Analysis of Volatile Compounds from CO_2 Removal Systems

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One of the primary concerns when designing CO_2 scrubber systems that will be integrated with a Sabatier reactor to produce water and methane is the amount of water released from the scrubber. Because the gas stream entering a Sabatier reactor must be compressed, water entering the reactor can condense and compromise the integrity of the system, thus rendering its valuable conversion capability useless. When the Johnson Space Center Environmental Chemistry Laboratory was tasked to develop an assay to quantify the water concentration in air samples from CO_2 scrubbers, additional testing was also performed to see if any other compounds were being concentrated on the scrubbers. It was thought that the efficiency of the scrubber systems could be quantified by comparing the differences in samples from the ambient air on the International Space Station (ISS) to the exit gas of the scrubber. As this analysis was carried out, it became evident that the concentrations of certain volatile compounds were higher in the samples from the scrubbers than they were in nominal environmental samples. This meant these compounds were being retained and concentrated on the scrubber beds. Based on this finding, concerns were raised about the potential for these compounds to poison the Sabatier reactor. Further investigation was required to identify these compounds due to their high concentrations and unique matrix of the CO_2 scrubber exhaust. This paper describes these events as well as the process that was developed to identify the volatile compounds that increased. An examination of how much the certain compounds can be concentrated by the scrubber systems is also included.

Nomenclature

CO_2	=	carbon dioxide
DF	=	dilution factor
ECL	=	Environmental Chemistry Laboratory
GC	=	gas chromatography
GC/FID	=	gas chromatography/flame ionization detector
GC/MS	=	gas chromatography/mass spectrometry
GC/TGA	=	gas chromatography/trace gas analyzer
GSC	=	grab sample container

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ISS	=	International Space Station
JPM	=	Japanese Pressurized Module
JSC	=	Johnson Space Center
OFP	=	octafluoropropane
ppb	=	parts per billion
ppm	=	parts per million
psi	=	pounds per square inch
SM	=	Russian Service Module
tech demo	=	technical demonstrations

I. Introduction

TO maintain the health of both crew and vehicles in human spaceflight, it is necessary to periodically monitor the spacecraft environment. For atmospheric monitoring, both real-time and archival methods are used. For decades, archival sampling has been performed using grab sample containers (GSCs). These containers come in various shapes and volumes, as described previously.[1] For general atmospheric sampling, the GSCs are evacuated and dosed with control compounds prior to delivery to the ISS. While on-board, samples are collected approximately every 45 days in the US Lab and in either the Russian Service Module (SM), Japanese Pressurized Module (JPM), or European Columbus Module. Upon return to Earth, these GSCs are returned to the Johnson Space Center (JSC) Environmental Chemistry Laboratory (ECL) for analysis using various gas chromatography (GC) and gas chromatography-mass spectrometry (GC/MS) techniques.

Besides their use for standard environmental monitoring, GSCs can be used to aid in the testing of technology demonstrations (tech demos) on board the ISS, including the development of systems used to remove carbon dioxide (CO_2) from the atmosphere. Currently, two different CO_2 removal systems are undergoing evaluation on board the ISS: the Thermal Amine Scrubber and a 4-Bed CO_2 Scrubber, both of which have been described previously.[2,3] For each of these prospective exploration technologies, instead of simply exhausting CO_2 overboard, there is a desire to concentrate the CO_2 for use in a Sabatier reactor, which will convert it to water and methane. Ideally, the exit stream from the CO_2 removal system will be very close to 100% CO_2, as the presence of water and some other compounds could lead to corrosion and poisoning of the reactor. We have recently described our efforts to quantify the trace levels of water in the exhaust streams from the different removal systems,[4] though these efforts have been ongoing for decades.[5] In addition to the samples returned for water analysis, GSCs have also been returned to the ECL for analysis of the exhaust streams for quantitative analysis of volatile compounds.

This paper discusses two compounds of interest that have been found in the ISS atmosphere: octafluoropropane (OFP) and isobutane. OFP is a refrigerant commonly identified as R-218 or Freon 218. It is a non-flammable compound with low toxicity that is used by the Russian heat exchange assembly. Historically, these compounds tend to be fairly difficult to scrub from the atmosphere due to their non-polar and non-reactive nature. Suspected leaks have occurred which were detected from the periodic monitoring of the ISS atmosphere. Isobutane is an odorless gas that has many applications across several industries, including as a refrigerant. The source of isobutane seen on-station is still unknown; however, spikes in isobutane concentration appear to correlate with docking of vehicles to the ISS.

II. Sample Preparation and Analysis

Upon arrival, the returned GSCs are cataloged, documented, and pressurized to ensure analysis can be performed on a number of different instruments required to provide information on the full suite of target compounds. Due to the fact that the technology demonstration samples typically arrive at sub-ambient pressure, the pressurization required results in a dilution factor (DF) ranging from 6x to 8x.

Once prepared, analysis of the samples proceeds along a standard path. First, the GC-trace gas analyzer (GC/TGA) is utilized to quantify methane, carbon monoxide, hydrogen, and CO_2. Next, a gas chromatograph with a flame ionization detector (GC/FID) is used to quantify several organic compounds normally present at high concentrations. This instrument is commonly used as a screening method for further analysis. Finally, a GC/MS is used to quantify over one hundred compounds down to low part-per-billion levels. Combined, these three techniques allow a full characterization of the samples. Due to the varied nature of the samples, some or all of the techniques may require further dilutions to quantify all compounds present.

III. Technical Demonstration Sample Analysis

During the analysis of one set of 4-Bed CO_2 Scrubber samples, a large unknown peak appeared in the GC/FID spectra. This peak was originally disregarded as it was unable to be identified on the GC/FID or the GC/MS instruments. The large peak appeared close to the retention time of OFP and seemed to impact the first section of the quantifiable peak. It was suspected that the large peak was related to the high CO_2 concentration of the samples and was a compound unable to be seen on any instruments used for analysis. This led the analyst to identify matrix interference for the OFP value in this set of samples. Unfortunately, the phenomenon of a large peak appearing before the OFP retention time continued in later tech demo samples, and it became clear that this would be a persistent issue.

In early 2023, another set of four 4-Bed CO_2 Scrubber samples were received by the ECL. The samples were analyzed with the original dilution factor applied when pressurizing the samples. In this instance, the DFs started at 7.78, 7.17, 6.65, and 6.97 for Samples A, B, C, and D, respectively.

When analysis began for the samples using the GC/FID, a large, sharp peak was seen several seconds before OFP's retention time. The quantified values on-column for OFP in each sample were as follows: Sample A-127 ppb, Sample B-124 ppb, Sample C-4003 ppb, Sample D-133 ppb. At the time, the large unknown peak (**Figures 1 and 2**) was suspected to have an impact on OFP's value due to the larger amount of OFP found in Sample C. This originally resulted in the decision to report only Sample C as matrix interference.

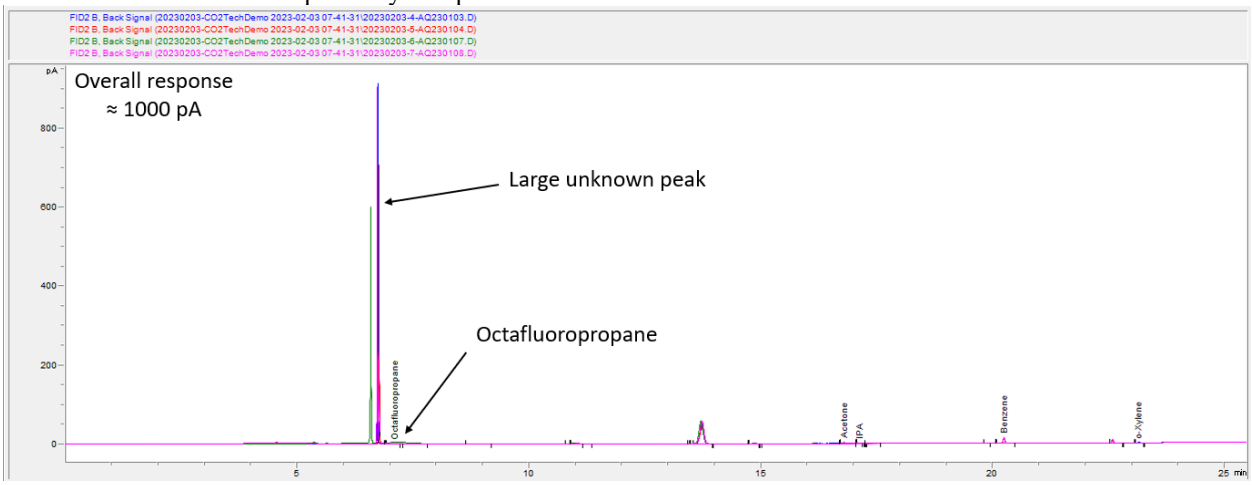

Figure 1: Original analysis of all four samples at their original dilution factors overlayed on top of each other.

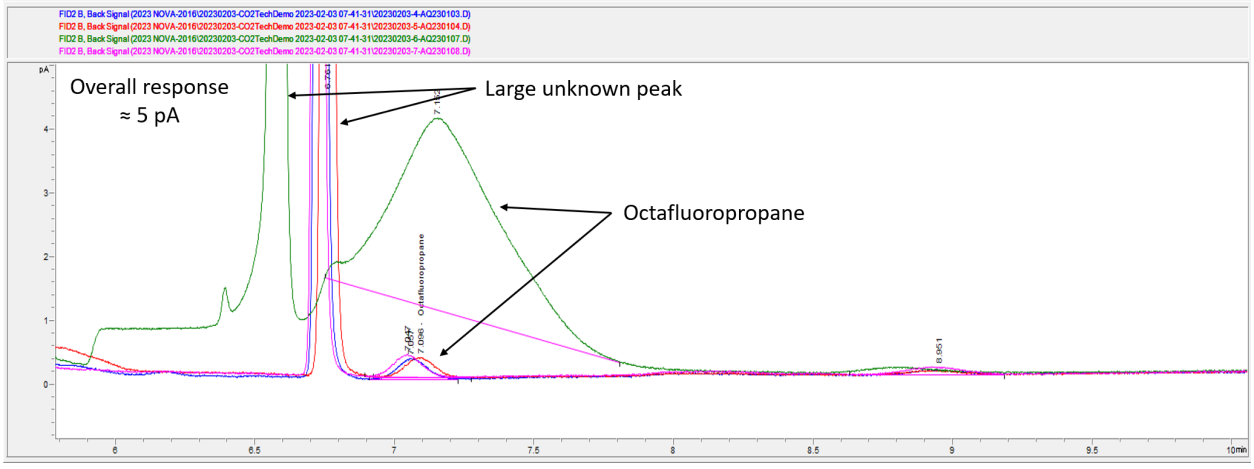

Figure 2: A zoomed-in view of the large peak as well as where the OFP retention time appears on the chromatogram.

IV. Identifying The Peak

The samples were diluted further to varying degrees after the GC/MS analysis had been performed, ultimately to very high dilutions to quantify the CO_2 concentration using the GC/TGA. It was decided to also run the new dilutions, now ranging from 250 to 290 DF, on the GC/FID to gain more understanding about the possible identity of the unknown peak. When analysis of the dilutions was performed on March 14th, 2023, there was only one peak that appeared. OFP was present in all samples at the same value, approximately 800 ppb on-column. The results averaged to a reported concentration of 213 ppm for the four samples. This led to further testing being necessary to determine if the large peak before the OFP retention time in the original run of the samples was OFP or impacting the ability to quantify OFP.

A. OFP Concentration

The goal of the first test was to identify the large peak as possible OFP overloading the injector and column. High concentration OFP standard and subsequent dilutions were run on the GC/FID to observe the behavior of large quantities of OFP entering the sample loop. A canister was filled with 1000 ppm OFP standard and then serial diluted with dry nitrogen gas to obtain a 500 ppm sample and a 250 ppm sample. Analysis of these samples showed that all high OFP standards appeared at the appropriate retention time of OFP, and all peaks were automatically identified by the software, as seen in **Figure 3**. This meant that simply having a high presence of OFP in a sample would not cause the peak to travel.

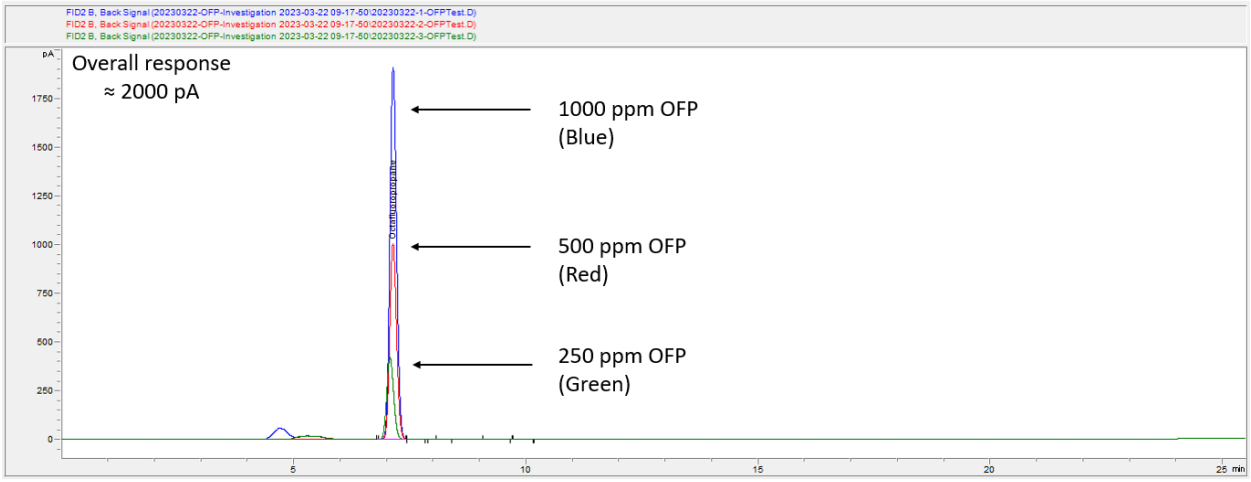

Figure 3: Results of the OFP dilution test overlayed on top of each other.

Another test involved spiking a diluted sample with a high concentration of OFP. The chosen sample was previously submitted for water analysis, originally had a DF of 6.58, and closely replicated the original samples run on the GC/FID seen in **Figures 1 and 2**. This sample was analyzed as a baseline before any spiking was performed. After establishing the baseline, the spike was introduced within the sample loop of the instrument, half of the injection being the original sample and half the high OFP standard. The spiking concentration recoveries appeared to align with what would be expected (**Figure 4**), though quantitative confirmation was unable to be performed due to the spike amount alone being outside of the calibration curve. This also confirmed that adding OFP to the samples would not cause the peak to shift in a similar manner to the unknown peak.

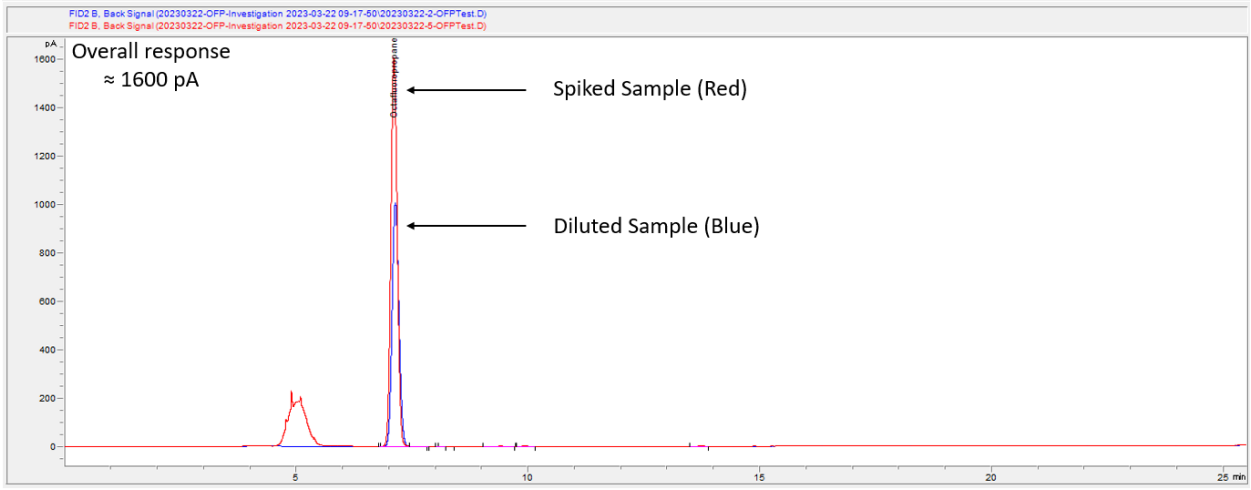

Figure 4: Overlay of the 500 ppm OFP standard in blue and the diluted sample spiked with 500 ppm OFP standard in red.

B. CO_2 Contribution

Another test performed involved only CO_2 and how it behaves in the GC/FID instrument. Two CO_2 standards were analyzed at different concentrations to determine if any peaks appear near the OFP retention time. One sample was filled with 10% CO_2 standard, and one sample was filled with 100% CO_2 standard. This analysis showed that no large peaks appeared on the GC/FID spectra, which was the expected outcome as CO_2 gas does not interact with the flame detector within this instrument. **Figure 5** shows the spectra of the 10% CO_2 sample and **Figure 6** displays the 100% CO_2 standard. Note that both spectra have very low responses when compared to other sample spectra.

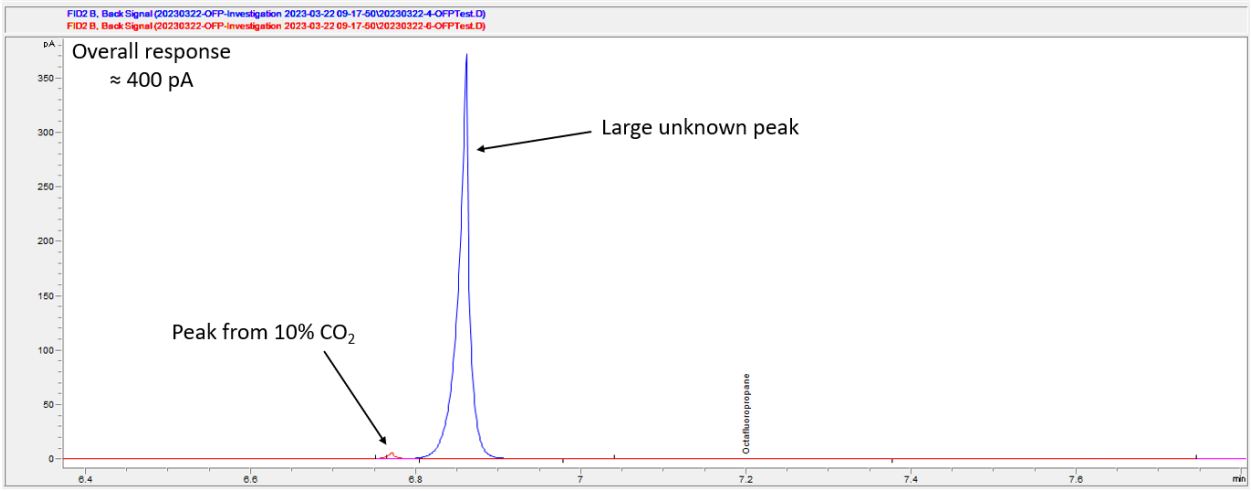

Figure 5: Spectra of the 10% CO_2 standard compared to a tech demo sample with the unknown peak.

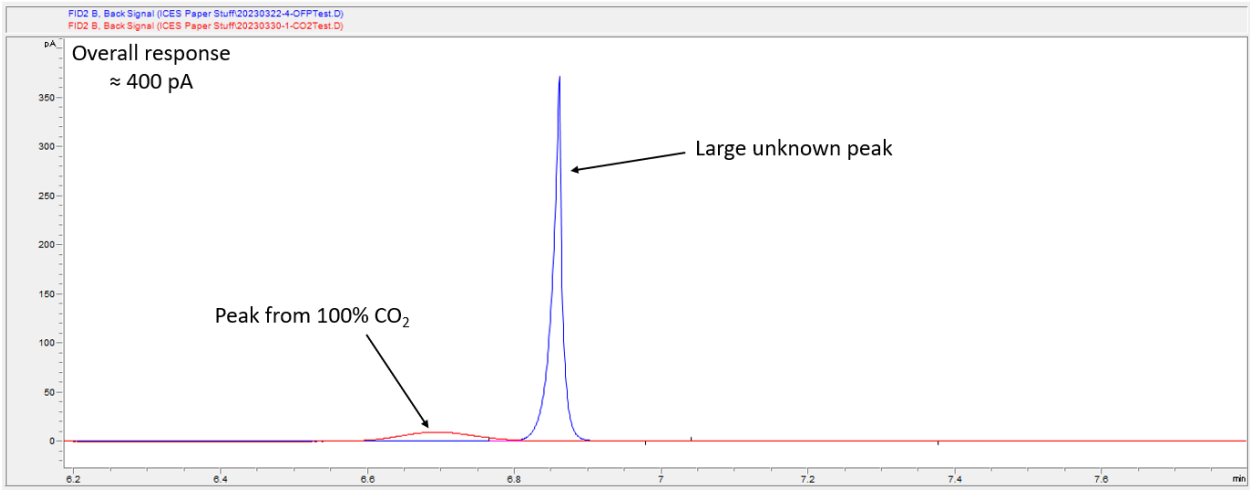

Figure 6: Spectra of the 100% CO_2 standard compared to a tech demo sample with the unknown peak.

C. CO_2 and OFP Combined

After the preliminary results from testing were complete, it was suspected that the large peak in the original tech demo samples was indeed OFP and that the CO_2 concentration combined with the OFP concentration created anomalous effects on the spectra.

A test was devised to confirm this by spiking a high concentration CO_2 standard with a high concentration OFP standard and then performing serial dilutions to recreate what was originally seen. One sample container was filled with 100% CO_2 standard. The sample containing only CO_2 was brought down to the pressure that mimicked the DF of the original samples, approximately 4 psi. The canister was attached to the 1000 ppm OFP standard bottle and allowed to fill to approximately 30 psi, then analyzed on the GC/FID. The expected final concentration was approximately 800 ppm, much larger than the concentrations seen from earlier samples, thus ensuring the peak-moving effect if it did occur. Dilutions were then performed at 50% increments using the dry nitrogen fill station. The dilutions analyzed were approximately 7, 14, and 28 DF.

Knowing that the canister being tested only contained CO_2 and OFP and that 100% CO_2 did not give a significant chromatogram, it was observed in **Figure 7** that the OFP peak indeed moved retention times and travelled towards its actual retention time as dilutions were performed. A DF of 28 ultimately allowed the peak to auto-integrate as OFP.

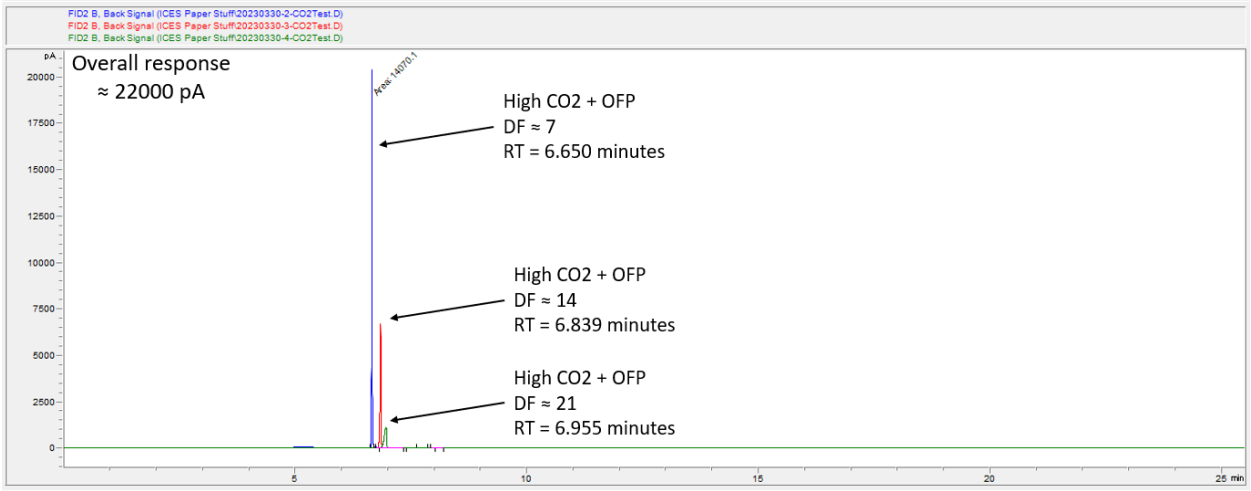

Figure 7: Combination test results show the forward movement of the large peak as dilutions are performed, slowly allowing the OPF peak to return to a normal retention time.

This test method now needed to be applied to a sample to show that the peak in the tech demo samples also acted in the same manner. This would further indicate that the large peak was OFP. A sample that was previously used for N_2/O_2 analysis was used for this process. This sample was run for a baseline and to confirm that it had similar

chromatography to the original samples. The sample was diluted 3 times from its starting DF of 10.34 down to a DF of 25, 50, and finally 100. With each dilution, the peak travelled to the right in the same way that the high OFP/CO_2 created standard did in the previous test. **Figure 8** zooms in to demonstrate the peak shape and location change as each dilution is made. Even more so, at DF of 100 the sample was able to be integrated and quantified. The results closely matched the original concentration of the original four samples.

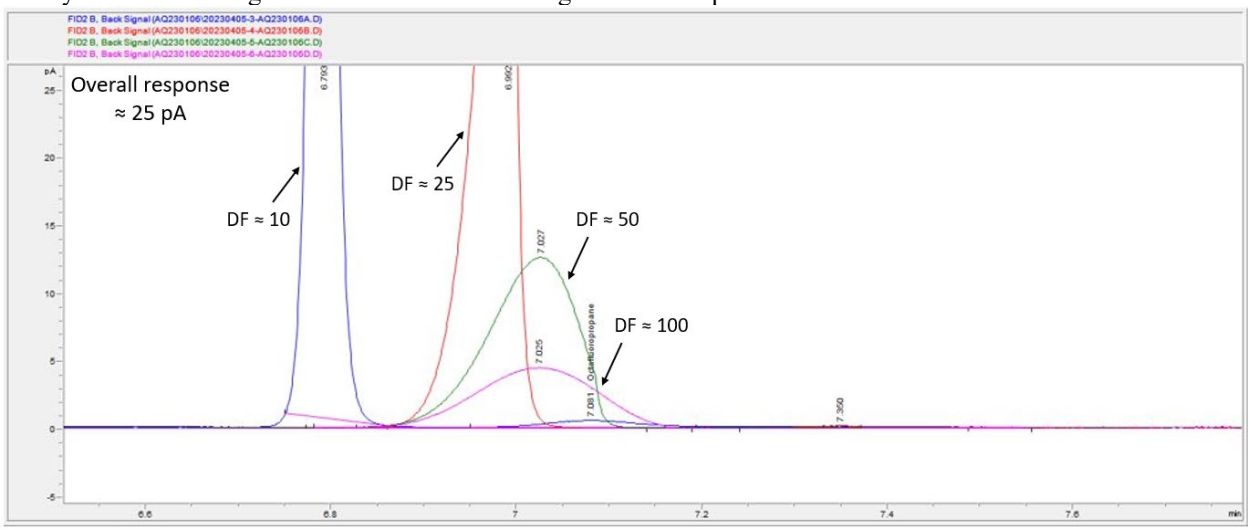

Figure 8: A zoomed-in image of the peak moving across the spectra.

Finally, a confirmation test consisted of spiking the diluted sample with OFP to determine if an acceptable percent recovery was possible. The sample was transferred into an empty container while an aliquot of 5 ppm calibration standard was created in another canister. The two canisters were joined and allowed to equilibrate. The final concentration expected after the spike was 3.69 ppm. The final result received was 4.04 ppm, resulting in a spike recovery of 109%. The spike recovery was within tolerance limits and made sense with the spike process performed. **Figure 9** is included to exhibit how both the sample peak and spiked sample peaks are at the same location in both spectra.

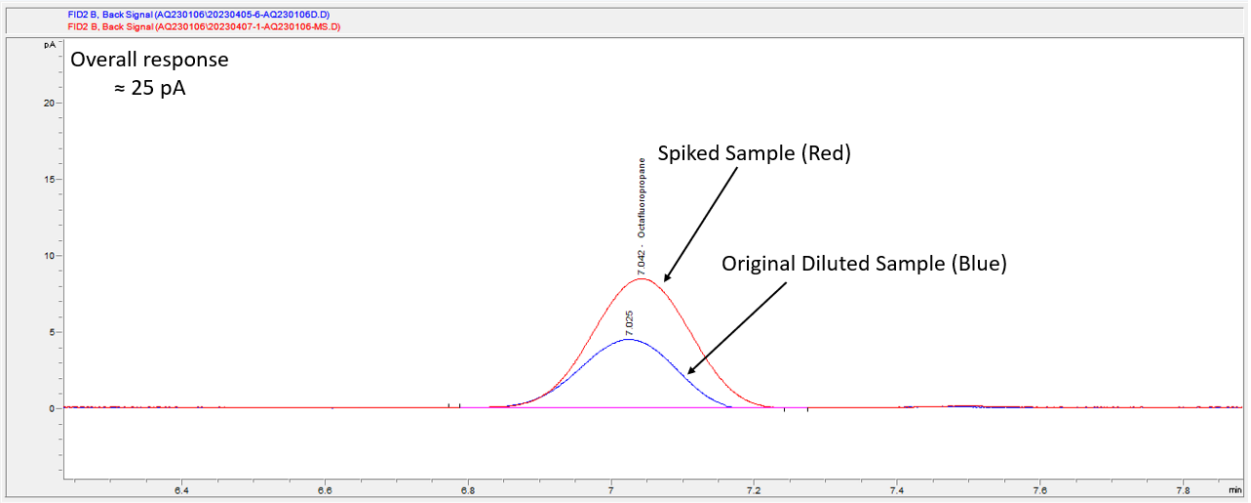

Figure 9: A zoomed-in view of the original diluted sample (blue) and the spiked sample (red).

V. Conclusions

Based on the testing performed, when a sample contains a high amount of CO_2 and a high amount of OFP, the interactions between the two gases causes the peak to distort and move from its typical retention time. This distortion also allowed for some of the OFP peak to tail and appear in the "correct" analytical window while still missing the remainder of the peak that eluted earlier. The high resultant values of OFP found in the tech demo samples led to the

question of its source. To find a possible explanation, analysts at ECL sifted through historical data for a possible correlation by assembling the graph in **Figure 10**. It was found that OFP in the nominal samples had suddenly increased due to a leak from a module aboard the ISS and remained at approximately 180 mg/m^3 for about two years. However, in late 2021 the OFP values from the ISS plummeted by a factor of 40 and remained low thereafter. Upon reviewing the tech demo timeline, this date coincided with the scrubber system installation and implementation on station. Therefore, it is possible that the 4-Bed CO_2 Scrubber system is actively scrubbing the OFP from the ISS atmosphere.

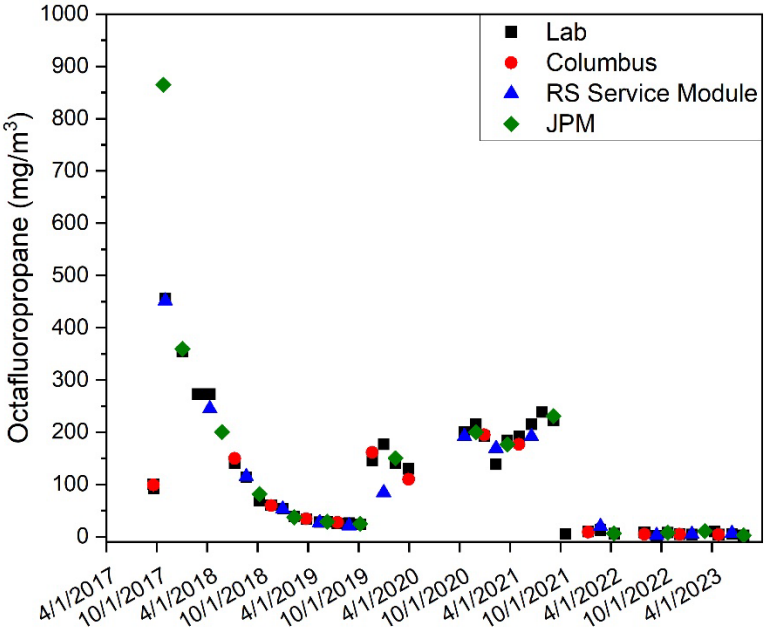

Figure 10: OFP concentration changes on ISS over time.

Another question arises from this discovery - if OFP can be removed and concentrated from the atmosphere, could other volatile compounds do the same? Unfortunately, more recent samples analyzed at ECL have found high levels of isobutane. Isobutane currently is not quantified on the GC/FID, although it can be seen in the spectra. By analyzing an isobutane standard, we have been able to identify the retention time within the current analytical method. The analysis for these samples requires significant dilutions for quantifying on the GC/MS, often an additional 10 to 20 DF.

Currently, the most recent tech demo analysis has shown a large amount of isobutane, but the OFP presence has completely disappeared from the GC/FID spectra. It is thought that because the tech demo is continuously running and its product is regularly sent overboard, the OFP that was present in the ISS atmosphere has since been removed below detectable limits. The OFP results in the most recent nominal samples has remained below detection limits.

VI. Future Impacts

Discovering the two compounds interacting with the CO_2 scrubber system has led the ECL to think ahead and make changes to the way it approaches air sample analysis from abnormal samples. Firstly, analysts involved with evaluating any air samples are now made aware of possible interactions from atypical sources. By being more observant of spectral differences and patterns, analysts can be more effective in finding anomalies that may need additional investigation.

Another influence includes adding more compounds to the GC/FID calibration curve to better screen for unknowns and high concentration compounds. The plan involves creating an isobutane curve to quantify in the short term, then adding isobutane to the calibration standard for the next cycle, permanently adding it as a new GC/FID-quantified compound. This would alleviate the need for unnecessary dilutions for GC/MS analysis.

Unfortunately, expanding the OFP window to include the larger and earlier eluting peak is likely unfeasible. The time difference between the erroneous large peak and the dedicated OFP calibration peak ranges by at least 30 seconds. While this is a relatively short time, it is a very large area to attribute to a single compound in chromatography. Typical

windows for compounds of interest in GC/FID analysis range from 6 to 12 seconds at most. There is also the limitation of the calibration curve. Currently, the curve only quantifies up to 20 ppm for all compounds. Calibrating for the expanded window and higher concentrations would therefore be impractical.

After this discovery, ground-based testing has been performed to find the cause of and ways to prevent this anomaly. ECL continues to support these efforts and analyze samples from test stands both on the ground and on the ISS.

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