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# DETERMINATION OF THE CONCENTRATION OF ATMOSPHERIC GASES BY GAS CHROMATOGRAPHY

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## ABSTRACT

The study of common greenhouse gases such as Carbon Dioxide (CO<sub>2</sub>) and Methane (CH<sub>4</sub>) is important because the concentration can be linked to added absorption of emitted terrestrial radiation, leading to the warming of the atmosphere<sup>1</sup>. This research measures the concentrations of common greenhouse gases in the air surrounding Eastern Michigan University. The development of an auto-sampler system for long term use on the EMU campus will create a viable way to monitor greenhouse gas concentrations throughout the year. Samples were analyzed using an Agilent 6890 Gas Chromatograph and a Valco Industries Thermal Conductivity Detector fitted with a Restek 5A Molsieve column (part # 80440-800) and a Varian poraPLOT column (part# CP7550) for proper molecular separation. Molecular data analysis is plotted using Peaksimple software by SRI Systems from Torrance, Ca. Although the experiment is ongoing, preliminary data suggest this methodology could be used to detect atmospheric methane.

## INTRODUCTION

Global monitoring of atmospheric greenhouse gases, in particular carbon dioxide (CO<sub>2</sub>), has been a goal of the U.S. government for over 40 years<sup>2</sup>. Charles Keeling developed the first instrument to measure atmospheric carbon dioxide and began taking samples at Mauna Loa Observatory, Hawaii, in 1958<sup>3</sup>. Other measurements and estimates of historic levels of greenhouse gases, dating back millions of years, have been obtained from ice core samples<sup>4</sup>. The levels of these gases have fluctuated throughout history, but the highest rates of increase were not seen until

the Industrial Revolution. During the last two centuries the concentrations of CO<sub>2</sub> and methane (CH<sub>4</sub>) never exceeded about 280 ppm and 790 ppb, respectively. Current concentrations of CO<sub>2</sub> are about 390 ppm, and CH<sub>4</sub> levels have exceeded 1700 ppb<sup>5</sup>. The use of hydrocarbon fuels such as coal, natural gas, and petroleum has been largely responsible for the rise in fossil carbon emissions. The Intergovernmental Panel on Climate Change<sup>6</sup> states that the study of the increase in the concentrations of these greenhouse gases is important, due to the effects these gases have on global temperatures. Climate change can be defined as a difference in average weather conditions, or the change in distribution of weather conditions<sup>1</sup>. Over time, some of the adverse effects due to these climate changes are increased temperatures and the severity of weather patterns<sup>6</sup>.

The Intergovernmental Panel on Climate Change states that greenhouse gases warm the planet by absorbing solar radiation<sup>6</sup>. As light from the sun penetrates the atmosphere, it is normally reflected back into space as infra-red (heat)<sup>7</sup>. Greenhouse Gases (GHG) absorb energy in the infra-red spectrum, and therefore heat the atmosphere, thus warming the planet<sup>1</sup>. This radiation would normally flow through the atmosphere and continue on into space, but the rapid rise in concentrations of these absorbent GHG's has led to some of the warmest years in the instrumental record of global surface temperature since 1850<sup>6</sup>.

Methane is an important greenhouse gas in the troposphere as it is not highly reactive with OH radicals in the atmosphere, and therefore, is a long lived substance. Its atmospheric lifetime has been calculated to be on the order of a decade<sup>5</sup>. Methane oxidation occurs through a series of reactions in which CH<sub>4</sub> is converted to CO<sub>2</sub> and other byproducts. The atmosphere is in a state of constant change, with many chemical reactions happening simultaneously. As we move forward with new technology, new ways of adding greenhouse gases to the atmosphere emerge.

"Fracking," a slang term for "fracture," describes a procedure involving fracturing rock formations that contain oil, petroleum or natural gas (CH<sub>4</sub>). "Fracking" is a relatively new procedure, first used in 1947; modern fracking technology was de-

veloped in the 1990's<sup>8</sup>. According to the Tyndall Centre report by Wood<sup>8</sup>, fracking occurs by a process that begins when sedimentary rock formations rich in organic materials are targeted for shale oil. The oil is extruded by first drilling vertically to the targeted deposit. Next a horizontal technique that can stretch for thousands of meters is employed. These horizontal wells are pumped full of water, additional additives and sand, to prop the well up. The pressure of the water fractures the rock, thus releasing the gases or oils held inside<sup>8</sup>.

While the gases and oils collected through fracking are not necessarily damaging to the environment, according to Howarth, et al<sup>9</sup>, a potentially important impact is created by methane leaking from the mining sites. Drilling and flow back release substantial amounts of methane into the atmosphere. Many of these fracking mines release methane that is trapped either in the rock or under it. Mines that are not interested in the methane either let it escape into the atmosphere or elect to burn it off<sup>8</sup>. As the increase in shale gas exploitation is only likely to increase, the next twenty years could see major increases in the amount of methane in the atmosphere due to fracking<sup>9</sup>.

It is impossible to do experiments on the planet's atmosphere as a whole, so we must take smaller usable samples and adapt ways of testing in order to measure the targeted subject. One of these testing methods involves the use of gas chromatography (GC) to separate molecules of interest from the bulk atmosphere<sup>11</sup>. Chromatography is one of the most widely used tools employed by analytical chemists. GC works by introducing a sample in the gas or liquid phase (the "mobile phase") through a tube that is either packed with, or lined with a material called the "stationary phase." This stationary phase can be composed of a number of things; usually either a polar or non-polar material is used to attract molecules of interest. An inert gas such as Neon (Ne), Helium (He), or Argon (Ar), is used as a mobile phase. The mobile phase pushes the sample through the column without reacting with the sample or the stationary phase. When heated, the molecules of interest begin to break their attraction with the stationary phase and break loose, moving through the column and into a detector.

Packed columns were the first type of columns used in GC; a packed column is filled with a stationary phase component. Perhaps the most important advancement in chromatography is the development of open tubular or capillary columns<sup>12</sup>. The “stationary phase,” rather than being in the form of beads, or an inert glass mesh throughout the length of the column, was instead coated on the inside of the tube. This allowed the columns to be longer, yet not require the pressure needed to move the sample through packing. Sensitivity has been greatly improved by being able to run the sample through longer columns<sup>12</sup>.

Thermal conductivity detectors (TCD's) are some of the earliest detectors used in GC. TCD is a powerful technique because it is a universal detector that has a range that begins at 500 pg/mL<sup>11</sup>. As the mobile phase exits the column it passes over a tungsten-rhenium wire filament<sup>12</sup>. When the sample passes over the wire, the electrical resistance is monitored, as it depends on temperature, which is determined by the thermal conductivity of the mobile phase. As the thermal conductivity of the mobile phase in the TCD cell decreases, the temperature of the wire filament and thus its resistance, increases<sup>12</sup>. Individual molecules and even atoms can be detected, since they all have different thermal conductivities. The VICI thermal conductivity detector that was used in this experiment works with a two channel reference system. TCD works by measuring the amount of electrical current required to keep the Tungsten-Rhenium filament the same temperature. The filament cools due to reference gas, or sample gas, running over it. There are two channels, A and B; channel B is used as a reference channel where only carrier gas is introduced to the filament. The reference channel measures the difference in conductivity created by the carrier gas so that it can be accounted for in sample gas measurements.

This research involves developing an auto sampler to be used in gathering and analyzing air samples around the campus of Eastern Michigan University. The air samples have been analyzed using an Agilent 6890 Gas Chromatograph with a Valco Industries Thermal Conduction Detector. The mobile phase ran hydrogen through a Restek Molsieve 5 angstrom packed column and a Varian poraPLOT column (part #CP7550), which was used to

separate our molecules of interest ( $\text{CO}_2$  and  $\text{CH}_4$ ). The molsieve column is a packed column that has a crystalline material inside to achieve molecular separation. The crystalline material has pores of 5 angstroms in diameter; the micro pores are able to filter larger molecules. Sample data was plotted using data analysis software (Peaksimple by SRI Systems) and compared to literature data to determine GHG concentrations found on central campus.

Developing an auto sampler for testing allows investigation of seasonal fluctuations of concentrations of greenhouse gases. As a first test of the auto-sampler system, the data can be compared to the literature concentration of these oft-measured species, which should give us confidence that the auto-sampler is a viable instrument for use in other atmospheric chemistry measurements.

## **METHODOLOGY**

Gas Chromatography is appropriate for this experiment because it is easy to use and detects a wide array of elements. It provides both quantitative and qualitative data on samples analyzed<sup>12</sup>. This method allows a sample containing many different substances to be analyzed at one time.

Air samples were collected at locations on the Eastern Michigan University campus. We collected atmosphere samples on the veranda from the third floor of the science complex. This provides good coverage of the central part of south campus. The samples were collected using Tedlar gas sample bags. The bags were connected to the machine via a gas pump and sample loop. The gas pump was used to draw sample gas from the bag into the sample loop. This allows for many samples to be analyzed quickly. Figures 1. and 2. show diagrams of the sample loop in fill mode and sample mode.

As described in Figures 1. and 2. (above), the equipment used to separate and detect the greenhouse gas molecules was an Agilent 6890 Gas Chromatograph fitted to meet our specific needs. There are two columns first a Restek Molsieve column the second is a Varian poraPLOT column and a single filament Thermal Conductivity Detector. The carrier gas and sample will be brought online with a 6 port sample gas valve system.

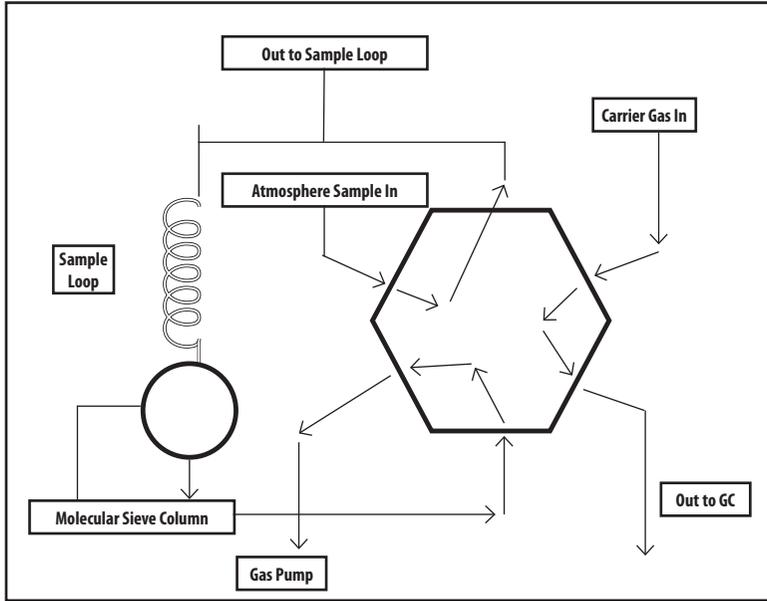


Figure 1. Diagram of gas flow in fill mode.

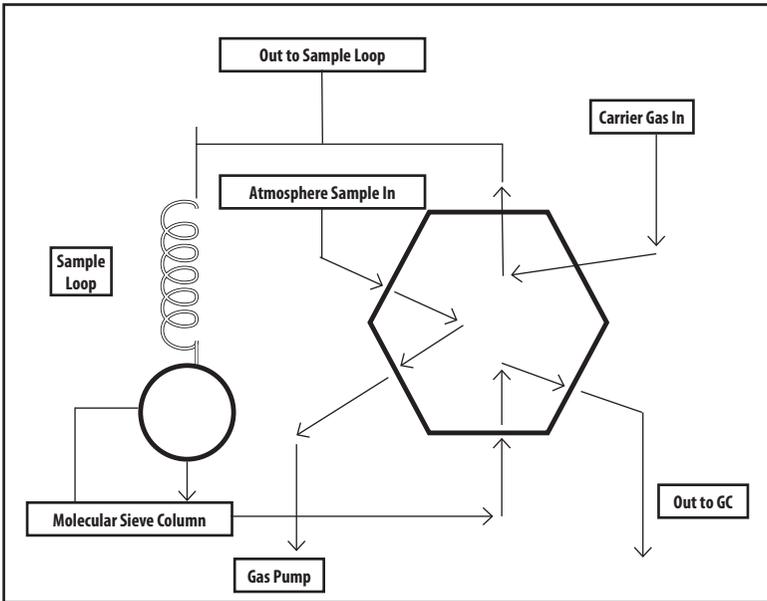


Figure 2. Diagram of gas flow in sample.

Sample materials are introduced to the system through an injection port, and into the columns. The temperature of the injection port is kept at temperatures above 200°C to minimize contamination sources until it is time to inject sample material. Our sample is held in a sample loop and pumped into the GC.

Measurements for this experiment were made using two separate columns. This was done to achieve maximum separation and retention times. A Restek 5A Molsieve packed column and a Varian poraPLOT column were used. "PLOT" stands for Porous Layer Open Tubular column. This is a capillary column that is lined with a 10 micrometer thick porous material made of fused silica. PLOT columns are especially sensitive for the detection of permanent gases. Permanent gases<sup>12</sup> are resistant to liquefaction under normal circumstances. This column, in particular, is good for both polar and non-polar molecules. The Varian poraPLOT is excellent for hydrocarbons up to C12. A C12 hydrocarbon is a carbon chain that contains 12 carbon atoms and 26 hydrogen atoms; hydrocarbons do not contain any other atoms. This column is especially good for C1 to C3 isomers. The column was conditioned in a GC, using a constant temperature of 200°C under a flow of 4 mL/min for 24 hours, to remove any residue from manufacturing and shipping.

The poraPLOT column has a working temperature range of up to 250°C. Samples are introduced with the injector port set at 50°C. The carrier gas is set on a constant flow at 6.0 mL/min. The column temperature is at 50°C for all data collection runs.

## **PROCEDURE**

### **Analytical Conditions**

The analytical conditions of our experiment were as follows: the test run began by turning on the pump and filling the sample loop for 0.6 min. At 0.6 min the valve was switched to the analysis mode and gas samples were pushed through the loop into the GC. The injector port was set to 50° C. The GC oven was set to 30° C and the flow rate remained at ~2mL/ min. TCD temperature was 100° C. Sample run time was 15 minutes monitored by Peak Simple software. Samples were directly injected to the port by syringe.

## Instrument Calibration

Calibration of the instrument occurred via samples of  $\text{CH}_4$  introduced by direct injection into the sample loop.  $\text{CH}_4$  standard was supplied by a house supply and the room air was gathered from the lab. The hydrogen carrier gas used was of high purity (AIRGAS). The sample loop and the pipeline feeding the system was purged to ensure that there were no residual gases in the system. The analyzer was brought up to temperature over the course of a few hours and allowed to remain heated while carrier gas was pumped through the system. Test runs were initiated after the TCD readings stabilized and there was a reliable baseline. The first sample was pure Hydrogen (H). This sample was run in order to check for proper TCD function. The carrier gas flow rate was adjusted to  $\sim 4$  mL per minute using a needle valve. Flow rate was determined using a bubble detector and stopwatch. The standard gas was then introduced to the system and given time to flow through the instrument. After analyzing these standards, a calibration curve was established to see retention times of our molecules of interest. A sample chromatogram was produced on the Peak Simple software, and the peak area was used to determine the concentration loading experienced by the detector.

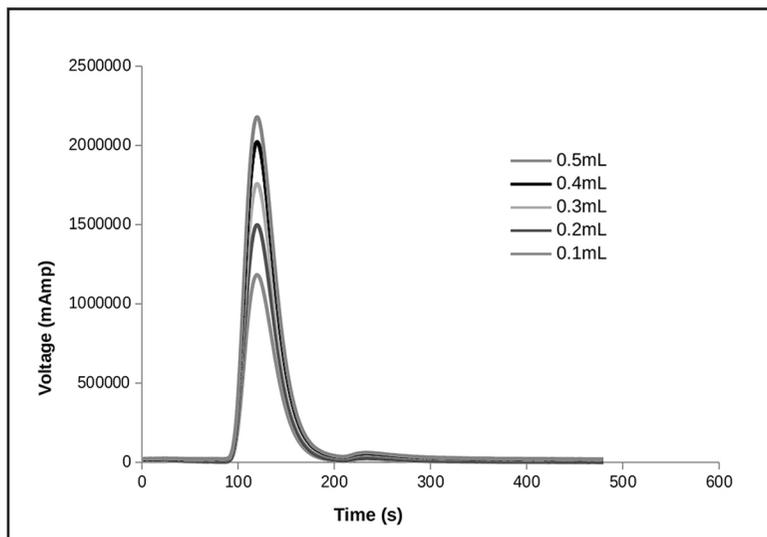


Figure 3. Series of Methane injections used to establish the calibration curve.

A calibration curve was established by injecting known amounts of CH<sub>4</sub> and measuring detector response. The first bags that were analyzed had pure methane from the house tap. A number of different volumes were used to build a calibration curve. Figure 3. illustrates the different peaks used to build the curve. In this case .1mL, .2mL, .3mL, .4mL, and .5mL methane samples were used.

After injecting known volumes of gas, the equation PV=nRT and Avogadro's number were used to calculate the number of molecules per sample. The calibration curve is shown in Figure 4 (below). The peaks on *Figure 3.* show the retention time and concentration of molecules of methane. Because the volumes were known, we were able to use the equation PV=nRT and determine the number of moles in the sample. Then, using Avogadro's number of 6.23x10<sup>23</sup> atoms per mol, the number of atoms per sample was calculated. The number of moles were then compared to the voltage. Using this information when sample gas was passed through the TCD, the voltage was then used to calculate concentration. *Table 1.* defines the variables of the ideal gas equation.

<b>P= Pressure = 1atm</b>
<b>V = Volume= volume of sample</b>
<b>N= number of moles= x</b>
<b>R= gas constant= .08206</b>
<b>T= temperature K°= 296.15 K°</b>

**Table 1.** Variables of the ideal gas equation.

By plotting the response of the TCD to varying volumes of methane, a line was established with a correlation (r<sup>2</sup>) value of .9883. This correlation shows the fraction of the value that was derived from the data, and what was derived from fitting the trend line. A value of 0.9883 shows that the line was derived at 98.83% of data, and that there is only a 1.17% error due to fitting the line.

Tests were run at a variety of temperatures, ranging from 30°C to 100°C, in order to ascertain where the best separation oc-

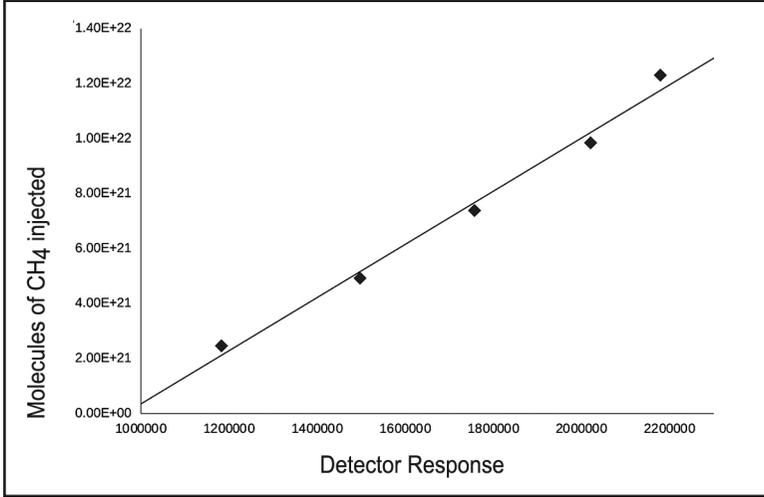


Figure 4. Calibration Curve 1.

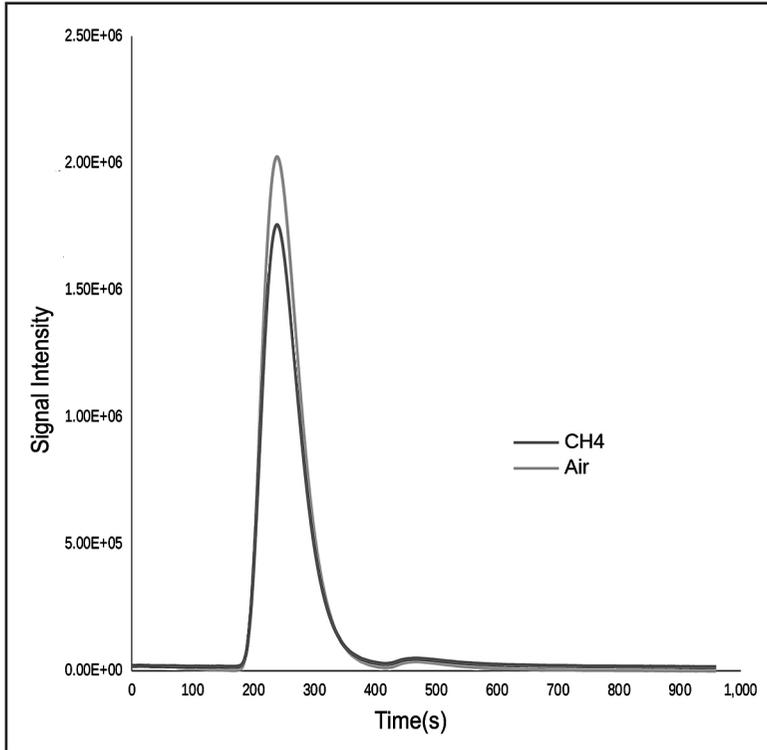


Figure 5. Room Air Compared to Methane using poraPLOT Column.

curs. Despite literature data showing otherwise<sup>13</sup>, it was decided that the poraplot column was not separating the atoms of interest ( $\text{CH}_4$ ). This is shown in *Figure 5*. By increasing the  $\text{CH}_4$  concentration, it was easier to map it, which led to the discovery that its peak may have been lost in the nitrogen peak.

*Figure 6*. compares the room air to room air with added methane. This graph shows that the room air sample (containing nitrogen, oxygen and methane) is not resolved into three component peaks. Because the methane peak begins so close to the end of the nitrogen peak, and the methane is very dilute in room air samples, it is very likely the two species are eluting at the same time. Measures were taken to add to molecule retention time and allow for a more distinct chromatogram, but at this time we have

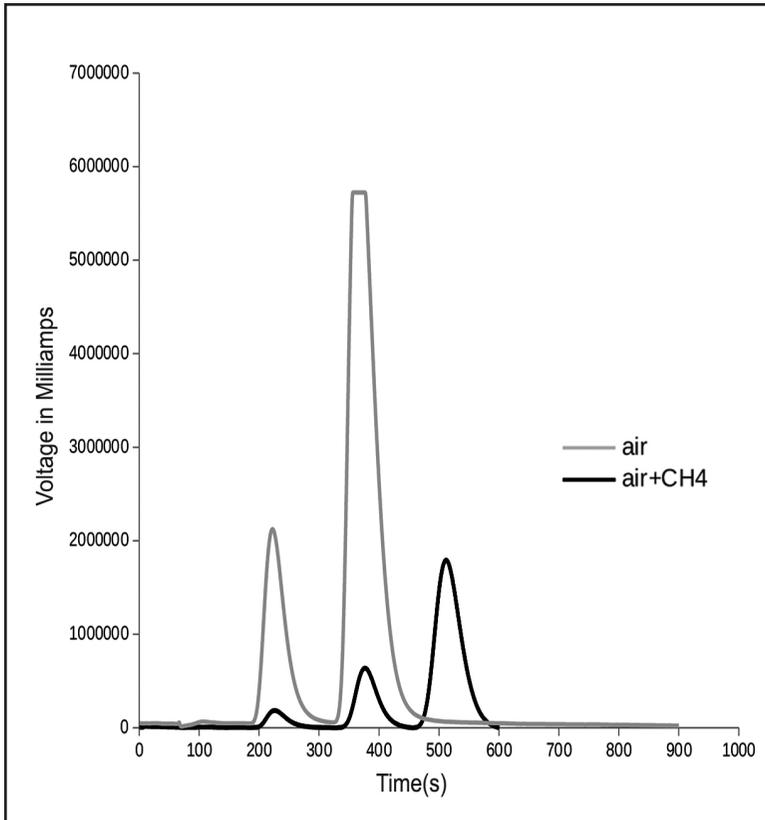


Figure 6. Comparison between Room Air and Room Air+Methane

not perfected the method. Also note that in *Figure 6*, the chromatogram of room air shows that the nitrogen peak is cut off, because the TCD only records voltage up to  $6 \times 10^6$  microvolts (6V).

To solve the problem of poor methane separation, a packed molecular sieve column was added to the loop. The column used is a Restek Moleseive column with a 2 mm inside diameter, packed with 5 angstrom diameter Zeolite packing. Tests were run with the new column added in the loop, yet there were still difficulties in isolating the methane. The flow rate was lowered to nearly 2mL/ min in order to give the molecules more time in the columns, and thus more time to adhere to the stationary phase. Problems with the separation continued, thus the next step was to place the sample loop into an ice bath in order to cool the sample molecules. By cooling the sample, the molecules should in turn have slowed down, increasing chances of separation. There were still problems differentiating a proper methane peak with room air samples. Our samples were then re-tested, using only the molecular sieve column. Successful separation of methane, oxygen and nitrogen was observed; the poraPLOT column was removed and the experiments continued with the molecular sieve column only.

### Sample Analysis

Sample atmosphere bags were connected to a 6 port valve system. This system has two settings: analyze mode and *fill mode*. In *fill mode*, the gas pump sucks sample atmosphere out of the bag and into the sample loop. The carrier gas must always run through the column, so in both analyze and *fill mode* the Hydrogen flows into the GC, and thus the column. Once the sample loop is full, the system is put into *analyze mode* and the valve switches so that the carrier gas pushes through the sample loop and into the GC. This in turn pushes the sample atmosphere into the GC and detector. After discovery of the poraPLOT not separating methane molecules, the poraPLOT was replaced by the mol sieve column. This provided better resolution and separation than the poraPLOT column. A septum port was also added to the sample loop for direct injections of atmosphere gas.

## Data Analysis

Once the calibration curve was established and TCD response was recorded, samples of room air were tested, as methane concentrations in indoor air are similar to those found outside. The room air samples delivered 2 peaks in chromatograms; the first was determined to be Oxygen ( $O_2$ ), and the second was determined to be Nitrogen ( $N_2$ ). The peaks were determined by introducing pure forms of the gases to the system in order to determine where Oxygen and Nitrogen eluted. *Figure 7.* shows a sample chromatogram of room air.

This chromatogram shows that the typical peaks of  $O_2$  and  $N_2$ , but  $CH_4$  seem to be below the limit of detection for this small (1mL) sample size. The  $CH_4$  retention time falls in the latter part of the  $N_2$  peak. In order to show the comparison of methane and room air, methane was added to a bag of pure air from a cylinder. In higher concentrations it is much easier to see where the peaks should be, and to compare them to room air. *Figure 8.* shows a comparison of room air and room air doped with methane from the house tap.

Using the sample bag with added methane shows the peak beginning as the large nitrogen peak is still flattening out. The fol-

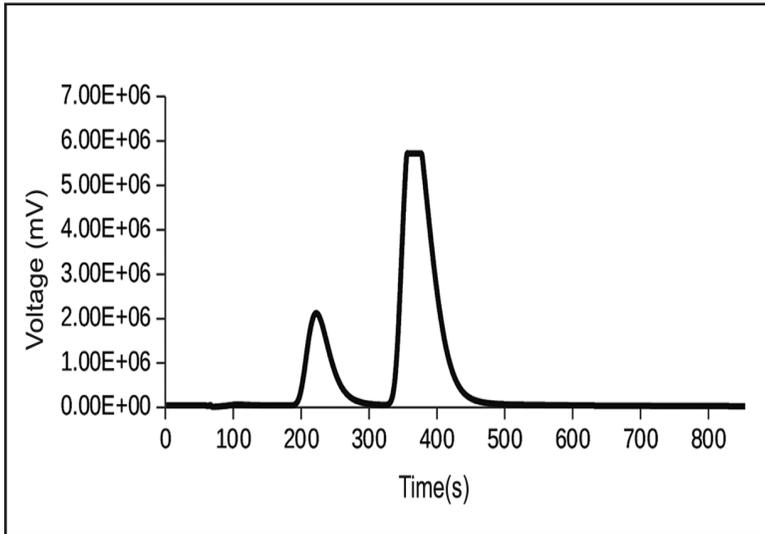


Figure 7. Sample Chromatogram of Room Air

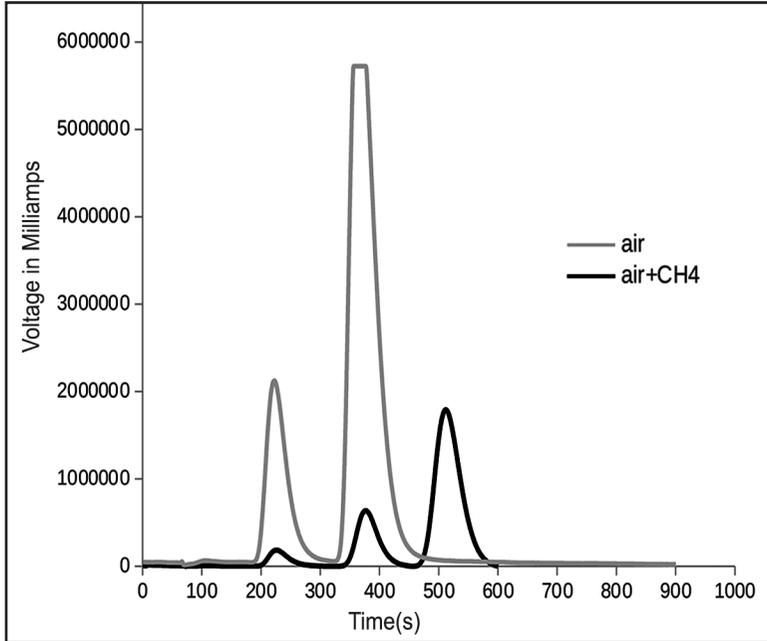


Figure 8. Illustration of a Bag of Room Air and Room Air + Methane

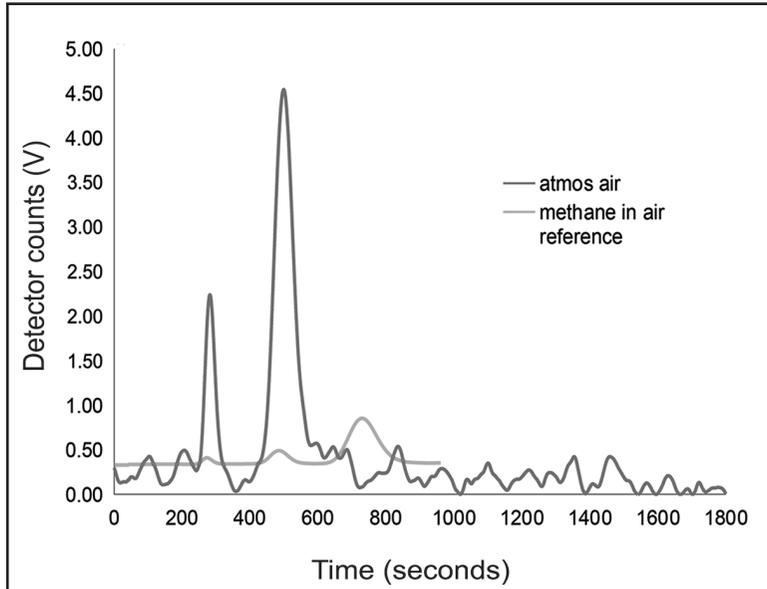


Figure 9 Chromatogram using Molsieve column

lowing diagram, *Figure 9.*, illustrates the air + methane reference sample matched up to atmospheric air analyzed using only the molecular sieve column. A discernible peak, although small, can be viewed just to the right of the nitrogen peak. *Figure 9.* shows the molsieve chromatogram.

## **DISCUSSION**

While the research is ongoing a viable separation technique for methane is within reach. As more adjustments are made the machine should prove quite useful for atmospheric measurements.

While previous data and the literature suggested that the poraPLOT column was the correct column for analyzing CH<sub>4</sub>, proper separation was never achieved with this column in place. One possible reason for this is that without proper equipment, the temperature of the sample could not be lowered enough. Cryogenic trapping is a technique used to narrow the width of sample peaks and thus improve resolution in chromatograms. The technique involves lowering the temperature of analytes far below ambient temperature (as low as -180° C), then releasing them from the trap by very rapid heating (60° C/ min). A version of this was attempted using ice baths, but was found not to be effective.

Another way that poor separation was addressed was by adding volume to the sample loop. It was thought that 1mL samples were not large enough to achieve proper separation. To fix this the sample, loop size was increased. Even with larger sample sizes good separation did not occur.

This experiment was conducted in order to prepare an instrument for further research. It has been shown that this is a viable instrument in atmospheric chemistry. This project will continue, and in future writings data from other sources and locations will be analyzed.

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