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Continuous Online Analysis of Amine Solvents Using Gas Chromatography

March 31, 2021

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EXECUTIVE SUMMARY

This project has successfully demonstrated some of the potential applications of Gas Chromatography as a technique for the continuous online monitoring of various critically important chemical properties of amine-based solvent systems used in Carbon Capture and Sequestration systems (CCS).

Several difficulties were encountered and overcome during this project. There are still further optimizations which need to be investigated before this technique could be considered mainstream. The information gathered during this project and presented here in this report provides an excellent basis for future work in developing these types of applications for use in permanent field installations.

There are unique challenges in performing continuous online analysis of amine-based solvent systems. The lack of commercially available, cost effective online analysis systems contribute negatively to the large-scale adoption of Carbon Capture and Sequestration (CCS) systems. Manually sampling and analysis is costly, complicated, and error prone. Development of these types of continuous online measurement systems will significantly help to reduce risk, improve operational efficiencies, and reduce operating costs of full-scale CCS systems. Establishing cost effect and reliable means of continuously measuring the critical parameters of these systems will help to speed up wide scale adoption of CCS technologies which are necessary to meet global carbon emissions reductions targets.

CONTRIBUTING AUTHORS

The research and authoring of this project was a collaborative effort between the International CCS Knowledge Centre and the University of Regina, Engineering Department.

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1. INTRODUCTION

Carbon capture processes are a critical element in meeting carbon emissions reductions targets from industrial point source emitters. Although there are many avenues of research currently being conducted into carbon capture technologies, the use of amine-based solvents to capture carbon dioxide from flue gas streams is currently the most mature process.

The health of the amine solvents in these processes are an important factor in managing the day-to-day operations of these units, as well as the overall costs of operation. Many of the critical chemical properties of the amine solvent are difficult and time consuming to measure. Currently, most operating facilities rely on a technician taking grab samples of the solvent from the process and sending them to a laboratory for analysis. This process is time consuming and labour intensive. Often, depending on the type of analysis, results can take hours, days or even weeks to be reported back to the process operators. These delays can prevent operators from making important operational decisions in a timely fashion, resulting in inefficiencies and risks in the operating process.

An important laboratory technique which is often used for measuring certain properties of the amine solvent, such as amine concentration, water concentration, carbon dioxide loading, and the concentration of certain degradation products of the amine, is Gas Chromatography.

Gas Chromatography is a mature, versatile, and well understood laboratory technique. Although primarily used as an offline analysis technique in the laboratory, a growing number of specialized applications have been developed which utilize this technique to carry out continuous online measurements of industrial process streams.

Gas Chromatography relies on the vaporization of a sample, without decomposition. The vaporized components of the sample are introduced to a mobile phase referred to as the carrier gas. The components in the carrier gas are passed through a stationary phase (the column) where they interact with the stationary phase. Each component of the sample will interact with the stationary phase to a varying degree. Components which interact weakly with the stationary phase will move rapidly through the column while those that interact more strongly will be retained in the column longer. This separates the individual components of the mixture into bands within the column. As the separated components exit the column, they are passed through a detector which is sensitive to the components of interest.

Specialized Gas Chromatography systems have been employed in the petrochemical industry for many years for the continuous monitoring of process streams for a wide range of properties. The volatile nature of these process streams makes them particularly suitable for Gas Chromatography.

Another specialized application of Gas Chromatography is the analysis of near pure CO_2 gas for

trace contaminants such as oxygen, nitrogen, hydrogen sulfide and water. As such, many carbon capture plants may already have a specialized gas chromatograph in place for monitoring the quality of the CO_2 product stream.

Although experience can be drawn from these specialized applications of Gas Chromatography, its uses in continuously monitoring amine solvent streams are not well established. This project seeks to demonstrate some potential applications of Gas Chromatography as a technique for the continuous online analysis of amine solvents.

2. EQUIPMENT

2.1 FULLY AUTOMATED SAMPLING CONFIGURATION

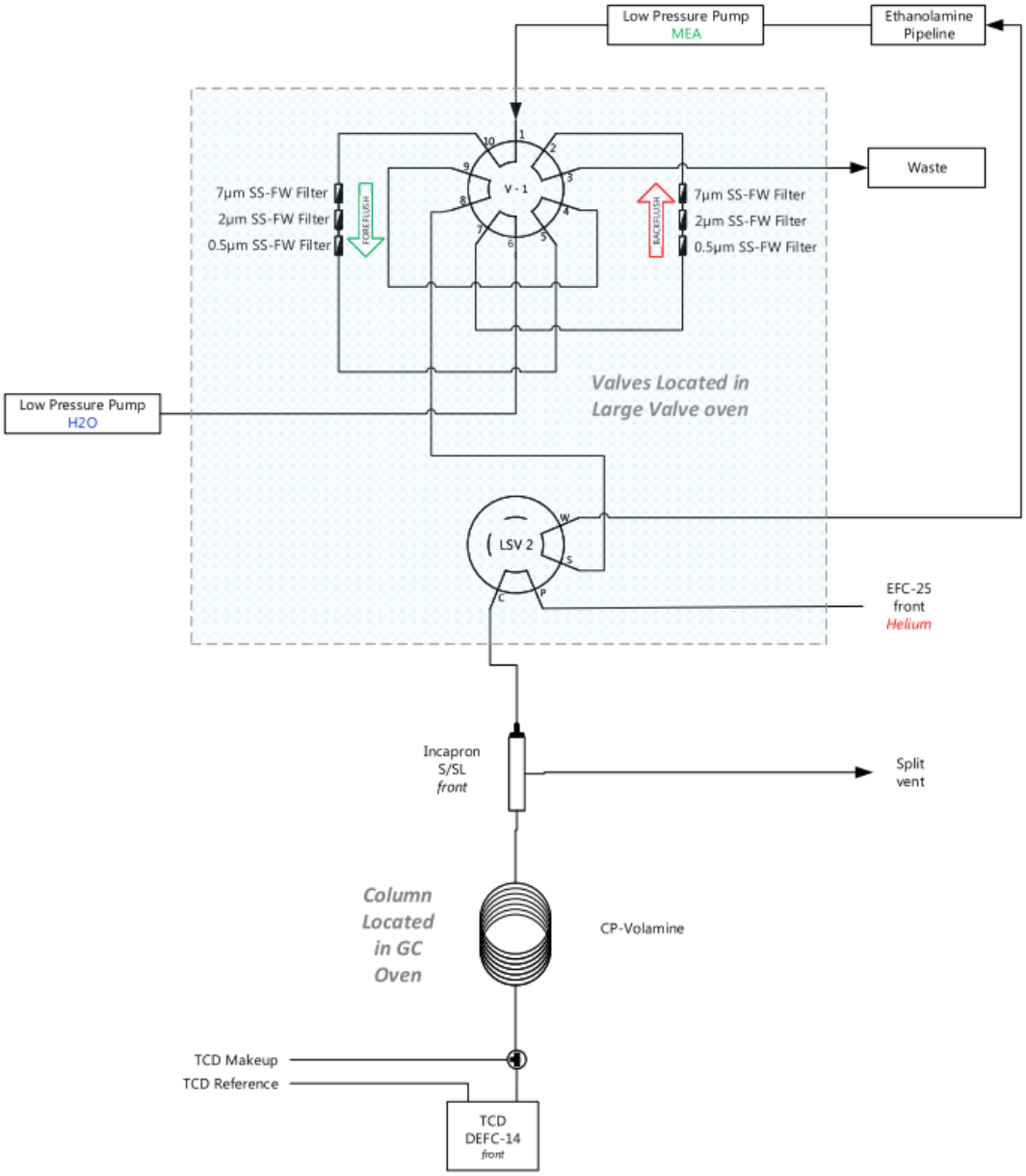
A Scion Instruments model 436 Gas Chromatograph was used for this project. The instrument was customized by Scion Instruments to allow for sampling a flowing stream of amine and directly injecting a small volume sample (0.2uL – 2.0uL) of the stream into the instrument for analysis. Figure 2-1 shows the configuration of the instrument for fully automated operation.

In this configuration, the box labeled 'Ethanolamine Pipeline' represents a continuously flowing amine sample stream. The sample is extracted from the process stream by a low-pressure peristaltic pump (Cole Parmer 74200-10). The sample then enters a 10-port valve where it passes through a train of stainless steel fitted filters to remove any particulate mater from the sample stream.

The 10-port valve is configured with two identical filter trains. The low-pressure water (H_2O) pump back-flushes the second filter train while the first filter train is in use. By changing the position of the 10-port valve, the sample will pass through the second filter train while the first filter train is back-flushed. In this way, the sample stream is continuously cleaned of particulates and the filters can be automatically cleaned when they begin to build up back pressure.

The cleaned sample coming from the outlet of the filter train then passes through to the second valve, which serves as the sample introduction valve for the GC. This valve is a Valco 4-port liquid sampling valve (LSV) which is equipped with a 0.2 µL core. This core controls the volume of the sample introduced to the GC injection port. The cleaned sample continuously flows between ports S and W. The cleaned sample stream is returned directly to the 'Ethanolamine Pipeline' to minimize the volume of sample removed from the stream.

Figure 2-1: Scion 436 GC Configuration for Liquid Stream Sampling



When the second valve is activated, the valve core rotates to the P, C position. This places a 0.2 µL volume of the sample into the helium stream. The helium carrier gas then carries the small liquid sample to the GC injection port. The standard syringe/septum style injection port typically seen on laboratory gas chromatographs has been replaced with a stainless steel direct injection port designed by Scion Instruments. This direct injection port is called an 'Incapron'.

From this point, the analysis is essentially identical to that used in a standard laboratory gas chromatograph. The sample is carried through the column by the carrier gas stream and then

through the detector. For this initial application, a Restek RTX-18078 Volatile Amine column was selected. See Table 2-1 for the specifications for this column.

A thermal conductivity detector (TCD) was selected for this application as the components of interest for this project, amine, water, and CO_2, are all detectable using this type of detector. There are many different types of detectors which could be used depending on the components of interest. Each have their own unique advantages and disadvantages.

Table 2-1: Restek Column Specification

Make	Restek
Model	Rtx-Volatile Amine
Length	60 meters
Internal Diameter	0.32 mm
Coating Thickness	5 µm
Catalog Number	18078

2.2 MANUAL DIRECT LIQUID INJECTION CONFIGURATION

Initially, the GC was delivered with only the fully automated liquid injection configuration. The initial testing runs, and calibrations were carried out using this automated configuration. However, it rapidly became apparent that some sort of manual injection would be highly beneficial to limit the volume of sample required during testing and method development.

Figure 2-3 illustrates how the `Ethanolamine Pipeline` sample stream was simulated in the laboratory environment. Because the volume of the flask used as a reservoir had less than 1 litre of capacity and the dead volume of the tubing in the external sample stream loop was significant compared to that volume, a large amount of each sample was required to be prepared to meet the minimum volume requirement. The significant dead volume of the tubing involved in this loop also required a significant sample to be wasted in flushing the system between samples.

It was decided that a manual means of directly loading the liquid sampling valve (LSV) would be useful. This would allow for small amounts of sample (< 1 ml) to be directly flushed into the LSV. This was accomplished by removing the stainless steel line connecting port #8 on the 10-port valve from port C on the LSV. A small piece of stainless steel line was then directly connected to port C on the LSV and adapted to a luer lock fitting to allow a 1-5 ml disposable syringes to be used to load samples directly into the LSV.

A picture of this arrangement can be seen in Figure 2-2.

2.3 MANUAL SYRINGE INJECTION CONFIGURATION

A third configuration was used to trouble shoot problems which were encountered when attempting to measure the monoethanolamine carbamates present in CO_2 loaded monoethanolamine (MEA) solutions. This configuration replaced the Incapron with a standard manual syringe injection/septum port, which would be typical of a manually operated laboratory gas chromatograph. This configuration allowed direct comparison of samples run on another Agilent gas chromatograph and proved very helpful in troubleshooting. This will be discussed more in section 9.

Figure 2-2: Syringe Adapter

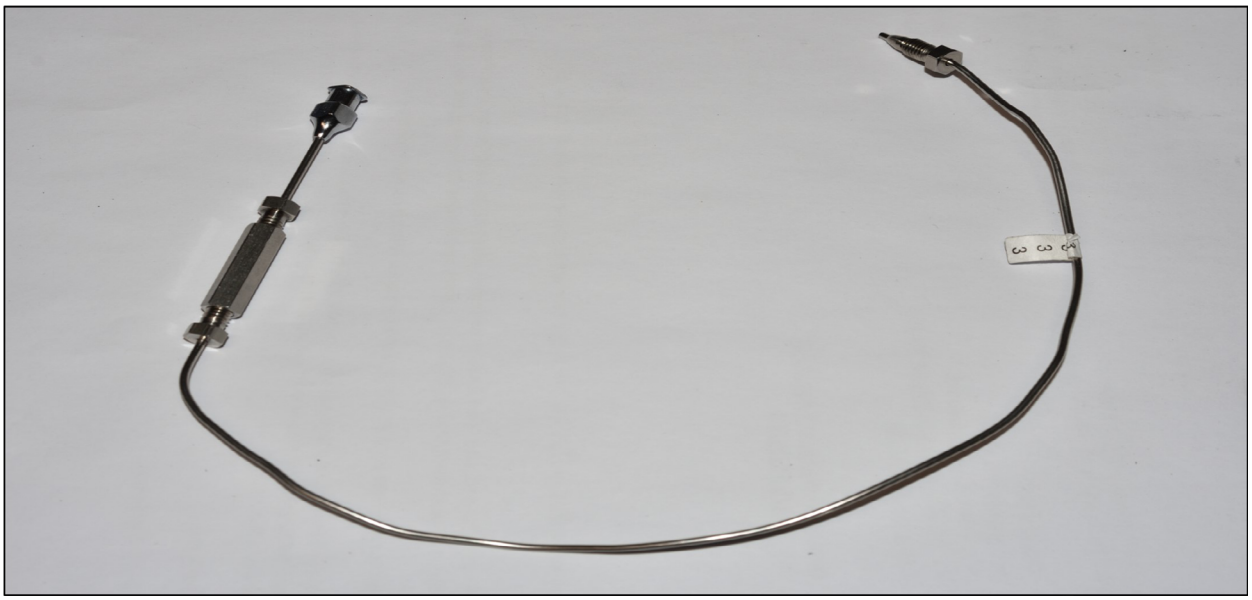


Figure 2-3: Experimental Setup for Automated Operation

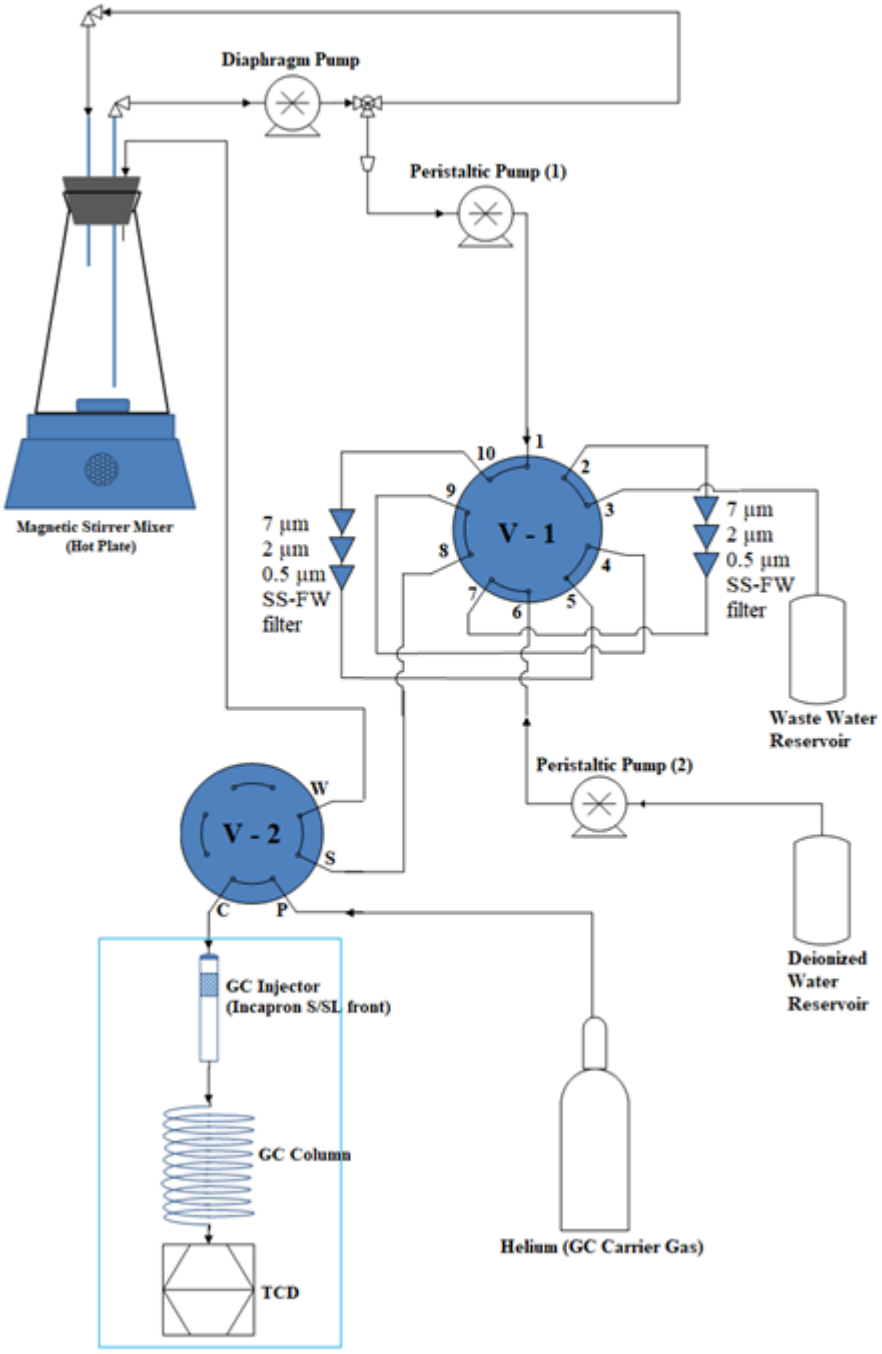


Figure 2-4: Photograph of Experimental Setup

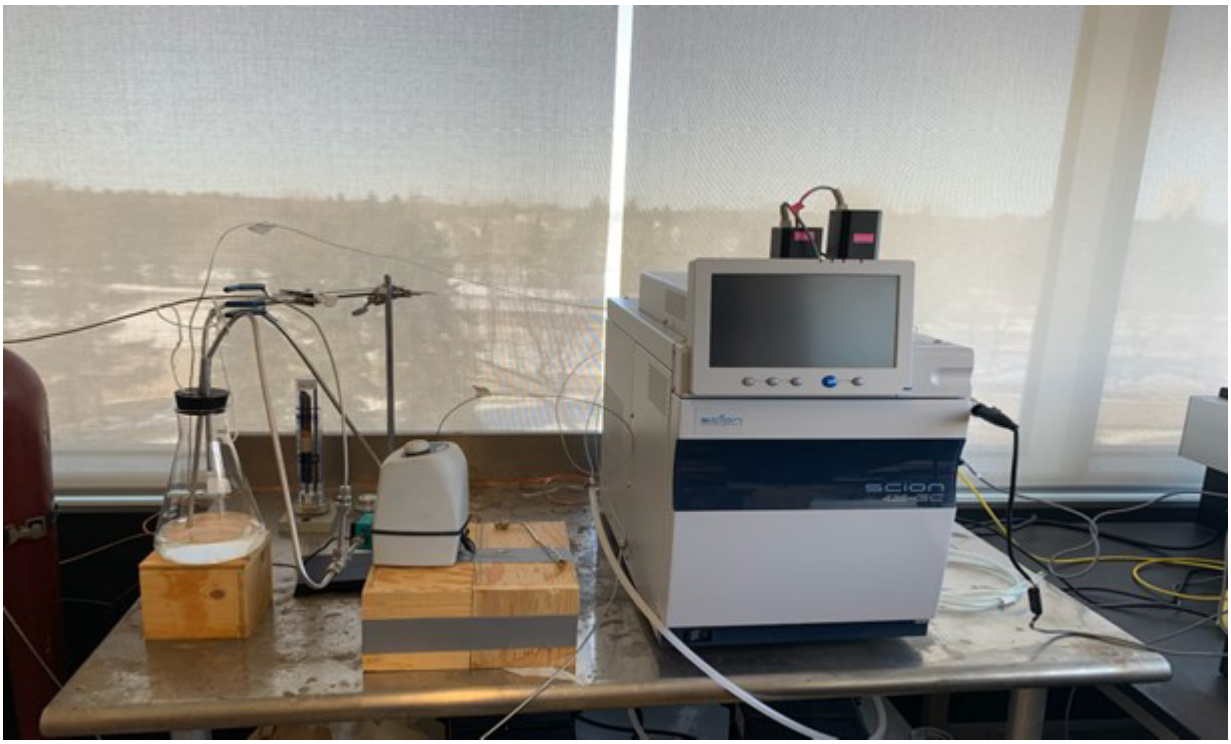


Figure 2-5: Photograph of Low-Pressure Pumps

3. REAGENTS

The following is a list of chemical reagents which were in this project.

- Ethanolamine (MEA, purity ≥ 98%)
- N-Methyl diethanolamine (MDEA, purity ≥99%)
- Sodium bicarbonate ($NaHCO_3$, purity ≥ 99.7)
- Sodium carbonate ($NaCO_3$, purity ≥ 99.5%)
- Ammonium bicarbonate (NH_4HCO_3, purity ≥ 99.0%)
- Potassium hydrogen phthalate ($C_8H_5KO_4$, purity ≥ 99.95%)
- Isopropyl Alcohol ($(CH_3)_2CHOH$ >99.7%)

4. INITIAL CALIBRATION OF MONOETHANOLAMINE AND WATER

4.1 PURPOSE

The intent of this initial experiment was to establish the performance of the selected chromatography conditions and calibrate the response factors for MEA and water.

4.2 EXPERIMENTAL DESIGN AND RESULTS

The initial experiments were done using three different concentrations MEA and water mixtures. The selected concentrations were 15, 30 and 45 wt% MEA. A volume of 1.0 litre of each of these solutions was prepared and run a total of ten times in fully automated mode. Table 4-1 contains the GC Conditions used for this run.

Figure 4-1 illustrates a set of typical chromatograms from these runs. Although the peak shapes are less then perfect, the reproducibility, measured as the relative standard deviation of the peak areas is <1.0%. Figure 4-2 and Figure 4-3 show the resulting calibration curves for water and MEA which were obtained from this data collected during this experiment. The curves are nicely linear and have excellent correlation coefficients.

4.3 CONCLUSIONS

These initial runs looked very promising. The system when configured in fully automated mode was able to measure the MEA and water concentrations. The calibration curves appear excellent, and the reproducibility is very acceptable.

Table 4-1: GC Program

Column	Rtx-Volatile Amine	
Split Ratio	10:1	
Flow	10	ml/min
TCD Temp	150 °C	°C
Filament Temp	250	°C
TCD Range	0.5	
Data Rate	25	Hz
Temperature Program		
Rate (°C/min)	**Step (°C)**	**Hold Time (min)**
Initial	50	2.00
30	210	2.67
	Total Time:	10

Table 4-2: Relative Standard Deviation of MEA/Water Standard

Standard	MEA Concentration (%wt/wt)	MEA Pk Area RSD (n = 10)	H_2O Concentration (%wt/wt)	H_2O Pk Area RSD (n = 10)
1	15	0.98%	85	0.15%
2	30	0.25%	70	0.09%
3	45	0.58%	65	0.98%

Figure 4-1: Sample chromatograms (15, 30, 45 %wt/wt MEA)

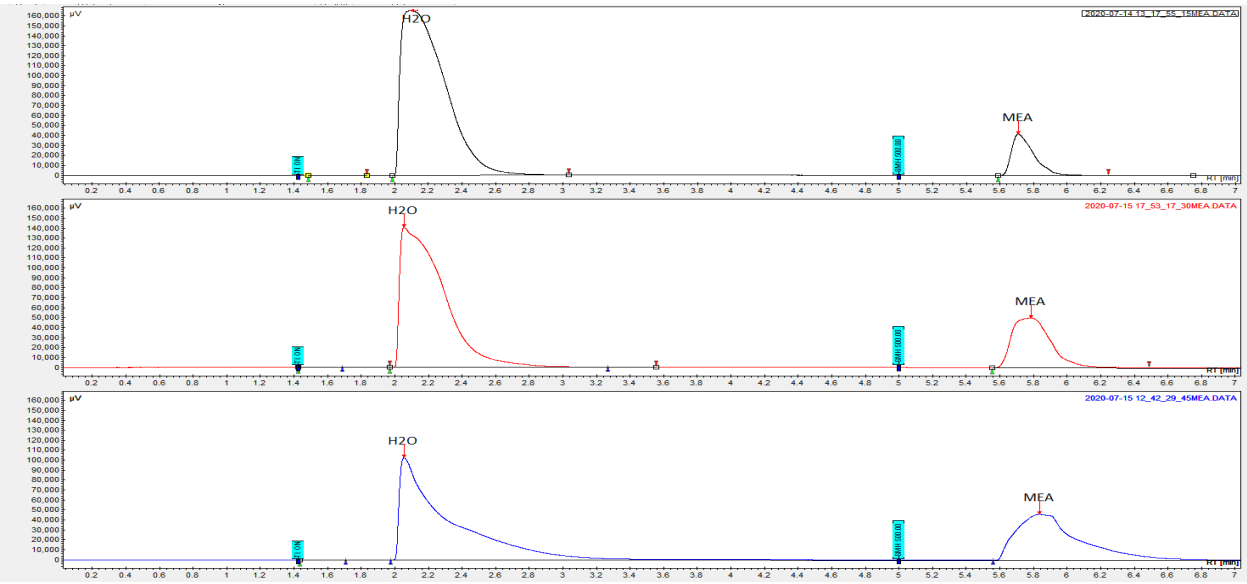


Figure 4-2: MEA Calibration

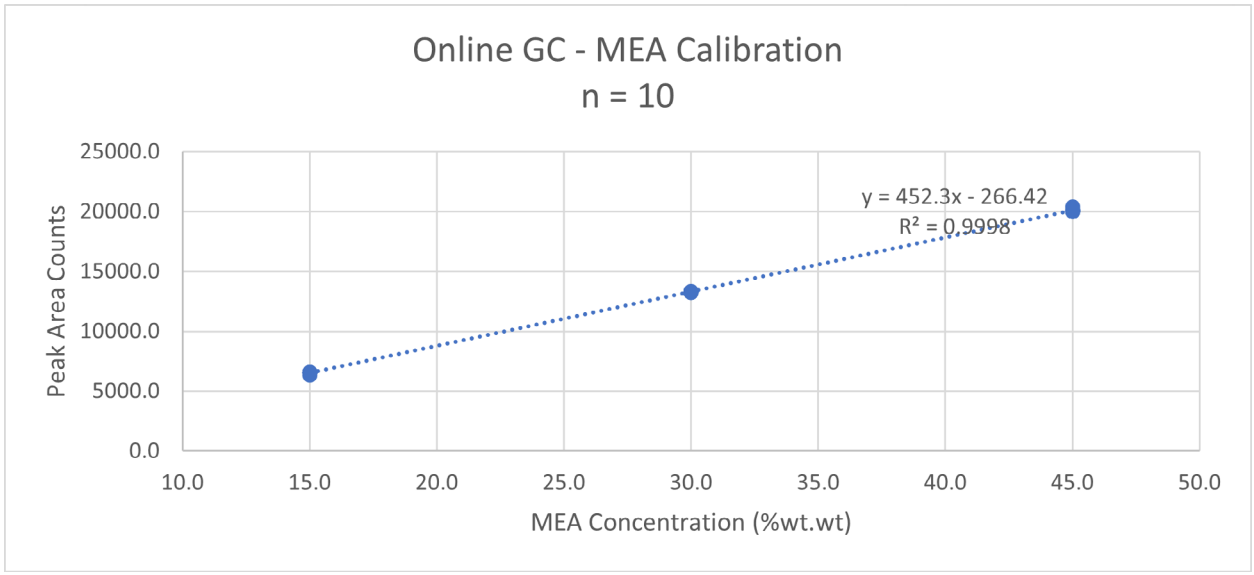
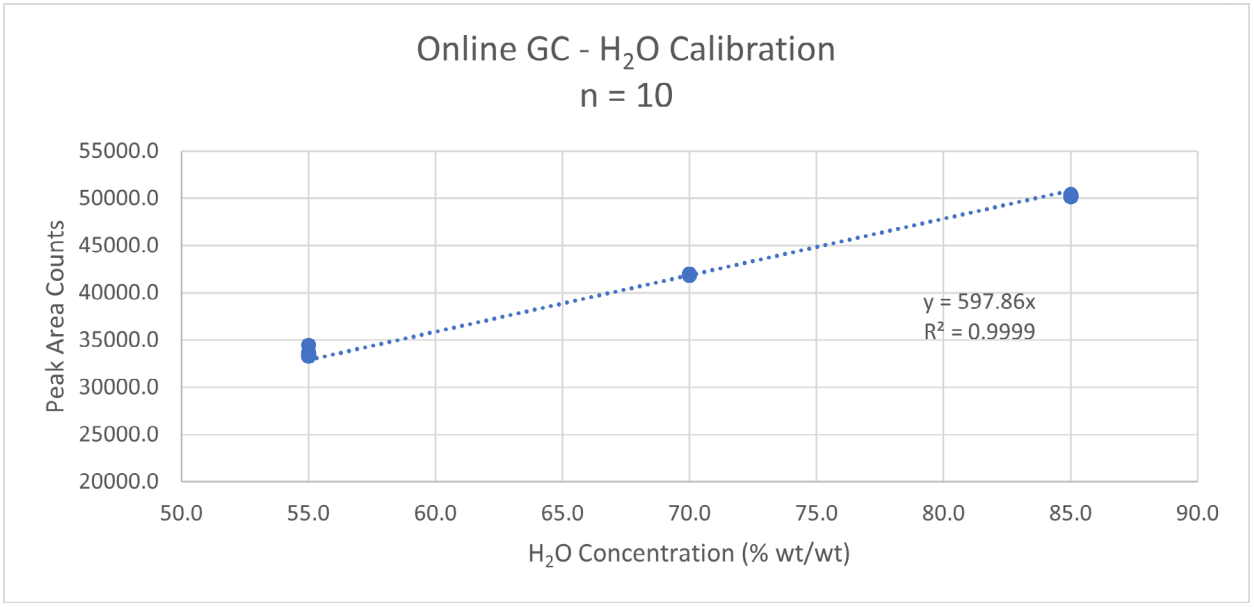


Figure 4-3: Water Calibration



5. MONOETHANOLAMINE AND WATER CALIBRATION USING ISOPROPYL ALCOHOL AS AN INTERNAL STANDARD

5.1 PURPOSE

The initial calibrations with MEA and water were quite acceptable. However, as the peak shapes were quite broad and, in some cases, somewhat mishappen, it was decided to see if an internal standard with a better peak shape might improve the reproducibility. To test this hypothesis, the calibrations carried out in section 5 were repeated, but with the addition of 10% wt/wt isopropyl alcohol (IPA).

5.2 EXPERIMENTAL DESIGN AND RESULTS

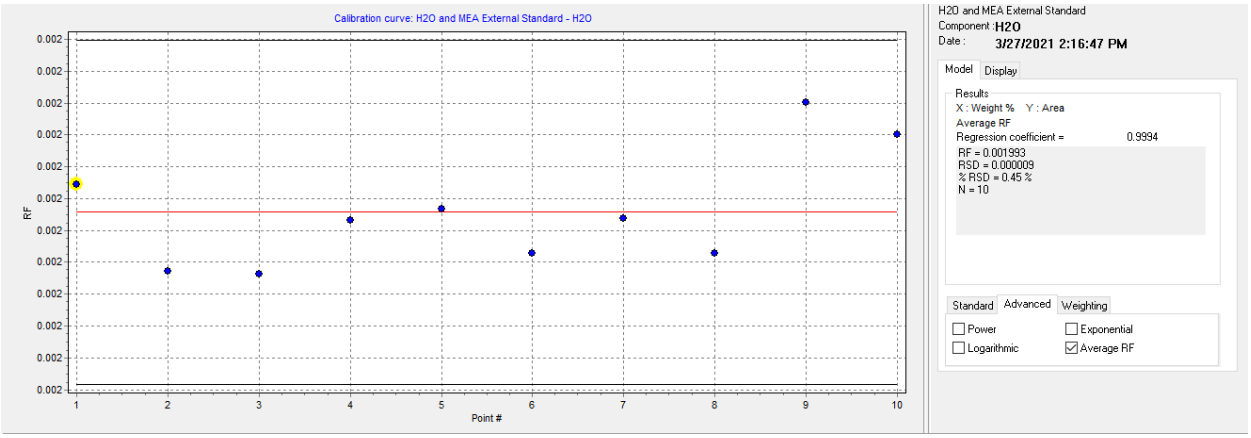
As in section 5, three different concentrations MEA and water mixtures where prepared. In addition to the MEA and water, each sample had 10% by weight IPA added to it. The selected concentrations were 10, 25 and 40 weight percent MEA. A volume of 1.0 litre of each of these solutions was prepared and each was run a total of ten times in fully automated mode. Table 5-1: GC Program contains the GC Conditions used for this run. Figure 5.6 illustrates typical chromatogram obtained for each sample concentration used in this experiment.

Table 5-1: GC Program

Column	Rtx-Volatile Amine	
Split Ratio	10:1	
Flow	10	ml/min
TCD Temp	150 °C	°C
Filament Temp	250	°C
TCD Range	0.5	
Data Rate	25	Hz
Temperature Program		
Rate (°C/min)	**Step (°C)**	**Hold Time (min)**
Initial	50	2.00
30	210	2.67
	Total Time:	10

Figure 5-1 illustrates a set of typical chromatograms from these runs. This figure shows the IPA peaks are nice and sharp. However, Figure 5-1, Figure 5-2, Figure 5-4, and Figure 5-5 show the average response factors for water and MEA, when calculated using the IPA as an internal standard, are worse than those when no internal standard is used. Figure 5-3 shows the average response factors for IPA. The reproducibility for IPA is 0.46%, which is excellent, however there is little correlation between the area of the IPA peak and that of the water or MEA. This is not altogether unexpected. If the variance in the areas of the water and MEA peaks were a result of a systematic error, such as an inconsistent volume being delivered from the LSV due to the formation of bubbles, a strong correlation would be expected. However, if the variance is due only to integration factors resulting from the poor peak shape of water or MEA, then the IPA peak area would not be expected to be highly correlated.

Figure 5-1: H_2O External Standard, Average Response Factor



5.3 CONCLUSIONS

This experiment has demonstrated that there is a low correlation between the response factor of the IPA and those of the water and MEA. From this we can conclude that the volume being delivered from the LSV to the injection port is consistent between injections. The use of an internal standard such as IPA is of little use in this situation.

Figure 5-2: H_2O with IPA IS, Average Response Factors

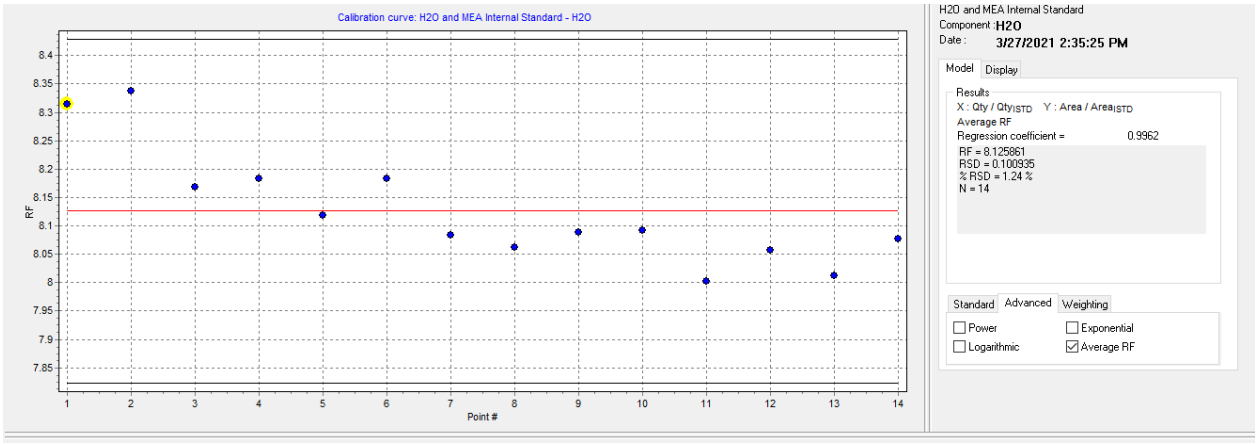


Figure 5-3: IPA Average Response Factor

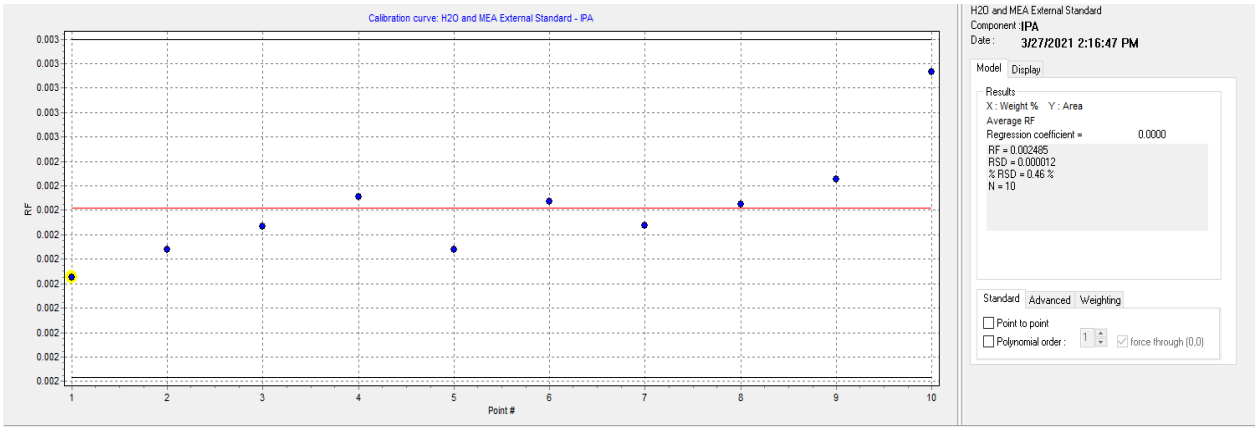


Figure 5-4: MEA with IPA Internal Standard

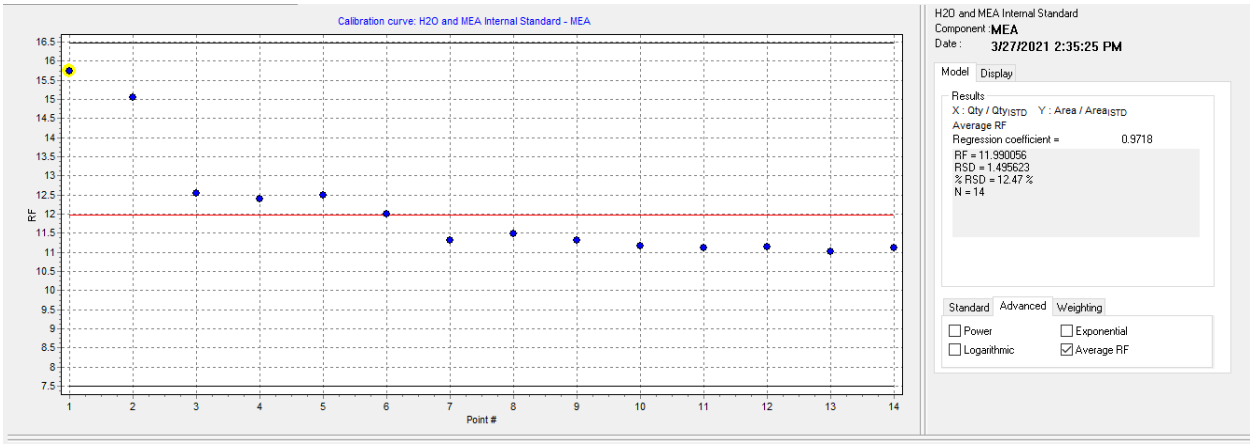


Figure 5-5: MEA External Standard

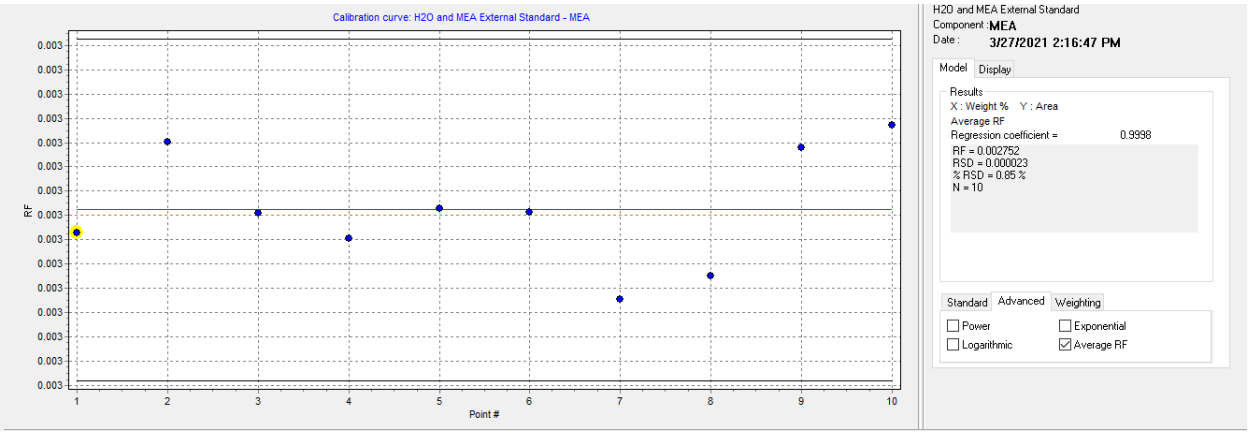
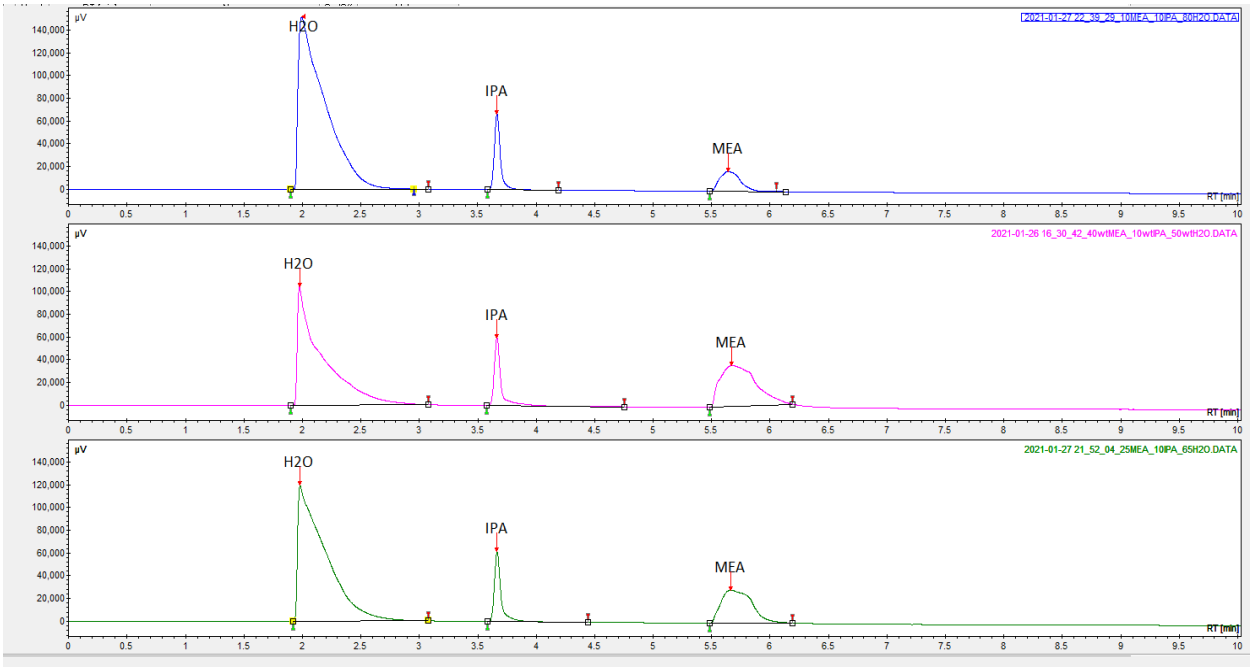


Figure 5-6: Sample Chromatograms (10, 25 and 40 % wt/wt MEA)



6. EXTENDED RUN OF 25% MONOETHANOLAMINE

6.1 PURPOSE

This experiment demonstrates the behaviour of the system in fully automatic mode over an extended period. This initial extended run was carried out with a pure MEA/Water mixture. No fly ash was added.

6.2 EXPERIMENTAL DESIGN AND RESULTS

A 1.0 litre volume of 25 weight percent MEA was prepared. Approximately 600 ml of this solution were added the volumetric flash which makes up the solvent reservoir. The amine recirculation pump was started and this solution was continuously recirculated for the duration of the test.

The Scion Instruments Compass software which controls the GC was configured to run a sequence file of >500 samples. Four methods were created. Each of these methods contained identical parameters for the GC settings and only differed in the valve activations to control the H_2O back-flush pump and the column selection position of the 10-port valve.

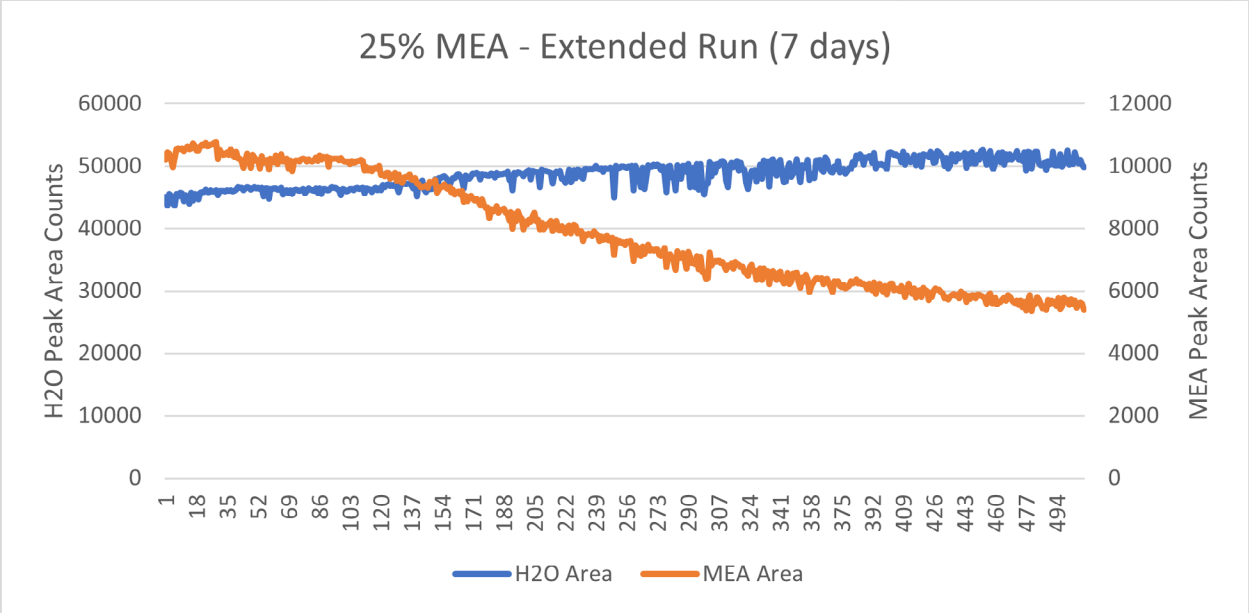
The sequence file was configured to run 10 samples on the first filter train. Then, it would switch to the second filter train for the next 10 samples. While the first two samples were running on the second filter train, the H_2O back-flush pump would run and wash the first filter train. Once a total of 10 samples had been run on the second filter train, the sequence file would cause the 10-port valve to switch back to the first filter train and the second would be back-flushed. This cycle was set to repeat for the duration of the extended run, which was 7 days.

Figure 6-1 shows the area counts of the MEA and the water peaks over the course of the run. It can clearly be seen that the water concentration increases over time and the MEA concentration decreases overtime. This is caused by contamination from the water used to flush the filter trains. Each time the filter train switch occurs, the dead volume of the filter train, which now contains the pure deionized water used to clean it, is added back into the amine reservoir loop.

When this type of system is used on a production process stream in an industrial setting, the volume of water present in the filter trains after back-flush would likely be inconsequential if added back into the overall stream volume, which could be many hundreds of thousands of litres in a typical production system.

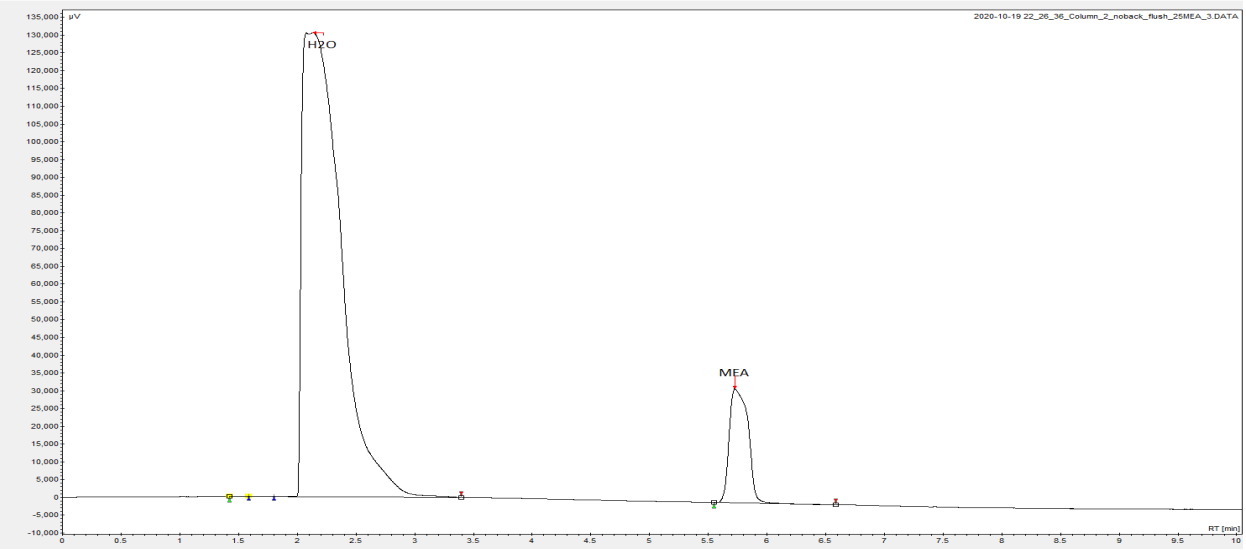
On smaller systems, such as an experimental skid testing system, where the total volume of the solvent in use might only be a few 100 litres, it may be desirable to have an initial purge cycle, which would send a small amount of the process amine through the filter train and then to waste before recirculating it back to the sample loop. It is likely though, that a small amount of pure water added back into a carbon capture solvent stream would simply not be noticed as the water balance in an operating system is usually in continuous flux. While removal of small amounts of amine from the system may require some amine make-up to be added.

Figure 6-1: Peak Area Counts from Extended Run



In Figure 6-1 some noise can be seen in the processed peak areas. This is particularly noticeable in the water area counts between about samples 230 and 360. This noise is due to slight variations in the way in which the peaks are being integrated by the Compass software. Compass is an extremely power software, with significant flexibility in configuring how the peak integration occurs. For this run, only basic peak widths and positions were considered in setting up the peak integrations. An example of a typical chromatogram from this extended run is shown in Figure 6-2. Because of the size and shape of these peaks the integration of the peak areas is occasionally sub optimal. Some time should be spent reprocessing these chromatograms with alternate integration settings to investigate optimizing the peak area integrations. This would likely reduce the noise.

Figure 6-2: Sample Chromatogram, 25% MEA/Water, Extended Run



6.3 CONCLUSIONS

The equipment ran very well for the entire 7 day run period. There were no major issues encountered. The control of the 10-port valve and the back-flush pump by the Compass software worked perfectly.

The dilution effect from the dead volume in the filter trains after cleaning with the back-flush pump caused a steady dilution effect over the course of the run. This problem is unique to the laboratory simulation of a continuous flowing process stream and occurs because the dead volume in the filter trains is significant compared to the relatively small total volume of amine in the simulated process loop. This effect should be noted but is unlikely to cause any real problems in either a full-scale process stream or a skid testing scenario due to the significantly larger volume of the process fluid in the sample stream.

7. EXTENDED RUN OF 25% MEA, 10% ISOPROPYL ALCOHOL (IPA) AND FLY ASH (12 DAYS)

7.1 PURPOSE

The second extended run was carried out with fly ash contaminated amine to test the effectiveness of the stainless steel filter trains in removing these types of particulate contaminants which might be expected to be encountered in a real-world application.

7.2 EXPERIMENTAL DESIGN AND RESULTS

A 1.0 litre volume of 25% MEA, 10% Isopropyl Alcohol and 65% water mixture was prepared for this experiment. To this solution 5 grams of fly ash collected from a coal burning power plant were added. The solution was stirred with a magnetic stirrer for approximately 1 hour. It was then allowed to settle for several hours and then ~ 600 ml were decanted to another flask leaving the heavier fly ash particles behind. The turbidity of this decanted solution was then measured using a Hanna Instruments Model HI83414 Turbidity and Free / Total Chlorine Analyzer. Figure 7.1 shows a photograph of the amine solution before and after addition of the fly ash.

The isopropyl alcohol was added to help correct for the dilution effect from the filter train backwashing that was observed in the first extended run. This run was carried out over a period of 12 days.

Table 7-1: Turbidity of sample at the start and end of the run

Date	Turbidity (NTU)
04-Nov-2020	26.06
12-Nov-2020	0.92

Table 7-1 shows the turbidity of the solvent mixture at the beginning of the run and at the end of the run. There were no issues encountered with the equipment over this 12-day period and it can be seen from the turbidity results that most of the fly ash was eventually removed by the filter trains.

As in the first extended run described in section 6 the amine in the solvent reservoir became diluted, over time, due to the water introduced by the back-flushing process. This can be seen in Figure 7-3. The peak areas corresponding to the water concentration are observed to increase gradually over the course of the run, while the peak areas corresponding to the MEA and IPA concentrations can be seen to gradually decrease.

Table 7-2 details the statistics collected from the individual runs. The ratios of the peak area of water to IPA and MEA to IPA are also calculated and shown here. When the MEA/IPA peak area ratios are calculated a relative standard deviation of only 3.1% over the course of the entire run is obtained.

7.3 CONCLUSIONS

The equipment ran very well for the entire 12 day run period. There were no issues

encountered. The control of the 10-port valve and the back-flush pump by the Compass software worked perfectly.

As before, the dilution effect from the dead volume in the filter trains after cleaning with the back-flush pump caused a steady dilution effect over the course of the run. Using the IPA as an internal standard to correct for this issue resulted in a relative standard deviation of the MEA/IPA ratioed peak areas of 3.1% over the 507 sample runs collected during the 12-day run period. Figure 7.3 illustrates the effect of the filter train dead volume dilution on the sample results. The areas of the water peaks can be seen to increase as a result of this dilution effect, while the areas of the IPA and MEA peaks decrease. Figure 7.2 shows the water to IPA and the MEA to IPA peak area ratios. As expected, the water can be seen to be increasing however, the MEA to IPA ratios are quite stable throughout the run.

Figure 7-1: Examples of MEA with and without fly ash

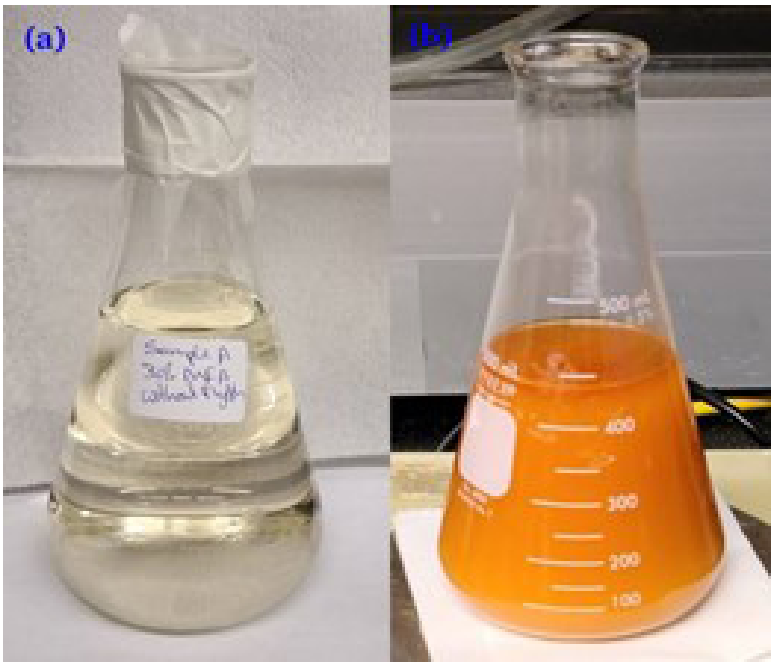


Table 7-2: Peak Area and Ratio Statistics

	Area/H_2O	Area/IPA	Area/MEA	H_2O/IPA	MEA/IPA
N	507	507	507	507	507
Mean	50319	1235	4339	57.6	3.6
Std Dev	3646	659	2244	35.3	0.11
Rsd %	7.2	53.3	51.7	61.3	3.1

Figure 7-2: Water and MEA to IPA Peak Ratios

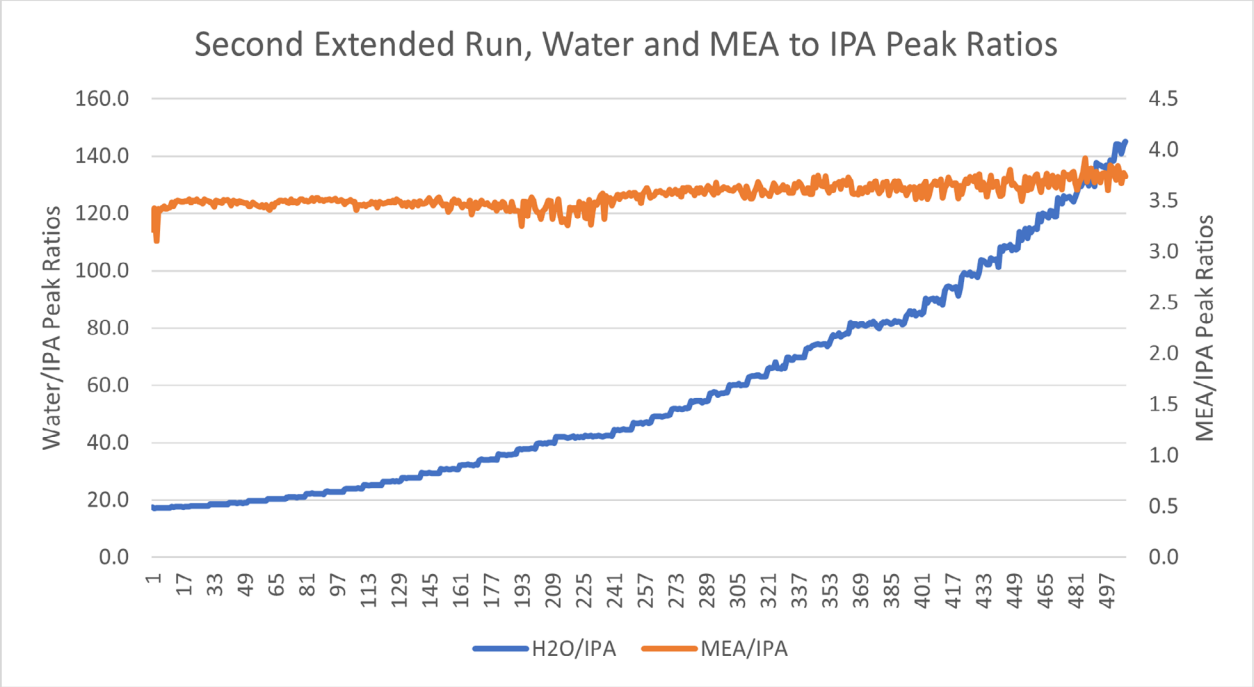
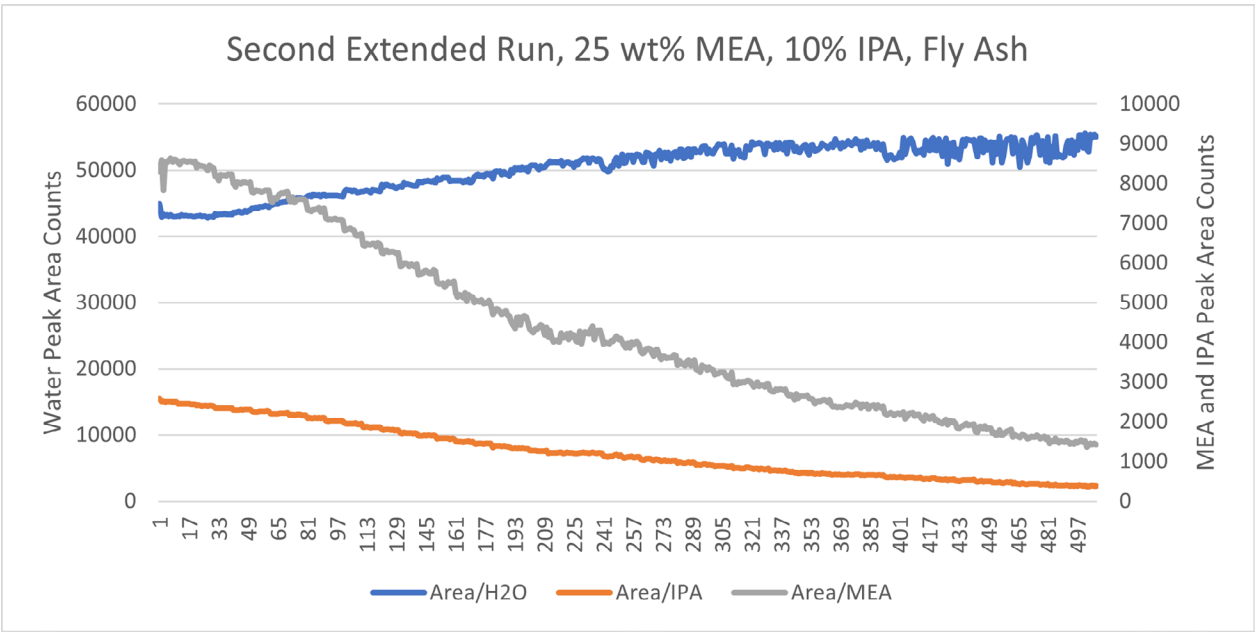


Figure 7-3: 25% MEA Second Extended Run, with IPA and Fly Ash



8. ANALYSIS OF CO_2 LOADED MONOETHANOLAMINE

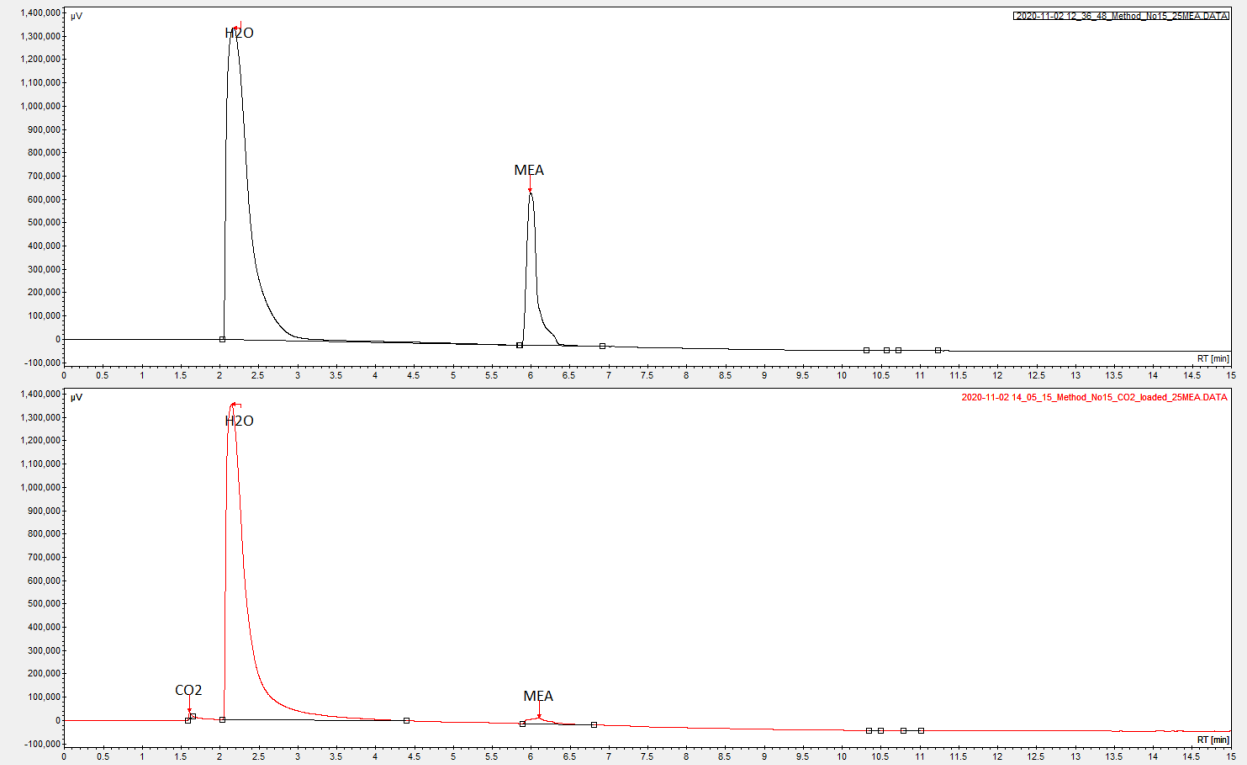
8.1 PURPOSE

The initial intent of this project was to demonstrate that Gas Chromatography could be used to continuously monitor the amine and water concentration in an amine sample stream. Although measuring the CO_2 loading of the amine was not initially in scope, it was decided to investigate whether this target parameter could also be determined in the same operating configuration as the amine concentration.

8.2 EXPERIMENTAL DESIGN AND RESULTS

A 1.0 litre volume of 15 weight percent MEA and water mixture was prepared. Approximately half of this solution was placed in an Erlenmeyer flask on a magnetic stirrer. Pure CO_2 was bubbled through this solution for approximately 1 hour. The original solution and the CO_2 loaded solution were each then injected manually into the gas chromatograph using the configuration described in section 2.2.

Figure 8-1: Unloaded and Loaded MEA (15% wt/wt)



This resulted in a completely unexpected observation. Figure 8-1 illustrates the chromatogram of the unloaded sample on the top and the CO_2 loaded sample on the bottom. A very small CO_2 peak can be seen at 1.6 minutes before the water peak. However, the MEA peak has almost completely disappeared. MEA typically forms more strongly bonded carbamates on absorbing CO_2 rather than weaker bonded carbonates. It was initially thought that the stronger bonded carbamates may not be decomposing back into MEA and CO_2 in the heated injection port. As the transfer line from the LSV to the Incapron is not heated, and the sample transfer lines terminates in the Incapron itself, rather than further down into the hot zone of the injector port, it was initially felt this may be the source of the problem. The MEA-carbamate could be depositing in the colder zone at the bottom of the Incapron towards the top of the injector port, where it might slowly bleed into the system. This would result in an elevated background but no apparent peaks.

Numerous different GC conditions were tested by increasing the temperature of the injection port, changing the split ratios and flow rates. None of these changes made an appreciable difference in the recovery of the amine or the CO_2.

8.3 CONCLUSIONS

There is a problem with the measurement of CO_2 under these experimental conditions. However, not only is the CO_2 measurement an issue, but the measurement of the MEA once exposed to CO_2 creates a serious problem with the use of this setup for monitoring amine and water concentration in a process environment. Significant effort was invested in understanding this problem and will be discussed in detail in section 9.

9. TROUBLESHOOTING CO_2 LOADED MONOETHANOLAMINE

9.1 PURPOSE

Understanding the problems with loaded MEA which were discovered in Section 9 are critical to the successful deployment of this technology to a real-world measurement scenario involving MEA. This section will discuss the procedures taken to identify the cause of this problem and the steps taken to resolve these issues.

9.2 EXPERIMENTAL DESIGN AND RESULTS

Initially, the poor recovery of the MEA was thought to be related to chromatographic conditions and/or the lower temperatures in the Incapron where the solvent sample first enters the gas chromatograph. Amines are known for interacting with all sorts of materials from glass to

stainless steels.

The first attempt to improve this was to wrap the top of the Incapron with thermal insulation to increase the temperatures closer to what would be expected in the hot zone of the injector. These attempts proved to make no measurable difference in the amine recovery.

The next approach was to modify the transfer line from the injection valve to the Incapron. The initial tubing used was approximately 10 cm in length and had an internal diameter of 0.76mm. It was thought that the larger diameter tubing may be causing the small 0.2µL sample to not be transferring cleanly from the injection valve core along the larger diameter tubing.

To investigate this a new transfer line was constructed from 0.25mm ID stainless steel tubing. This change also had no appreciable effect on the amine or CO_2 recovery.

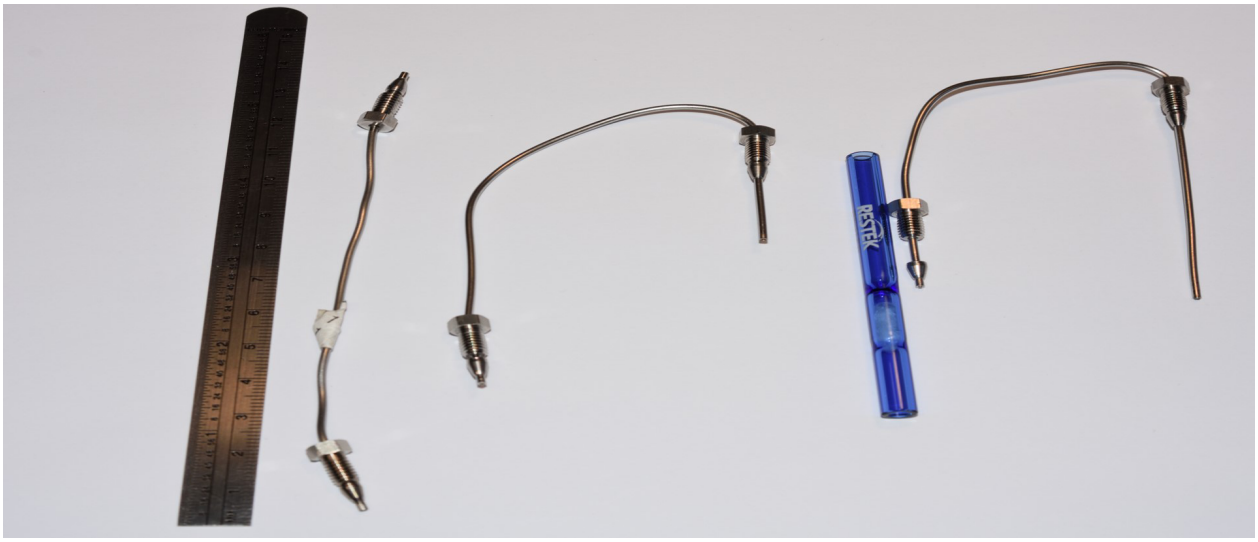
Two additional sample transfer lines were constructed of the 0.25mm ID stainless steel tubing. These transfer lines were fitted to the Incapron in such a way as to allow for their penetration into the injection port at different depths. The first one penetrated into the injection port to approximately 20mm. This transfer line also had no impact on the amine and CO_2 recovery. The second was measured to extend 50mm into the injection port which is the maximum depth that in syringe needle would be able to reach if the port were configured with a standard syringe septum port. This also had little to no effect on the amine recovery. Figure 9-1 is a photograph of the different stainless steel sample transfer lines described here. The leftmost line was the original, with zero penetration through the Incapron and an internal diameter of 0.76mm. A glass injection port liner is included for size reference.

At this point, samples of loaded and unloaded MEA were run on a different laboratory GC equipped with a standard syringe septum port. Although this instrument was equipped with a different column, and the injection volumes were considerably larger (1µL), the amine and CO_2 recoveries were roughly as would be expected.

This verified that these types of samples were measurable using Gas Chromatography. But this still provided little clear evidence as to the cause of the poor recoveries on the instrument used in this project.

To eliminate the injection port and column as the source of the problem this GC was configured back to a more typical manual syringe septum injection port as described in section 2.3. Identical GC conditions were used as with the Incapron and LSV. The only other difference with these injections was a larger sample volume necessitated by the size of the gas tight syringe which was available for troubleshooting.

Figure 9-1: Stainless Steel Sample Transfer Lines

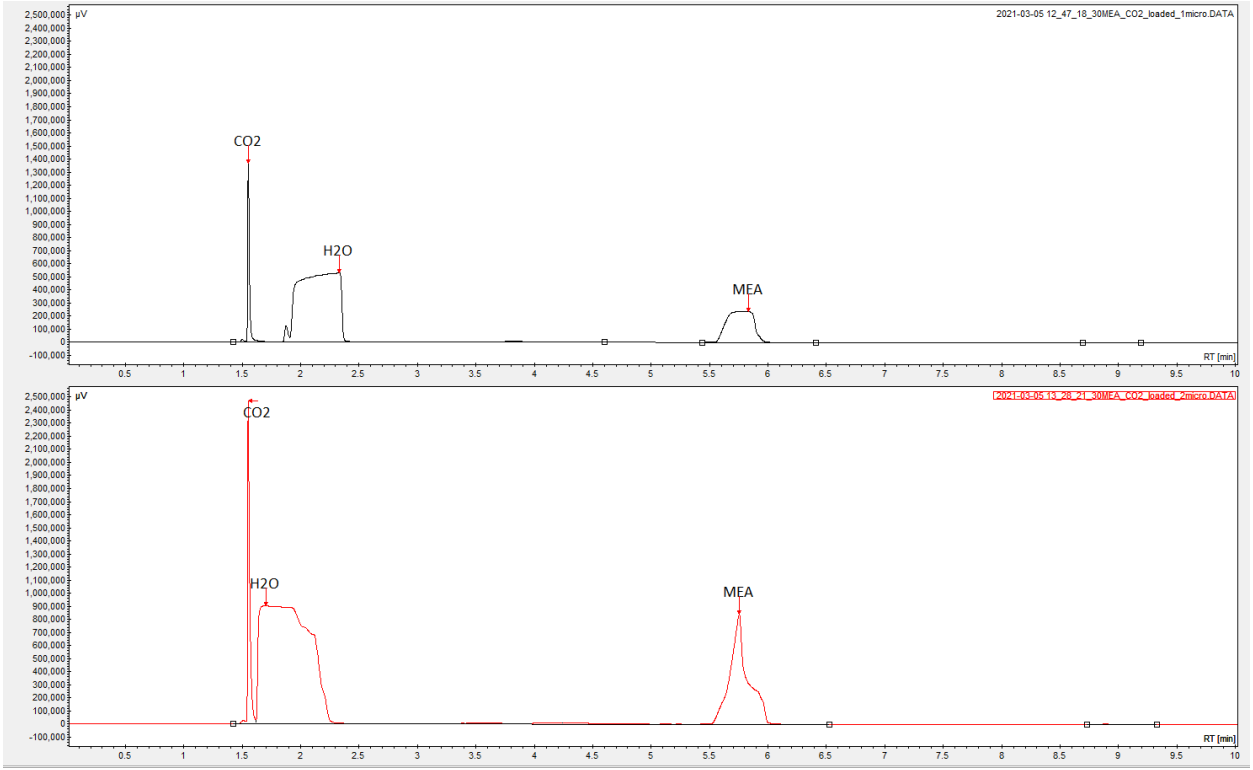


Rather than the 0.2µL volume generated by the LSV, 1.0 µL and 2.0 µL injection volumes were used. These larger volumes are too large for the 0.32mm ID of the Restek column. As a result, the peaks shapes are poor due to column overloading. However, the CO_2 and amine peaks were returned. Figure 9-2 shows the results of a 1µL (Top) and a 2µL (Bottom) injection of a 30% wt/ wt CO_2 loaded MEA.

Since the last stainless steel sample transfer line was tested at the same injection depth within the manual syringe with the septum port, this eliminated the hypothesis that the sample recovery issue was a problem with temperature or injection location within the injection port.

This left only the sample transfer line and the liquid injection valve itself as the probable source of the issues. At this point, the working hypothesis was that the 0.2uL sample from the injection valve was not moving cleanly through the sample transfer line. Perhaps due to viscosity and/ or wetting behavior of the solvent within the transfer line. The loaded MEA carbamate does have a significantly higher viscosity and may also exhibit different wetting behavior against the stainless steel material of the sample transfer line.

Figure 9-2: Syringe Injections (Top = 1µL, Bottom = 2µL)



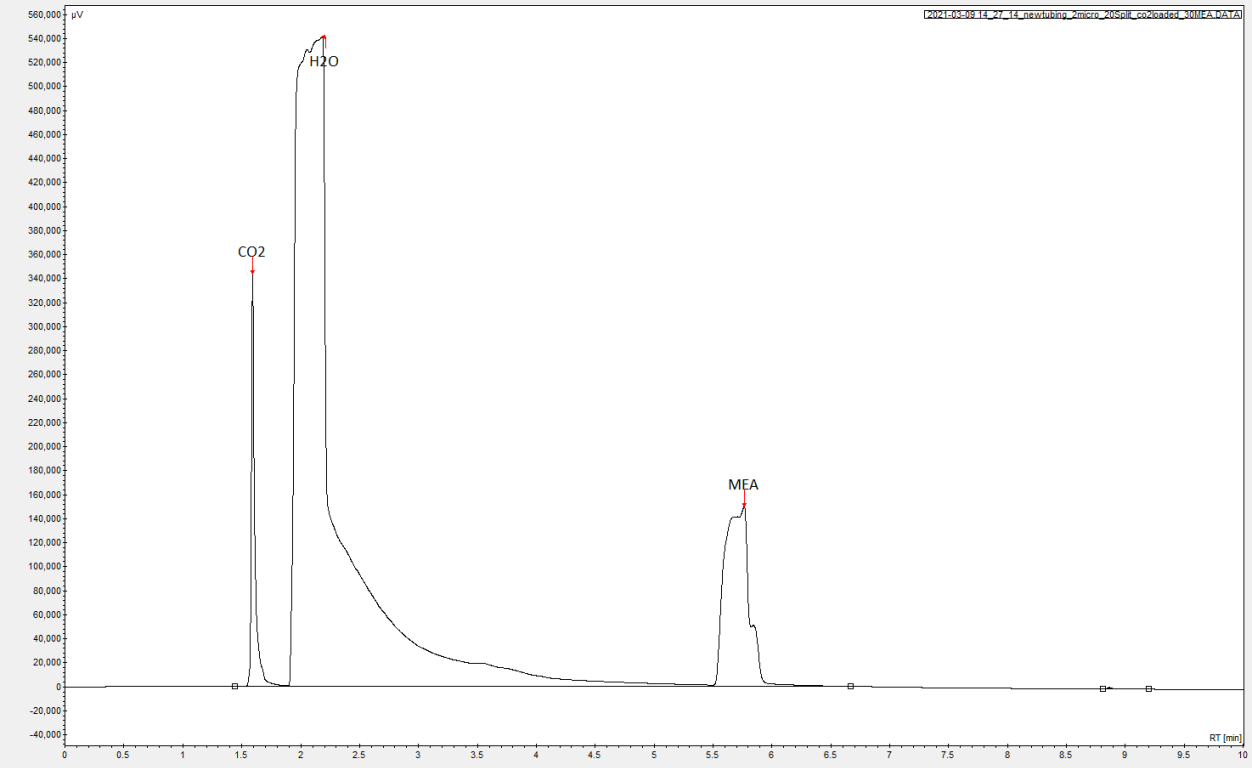
Further discussions of these issues with Scion Instruments resulted in their recommendation to try a different material for the sample transfer line. Due to shipping issues caused by Covid-19, there was insufficient time available to obtain all the recommended tubing materials. However, Scion Instruments was able to provide a sample of Restek "Hydroguard Deactivated Stainless Steel Tubing".

This tubing was provided in a 0.53mm ID. Roughly halfway between the two types of stainless steel tubing previously used for the sample transfer lines. This tubing however has a different outer diameter of 0.8mm as opposed to the 1/16" outer diameter of the stainless steel tubing.

This necessitated the use of a different type of fitting. The fittings provided adapted the smaller OD tubing to the standard 1/16" fittings used in the instrument. However, because of the nature of these fittings, it was not possible to penetrate the Incapron to deliver the sample to the same depth within the injection port as the syringe needle would reach.

The GC was converted back to manual injection through the liquid sample valve as described in section 2.2. A new sample transfer line was constructed from the Hydroguard tubing. A sample of CO_2 loaded MEA was injected under these conditions, however, there was still no significant improvement in the recovery of the amine and CO_2.

Figure 9-3: 2µL CO_2 Loaded 30% wt MEA with Hydroguard



The only remaining significant difference was the sample volume size between the manual syringe injection and the manual LSV injection. To test this condition, the LSV was modified from the 0.2uL injection core to a 2µL injection core.

The chromatogram of the sample injected using the 2µL core and the Hydroguard transfer line is shown in Figure 9-3. This configuration produces a similar chromatogram to that of the manual syringe injection. The MEA and CO_2 are recovered, at least to a degree.

To determine if the sample volume change alone was responsible for the improved amine and CO_2 recoveries, the Hydroguard transfer line was again replaced with the 50mm penetration stainless steel line. When the same CO_2 loaded 30% weight MEA was injected, the CO_2 and MEA peak again completely disappeared.

This clearly indicates that both the Hydroguard tubing and the change in sample volume were responsible for the improved recoveries.

9.3 CONCLUSIONS

It is clear there are sample transfer issues with this configuration. It is likely that the key factors effecting the transfer efficiency from the LSV are related to both the sample viscosity and the samples wetting behavior when in contact with the material of the sample transfer line.

Future work should investigate different options for the sample transfer line as well as determining the optimum tubing diameter, sample volume size and carrier gas flow rate to maximize the sample transfer efficiency for highly viscous samples.

The 2µL sample loop significantly improved the recovery of CO_2 and MEA, however, this volume is very large for the Restek Vol-Amine column. The performance of the Valco 0.5µL and 1.0 µL valve cores for the LSV should be tested.

10. FILTER TRAIN PERFORMANCE

10.1 PURPOSE

For this technique to be used in a permanent online field installation it is critical that the system require minimal maintenance. Real-world amine sample streams contain a wide variety of chemical and physical contaminants. This system was designed with two alternating sequential filter trains to prevent fine particulates from entering the LSV or the Gas Chromatograph. During the previous extended runs described in sections 7 and section 8, no problems were encountered with the filters or the back-flushing processes. However, these runs were relatively short compared to what would be expected of a system in a permanent field installation.

This experiment was designed to understand the rate at which these filters might plug in a worst-case field setting, and how effective the back-flushing system is at removing contaminants on the filters.

10.2 EXPERIMENTAL DESIGN AND RESULTS

Each filter train consists of three stainless filters of decreasing pore size. The first filter is a 7µm, followed by a 2µm and finally a 0.5µm filter. The position of these filters in the system can be seen in Figure 2-1. Particles smaller than 0.5 µm expected to pass right through the column and should cause no significant problems.

During the extended runs described in sections 7 and section 8 the back-flushing system was

triggered based solely on a certain number of sample injections. In a real-world scenario, it would be more appropriate to monitor the build up of pressure in the filter trains and trigger a back-flush cycle only when required.

In addition, controlling the duration of the back-flush cycle based on back-pressure rather than simply a fixed time, as performed in the previous extended runs, would minimize water consumption, and maximize online time.

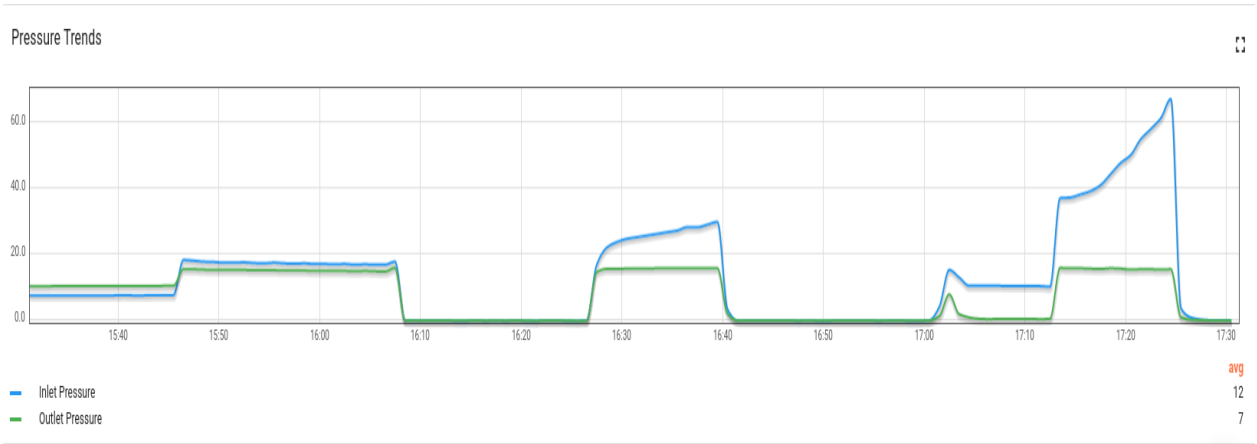
To measure the backpressure across these filter trains, a small data acquisition system was designed and configured to measure the pressure at the inlet and outlet of the channel #1 filter train. A permanent installation would need to measure the inlet and outlet of both filter trains. However, for the purposes of this experiment and to reduce costs, only the first filter train was configured for pressure monitoring.

The data acquisition system was built using a Raspberry PI, an off the shelf 16-bit 4 channel data acquisition module, and a small custom designed scaling and calibration circuit. The data was logged using a short python program and stored on the Raspberry PI in a CSV file. The data was also uploaded once per minute to a web-based internet of things (IOT) application which allowed for real time monitoring of the back pressures using a standard web browser.

For the purposes of this experiment, a 30% MEA solution was prepared. Fly ash was added to the sample to make a resulting mixture with 0.5% wt/wt fly ash. This is an extremely high concentration and is well beyond what would be expected in most field situations.

This solution was placed on a magnetic stirrer and stirred constantly while the amine

Figure 10-1: Increasing back pressure

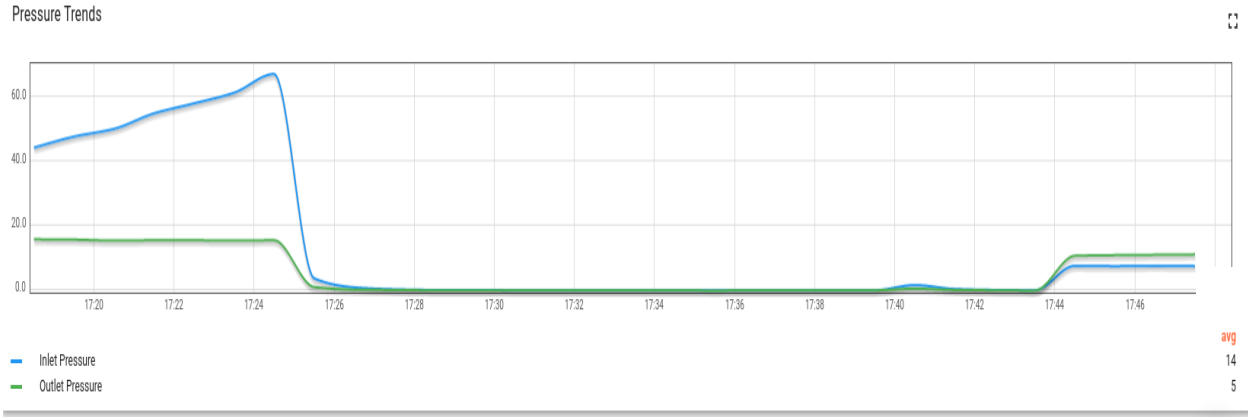


recirculation pump recirculated the contaminated amine through the 'ethanolamine pipeline' portion of the experimental setup. Figure 10-1 shows the build up of pressure on the filter train

as the low-pressure amine pump is cycled on and off, loading fly ash from the contaminated amine reservoir onto the channel #1 filter train. The blue trace represents the inlet pressure, and the green trace represents the outlet pressure. The difference between these to pressures represents the backpressure or plugging of the filter train with fly ash.

Figure 10-2 represents a final loading pulse followed by switching the system to back-flush mode and running the low-pressure H_2O pump to back-flush the filter train with deionized water. It can be seen at time 17:44 in this figure, that the inlet and outlet pressures reverse, and the pressure differential very rapidly returns to approximately the original level. This loading and backwash cycle resulted in a 0.5PSI increase in the total pressure across the filter train. This likely represents material which was not successfully removed from the filter train in the short back-flush cycle.

Figure 10-2: Increasing back pressure



10.3 CONCLUSIONS

This filter train design appears to be highly effective at controlling particle ingress into the LSV and the Gas Chromatograph. Despite the efficiency of the filter trains a problem was encountered at the end of this experiment with plugging of the pump and the inlet line to the 10-port valve. Although the contaminant level in the amine solution used for this experiment is well beyond what would be expected in a typical field application, this is still a weak point in the system. Future work should investigate ways to protect the 10-port valve and the low-pressure amine pump from system upset conditions which could potentially introduce extreme levels of particulate contamination into the system.

11. FINAL CONCLUSIONS AND FUTURE WORK

11.1 CONCLUSIONS

This project has demonstrated that Gas Chromatography has significant potential as a method for the continuous online monitoring of amine-based carbon capture solvents. Work during this project focused primarily on the measurement of amine and water concentrations. However, the measurement of carbon dioxide loading is also possible. More work is required on this parameter to develop better calibration options and to optimize the sample transfer to the GC of the high viscosity CO_2 loaded MEA solutions

The best calibration options for CO_2 which were found in this project are to use a number of CO_2 loaded MEA solutions as a secondary calibration standard. These calibration solutions can be prepared easily in the lab and then measured against a primary calibration standard, such as Sodium Carbonate or Sodium Bicarbonate using other laboratory techniques such as the Schimadzu TIC/TOC analyser or by titrimetry.

Once prepared, these standards should be stable for a long period and could be used to perform periodic online calibration checks of the instrument using a separate stream selection valve.

This project found that excellent reproducibility for MEA and water was achievable over extended run times. If the total degradation levels in a production amine solvent approach or exceed 1% by wt, it may be possible to estimate the total amount degradation present in the solvent by difference.

Direct measurement of certain key degradation products of certain solvent systems should also be possible. Specific method development would be required to establish chromatographic conditions for each unique amine solvent. In the case of primary amine-based solvents like MEA, where the major degradation products are organic acids, Gas Chromatography is likely not an optimal solution. However, in the case of secondary and tertiary amine-based solvents, where the major degradation products are more likely to be amides it should be possible to develop chromatographic conditions to measure the amines and their degradation products under the same chromatographic conditions.

The filter trains used in this project proved very effective at protecting the LSV and the Gas Chromatograph from particulate contamination in the solvent system. In the final tests, an extremely high loading of fly ash was used which might be representative of a system upset condition in a field application. The filter trains and back wash system performed well under these conditions, however, the 10-port valve and the amine sampling pump, which are both upstream of the filters, eventually plugged. Future work should investigate a means of protecting the pump and 10-port valve in the event of a severe system upset condition.

11.2 FUTURE WORK

11.2.1 Use of Hydrogen as a Carrier Gas

Helium was chosen as the carrier gas in this project for reasons of convenience and to avoid the capital costs of a hydrogen generator. This choice was optimal for the laboratory. However, in a field application where the system is intended to operate unattended for an extended period, hydrogen would be a better choice. In the long term, it would be cheaper and having a hydrogen generator available would allow for extremely long run times without the requirement of changing compressed gas cylinders. The total run time would only be limited by the availability of a high purity water supply to keep the hydrogen generator running.

The use of hydrogen as a carrier gas would require some tuning of the chromatographic methods. Although, hydrogen often produces superior chromatographic results to helium.

11.2.2 Optimize Sample Transfer from the LSV to the Gas Chromatograph

Significant difficulties were encountered with the sample transfer from the LSV to the Gas Chromatograph injection port. This transfer is critical to the reproducibility and overall performance of the system. These issues only appeared with the highly viscous CO_2 loaded MEA solutions. It is critically important that the transfer from the LSV to the GC be optimized. This will involve some experiments with different sample injection volumes, the internal diameter of the transfer tubing and the material composition of the transfer line and the carrier gas flow rate. Minimizing the length of the sample transfer line should also prove beneficial.

Once these optimizations are completed, the choice of analytical column should be revisited to ensure compatibility with selected sample volume.

Heating the transfer line from the LSV to the Incapron may also be beneficial in reducing the sample viscosity and improving the sample delivery.

11.2.3 Analytical Column Selection

The Restek column used for most of the experiments in the project proved adequate. There may be other columns which would be more suitable, particularly if larger sample volumes prove beneficial in the optimizing the sample transfer from the LSV to the Incapron.

The Agilent column used for the final testing has a much higher capacity and provides improved chromatography for larger injection volumes.

Final column selection will of course depend on the specific amines present in the solvent under study as well as the targeted analytes.

11.2.4 Detector Selection

There are a wide varieties of detector types available for use in Gas Chromatography. The Thermal Conductivity Detector (TCD) used in this project is a generic type of detector. It can be used for most types of compounds, including inert gases, oxygen, carbon dioxide and water. It has a much lower sensitivity than many more compound specific detectors. In this use case, where the bulk components, amine and water were the target compounds, this lack of sensitivity is an advantage.

Other detectors such as Flame Ionization (FID) may be more suitable for experiments directly targeting the measurement of specific degradation product or contaminants within the solvent system.

It is also possible to use multiple detectors on a single GC. This can prove valuable for certain types of analysis; however, the added complexity is often detrimental, especially in a field application intended for unattended operation for extended periods of time.

11.2.5 External control of back-flush system

The current back-flush system is controlled by the Compass chromatography software. This works well but can only trigger column changes and back-flushing based on a fixed number of samples. A better approach would be to monitor the differential pressure across each filter train and control the start of a back-flush cycle and the duration of a back-flush cycle based on the differential pressure.

The Raspberry PI data acquisition system designed for this project could easily be modified to perform these capabilities. The Scion GC can be monitored and controlled from remote through a control input and a ready state output on the back of the instrument. The software and hardware of the Raspberry PI could be updated to read the ready state of the GC and, wł the differential pressure reaches a threshold level, to pause the GC at the end of a run. Then, trigger the 10-port valve to switch channels and then resume the GC operations.

The Raspberry PI would then perform a back-flush cycle on the offline channel by starting the low-pressure H_2O pump while monitoring the differential pressure. Once the pressure returned to normal, the Raspberry PI could stop the back-flush, thus saving water and ensuring maximum online time of the system.

11.2.6 Stream Selection

In a practical field application, it would be desirable to monitor multiple sample streams with a single GC. The Raspberry PI used for the pressure monitor in this project would be quite suitable for control of a stream selection valve. Further investigations into this option should be conducted.

11.2.7 Direct interfacing of Compass results with a Human Machine Interface (HMI)

In a practical field application, it would be important to get results delivered in real time from the Compass software directly to a HMI system. This would allow system operators to view the chromatographic results in near real time.

Compass has several ways in which this might be achieved. There is a software application interface (API) as well as options for writing result files after each run to a comma separated value (CSV) file. The Raspberry PI may also prove useful in meeting this requirement.

Further investigation into the best approach of delivering near real time data to a HMI should be investigated.

11.2.8 CO_2 Calibrations

Further investigations into optimal standards for CO_2 calibrations should be conducted. Although the CO_2 loaded MEA solutions may be suitable for certain situations, a preferred solution would be to find an organic compound which would decompose at the temperature in the injector port into CO_2 gas and another organic compound which would pass through the system without negatively affecting the analytical column.

In this project, sodium bicarbonate and ammonium bicarbonate were investigated. However, neither compound proved satisfactory. The sodium bicarbonate decomposed in the injector port, but produced carbon dioxide and sodium carbonate, which is stable to very high temperatures. This would result in contamination of the injector port liner and/or the analytical column over time.

The ammonium bicarbonate was a better choice as it decomposes at a low temperature (~35 °C) into ammonia and carbon dioxide. This was only tested on the Restek column and the ammonia tended to interfere with the reliable integration of the water and CO_2 peaks. In addition, the solubility of ammonium bicarbonate is insufficient to prepare CO_2 calibration standards at the levels which might be expected in a fully CO_2 loaded 30-40 % MEA solution.

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