Regolith and Environment Science and Oxygen and Lunar Volatile Extraction (RESOLVE)

Lunar Advanced Volatile Analysis (LAVA)
Capillary Fluid Dynamic Restriction Effects on Gas Chromatography

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Nomenclature

Abbreviation	Meaning
COTS	Commercial off the Shelf
GC	Gas Chromatography
GCF	Gas correction factor
ID	Inner diameter
ISRU	In-Situ Resource Utilization
LAVA	Lunar Advanced Volatile Analysis
MS	Mass Spectrometer
MXT®	Restek metal capillary tubing
OVEN	Oxygen Volatile Extraction Node
PT	Pressure Transducer
RESOLVE	Regolith and Environment Science and Oxygen Lunar Volatile Extraction
RP-15	Resource Prospector 15
RPM	Resource Prospector Mission
SBIR	Small Business Innovation Research
SCCM	Standard cubic centimeters
ST	Surge tank
TCD	Thermal Conductivity Detector
Symbol	**Meaning**
F	volumetric flow rate
P_{down}	downstream pressure
P_{up}	upstream pressure
ΔP_{Col}	column pressure drop
ΔP_{TCD}	Thermal Conductivity Detector pressure drop

I. Introduction

NASA interest in the colonization of Mars requires In-Situ Resource Utilization (ISRU) in order to eventually become Earth independent. The Resource Prospector (RP) mission is one of the first moves within the proving ground steps towards understanding utilization of planetary bodies for exploration life support. The Regolith and Environment Science and Oxygen Lunar Volatile Extraction (RESOLVE) Payload will allow for the quantitative recognition of water on the moon. With water as an absolute necessity for human life, harvesting lunar resources may relieve exploration design and costs, as well as enabling space pioneering.

The RESOLVE payload will be the main component of a rover that aims to reach the lunar South Pole and analyze lunar volatile components. The main process steps of the system involve the Oxygen Volatile Extraction Node (OVEN) and the Lunar Advanced Volatile Analysis system (LAVA). OVEN consist of a drill that removes lunar regolith sample and heats it for analytical preparation. The sample volatiles move through the LAVA Fluid Sub-System (FSS) for evaluation by means of Gas Chromatography and Mass Spectroscopy (GC-MS). A schematic of these components can be viewed in **figure 1** below [2].

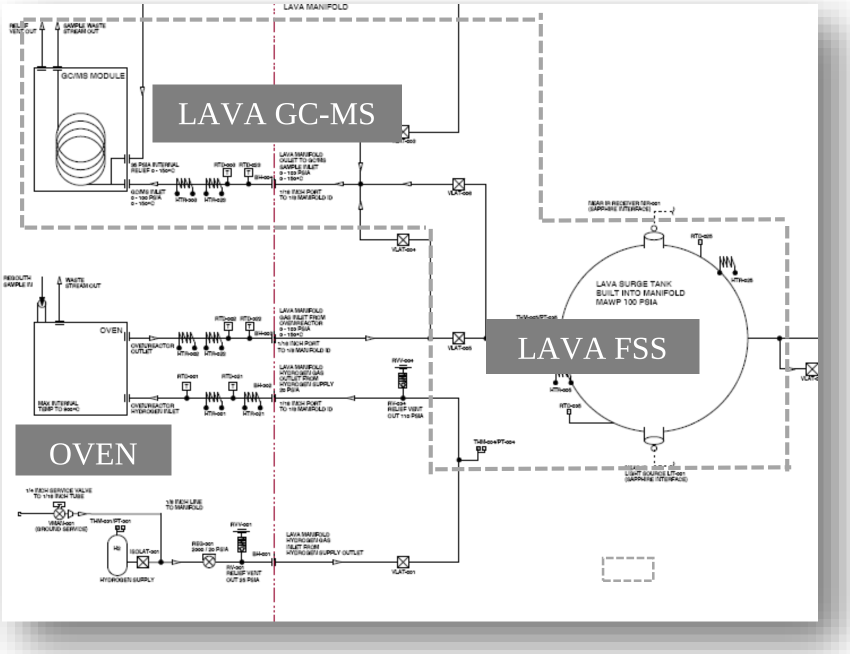


Figure 1. Portion of Fluid Sub-system mechanical schematic [2]

This study aims to better understand fluid dynamics of the payload's Fluid Subsystem (FSS), specifically within LAVA. The FSS establishes micro-scaled flows by series of various sized capillary tubing. The GC-MS unit will be exposed to lunar vacuum; therefore, computational modeling with these parameters can be challenging. It is of great interest to have an ability to model the unit, so as to prevent over-pressurization to the MS and ensure the production of dependable GC data. The GC works by measurement of retention time throughout capillary columns. There are two isolated flows, one being analytical flow with the carrier gas and volatile sample, while the reference flow contains only the carrier gas. After the fluids pass through the these columns, they reach a Thermal Conductivity Detector (TCD) seen in **figure 2** that uses hypodermic tubing to compare the heat transfer properties between the two streams and output a signal from its Wheatstone bridge. As filaments heat the material of the TCD, a change in resistance is caused by the difference between the temperate and heat removal rate of each flow. The GC can then generate a graph conveying microvolts versus retention time peaks that signify different chemical volatile components. Once the micro-flows exit the TCD, they are combined in a transfer line and sent to the mass spectrometer for further analysis.

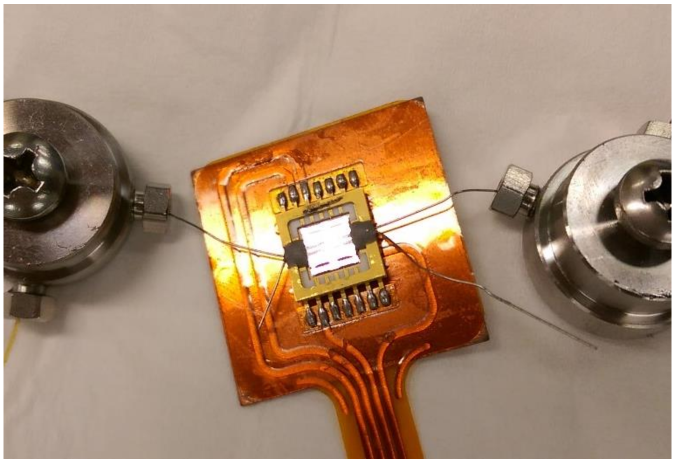


Figure 2. Close view of a thermal conductivity detector

Kennedy Space Center utilizes a GC Commercial of the Shelf (COTS) instrument from a gas instrumentation company, called Inficon. The GC instruments from this provider are not designed to operate under vacuum. In addition, the TCD was designed to work at atmospheric pressure. Due to the intended nature of this equipment, there is little understanding about how the GC will perform in the lunar environment. KSC’s involvement with the Small Business Innovation Research (SBIR) program permitted cooperation with Creare, a research and development company, and Inficon. This allowed for further investigation of GC-MS technologies. This research is of interest to the payload design, since the system was able to obtain GC data without over-pressurization events. It utilized a 0.050 mm ID transfer line that connected the flow from the GC to the MS, which is the main topic of this investigation.

The objective of this study is to ultimately aid towards the development of a computational model of the GC-MS portion of the LAVA by obtaining physical data that shows the pressure conditions, flow rates and retention times of the GC unit and how transfer line restriction along with vacuum conditions affects these values. Overall, it aims to provide more knowledge of capillary micro flow systems that may be used for ISRU related missions.

II. Procedure

To prevent potential damage to a test GC device, an experimental set-up was built instead. After pressure and flow results were generated from this apparatus, testing of an actual GC was permitted to find the changes in chromatography data. By conducting these two experiments, the validity of volatile component data can be determined.

A. GC Experimental Set-up Procedure

A experimental set-up was built to mimic the flow of the GC unit, which included a pressurized gas source, Restek fused silica capillary column, TCD from an Inficon MicroGC 3000 model, a model 740 Paroscientific Pressure Transducer (PT), Restek MXT® or fused silica capillary transfer line, MKS laminar mass flow meter, MKS type 247D four-channel readout, and a KNF UN813.3ANI model rough pump. The details and dimensions of the set-up are portrayed in **figure 3** below.

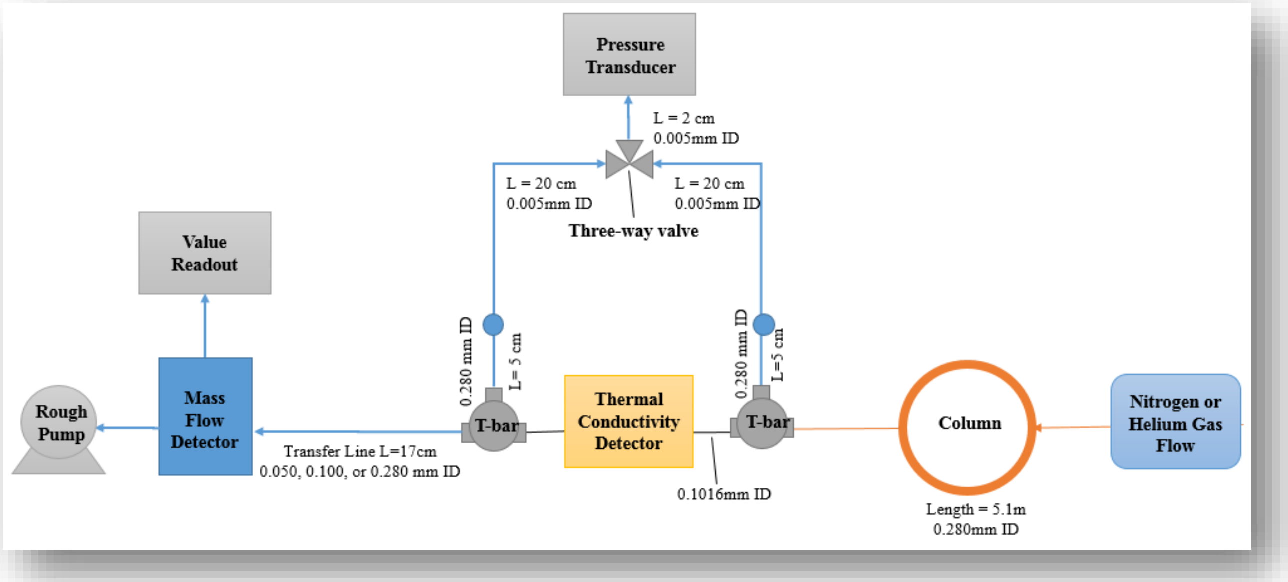


Figure 3. GC experimental set-up

Flow is connected to only one side of the thermal conductivity detector; both flows would only be of interest to the GC data, which will be observed in the next procedure. Nitrogen enters the system at 20-25 psig from a pressurized cylinder. Nitrogen was chosen as the test reference gas due to the available flow rate detection equipment calibration capabilities; although helium was preferred, the equipment could not accommodate. The mass flow readout was calibrated for nitrogen using the appropriate gas correction factor (GCF). As the gas travels from the column to the TCD, a PT can generate a reading for either the upstream or downstream side of the TCD, depending on the orientation of the three-way valve on the PT. A transfer line then directs the fluid flow towards a mass flow detector and rough pump at 2.056 psia. The pressure of the rough pump was determined by the resulting downstream pressure with a 0.280 mm ID line and no gas flow. This system was tested with various transfer line inner diameters of 0.280, 0.100 and 0.050 mm ID. Their lengths were kept constant at 17cm in order for valid pressure and volumetric flow rate value comparisons. A closer look at the column, TCD, PT and the corresponding fittings can be seen in **figure 4** below.

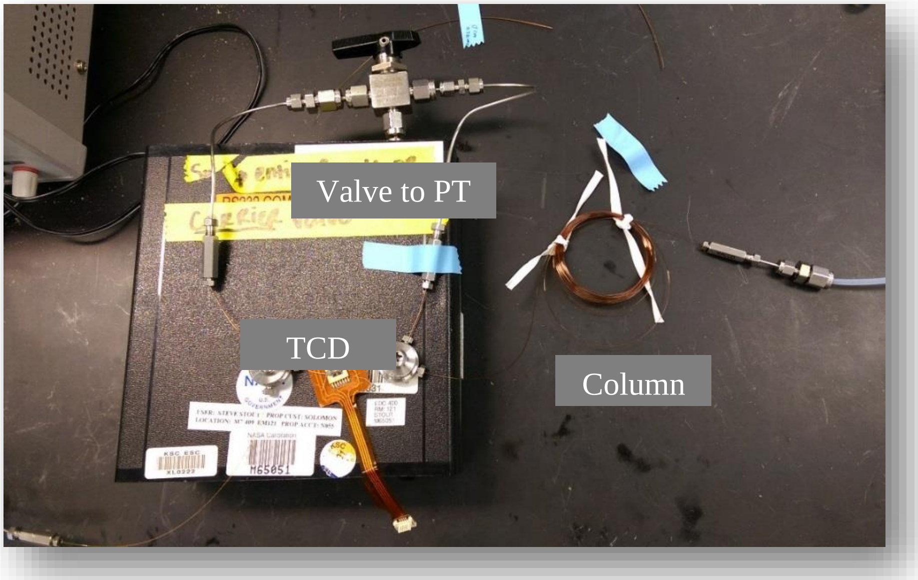


Figure 4. GC model close-up of column, TCD and PT

For each transfer line run, pressure data was taken from upstream until the system appeared to stabilize. The downstream pressure data and the volumetric flow rate in standard cubic centimeters (SCCM) were recorded thereafter. The time pressure data would then be plotted for further analysis. A look at the flow meter pressure equipment is shown in **figure 5**.

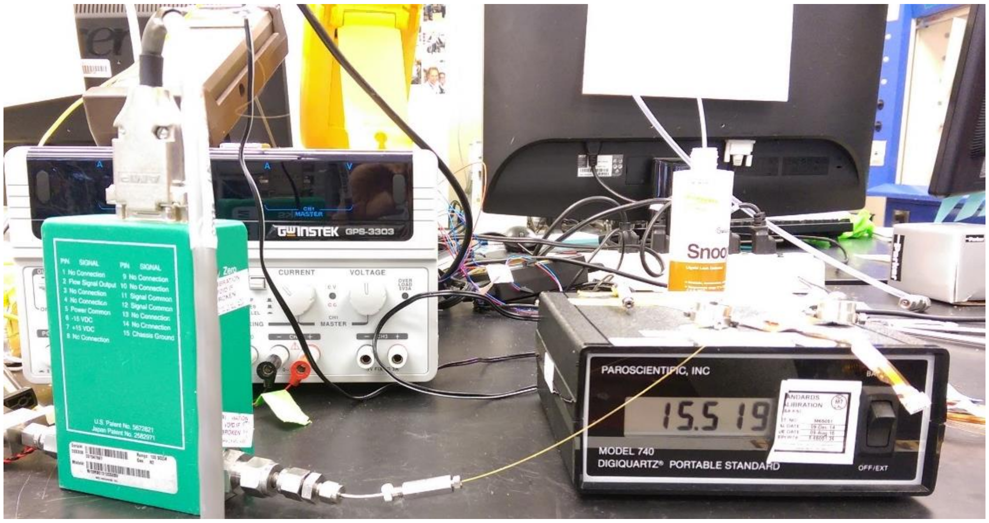


Figure 5. Mass flow meter and pressure transducer

B. Micro GC 3000 Procedure

The pressure and flow rate conditions directly affect the GC data, which ultimately will determine how the presence of lunar volatiles will be evaluated. In order to study the changes in GC data, the same transfer lines were applied to the end of an Inficon Micro GC 3000. A simple schematic of the experiment is seen in **figure 6**. Choosing the right column temperature and pressure conditions is important for sufficient GC data. The optimal method for the MicroGC 3000 that has an 8m column is a pressure of 30 psig and temperature of 70ºC [1].

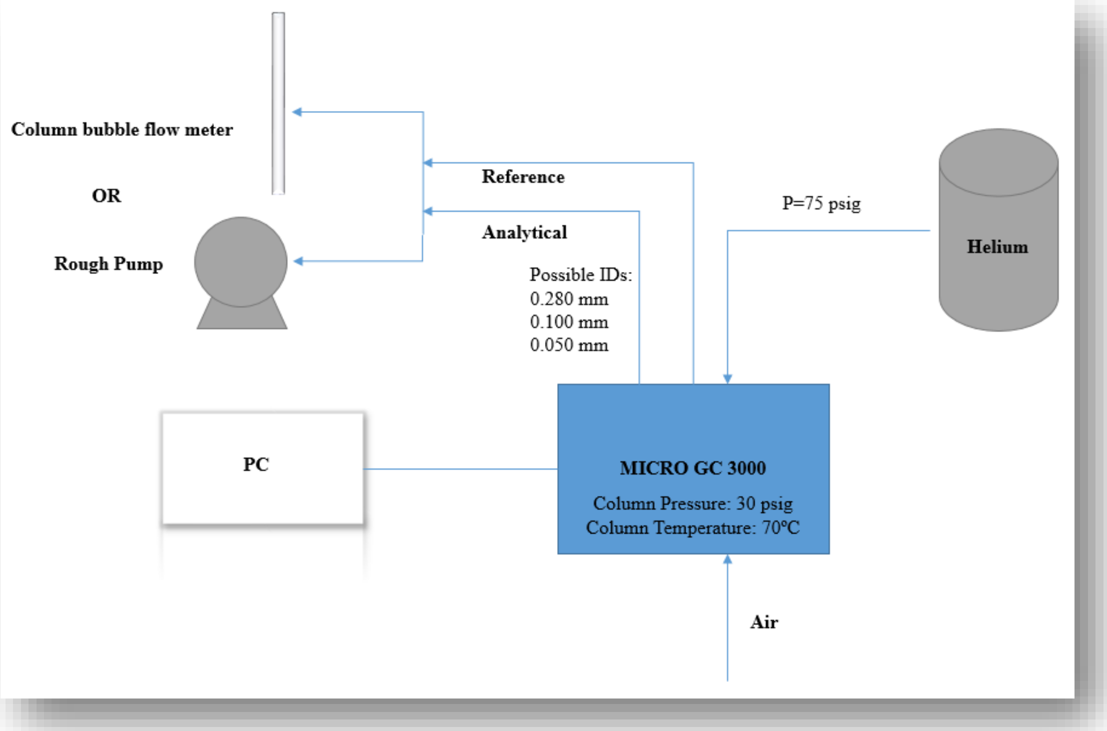


Figure 6. Inficon MicroGC 3000 process schematic

Helium is used as the reference and carrier gas for GC analysis; the gas cylinder was set to 75 psig. Room is air is pumped into the instrument as the analytical sample. The MicroGC 3000 sends the data to a connected personal computer. The back of the GC has external tubing where different transfer lines can be applied as seen in **figure 7**. Data analysis was performed by the Inficon software, EZ IQ. All data was export to excel for graphical comparison.

Figure 7. Rear of MicroGC 3000 channel access

The 0.280, 0.100, and 0.050 mm ID 10cm length transfer lines were connected in various ways: analytical only, reference only, analytical and reference to atmosphere, analytical and reference to a KNF UN813.3ANI model rough pump. These connections were converted by Valco unions and were leaked check for helium prior to GC analytsis. A portrayal of how the lines were T-connected to the pump can be seen in **figure 8**.

Figure 8. Fitting connection to rough pump

For the runs that had a transfer line attached to only one of the flows, the volumetric flow rate was determined by a glass bubble meter vented to atmosphere. Snoop solution, typically used to detect leaks, was pumped through the glassware by the exiting gas. The flow rate was calculated by travel time of a bubble across 1 mL of volume. The experimental set-up can be seen in **figure 9** below.

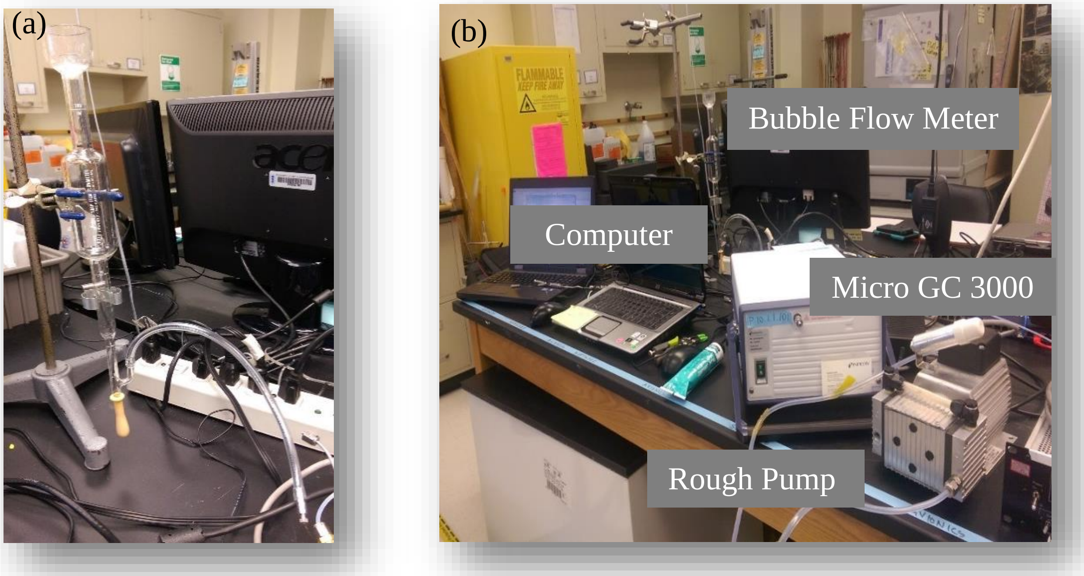


Figure 9. (a) Bubble flowmeter (b) MicroGC 3000 experimental set-up

For each run classification, at least ten GC runs were executed; the data picked for comparison was among the ending runs, so as to account for the time it takes for the GC to reach steady state. Each classification was completed within the course of a full work day, where the transfer line runs were compared to an initial "original" run without any added connections. In order to see the impact of line length to the GC data, several runs were performed usings a 20cm 0.050 mm ID line on the analytical flow to atmospheric pressure. And lasty, to also further observe the line restriction effect on steady state equilibrium, a 0.050 mm ID transfer line was applied for each option over the course of about 3 hours.

III. Results and Analysis

The resulting data from both the GC experimental set-up and the MicroGC 3000 procedures are presented graphically. This is to provide a visual understanding of the values occurring in different components of the GC system and for comparison of the data generated by the TCD.

A. GC Experimental Set-up Results

A graphical and tabulated comparison for the different transfer line GC set-up data can be seen below in **figure 11**. The location of the determined tabulated values on the system is displayed in **figure 10**. This includes final upstream and downstream pressures, flow rate, pressure drop across the TCD and pressure drop relative to the column.

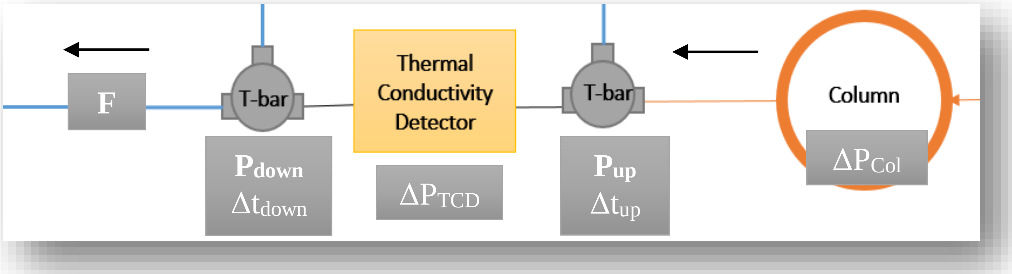
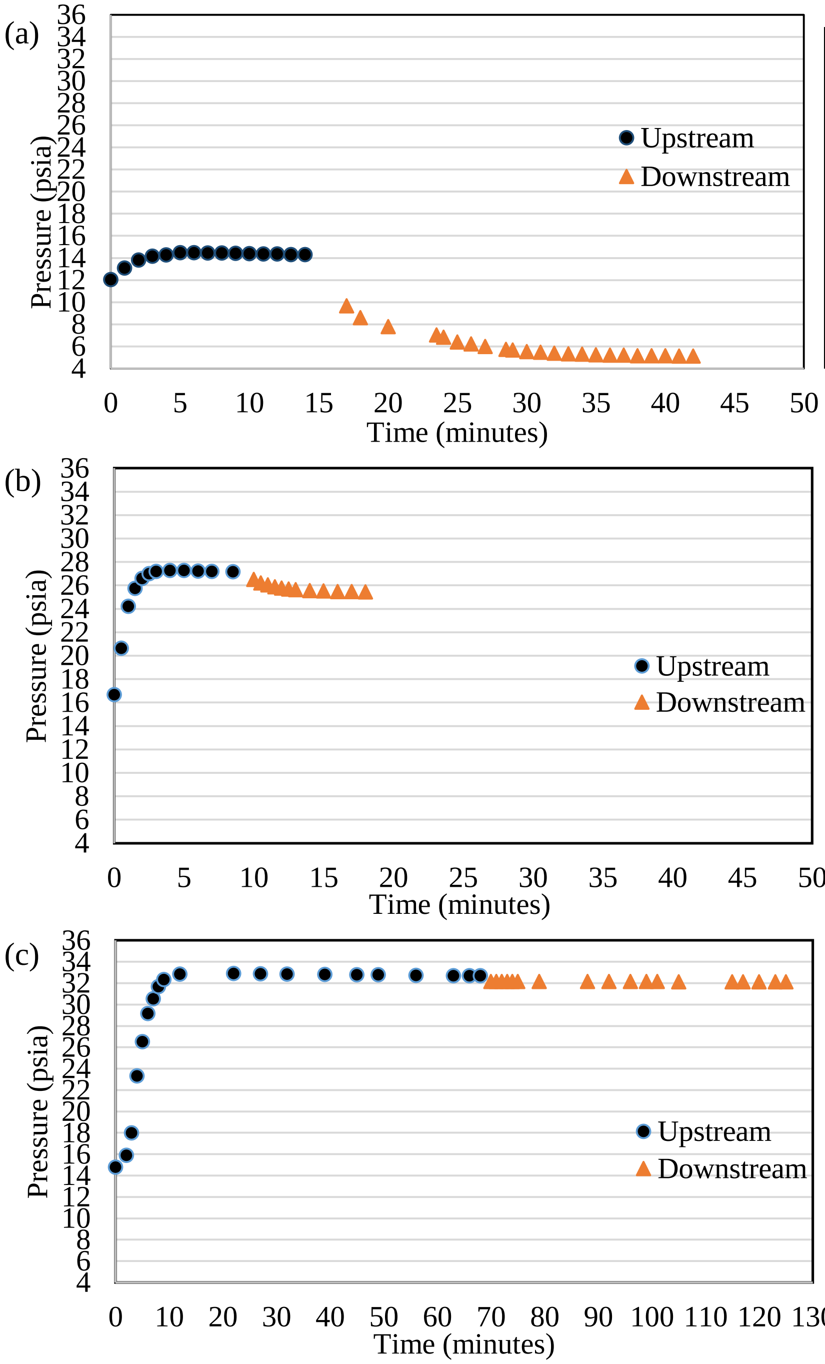


Figure 10. Location of readings and values on the GC experimental set-up

The upstream and downstream data are plotted together to portray an overall approach to steady state as the pressure readings stabilize. Stabilization time was evaluated based on the PT reading producing a value with the same tenth decimal digit over the course of at least 3 minutes for upstream; this also applied for the downstream data for the 0.280 mm ID line. Since the ΔP_{TCD} became smaller for the other lines, stabilization was based on the one-hundredth decimal digit's constant value. The values for P_{up} and P_{down} were based on the average of the three stabilization readings per run. For upstream data, Δt_{up} was calculated from the time gas was pressurized into the system until it stabilized. The downstream time Δt_{down} was determine from the time the three-way valve was switched, up to pressure stabilization.



(a)

Data Name	**Value**
P_{up}	14.440 psia
P_{down}	5.143 psia
F	13.2 SCCM
ΔP_{TCD}	9.297 psia
ΔP_{Col}	20.260 psia
$\Delta P_{Transfer}$	12.384 psia
Δt_{up}	9 min
Δt_{down}	19 min

(b)

Data Name	**Value**
P_{up}	27.248 psia
P_{down}	25.462 psia
F	6.2 SCCM
ΔP_{TCD}	1.785 psia
ΔP_{Col}	7.452 psia
$\Delta P_{Transfer}$	25.192 psia
Δt_{up}	6 min
Δt_{down}	8 min

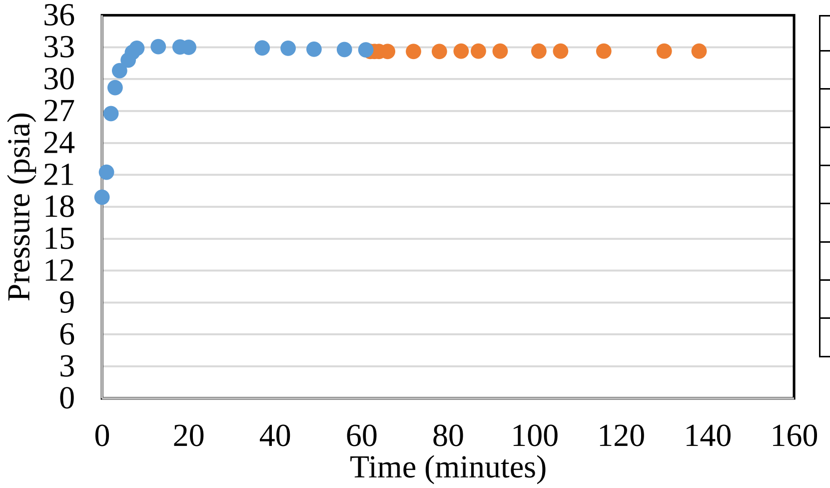
(c)

Data Name	**Value**
P_{up}	32.869 psia
P_{down}	32.147 psia
F	$\leq$ 0.03 SCCM*
ΔP_{TCD}	0.722 psia
ΔP_{Col}	6.831 psia
$\Delta P_{Transfer}$	30.813 psia
Δt_{up}	32 min
Δt_{down}	2 min

Figure 11. GC experimental set-up pressure readings, time and flow values of nitrogen gas to rough pump outlet: Transfer lines (a) 0.280 mm ID (b) 0.100 mm ID (c) 0.050 mm ID

**Out of equipment accuracy range*

When the system is run without the rough pump, vented to the atmosphere, the pressure drop values for the column and TCD decreased. This was expected, since applying a vacuum to the system causes a pulling of the fluid flow towards the end of the transfer line. These results are seen in **figure 12.**



Data Name	Value
P_{up}	32.950 psia
P_{down}	32.607 psia
F	≤ 0.01 SCCM*
ΔP_{TCD}	0.342 psia
ΔP_{Col}	6.750psia
$\Delta P_{Transfer}$	18.250 psia
Δt_{up}	20 min
Δt_{down}	1 min

Figure 12. GC experimental set-up pressure readings, time and flow values of nitrogen gas to atmosphere

It is evident that the pressure readings are increased as more restriction is put on the system by a smaller transfer line. The pressure difference across the TCD and column become more negligible with this restriction, as seen by the ΔP results. In regards to the flow rate, there is also a decreasing trend. The pressure determination for all runs had a certain wait time, depending on the initial pressure and the transfer line. Yet, no linear relationship is shown between transfer line ID and wait time; the 0.100 mm ID run seems to have a fastest overall stabilization time.

The most difficult part of the system to model computationally is the last portion of the flow process, due to the vacuum caused capillary slip. Looking at the pressure differential across the transfer line and its relationship to the flow rate in **figure 13**, it can further verified that the pressure drop across the transfer line becomes larger with smaller transfer lines, but that the flow rate is limited due to the amount of restriction.

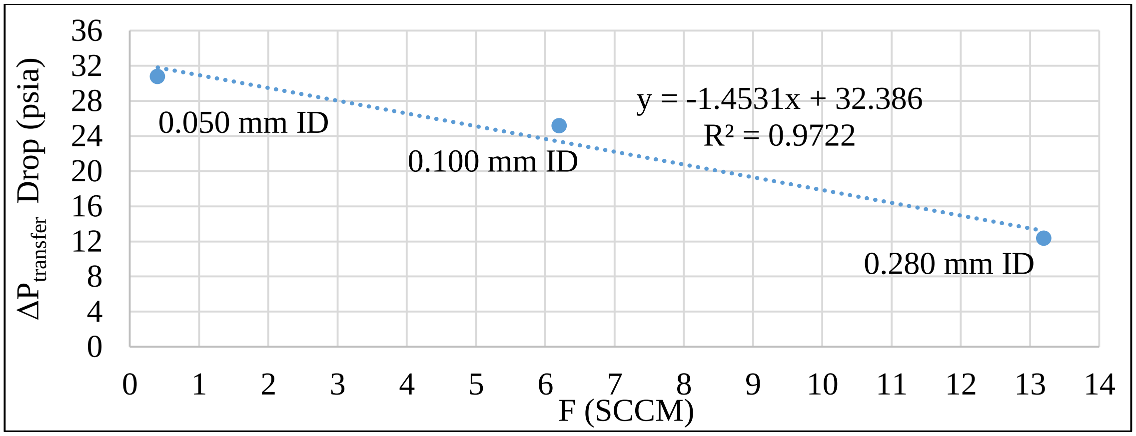


Figure 13. Transfer line pressure drop and flow rate

B. MicroGC 3000 Results

As GC data was obtained, the bubble flow meter was used to measure the volumetric flow values with exposure to atmosphere. A summary of these results are displayed in **table 1**.

Transfer line (mm ID)	Analytical (mL/min)	Reference (mL/min)
None	2.99	1.893
0.280	2.00	1.863
0.100	1.08	1.411
0.050	0.910	0.694

Table 1. Volumetric flow rates for transfer lines to atmosphere: Helium as carrier gas

As expected, the flow rates decrease with smaller transfer lines. Notice that the flow rates for the reference flow are smaller.

When transfer lines were applied to the reference flow, there was no significant change in chromatography in comparison to the initial original runs. Broadness and areas of the peaks stayed constant. Although there was also no change in retention times, there were small changes in the baseline with no apparent trends. The corresponding GC graphs can be seen in **figure 14**.

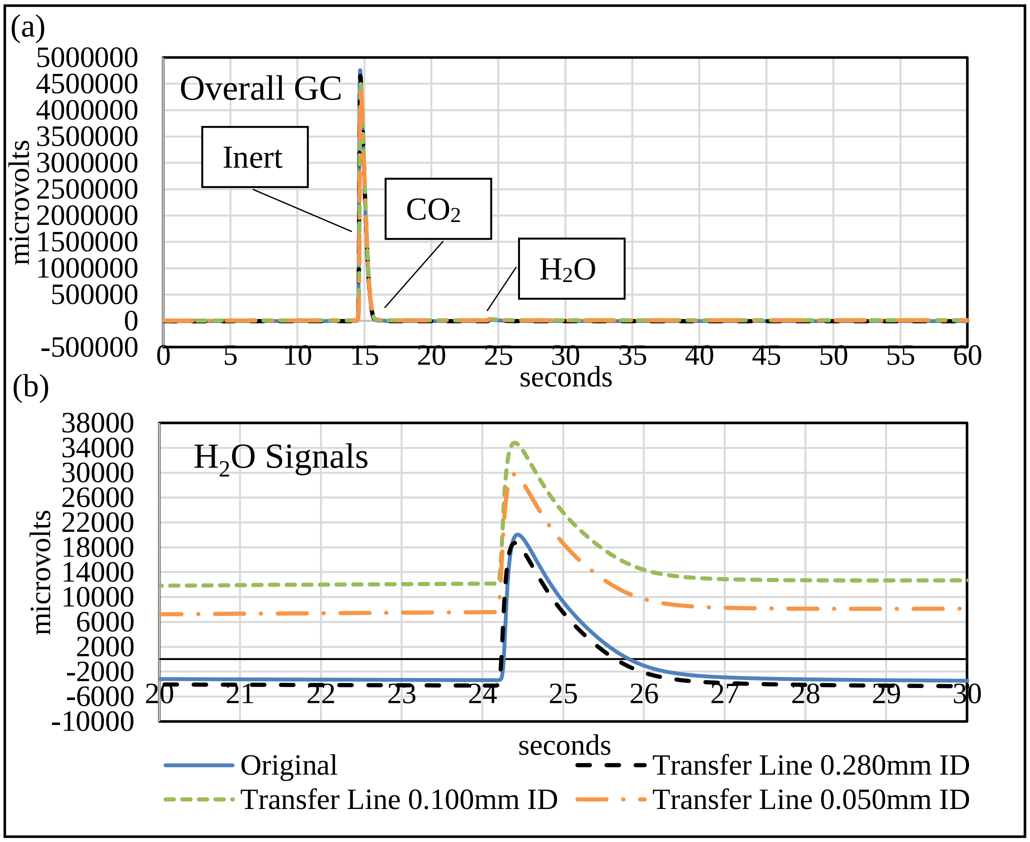


Figure 14. Reference to atmosphere (a) All transfer lines comparison
(b) Close-up of water peaks

The retention time and integration values are shown below in **table 2**. There was no significant distinction between the different sized transfer lines. This suggests that the signals are independent of flow changes to the reference line alone.

Transfer Line ID (mm)	**Inert (seconds)**	**Carbon dioxide (seconds)**	**Water (seconds)**
None	14.66	16.34	24.42
0.0280	14.68	16.34	24.38
0.100	14.7	16.36	24.38
0.050	14.7	16.36	24.38
Transfer Line ID (mm)	**Inert Area (µV)**	**Carbon dioxide Area (µV)**	**Water Area (µV)**
None	2257179	3630	21959
0.0280	2200225	3600	21360
0.100	2121854	3537	21675
0.050	2119799	3133	20341

Table 2. Reference flow retention time and peak area comparisons

On the other hand, applying these transfer lines to the analytical flow made a tremendous difference in retention time and peak traits, as seen in **figure 15** and **table 3**. It appears that the smaller transfer line means larger retention times. The sample takes longer to travel through the GC column due to the increased restriction and lower flow rate. The 0.280 mm ID line had no shifts when compared to the original data. The 0.100 mm and 0.050 mm had shifted to the right about 15 seconds and 50 seconds, respectively. As the transfer lines got smaller, broader peaks were signaled due to longer diffusion time of sample gas in the column. This resulted in larger integration values.

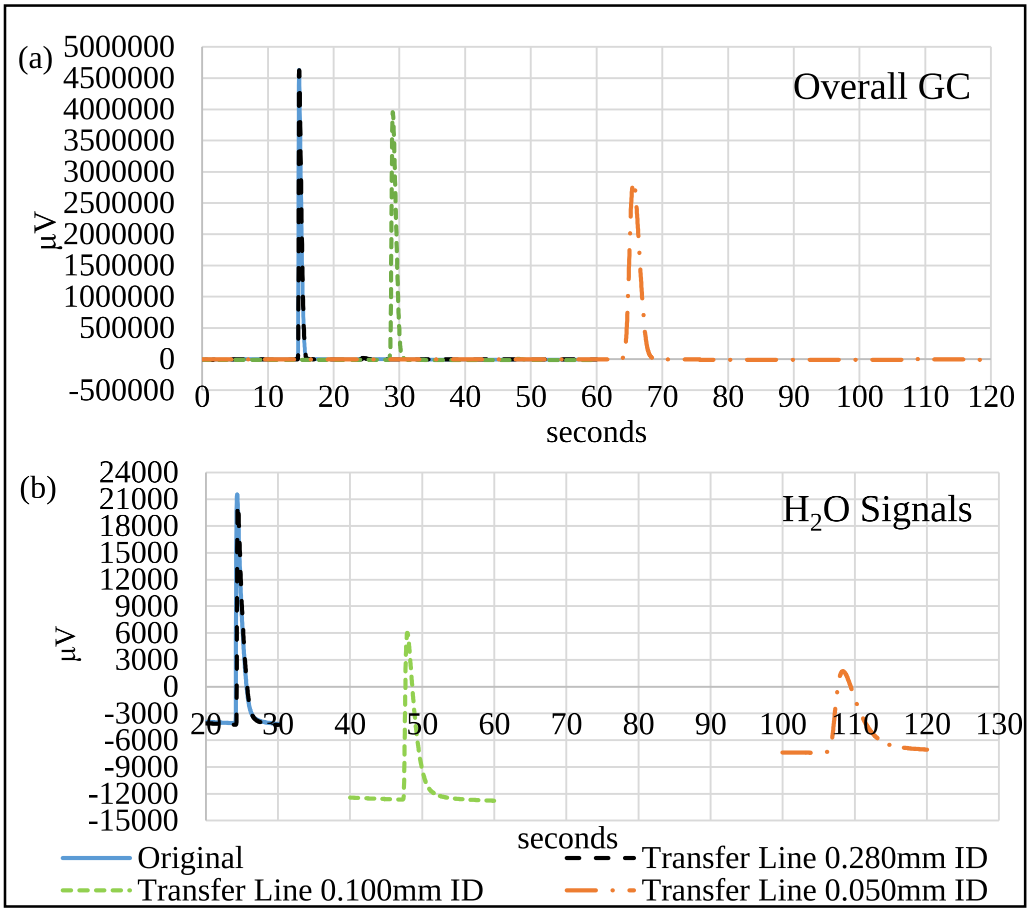


Figure 15. Analytical flow to atmosphere (a) All transfer lines comparison (b) Close-up of water peaks

Transfer Line ID (mm)	Inert (seconds)	Carbon dioxide (seconds)	Water (seconds)
None	14.68	16.34	24.32
0.0280	14.74	16.4	24.42
0.100	28.98	32.2	47.92
0.050	65.58	72.6	108.32
Transfer Line ID (mm)	**Inert Area (µV)**	**Carbon dioxide Area (µV)**	**Water Area (µV)**
None	2189720	3130	23751
0.0280	2184793	4460	22966
0.100	3188925	6778	31081
0.050	5280744	4575	35901

Table 3. Analytical flow retention time and peak area comparisons

As the reference line was untouched, these results show that the analytical line has a primary influence on the GC data. When putting disturbances on the analytical sample, the peak characteristics will change dramatically.

When transfer lines were applied to both the reference and analytical flow and exposed to atmosphere, all the retention times for each line remained the same when comparing it to the previous runs, with the exception of the 0.050 mm ID line. Its data had shifted about 10 seconds. This potentially demonstrates that the data is independent of the changes to the reference flow, only if the transfer line inner diameter is sufficiently large. The increasing peak areas are also evident. The corresponding data and values can be viewed in **figure 16** and **table 4**.

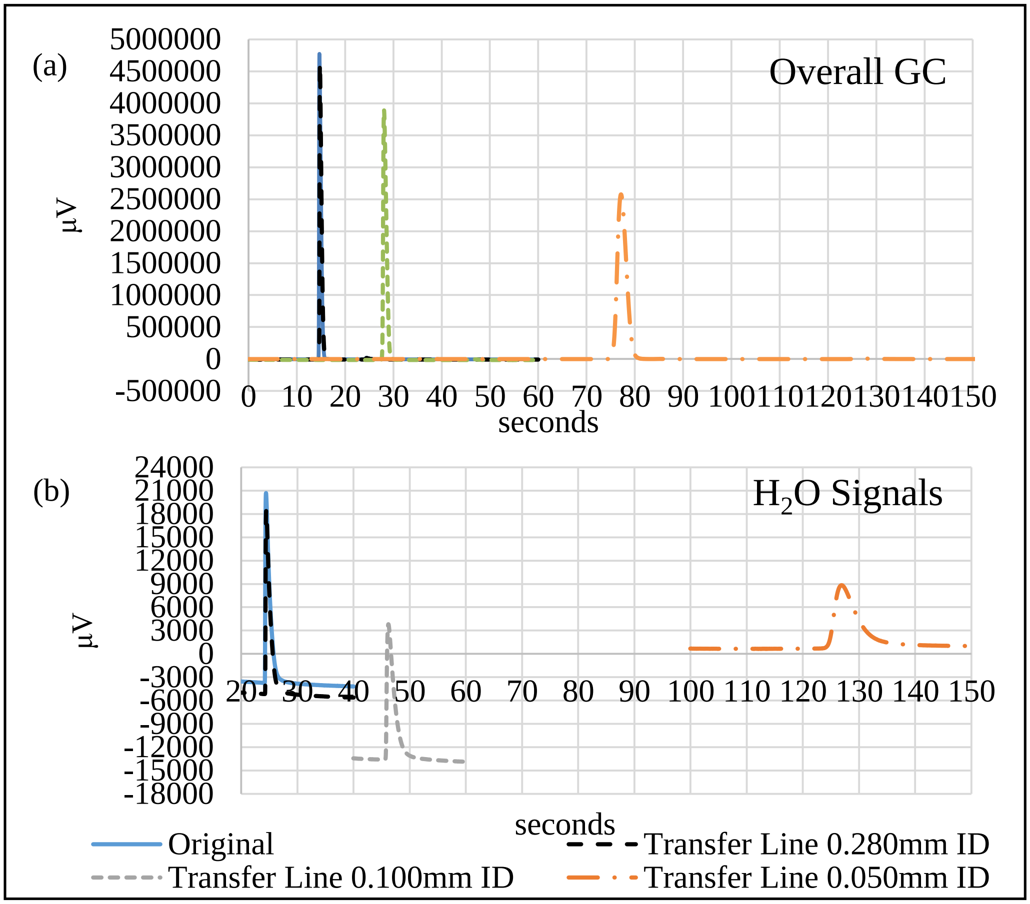


Figure 16. Reference and analytical flow to atmosphere (a) All transfer lines comparison (b) Close-up of water peaks

Transfer Line ID (mm)	Inert (seconds)	Carbon dioxide (seconds)	Water (seconds)
None	14.66	16.34	24.4
0.0280	14.76	16.44	24.46
0.100	28.04	31.12	46.18
0.050	75.9	83.94	125.08
Transfer Line ID (mm)	**Inert Area (μV)**	**Carbon dioxide Area (μV)**	**Water Area (μV)**
None	2252243	3679	22679
0.0280	2182354	3725	21953
0.100	3060254	4237	28214
0.050	5752353	6415	39107

Table 4. Reference and analytical flow to atmosphere retention time and peak area comparisons

When both flows were connected to a rough pump, in **figure 17** and **table 5**, the retention times decreased for all the sized transfer lines relative to the other category runs. The column saw a larger pressure drop, which resulted in faster flow rates and shorter retention times from the TCD, as expected. It was predicted that the smallest transfer line would prevent a significant shortening of the retention time. On the other hand, the results showed that the 0.050 mm ID line differed the most at 18 seconds. Perhaps the vacuum allowed for more capillary slip flow and eased the large restriction on the system caused by the 0.050 mm ID tubing.

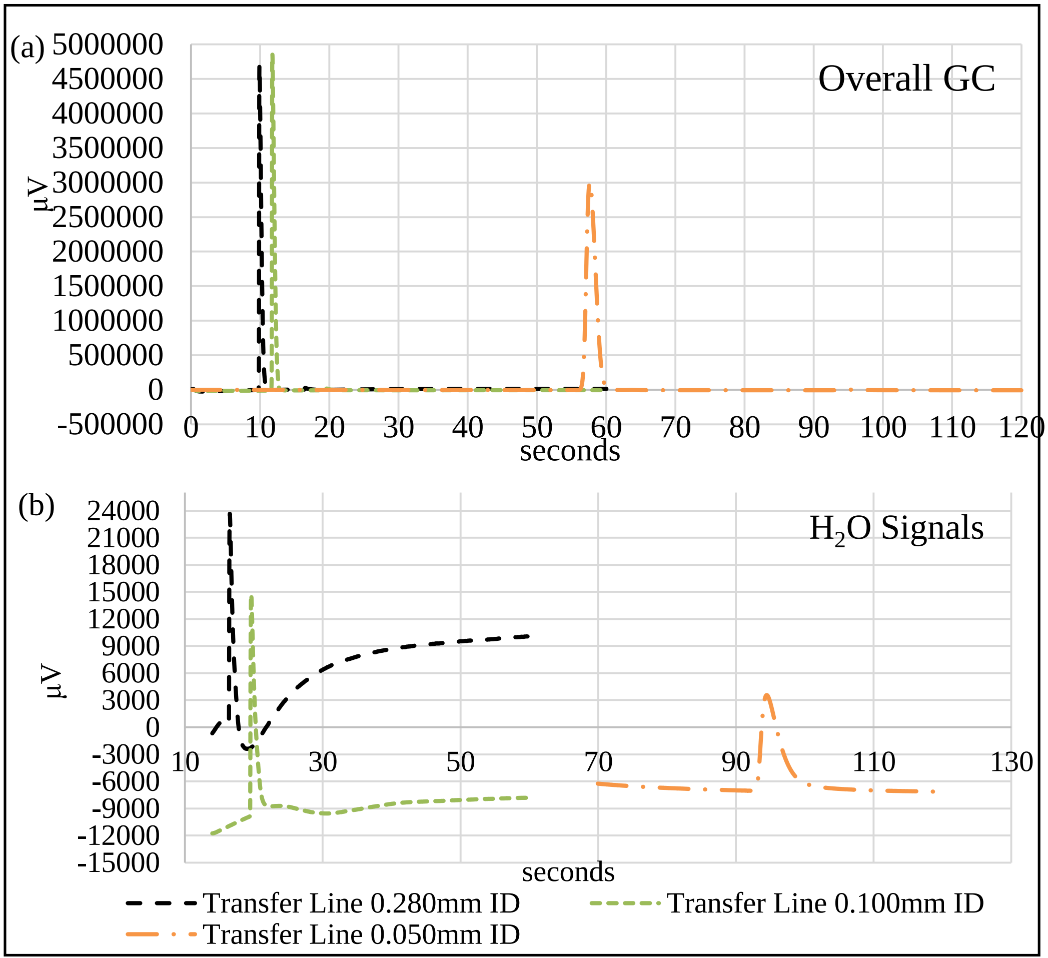


Figure 17. Reference and analytical flow to rough pump (a) Overall GC comparison (b) Close-up of water peaks

Transfer Line ID (mm)	**Inert (seconds)**	**Carbon dioxide (seconds)**	**Water (seconds)**
None	14.64	16.3	24.24
0.0280	9.86	n/a	15.64
0.100	11.74	n/a	19.58
0.050	57.62	63.74	94.46
Transfer Line ID (mm)	**Inert Area (µV)**	**Carbon dioxide Area (µV)**	**Water Area (µV)**
None	2187384	14540	26161
0.0280	1808660	0	42057
0.100	2009769	0	47659
0.050	4739136	4604	36323

Table 5. Reference and analytical to rough pump flow retention time and peak area comparisons

Table 5 suggests that the vacuum data is not in agreement with the peak broadness and integrations trends for water as previously observed. In addition, the larger lines exposed to vacuum were unable to separate the small composition of carbon dioxide. It appears that the 0.100 mm ID line is the best for achieving larger water peak integrations. But, the 0.0280 and 0.100 mm ID lines formed co-elutes, or combined peaks, in the chromatography. The carbon dioxide signal had shifted into the retention time region of the inert gases.

To observe the effect of line length on chromatography, a 20 cm 0.050 mm ID line was attached to the analytical flow.The GC data had a tremendous shift with broader peaks when a longer transfer line was applied, as seen in **figure 18**. The change in inert retention time was proportional to the length increase; both values about doubled as expected. In reference to the other peaks, this change was not as predictable since the compounds react to the column inner wall. The water signal had moved about 80 seconds. It is evident that signals are much shorter in height and broader compared to the 10cm line. The helium flow rates for the longer line were determined from the bubble flow meter to be 0.645 mL/min on the analytical side, and 0.333 mL/min when applied on the reference side. These smaller flow rates indicate friction influences present in the capillary line. This pattern of increasing length and decreasing flow rate is used for flow control in fluid systems. On the contrary, the results above show that a vacuum can make an impact on this relationship.

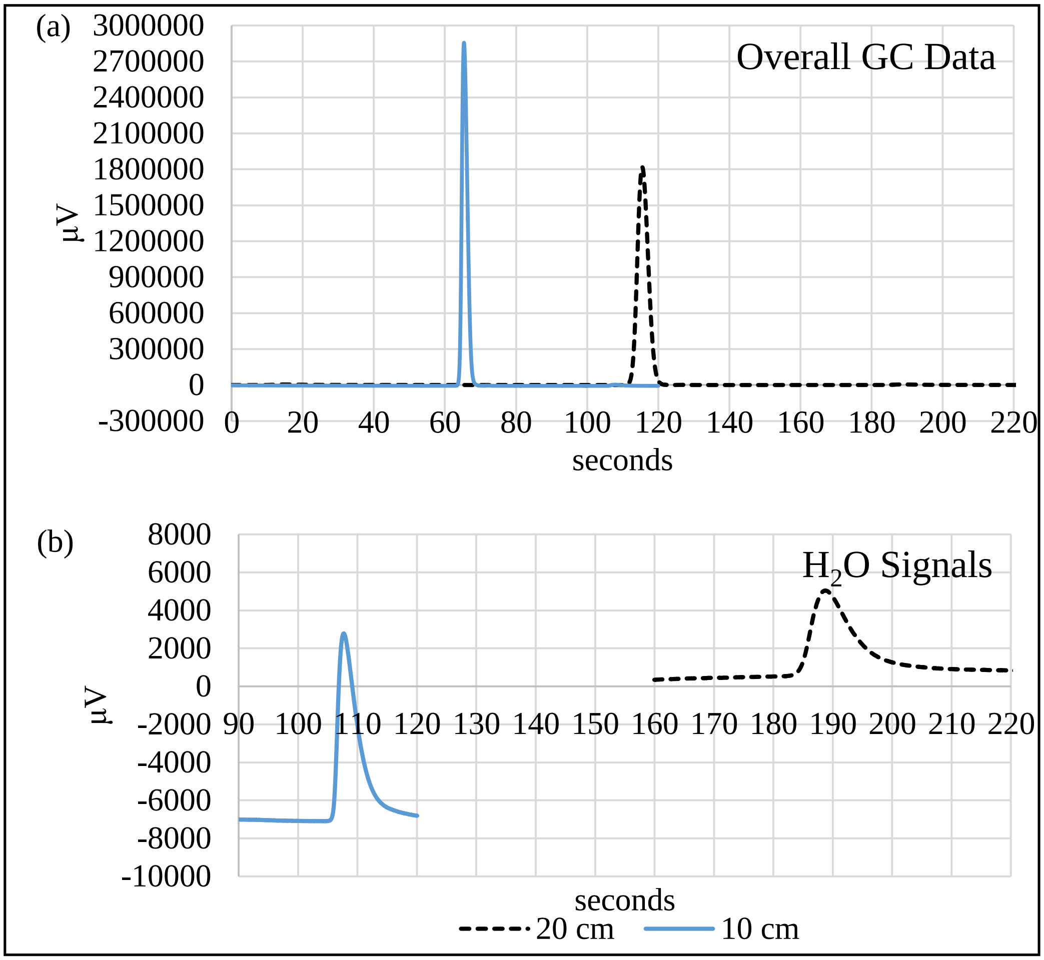


Figure 18. GC comparison of 10 cm and 20 cm length with a 0.050 mm ID (a) Overall GC comparison (b) Close up of water peaks

To fully understand how long the system takes to reach true equilibrium, the retention times were compared throughout a 3 hour period for the 10 cm length 0.050 mm ID transfer line in each scenario. The overall signals and a close-up water peak in **figure 19** shows the difference between the runs in the first and last series. The difference in retention time for the inert gases was 0.02 seconds. The other components showed no difference in retention time.

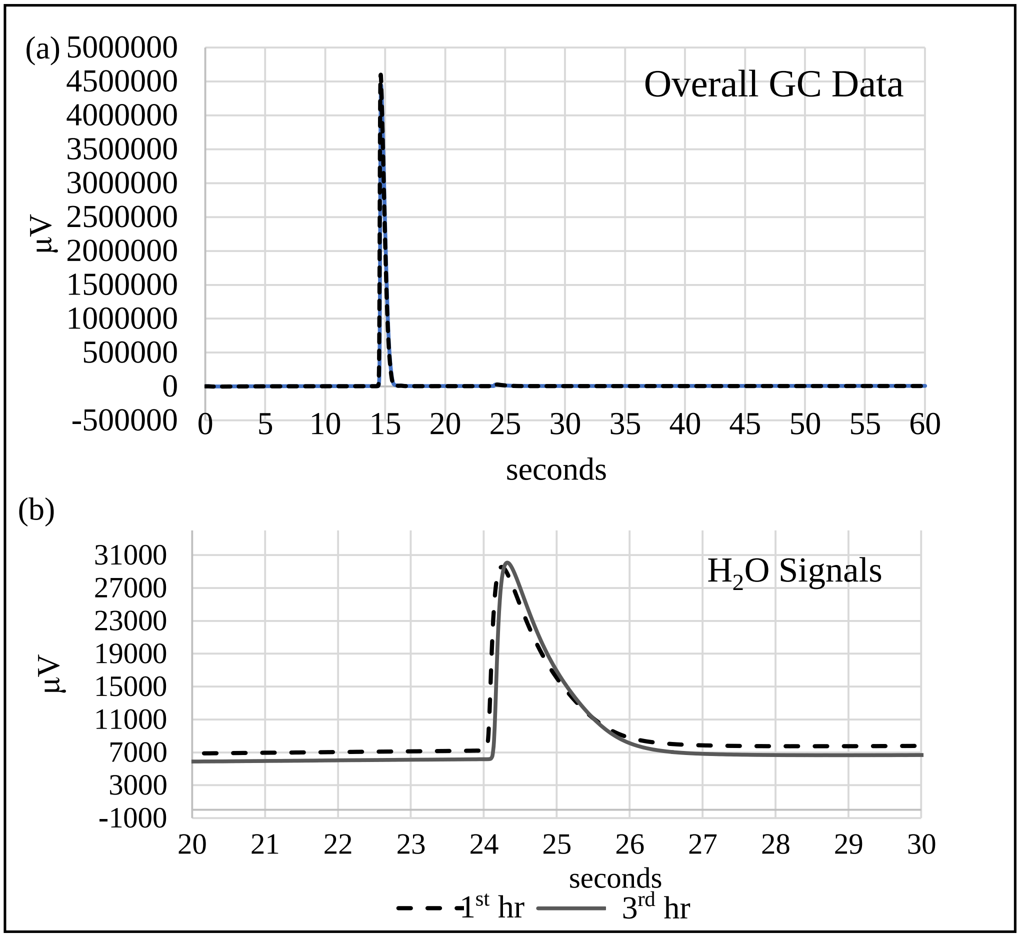


Figure 19. Reference flow to atmosphere 0.050 mm ID first and last run comparison (a) Overall retention time (b) Water peaks only

The analytical flow tests showed more horizontal shifts in **figure 20**. The retention time changes for inert, carbon dioxide and water were 0.22, 0.28 and 0.36 seconds. This further suggests the impact of the analytical line on the system's data output and steady state condition.

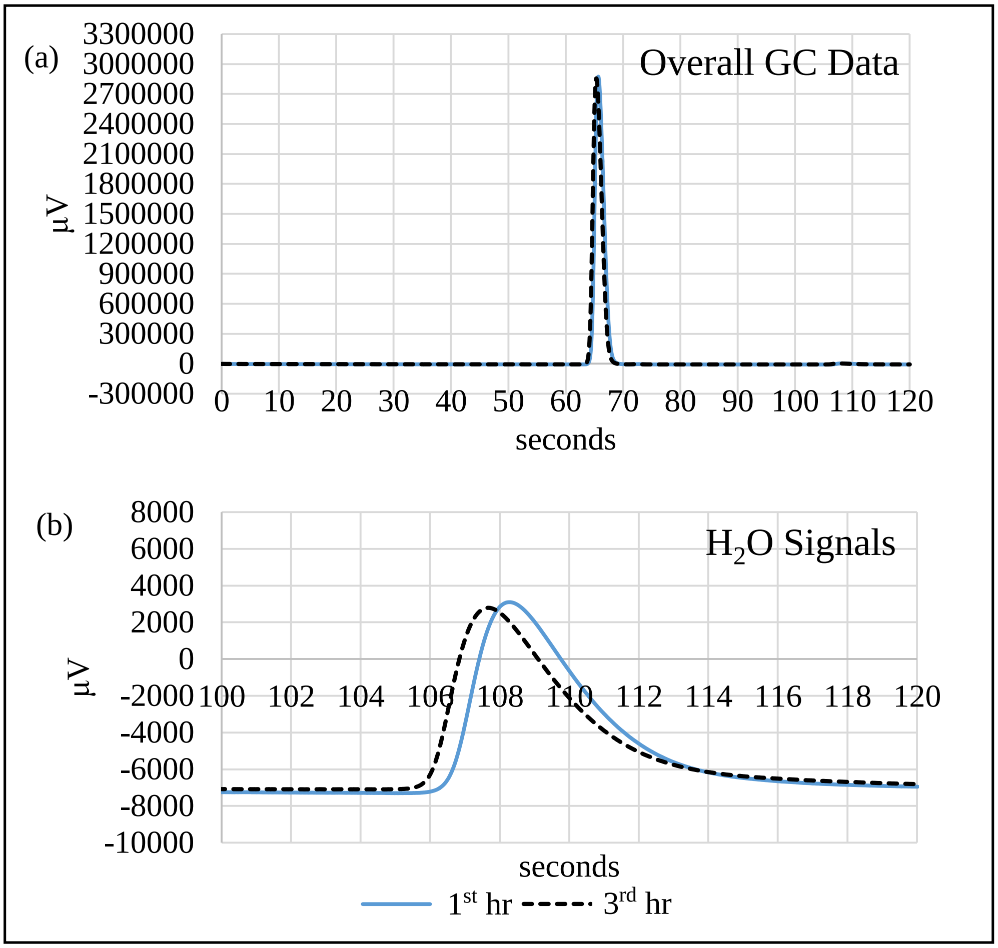


Figure 20. Analytical flow to atmosphere 0.050 mm ID first and last run comparison (a) Overall retention time (b) Water peaks only

When both lines were applied to the reference and analytical exit points, the shift was smaller compared to the analytical runs. The difference values were 0.02 seconds for inert and carbon dioxide, while water had a change of 0.12 seconds. The results are seen in **figure 21**.

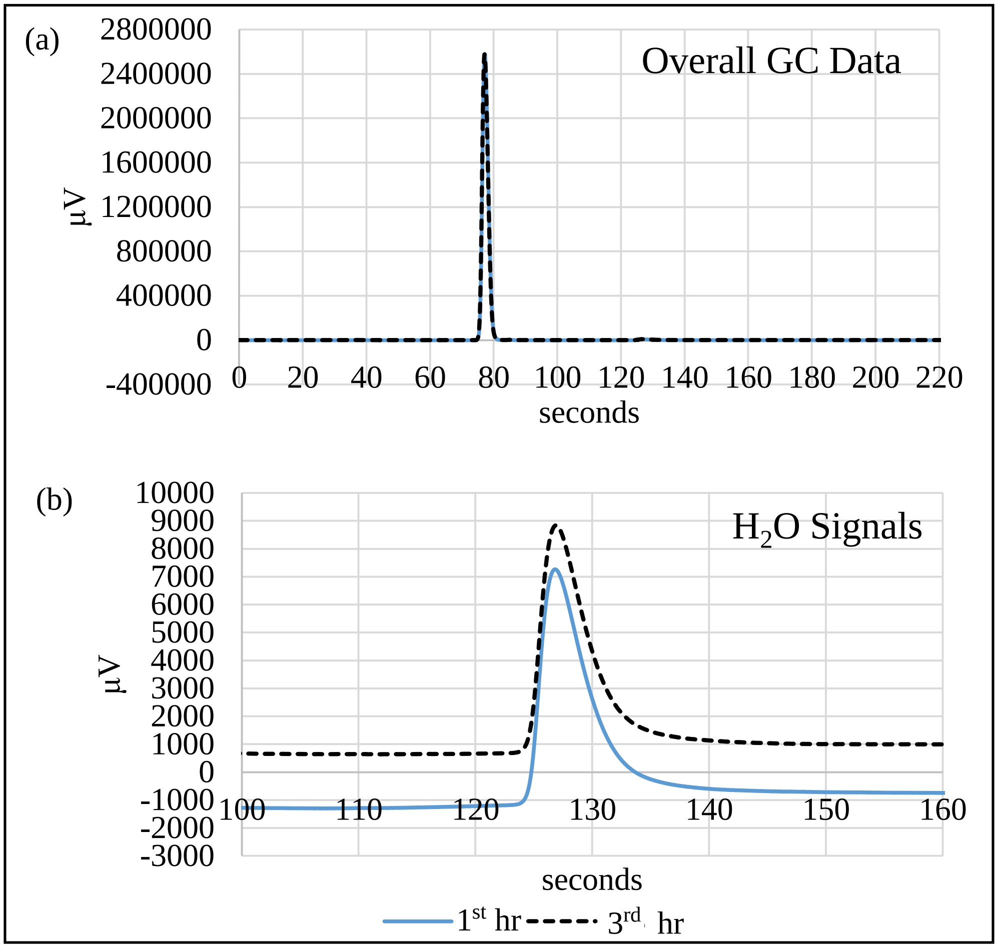


Figure 21. Reference and analytical flow to atmosphere 0.050 mm ID first and last run comparison (a) Overall retention time (b) Water peaks only

Reference and analytical flow to the rough pump showed the biggest change in retention time throughout the run time period. Water showed the most change at 3.18 seconds. The inert and carbon dioxide peaks shifted 1.96 and 2.16 seconds, respectively. It visually evident that the entire chromatography is considerably shifted, seen in **figure 22**. Incorporating a vacuum into the system causes an increased time to reach equilibrium.

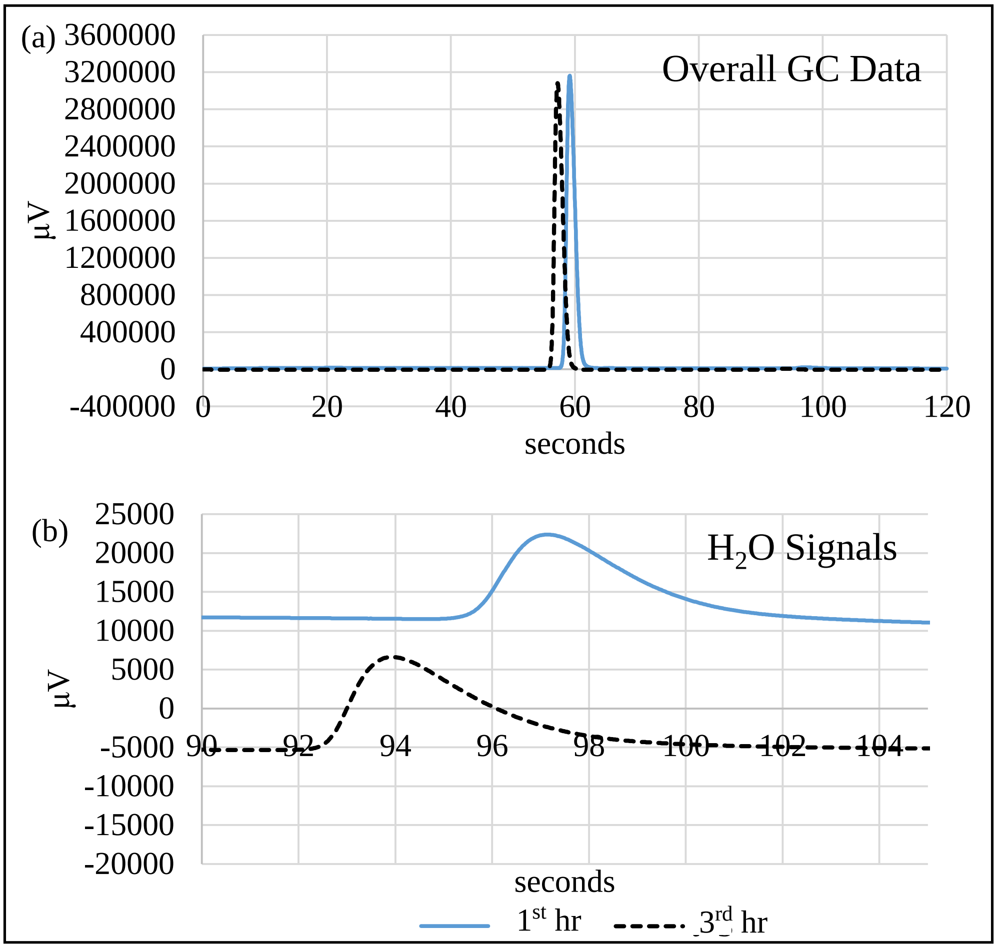


Figure 22. Reference and analytical flow to rough pump 0.050 mm ID: Retention time trends

Water is the sample component that is most affected by long term runs of the GC. All four cases showed that water retention time had shortened the most, compared to the other air components.

IV. Conclusion

Overall, the various combinations of line applications and diameters produced diverse signals. The expected patterns did occur consistently for a majority of the runs. It can be concluded that the TCD had performed sufficiently enough, despite the changing parameters and its originally intended design. These observations should be noted for missions that plan to conduct volatile analysis in the vacuum of space. It may be the case that limiting flow to the mass spectrometer is highly important. This requirement may come at the expense of the GC data’s signal characteristics.

It is important to note that water was largely influenced by the GC’s ability to approach a steady state. Since finding water is the essential goal of the lunar prospector, having a better knowledge of the GC’s ability to perform in the micro-flow system is important. Being able to identify water peaks at potentially different retention times is vital to mission success. One may consider the amount of water predicted to be present on the moon and associate these assumptions with the given data in this study. The lack of atmosphere on the moon permits the 0.050 mm ID transfer line for use, considering the results that shows a minimal influence of vacuum conditions in regards to the identification of all chemical components. With this size transfer line, it may also prevent over-pressurization to the MS.

This study approach was conducted with the purpose of enabling COTS instrumentation for NASA and proving that the GC-MS can be operated in ambient conditions, as well as in outer space. It would be of great interest to further investigate the reasoning for the GC patterns for the 0.050 mm ID line. This can be explored in future experimentation where the line length is varied and exposed to different outlet pressures. Studying how the TCD will react is potentially vital for future ISRU related missions with an incorporated GC-MS fluid sub-system design.

V. References and Acknowledgements

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