Analysis of Gas Samples Collected from the 10 MW_e Supercritical Transformational Electric Power (STEP) Demonstration Plant

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ABSTRACT

The STEP Demo pilot plant is an advanced Brayton power cycle with carbon dioxide (CO_2), at supercritical state, as the working fluid that operates under extreme turbine inlet conditions (700°C, 20 MPa). The presence of impurities in the sCO_2 working fluid can significantly affect system performance and material integrity. Impurities such as oxygen (O_2), nitrogen (N_2), argon (Ar), water (H_2O), methane (CH_4), and carbon monoxide (CO), originating from air ingress or interactions with structural alloys, can alter the thermophysical properties of the working fluid and turbomachinery performance, as well as promote oxidation or carburization, under prolonged service conditions. Therefore, understanding and monitoring the gas composition are critical to maintaining system efficiency and long-term durability for commercial deployment.

A gas sampling procedure was established under a collaborative research agreement with GTI Energy (GTI) to analyze and quantify the presence of potential supercritical CO_2 (sCO_2) impurities in the power cycle loop of STEP plant, located in San Antonio, Texas. The procedure was used to collect 10 gas samples from STEP Demo plant that were subsequently delivered to CE-O for analysis. It should be noted that the samples presented here correspond to a very limited number of hours of operation and thus do not represent the long-term trends. This effort intends to create a baseline for the sampling and analysis procedures that can eventually be applied to longer hours of operation to effectively study the type and impact of impurities in sCO_2 working fluid. Additional gas samples will be taken later from STEP's Recompression Brayton Cycle (RCBC) operation. Gas sample analysis was performed using a modified ASTM D7833 method on a gas chromatograph (GC) unit, suitable for dry gases with detection limits below 0.01%. Due to the

limitations of GC to determine water content, supplementary analysis with Mass Spectrometry (MS) was performed to verify the presence of moisture in the gas samples.

GC and MS were both used in combination to provide a comprehensive assessment of the gas mixtures. Trace amounts of O_2 and N_2 were detected. It seems they were introduced during sampling, as these species were not present in significant concentrations in the source gas. MS analysis also confirmed the presence of moisture in the process gas. Additionally, GC analysis identified trace levels of some hydrocarbon compounds.

1. INTRODUCTION

Recent studies have demonstrated that the performance of sCO_2 power cycles can be influenced by the composition of the working fluid. Variations in gas composition, such as oxygen concentration, water vapor, and other impurities, directly impact system efficiency [1-4]. Even small amounts of impurities such as N_2, Ar, O_2, H_2O, and CH_4 in source CO_2 working fluid can reduce the efficiency of sCO_2 Brayton cycles. For example, a study found that with a typical industrial CO_2 mixture (99.076% CO_2), cycle efficiency dropped by 0.32–0.39% compared to pure CO_2. This reduction is due to changes in the working fluid's physical properties, which affect heat transfer and component performance [5]. It was also shown that the addition of trace gases like N_2 and Xe decreased the isobaric heat capacity of the working fluid, which can impact cycle design, further influencing efficiency [6]. The STEP facility is supplied with "beverage grade" CO_2, which has 0.1% impurities.

Industrial CO_2 is often supplied with a stated purity (e.g., 99.9%), but actual composition can vary. Laboratory purity tests, such as gas chromatography (GC) or mass spectrometry (MS), can be used to quantify the concentrations of impurities such as N_2, Ar, O_2, H_2O, and CH_4 before and during system operation. After determining the impurity composition, sensitivity analyses and design point studies can be performed to assess how these impurities affect system performance, including cycle efficiency, power output, and component operation. Laboratory exposure tests subject structural alloys to sCO_2 with and without controlled impurities at relevant temperatures and pressures. Post-exposure analysis (e.g., weight gain measurements, microstructural examination) helps to determine the impact of impurities on corrosion and carburization rates. In this study, we present a case-specific procedure for gas sampling and analysis for the STEP Demo pilot plant. The goal is to establish a reliable baseline for impurity detection in sCO_2 cycles, enabling future impact assessments of long-term operation on system performance and material integrity.

2. EXPERIMENTAL APPROACH

The STEP facility utilizes a pre-assembled, panel-mounted sampling system procured through Swagelok to collect gas samples from dedicated sampling points throughout the process. This system can accept high-pressure gas (up to 2,000 psig) and regulate it down to less than 60 psig. When depressurizing the CO_2, it cools due to the Joule-Thompson effect. This poses challenges to ensure proper sampling, and steps must be taken to avoid coalescence or condensation of contaminants that can lead to inconsistent results. To mitigate this risk, the sampling panel at the STEP facility employs a vaporizing regulator, which heats the flow as it depressurizes to maintain the integrity of the sample. A flow control device is also utilized to maintain flow of the sample within a specified range. This prevents overheating of the sample in the event the flow is too slow and prevents exceeding the heat rate of the heater if the flow is too high, which would lead to cooling. The bottle on the panel also allows flow to travel through to aid in clearing out contaminants and ensuring a representative sample is collected.

The process of purging the gas sampling panel and sample bottle and collecting the sample are performed in three major steps. First, the panel and sample bottle are connected to the process source and CO_2 is allowed to flow through the entire system. This is displayed in the left half of Figure 1. A check valve on the outlet with an adjustable cracking pressure helps maintain back-pressure on the sample cylinder. Second, the geared 3-way valves (operated by a single handle) are closed to stop all flow. The sample cylinder isolation valves are closed while pressure is maintained. Third, the geared 3-way valves are opened to vent any remaining pressure in the panel so the sample cylinder can be removed.

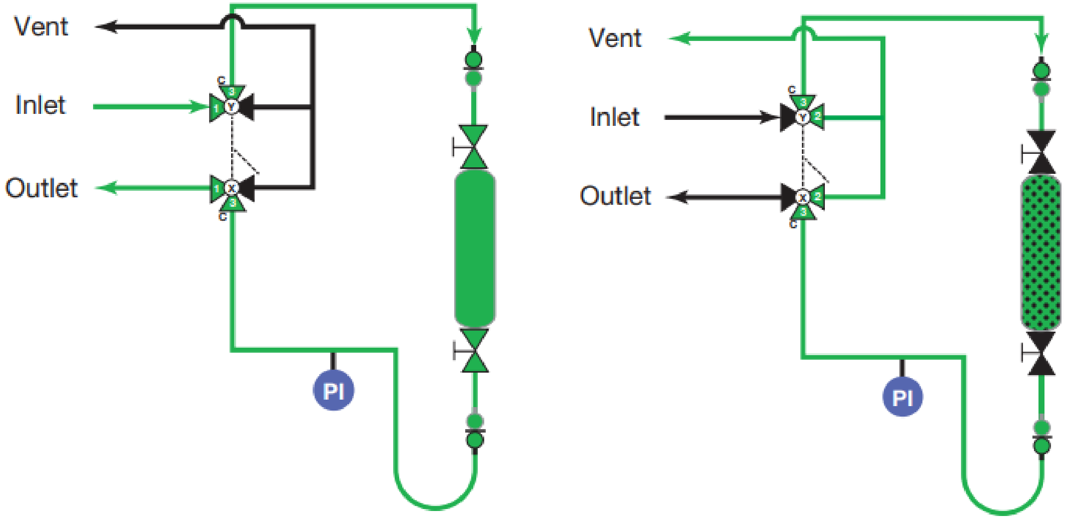

Figure 1 Representative layout of Grab Sample Panel operating modes [7]

The low-pressure sample is stored in a 300 cm^3 stainless steel sample cylinder, which can be detached from the system for transport. However, since multiple gas samples need to be transported from the STEP facility in San Antonio to CE-O's facility in Ottawa, an economical shipping method was required. CE-O proposed using multilayer foil gas sample bags. These bags are lighter, significantly less expensive, and more easily flushed clean, compared to stainless steel sample cylinders. To facilitate the transfer of gas samples from stainless steel sample cylinders to disposable sample bags, CE-O developed and assembled a dedicated apparatus (**Figure 1**). A flexible hose on the gas sampling panel was disconnected from the bottle, and a sampling bag apparatus was connected in its place. The grab sampling panel was moved to a condition where the CO_2 sample was flowing through the Swagelok bottle and out to the atmosphere through the sampling bag apparatus. This established a purge of any contaminants in the fixed components of the sampling system. While the CO_2 continued to flow, a sample bag was connected. Each sample bag followed the procedure below:

1. The sample bag was connected and filled.
2. The bag was disconnected and evacuated using externally applied force to empty the bag.
3. The bag was re-connected and filled a second time.
4. Once full, the bag valve was closed, and the sampling panel was turned off simultaneously (two-person step).
5. The bag was disconnected and sealed for transport.

The goal of this evacuation in step 2 was to minimize the amount of contaminants that may have been present in the bag prior to taking the sample.

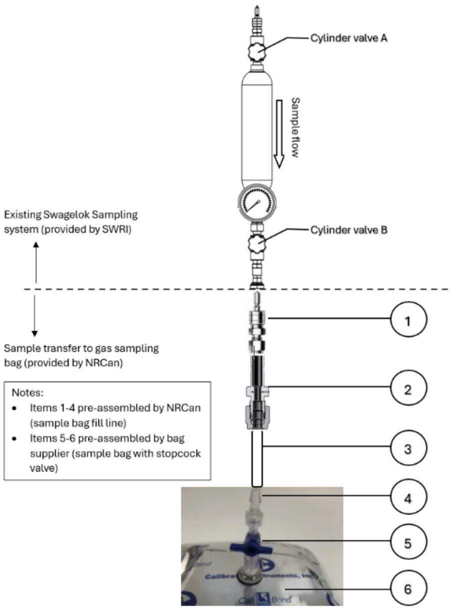

Figure 2 Cylinder to pillow-style gas sampling bag

Ten gas samples were received by CE-O from the STEP plant, with the goal of performing a qualitative and quantitative analysis to determine the composition of the gas mixtures, including identification and quantification of the individual components. Two analytical methods were employed for comprehensive gas analysis. First, gas analysis was conducted on a Wasson ECE RGA based on Agilent 7890A GC-FID/TCD, using an in-house modified method similar to ASTM D7833 Standard Test Method for Determination of Hydrocarbons and Non-Hydrocarbon Gases in Gaseous Mixtures by Gas Chromatography. Afterward, a Pfeiffer Vacuum GSD 350 OmniStar mass spectrometer with a quadrupole mass analyzer was employed for analysis of the gas samples.

3. RESULTS AND DISCUSSION

Table 1 details the received samples and the corresponding analytical techniques employed for each sample, which will be elaborated on in subsequent sections. The STEP operating data plot pertinent to the sampled gases is depicted in **Figure 2**.

Samples #1 to #8 were collected at the cooler outlet/compressor inlet at two-time steps during testing, and once at the end of the run. For each sampling event, two gas bags were filled to provide redundancy in case of leakage during shipment and to enable verification during analysis. All samples were taken when the system was not flowing, ensuring non-interference. At the time of sampling, the loop was in a settled-out state but remained at high pressure. Whenever possible, samples were collected while the CO_2 was in the gaseous phase. Samples #9 and #10 were collected directly from the CO_2 supply source to investigate the potential baseline contamination in the supply gas.

Table 1 The list of received gas samples and the corresponding gas analysis performed

	Assigned Name*	Date and Time of Sampling	Time in Figure 2 (sec)	GC	MS
1	GTI#1	9/26/2024 23:09	83,340	X	
2	GTI#2	9/26/2024 14:15	51,300	X	
3	GTI#3	9/26/2024 14:14	51,240	X	X
4	GTI#4	9/26/2024 23:09	83,340	X	X
5	GTI#5	9/27/2024 22:30	167,400	X	X
6	GTI#6	10/2/2024 18:30	N/A	X	X
7	GTI#7	10/2/2024 18:30	N/A	X	X
8	GTI#8	9/27/2024 22:30	167,400	X	X
9	GTI#9	12/30/2024 11:00 Sample1 CO_2 Sample of Process Vaporizer	N/A	X	X
10	GTI#10	12/30/2024 11:00 Sample2 CO_2 Sample of Process Vaporizer	N/A	X	X

*The sample numbers do not follow the actual timestamp.

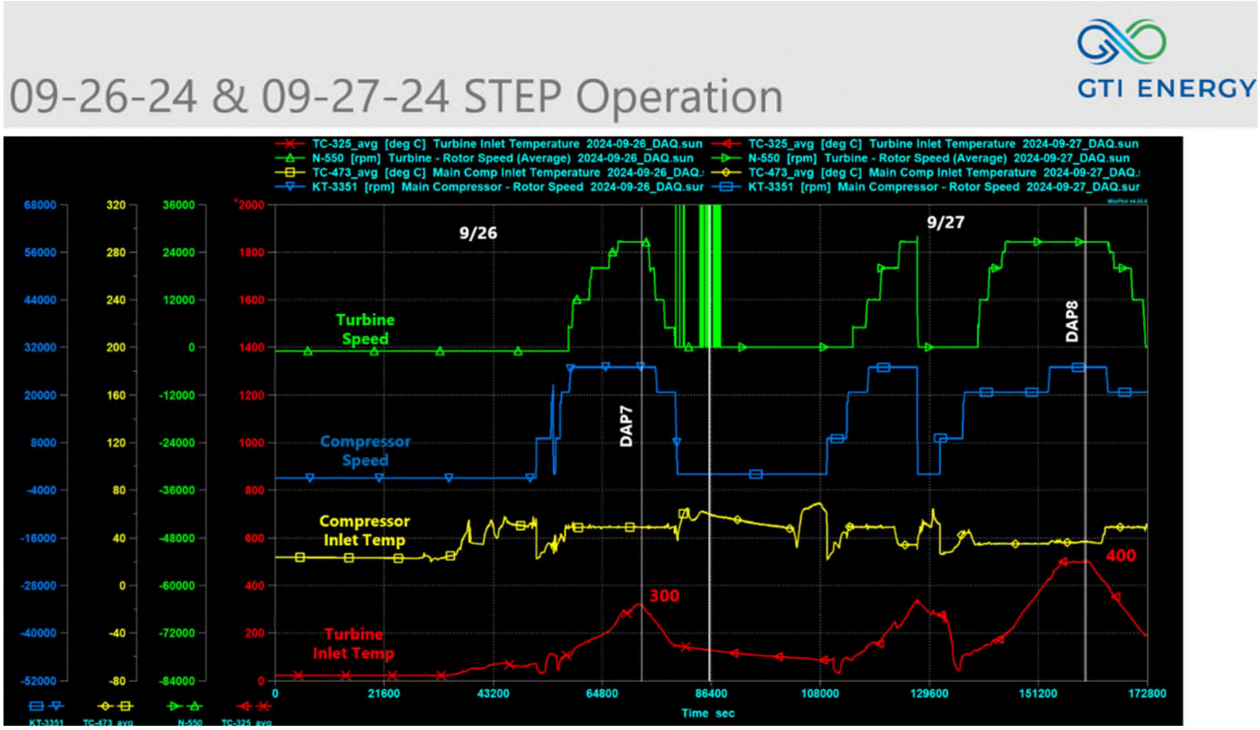

Figure 3 STEP operating data plot relevant to the gas sampling times

3.1 GAS CHROMATOGRAPHY (GC)

All gas bags were analyzed using gas chromatography (GC). To ensure analytical performance, one gas bag was randomly selected for duplicate analysis, while the remaining bags were analyzed in single runs. Performance specifications required that each reported analyte in duplicate analyses must not differ by more than the greater of 0.1 mol% or 10% of the reported value. The following should be noted for the GC analysis:

1. The analysis is limited to dry gas; water content cannot be detected.
2. All gas concentrations below 0.01% are reported as zero due to limitations of the analytical method.
3. The lower detection limit for helium, hydrogen, carbon monoxide, carbon dioxide, carbonyl sulfide, and hydrogen sulfide is 0.04%. This limitation is related to the detector's sensitivity to these specific gases.

Direct analysis of moisture by GC is challenging because water has low volatility relative to many analytes, shows weak (and often problematic) interaction with conventional GC stationary phases, and tends to degrade peak shapes or interfere with analyte separation [8]. This often results in water not producing a clear peak or interfering with the analysis of other compounds. To verify the existence of moisture in the gas, MS was used as described in Section 3.2.

The GC analysis results, visually represented in **Figure 3** and numerically summarized in **Table 2**, indicate a predominant presence of CO_2, ranging from 96.47% to 99.21% of the total gas composition. N_2 was detected in a relatively lower concentration, varying between the range of 0.56% and 5.25%. O_2 and Ar, grouped due to their similar chromatographic behavior (though the presence of Ar is unlikely given the process conditions), were present in a low concentration in the range of 0.23% to 2%. Methane and ethane were detected, but not quantifiable. The presence of other hydrocarbon compounds was negligible (i.e., below the detection limit of 0.01%) for all gas bags except for Gas Bag #6.

Table 2 Analysis results (dry basis) using the gas chromatograph (GC)

Components	**Amount [mol %]**									
	#1	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**#8**	**#9**	**#10**
Carbon Dioxide	96.47	97.92	99.03	93.69	99.21	98.71	92.75	97.08	98.8	99.28
Methane	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ethane	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Argon/Oxygen	0.99	0.58	0.28	1.74	0.23	0.36	2	0.82	0.53	0.51
Nitrogen	2.55	1.5	0.68	4.56	0.56	0.92	5.25	2.1	1.38	0.2
t-2-butene	-	-	-	-	-	<0.01	-	-	-	-
1-butene	-	-	-	-	-	<0.01	-	-	-	-
3-Methyl-1-Butene	-	-	-	-	-	<0.01	-	-	-	-
t-2-Pentene	-	-	-	-	-	<0.01	-	-	-	-
C6 Plus	-	-	-	-	-	<0.01	-	-	-	-

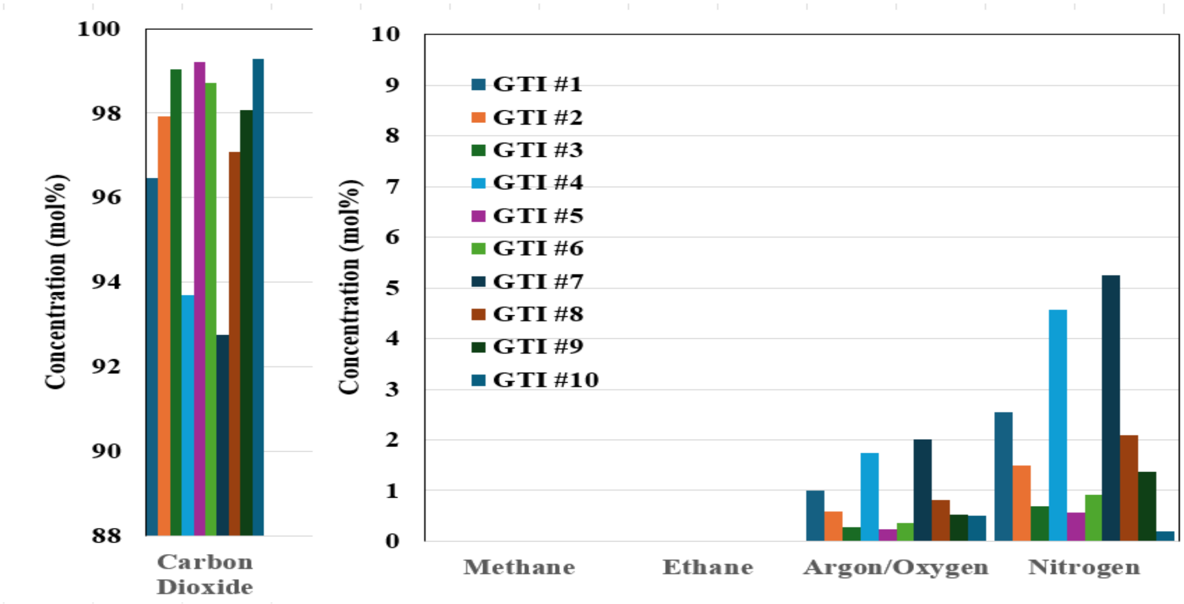

Figure 4 Comparative results of gas sample analysis using GC

3.2 MASS SPECTROMETRY (MS)

The mass spectrometer, equipped with a quadrupole mass analyzer, was used to analyze gas samples from bags #3–10. When possible, duplicate runs of the samples were performed to confirm the presence of species. Equipped with an electron impact ionization source with the energy 70 eV, the system operated under high-vacuum conditions maintained by a Pfeiffer Vacuum pumping system. The MS analysis began with a mass range of 1-100 amu (atomic mass units) to identify gas components and was eventually narrowed to 1-50 amu for further analysis.

Unlike GC, which cannot detect moisture, MS can provide further information about the composition, especially unknown compounds. It analyzes the mass-to-charge ratio (m/z) of ionized particles or mass in amu, generating a spectrum that plots intensity versus m/z or amu. This spectrum enables the identification of the molecular ion (revealing molecular weight) and fragment peaks (providing structural insights) [9].

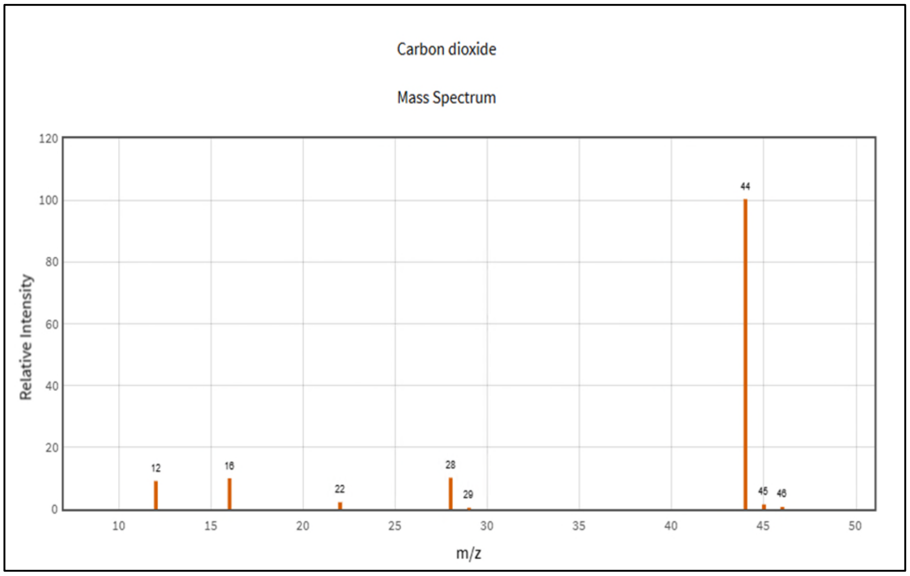

Figure 5 The NIST mass spectrum of CO_2 (NIST webbook-SRD69)

The NIST Mass Spectral Database aids in interpreting mass spectra. Comparing experimental spectra to the database allows for the identification of unknown compounds, access to structural details, and analysis of fragmentation patterns. **Figure 4** illustrates the NIST fragmentation pattern of CO_2, with its main component at 44 m/z and fragment peaks for C^+, O^+, and CO^+ at 12, 16, and 28 m/z, respectively. The intensities of other peaks are negligible. The NIST database also aids in confirming isotopic distributions and simulating fragmentation to predict spectral behavior.

Figure 5 displays a typical MS spectrum of the analyzed gas, which confirms the presence of water (H_2O, 18 amu). The peaks corresponding to C (12 amu – from CO_2), N (14 amu – from N_2), O (16 amu – from either CO_2, CO, and H_2O) CO_2 (28, 44, 45 amu), O_2 (32 amu), and N_2 (28 amu – combined with CO from CO_2) further validate the presence of CO_2, N_2, and O_2 in the gas, which was shown by the GC results. Methane and ethane may be present in the samples; however, their quantities are too small to validate, as their significant peaks exist under similar peaks as N/O (14, 16 amu) and CO/N_2 (28 amu), respectively. Other signature peaks would be out of the detection limit; therefore, these species cannot be confirmed to be present in any significant quantities. The use of combined GC/MS would be able to do a full separation and quantification of these species. The comparative spectrums of three samples (GTI #3-5) are shown in **Figure 6**.

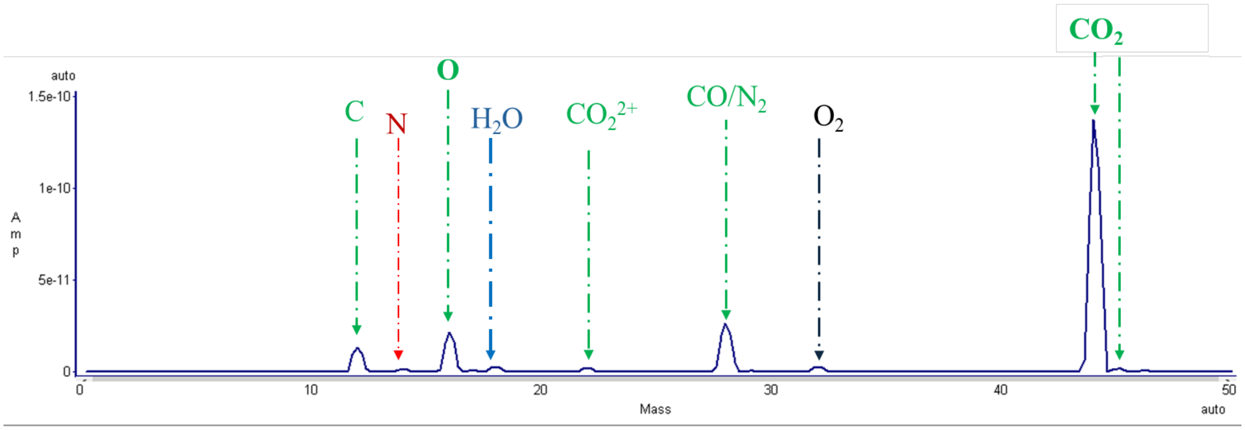

Figure 6 Mass spectrum of GTI#3 sample and relevant components

For clarity, the other three samples (GTI #6-8) are presented in **Figure 7**. Samples 1 and 2 were not analyzed further because the gas bags were emptied after the initial GC analysis. **Figure 8** shows the comparison of the two source gas bags (GTI #9, 10). It should be noted that when available, duplicate test runs were completed for the gas bags. The spectrum shows both molecules and their ionized fragments. For example, the O peak at 16 represents the combined fragments from $C\mathbf{O}_2$, $H_2\mathbf{O}$, and $\mathbf{O}_2$. Similarly, the N_2 peak combines fragments from CO_2 (i.e., CO) and N_2 due to their identical molecular weight (m/z=28).

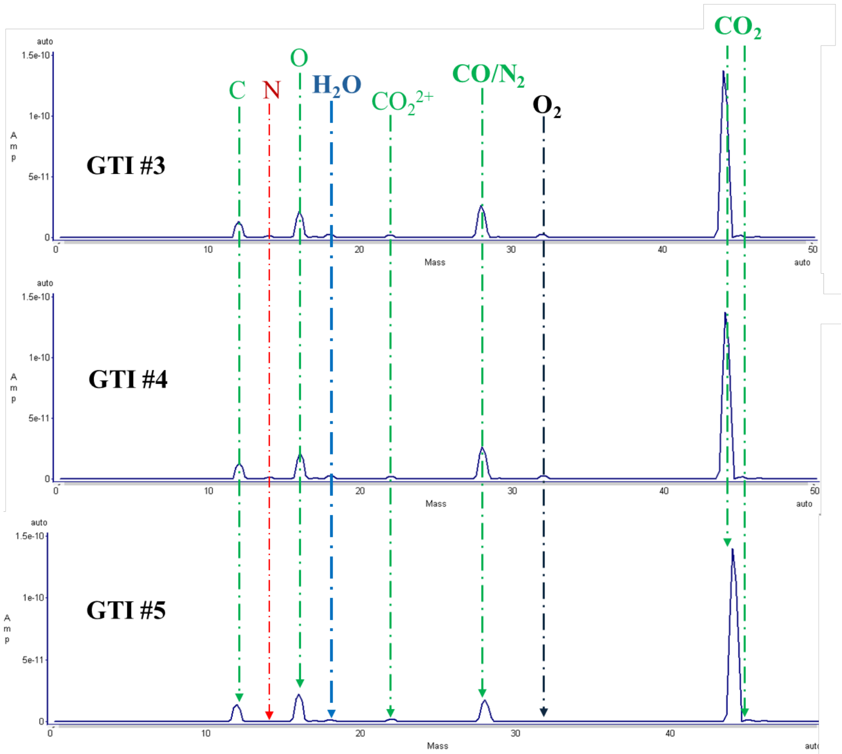

Figure 7 Comparative mass spectrum of samples GTI #3-5 and the components

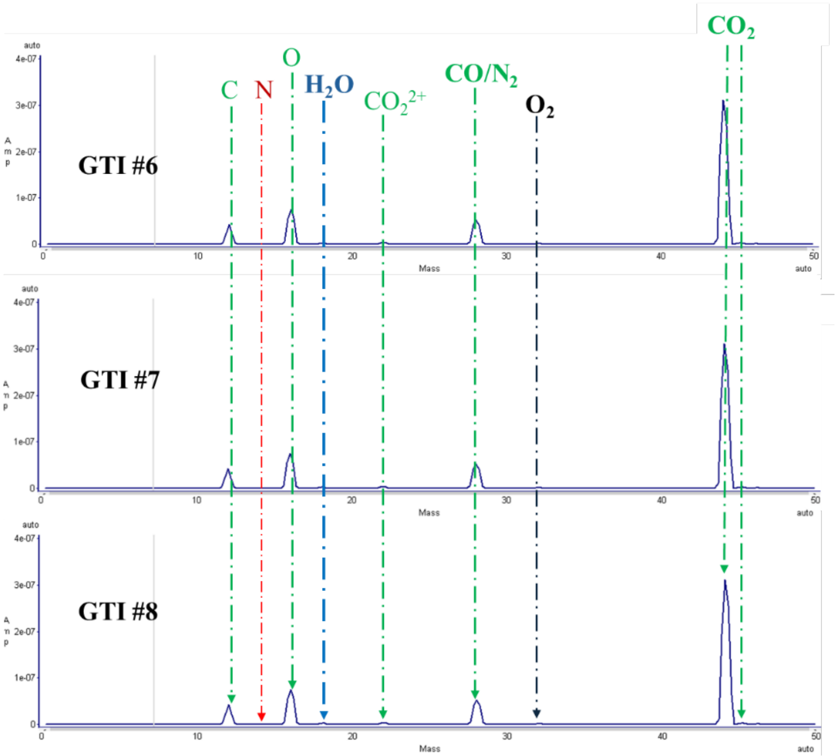

Figure 8 Comparative mass spectrum of samples GTI #6-8 and the components

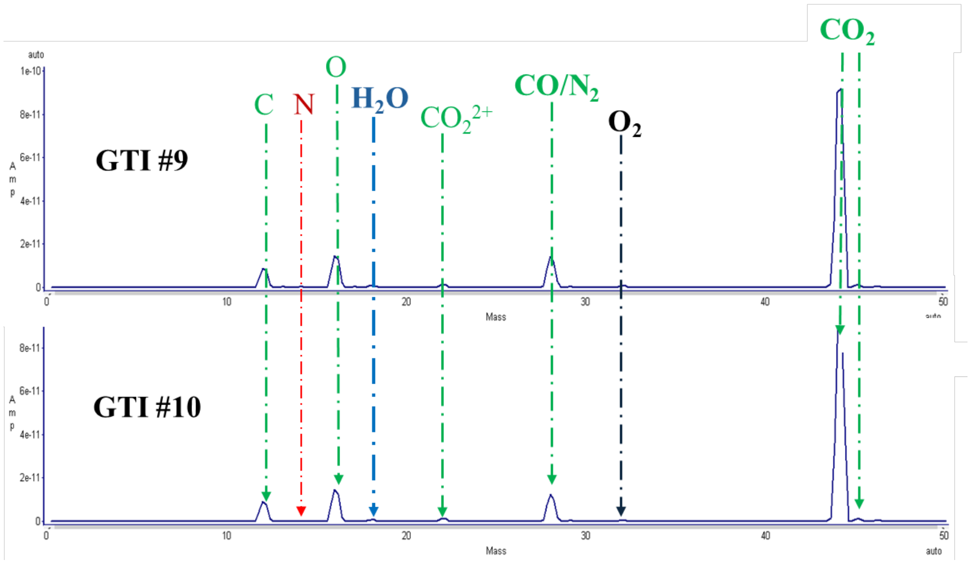

Figure 9 Comparative mass spectrum of samples GTI #9, 10 and the components

The qualitative outcomes from both the MS and GC for samples GTI #3-8 are consistent, with the mass spectrometer also detecting the presence of water (H_2O – 18 amu). Quantitative analysis is achievable through the utilization of calibrated standard reference gases; however, due to the overlap with many species in this case, it posed a challenge to separately quantify each species. In addition to CO_2, the presence of water was observed, along with some N_2 and O_2. It should be noted that gas bag samples GTI #9 and 10, from the source gas, exhibit a smaller peak of water, N_2 or O_2 relative to the other gas sample bags.

4. DISCUSSION AND CONCLUSION

Gas Chromatography (GC) and Mass Spectrometry (MS) were employed in tandem to conduct a comprehensive analysis of the gas samples collected from STEP Demo plant. The results of this analysis have confirmed that CO_2 constitutes the predominant component within all the samples. The presence of trace amounts of O_2 and N_2 is attributed to potential air ingress during the sampling process, as it is observed in relative amounts from the source gas samples (GTI #9, 10). Future samples may employ a modified sampling method to reduce this potential source of error, for instance with the use of a sample bag with two ports that allows flow through similar to the cylinders on the sampling panel. From the MS analysis, water was also observed in a detectable amount in the process gas samples. Furthermore, the utilization of the GC facilitated the detection of trace quantities of various hydrocarbon compounds, including ethane, butane, t-2-butene, methyl-1-butene, and t-2-Pentene. These could not be confirmed using MS, as they were under the detection limit of this unit. The samples presented here correspond to a very limited number of hours of operation and thus do not represent the long-term trends. This effort created a baseline for the sampling and analysis procedures that can eventually be applied to longer hours of operation to effectively study the type and impact of impurities in sCO_2 working fluid. Additional gas samples will be taken later from STEP's Recompression Brayton Cycle (RCBC) operation.

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