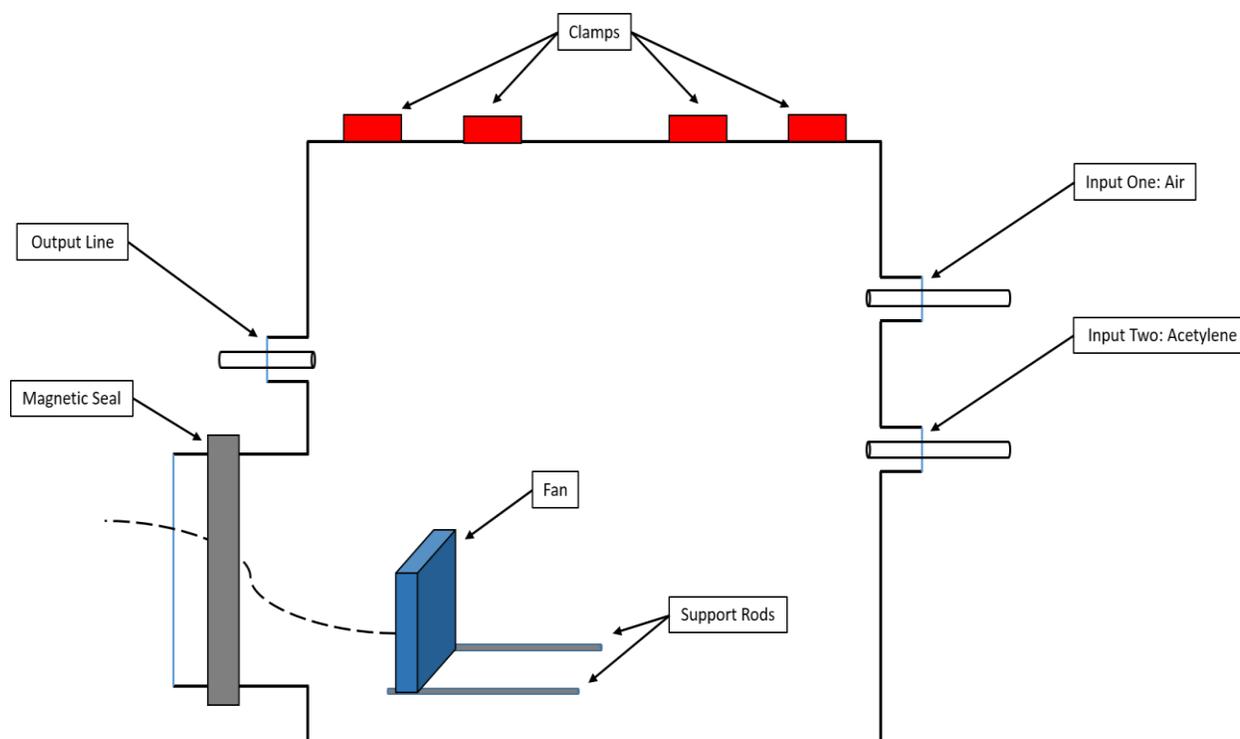
Figure 2: Atmospheric chamber schematic.

Two input lines feed into the chamber, each connected to tanks of compressed gas by which the sample mixtures were introduced into the chamber. On the opposite side of the chamber, two openings serve as an output line and chamber evacuation vent respectively. The input and output lines were secured using electrical tape wrapped securely around the 1/4-inch polyethylene tubing inserted into each opening. The evacuation vent was closed using two iron bars sealed to bar magnets on the other side of the opening. The inside of the vent was sealed using vacuum grease to minimize gas leakage and avoid chamber outgassing.

A low-speed fan was inserted into the chamber through the evacuation vent to maintain consistent air-circulation throughout the chamber. This served to prevent sample mixtures from becoming stagnant inside of the chamber. The fan was supported by two small glass rods to ensure

the fan maintained its orientation inside the chamber. The fan was a repurposed computer component, its wiring spliced to the A/C power supply of an old phone charger. The spliced wiring was tightly wound with Teflon tape to prevent gas leakage via the wiring and keep the wires together compactly.

Each input line was connected to a compressed gas tank by means of a rotameter. Input one was connected to a tank of Grade-D compressed breathing air, and input two was connected to a tank of dissolved Acetylene gas. Both gas sources were purchased from Red Ball Oxygen Co., Inc. (Shreveport, LA). The rotameter control valves measured gas throughput in standard cubic feet per hour (SCFH), with maximum measurable gas flows of 1.0 SCFH for input one and 0.4 SCFH for input two. The input valve schematic is shown in Figure 3.
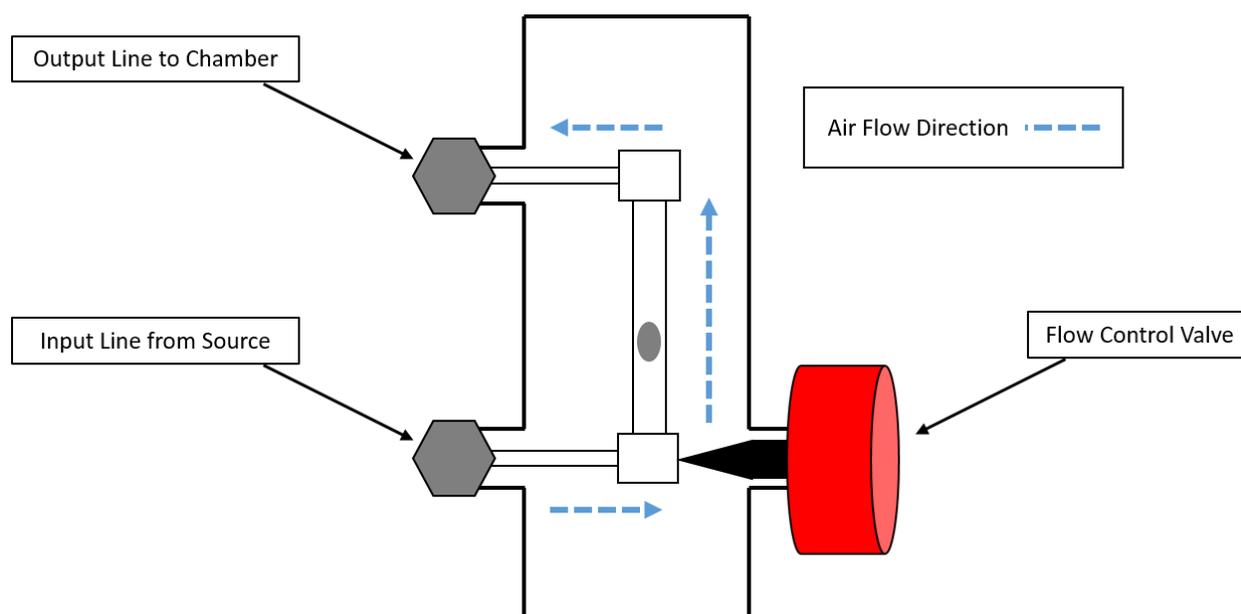
Figure 3: Schematic for the rotameter input valves.

Both rotameters were fitted with identical pairs of stainless steel Swagelok fittings connecting the control valve to 1/8-inch polyethylene tubing. Both the input and output tubing were in turn connected to a 1/8-inch to 1/4-inch adapter. The rotameters were connected to 1/4-

inch tubing leading from the compressed gas sources and also to 1/4-inch tubing leading into the atmospheric chamber.

Beginning at the sources, 1/4-inch tubing was connected directly to the tank regulator. The opposite end of the tubing was connected to the rotameter input valve via the Swagelok adapters fitted to the rotameter input lines. On the opposite side of the chamber, the output line was capped with a 1/4-inch stainless steel septum fitting for the purpose of sample extraction. The chamber output was designed so that samples could be extracted using a 1000μL gastight syringe.

Leak Testing

When chamber assembly was completed at the end of spring 2015, leak testing began immediately thereafter. Throughout the course of leak testing, the sealing method for the chamber went through several iterations for both the input/output lines and the evacuation vent.

Leak testing was accomplished qualitatively by capping all input/output lines and filling the chamber with compressed air until the walls of the chamber were drawn taut from internal pressure. The chamber was then visually and tactilely inspected after a period of 24-36 hours to determine how much air was retained over the interval. Because of the relatively low internal pressure of the chamber, it was not possible to test the chamber using traditional leak testing methods.

The input/output lines were sealed using tape wound around both the 1/4-inch polyethylene tubing and the outside of the chamber. Multiple types of tape were tested before electrical tape was selected for its ability to bind the chamber effectively to the outside of the polyethylene tubing. In the prototype stages of leak testing, the evacuation vent was sealed using a reinforced rubber

gasket. However, the primary result of the testing revealed that a more effective sealing method was necessary.

Based upon the leak testing results, the final evacuation vent seal was completed using two iron bars on one side of the chamber transfixed by a series of ceramic bar magnets on the other side. The inner space of the vent was lined with vacuum grease to ensure that gas leakage through the opening was prevented. The vacuum grease was crucial in compensating for the fan wiring exiting through the evacuation vent.

Headspace Analysis

Before sample testing could begin, it was imperative that a proper method be determined to analyze chemicals already in the gaseous phase. This was because the gas chromatography component of the GC/MS instrument often depends on the boiling temperatures of volatile compounds. Because the samples were already in the gaseous state, it was necessary to ensure that the GC/MS at ETBU was properly equipped to analyze gas-phase samples. Because the intended analyte compound was acetylene gas (molar mass: 26.04 g/mol), it was decided that a method should be derived from analyzing another gas-phase organic compound. For this reason, ethanol (molar mass: 46.068 g/mol) was selected as a reasonable approximation for developing a testing method for gaseous acetylene to approximate the void time for the GC/MS column.

To test ethanol, a method was taken from the work of André Généreux and John Head at Concordia College in 2011.[46] In their research, they attempted to quantify the concentration of ethanol and other VOCs using GC/MS. Their method used an instrument similar to the Shimadzu GCMS-QP2010 at ETBU with the following parameters: An initial column temperature of 38°C was held for one minute, then the column temperature was ramped to 60°C at a rate of 2°C/min.

Immediately after the column had reached 60°C, the column temperature was increased to 200°C at a rate of 70°C/min and held at the maximum temperature for six minutes. At the same time, the injector temperature was 250°C with a split ratio of 10:1. In the method, a solvent delay took place at 0.5 minutes. The mass spectrometer was set with an ion source temperature of 230°C and an interface temperature of 200°C.

Because the above method was developed for use with liquid ethanol, it needed to be tested with vaporized ethanol. Ethanol samples were prepared in 1.5-mL bottles by adding 20µL of liquid ethanol to each sample bottle. The bottles were then sealed, placed in an oven, and baked at 38°C for 45 minutes to ensure the ethanol was fully evaporated before analysis. The results of the ethanol analysis can be found in Figure 4.
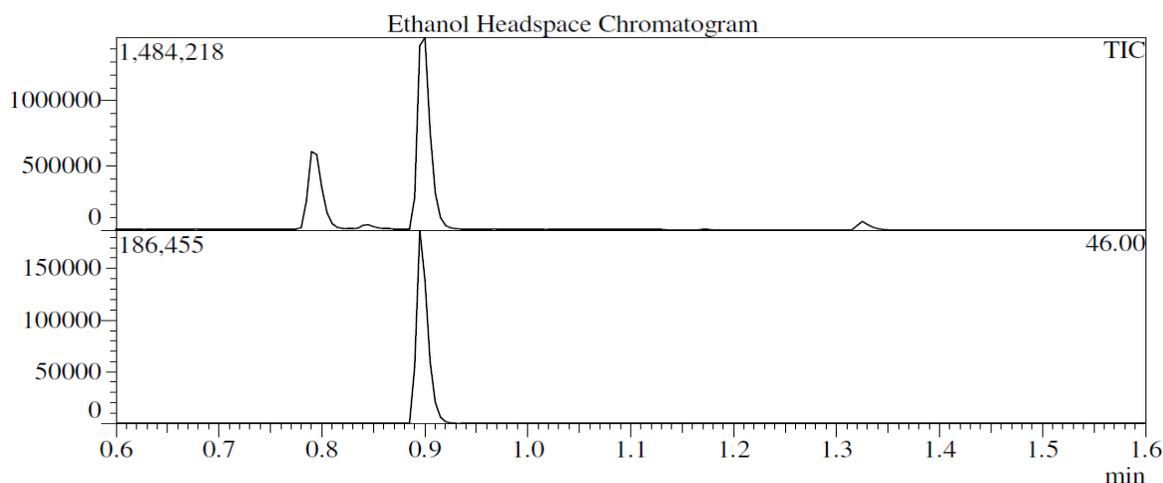
Figure 4: Chromatogram results of the Ethanol headspace analysis.

Figure 4 shows the Total Ion Count (TIC) chromatogram as well as the Selected Ion Count (SIC) for the mass at 46.00 amu, the approximate mass of ethanol. The TIC is integral to any GC/MS analysis because it illustrates the total number of ions passing by the instrument's detector as a function of time, regardless of molar mass. In the top half of Figure 4, the large peak at approximately 0.9 min shows the primary elution time for the analyzed sample, where the greatest

number of ions passed the detector. In the bottom half of the figure, the SIC for 46.00 amu is shown. This selected count reflects the number of ions at 46.00 amu that passed the detector over the course of the experiment run. The conclusions taken from these data show that a large elution of ethanol occurred around 0.9 min, alongside the primary elution time from the TIC. Because the ethanol was successfully picked up by the instrument, it was determined that the GC/MS at ETBU would be able to properly analyze gaseous chemical species such as vaporized ethanol and acetylene. This confirmation was crucial before any further testing attempts were made.

Acetylene Testing

The next step of the experimental process was to develop a method to properly analyze the concentration and presence of acetylene in the sample mixture. This was accomplished by pumping a series of air and acetylene mixtures into the chamber then subsequently extracting and testing those mixtures with the GC/MS.

Through a series of tested sample batches, an optimized method was reached. During the method optimization, the final column temperature was lowered to 100°C instead of 200°C so that the sample could be fully tested more quickly, and also because the sample was already in the gas phase. In addition to the final temperature being lowered by 100°C, the rate of change for column temperature was lowered to 20°C/min instead of 70°C/min to generate a more gradual change in temperature. Both of these changes were intended to make the method faster and more efficient for the gaseous analyte. In the final analysis, the method began with an initial column temperature of 38°C, which was held for one minute. This was then ramped to 60°C at a rate of 5°C/min. After the column had reached 60°C, the temperature was again ramped up to 100°C at a rate of 20°C/min. The column was then held at the maximum temperature for 5 minutes. An injection temperature

of 250°C and a split ratio of 10:1 were utilized just as in the method developed by Généreux, et al.[46] A mass range of 20-50 *m/z* was selected for analysis because of the molar masses of acetylene (molar mass 26.02 g/mol) and the compounds present in air.

In preparing the sample mixture, air was vented into the chamber at a rate of 1.0 SCFH (0.4717 L/min) and acetylene was vented in at a rate of 0.4 SCFH (0.1887 L/min). Acetylene was vented into the chamber for roughly one-half the time that air was pumped in. This was to ensure two things about the internal state of the chamber: first, that a large enough concentration of acetylene would be present to properly analyze, and second, that the amount of acetylene would be small enough to maintain in-lab safety during the process of chamber evacuation.

IV.   Results

Through testing, it was seen that the elution time occurred consistently between 0.7 and 0.9 minutes, well before the GC column had reached its maximum temperature. The elution time of the acetylene indicates an elution temperature of 38°C, before the column temperature began ramping.

Using the optimized method, an acetylene sample was analyzed that showed a large amount of acetylene elute at 0.8 minutes. The chromatogram in Figure 5 shows the TIC and the SIC at 26.00 amu, approximately equal to the atomic mass of acetylene.
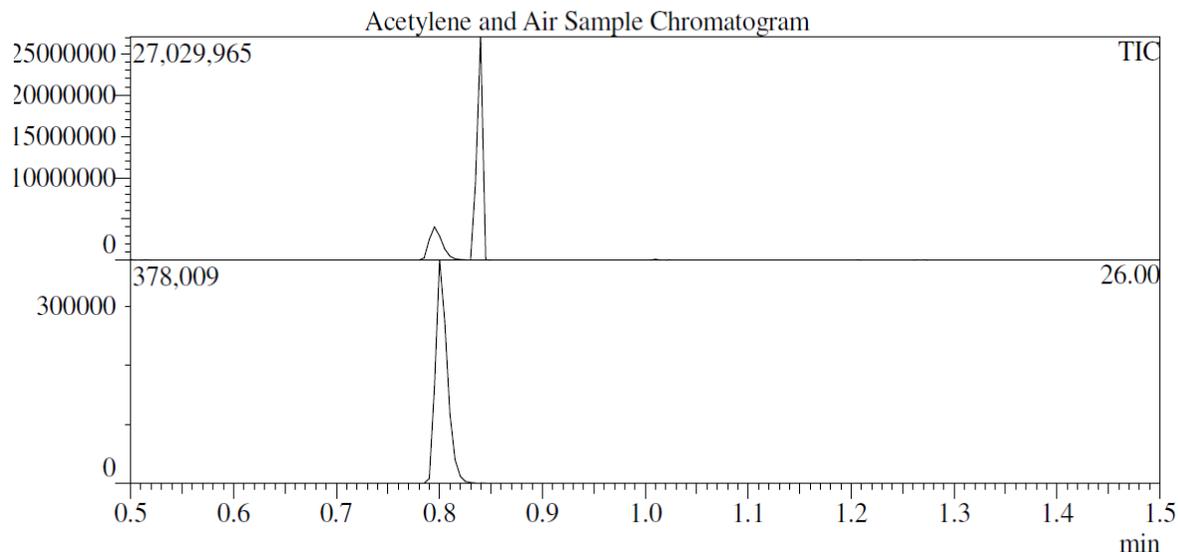
Figure 5: GC Profile for the total ion count of the sample and 26.00 m/z.

In Figure 5, the intensities of the base peaks in the chromatogram were both normalized to show the most intense peak as 100% of its respective scale. The top chromatogram shows the TIC for the sample while the bottom chromatogram shows the SIC for 26.00 amu between 0.5 and 1.5 minutes. The results of Figure 5 show a relatively large quantity of acetylene leaving the GC column at 0.8 minutes, which means that the results from Figure 4 were repeated with the gaseous samples in the acetylene test. The instrument was able to successfully detect and differentiate the analyte in the gaseous sample.

At 0.8 minutes, a mass spectrum was used to determine whether the elution of acetylene was significantly present in the spectral data as well as the chromatogram. The mass spectra for the sample at 0.8 minutes is shown in Figure 6.
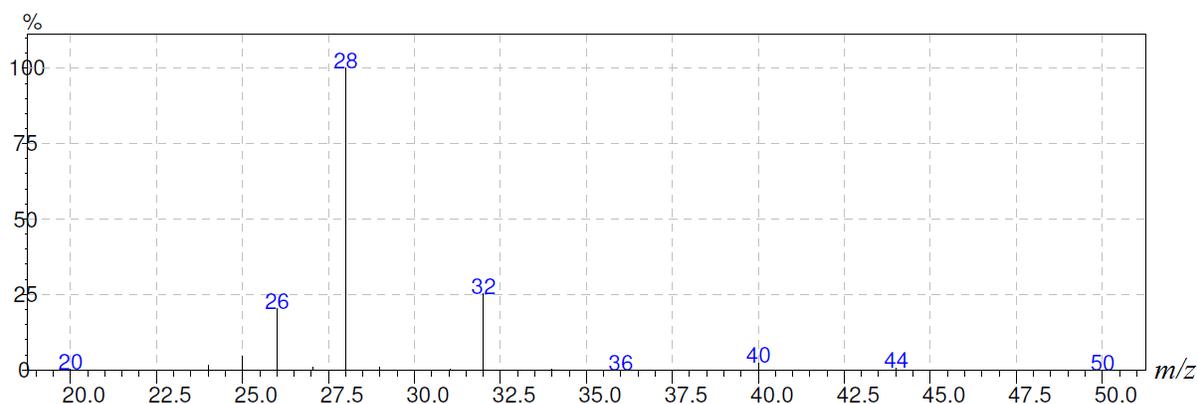
Figure 6: Mass spectrum analyzing the relative amount of acetylene vs. the component compounds of air.

In the spectrum from Figure 6, the base peak—the most abundant mass present—occurred at 28 *m/z*, which is consistent with diatomic nitrogen (N_2) being the most abundant compound in air. The relative intensity of the peak at 26 *m/z* was 20.26% of the nitrogen peak.

To understand how the relative intensity of the acetylene peak compared to the N_2 peak, approximate numbers of moles of both acetylene and air were calculated using the approximate flow rates of each gas scaled against how much time was spent pumping each gas into the chamber. The air mixture was vented into the chamber for 23 minutes and 17 seconds (23.28 min) at a rate of 0.4717 L/min. After the air sample was introduced to the chamber, acetylene was vented into the chamber for 13 minutes and 10 seconds (13.17 min) at a rate of 0.1887 L/min. Then, approximate volumes of each gas sample were calculated via Equation 1:

$$V \approx t * Q \tag{1}$$

where V is defined as the sample volume in liters (L), t is the time measurement in minutes (min), and Q is the flow rate in liters per minute (L/min).

$$23.28 \ min * 0.4717 \ \frac{L}{min} = 10.98 \ L \approx 11.0 \ L \ of \ air$$

$$13.17 \ min * 0.1887 \ \frac{L}{min} = 2.48 \ L \approx 2.50 \ L \ of \ acetylene$$

The volumes of each sample were then converted to moles using the ideal gas law as shown in Equation 2. The gas samples in the chamber were assumed to behave ideally because all calculated values were approximations. Therefore, use of the van Der Waals equation was not required for the system in question in this research:

$$PV = nRT \tag{2}$$

where P is the pressure inside the chamber in bar, V is the sample volume in liters (L), T is the temperature of the room and chamber in Kelvins (K), n is the number of moles (mol) in the sample, and R is the gas constant with a value of 0.083144 bar*L*K^{-1}*mol^{-1}.

In order to calculate moles from the obtained sample volumes, two assumptions were made. First, a constant room temperature of 21°C (294 K) was assumed because both samples were vented into the chamber and analyzed instrumentally within a short period of time (less than 45 minutes). Second, an internal pressure for the chamber needed to be estimated; this was accomplished by assuming that the pressure outside of the chamber was approximately equal to 1 bar. Then, a manometer was attached to one of the input valves and the chamber was filled to tautness. The manometer reading was 0.3 bar, meaning that the internal pressure of the chamber was 1.3 bar. This estimate was used as the internal pressure of the full chamber when samples were introduced into the chamber. Because these assumptions were made, the calculated results are, therefore, approximate values.

$$\frac{10.98 \ L * 1.3 \ bar}{0.083144 \ \frac{bar * L}{K * mol} * 294K} = 0.58196 \ mol \approx 0.58 \ mol \ of \ air$$

$$\frac{2.48\ L * 1.3\ bar}{0.083144 \frac{bar * L}{K * mol} * 294K} = 0.131891\ mol \approx 0.13\ mol\ of\ acetylene$$

The final step before comparing the number of moles for the two sample species was to determine the approximate number of moles of N_2 in the air sample. Atmospheric air mixtures are known to have a composition of approximately 75.5% nitrogen, 23% oxygen, 1.28% argon, and 0.012% carbon with trace amounts of other gases interspersed.[47] Therefore, an estimate of the molar amount for N_2 could be determined by multiplying the number of moles of the air sample by the percentage of nitrogen in the air.

$$0.58\ mol * 0.755 = 0.4395\ mol \approx 0.44\ mol\ of\ N_2$$

After estimating the amount of nitrogen gas in the sample, the ratio between the moles of acetylene and nitrogen was taken and compared to the relative intensities of each compound from Figure 6.

$$\frac{0.13\ mol}{0.44\ mol} = 0.295\ \frac{acetylene}{nitrogen}$$

Because the chamber was not completely evacuated before sample introduction, the calculated ratio of acetylene to nitrogen is a feasible estimation of the sample composition inside the chamber. The above value indicates that air from the laboratory surrounding the chamber was trapped inside it upon sealing. Therefore, it was reasonable to expect a higher theoretical ratio of acetylene to nitrogen because the calculations were unable to account for the air already inside the chamber, thus leading to a lower observed ratio of acetylene to nitrogen. However, the relative abundance of acetylene in the sample spectra indicated that acetylene was successfully extracted from the chamber after sample input.

Post-sample Blank Analysis

After the acetylene samples were analyzed to produce the results found in Figures 5 and 6, the evacuation vent on the chamber was opened and the sample mixture was released into an air scrubber to dispose of any remaining acetylene. The chamber was then left open for a week so that any trace amounts of gas could dissipate before a final test was administered to the chamber.

The chamber was filled with clean air, with the acetylene input valve completely shut off but still connected. After the air was allowed to circulate for 35 minutes, a sample was taken out of the chamber in exactly the same way that the acetylene samples were extracted. A 2mL sample was extracted through the output septum via a 1000μL gas-tight syringe and run through the GC/MS for analysis. The purpose of the testing was to confirm that a clean air sample could be run through the chamber and instrumentally verified as uncontaminated after having run a chemical such as acetylene through the system.

The chromatogram and mass spectra results from the post-sample blank showed no spikes of acetylene in either a TIC or an SIC focused about 26.00 amu. This confirmed that the chamber was able to be sufficiently cleaned of gas samples simply by forcing the existing sample through an air scrubber and allowing the chamber to vent to the air in the surrounding lab.

V.   Conclusion

Discussion of Chamber Performance

The combination of results from the acetylene sample test and the post-sample blank run show that the chamber is a potentially viable research asset to the Department of Biology and Chemistry at ETBU. At this stage of development, the chamber does need additional modification

for other sample introduction methods. However, the verdict drawn from this research is that the chamber itself is a project that warrants further funding and effort. Variance seen in the collected data falls within reasonable expectations given the initial stage of chamber development that this research was designed to address.

Discussion of Project Goals Accomplished

In the initial proposal to this research, several possibilities were indicated as supplements to the project. Specifically, the selection and computational modeling of an atmospheric gas complex was proposed as a supplement to the chamber testing itself. This portion of the project was unable to be completed for two primary reasons: hardware complications and time. In the original project prospectus, chamber leak-testing was scheduled to take place only during the spring of 2015, with sample-testing beginning by early September of 2015. However, leak-testing was not finished until early November of 2015. This meant that no attention could be diverted from successfully sealing the chamber until that was accomplished. Therefore, these supplemental aspects of the project were limited or cut entirely to ensure the safety of those in the Murphy Science Building.

Although a computational assessment of an atmospheric complex was not completed during the course of this research, the primary goals of the research were accomplished. Those goals were to verify the feasibility of using the atmospheric chamber for gas-phase testing with the GC/MS on-campus at ETBU by assembling the chamber, determining a proper experimental method, standardizing a testing methodology, and comparing the efficacy of the chamber to standard-sized equivalents. All but the last of these were successfully accomplished, and the goal withstanding was unable to be accomplished because of the qualitative nature the research took on

out of necessity. Because approximate values were calculated, it would have been impossible to accurately compare the chamber's performance to other methods statistically with any degree of viability. Additionally, because of the system tested in this analysis, it would not have been possible to find a proper point of statistical comparison.

Overall, the chamber performed promisingly. Therefore, the only major omissions from the project are the supplemental statistical and computational results that could only have been accomplished had the leak-testing of the chamber gone as scheduled.

Discussion of Future Possibilities

The chamber can be useful in a large variety of ways. Primarily, the chamber serves as a low-cost atmospheric chamber that does not require specialized machining expertise or large amounts of funding to acquire and assemble. Therefore, barring the cost of the GC/MS instrumentation, this method should be accessible to other small liberal arts institutions. The low-cost emphasis of the project was one of the primary reasons this research was initially selected and would be a boon to any other small schools looking to contribute to the field. This means that atmospheric chemistry research could potentially be opened to many universities of comparable size to ETBU.

Possibilities for further research at ETBU specifically are three fold, dependent on possible sample introduction methods yet to be determined. The first possibility is the quantitative analysis of the chamber's performance and the computational study of an atmospheric gas complex. This could be accomplished with a sufficiently large dataset, as long as each sample is prepared in a similar manner according to an established experimental method. The second possibility is to use the chamber to simulate the formation of atmospheric complexes by injecting specific sample

mixes into the chamber. The mixtures could then be analyzed using the GC/MS in the same way that the acetylene samples were analyzed. In simulating these atmospheric systems, it could also be possible to isolate the chamber from outside light sources and expose the sample mixture to light from a UV lamp to catalyze photochemical reactions, which commonly take place in atmospheric conditions in the presence of sunlight. The third possibility would require a different sample introduction method; however, it could prove equally useful in the long-term. Since the chamber is suspended in a support-cage, it could be taken out of the lab for possible field-testing applications. Although a sample-introduction method would have to be developed for on-site collection, it would allow the department to engage in atmospheric research in a very practical sense. This would also allow future students at ETBU to experience and contribute to research in a major field of chemistry and interdisciplinary study.

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