

Effects of Ambient CO₂ on Monitoring of the International Space Station Atmosphere with the Air Quality Monitor

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Since 2009, gas chromatography-differential mobility spectrometry (GC/DMS) has been used on-board the International Space Station (ISS) to monitor the atmosphere for volatile organic compounds. The technology was originally tested as part of a Station Detailed Test Objective (SDTO) and then transitioned to operational hardware. The operational version of this hardware, the Air Quality Monitor (AQM), currently monitors 22 compounds, though the target list is flexible and can be adjusted depending on changes in materials or the spacecraft environmental control systems.

After separation on the GC column, target compounds are ionized via charge transfer from a Reactant Ion (RI). In the positive mode, H⁺(H₂O)_n is the RI while O₂⁻(H₂O)_n acts as the RI in the negative mode. In the early stages of the SDTO, it was discovered that the position of the RI Peak (RIP) in the negative mode was shifting with time on orbit, and the instrument was losing sensitivity to certain compounds. This shift of the RIP appeared to be correlated with increasing concentrations of CO₂ in the recirculation system of the instrument. The operational version of the AQM uses larger, replaceable sieve packs to clean the recirculated carrier gas. It was hypothesized that incorporation of the large sieve packs would minimize the effect of CO₂ on the position of the RIP. Unfortunately, this phenomenon has also been observed on the first two sets of AQMs operating on the ISS.

In this paper, we will discuss the mechanisms behind the shifting RIP as well as the effects on the ionization of selected target compounds. Additionally, we will discuss potential approaches to mitigate the impact of the RIP shift and extend the current 6-month life of sieve packs on-orbit.

Nomenclature

<i>AQM</i>	=	Air Quality Monitor
<i>AQM-GFE</i>	=	Air Quality Monitor-Government Furnished Equipment
<i>AQM-SDTO</i>	=	Air Quality Monitor-Station Detailed Test Objective
<i>CH₄</i>	=	Methane
<i>CO₂</i>	=	Carbon dioxide
<i>DCE</i>	=	1,2-dichloroethane
<i>DCM</i>	=	Dichloromethane
<i>EA</i>	=	Electron Affinity

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<i>GC-DMS</i>	= Gas Chromatograph-Differential Mobility Spectrometer
<i>GC-IMS</i>	= Gas Chromatograph-Ion Mobility Spectrometer
<i>GC-MS</i>	= Gas Chromatograph-Mass Spectrometer
<i>H₂</i>	= Hydrogen
<i>H₂O</i>	= Water
<i>HCRMS</i>	= Hydrocarbon and Moisture Trap Absorbent Media
<i>ISS</i>	= International Space Station
<i>LiOH</i>	= Lithium Hydroxide
<i>N₂</i>	= Nitrogen
<i>O₂</i>	= Oxygen
<i>RF</i>	= Radio Frequency
<i>RIP</i>	= Reactant Ion Peak
<i>SDTO</i>	= Station Detailed Test Objective
<i>SF₆</i>	= Sulfur hexafluoride
<i>VOA</i>	= Volatile Organic Analyzer
<i>VOC</i>	= Volatile Organic Compound

I. Introduction

With the longer missions and decreased opportunities for archival sample return from the International Space Station (ISS), it is imperative to develop real time environmental monitoring capabilities to ensure the health of the crew and the spacecraft. In the case of the atmosphere on the ISS, major constituents such as nitrogen (N₂), oxygen (O₂), carbon dioxide (CO₂), methane (CH₄), hydrogen (H₂), and water vapor (H₂O) are monitored by the Major Constituent Analyzer (MCA), which is a magnetic sector mass spectrometer.¹ For trace volatile organic compound (VOC) monitoring, a number of different instruments have been used. From 2001-2009, a combined gas chromatograph-ion mobility spectrometer (GC-IMS) known as the Volatile Organic Analyzer (VOA) was used to monitor trace VOCs.² However, with the need to reduce mass, volume, and crew time while maintaining performance for exploration missions, a “next generation” VOA was developed. This gas chromatograph-differential mobility spectrometer (GC-DMS) improved upon the original VOA in several ways. These included a volume decrease (5.2×10^3 cm³ versus 9.2×10^4 cm³), a mass decrease (3 kg versus 44.5 kg), cost savings (~ \$25k each versus \$6M for 2 units), and a reduced reliance on ISS resources, as the carrier gas for the GC was recirculated air instead of ISS N₂. This device, built by Sionex, was delivered to the ISS as a Station Detailed Test Objective (SDTO) in March 2009. The SDTO was successful in accomplishing its goals,³ but there were certain aspects of the testing that indicated improvements could be made prior to developing an operational version of the hardware. The improved instrument had an onboard computer with wireless capability that eliminated the need for it to be hardwired to the ISS communication bus. Furthermore, the instrument operation was totally automated after the power switch was moved to the “on” position. There was also remote desktop capability so the instrument could be controlled from the ground to complete extra runs or perform troubleshooting without needing crew time.⁴

The principles of DMS and GC-DMS have been described in detail previously⁵⁻⁷ and will only be described briefly here. As analytes of interest exit the GC and enter the DMS detector cell, they are ionized and exposed to asymmetric radio-frequency (RF) fields that displace the ions perpendicularly to the gas flow. To prevent the neutralization of the ionized analyte on the cell walls, a small DC voltage (compensation voltage, C_v) is applied to steer the ions away from the walls and towards the detector. The optimal C_v value for an individual compound is related to the interaction of the ion with the RF field.^{8,9} The combination of RF and C_v parameters, combined with GC retention time, are used to identify the compounds present in the sample.

One advantage of using DMS over IMS is that fact that both positive and negative ions can be monitored simultaneously. The ionization of analytes is achieved via charge transfer from a Reactant Ion Peak (RIP). In the positive mode, the RIP signal is generally recognized as an overlapped signal consisting of a hydrated proton with a variable number of water molecules arising from the ⁶³Ni ionization source. Analytes with a higher proton affinity than water will be ionized via proton transfer.¹⁰ In the negative mode, the RIP consists of a cluster of O₂⁻ surrounded by a variable number of water molecules. The ionization of species in the negative mode is not as straightforward. It has been stated that the formation of an adduct with the RIP is the initial ionization step in negative reactant ion chemistry in air, and the ion may subsequently remain as an adduct or undergo charge transfer or proton abstraction.¹¹ As such, an actual electron transfer step may or may not play a role in the ionization of species detected in the negative mode.

During on-orbit testing of the AQM-SDTO, it was found that the negative mode RIP began to shift to less negative values, and this shift appeared to correlate with a decrease in sensitivity towards dichloromethane (DCM)^{3,7,12} as shown in **Figure 1**. Note that, while the DCM concentration is normally found at trace levels or below, this change is still dramatic, as is the fact that no other target compound appeared to react in this manner. Initial thoughts as to the source of this shift centered on the potential breakthrough of water in the sieve packs used to clean the recirculated carrier gas. However, the fact that there was no corresponding change in the positive mode RIP suggested that water was not the cause.⁷ Other contaminants present at high levels in the ISS atmosphere, such as Freon 218 (octafluoropropane) and sulfur hexafluoride (SF₆), were also ruled out through ground testing.⁴ Another potential contaminant on board the ISS is CO₂. Concentrations of CO₂ in the ISS atmosphere are generally in the range of 2000-3000 ppm, though the concentrations have been known to approach 5000 ppm.⁷ Currently, the CO₂ levels are managed to a 24-hour average of 3 torr or less (~3900 ppm) by a combination of techniques.¹³ During the time period that the AQM-SDTO was on board the ISS, the units were required to be turned off following their use due to acoustic concerns. This resulted in CO₂ being ingested every time that the unit was activated. With non-replaceable sieve cartridges in these units, it is believed that continuous exposure to CO₂ simply overwhelmed the sorbent material.⁷ With the on-orbit activation of the GFE version of the AQM and its larger, replaceable sieve packs, as well as the ability to run constantly due to improved acoustic characteristics, it was assumed that CO₂ effects on the RIP would be minimal. However, as seen in **Figure 2**, the negative mode RIP continually and reproducibly shifted to a less negative C_v following the installation of new sieve cartridges, indicated by green stars in the figure.

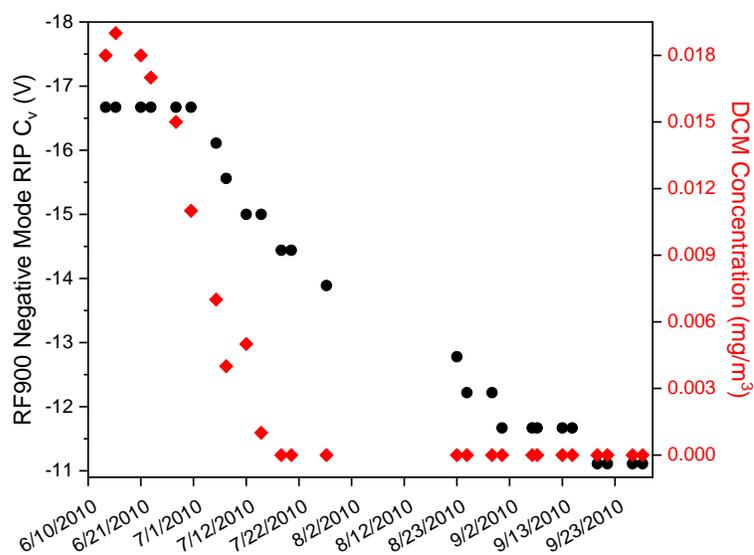


Figure 1 – On-orbit data from the AQM-SDTO from June to October 2010 showing changes in the negative mode RIP (black circles, left axis) and the dichloromethane concentration (red diamonds, right axis).

Studies to understand this change in C_v with CO₂ were performed by interfacing AQM-SDTO with a mass spectrometer.^{7,12} Analysis of the mass spectrum obtained from the AQM-SDTO upon activation indicated that the negative mode peak (at C_v = -17 V) consisted of O₂⁻ and its hydrates, as would be expected. After deactivating the AQM and placing it into a bag with dry ice for several hours, the AQM was activated, and the mass spectrum of the negative mode RIP (now at C_v = -12 V) contained mostly O₂(CO₂)⁻ and its hydrates. Due to a large charge transfer from O₂⁻ to CO₂, it has been postulated that the O₂(CO₂)⁻ moiety is actually a molecular CO₄⁻ ion.¹⁴⁻¹⁷ Limero et al.⁷ found that this process could be reversed by flushing the system with purified air, confirming the findings of Spangler and others¹⁵ that the CO₄⁻ species is preferred only at high CO₂ and low water concentrations.

If one assumes that the ionization of negative-mode species is indeed related to electron transfer from the RIP, then the electron affinities (EA) of the potential RIP species could conceivably affect the processes in which the electron interacts with analytes of interest. This potentially could reduce the sensitivity towards those compounds, specifically DCM and DCE in the case of the AQM. **Figure 3 (A, B)** shows the effects of a changing negative mode RIP on the detection of these compounds observed during flight preparation of new AQMs. While the effects on DCE are not as pronounced as with DCM, the increase in peak areas with a more negative RIP are obvious. The EA of O₂ and its hydrates is significantly higher than that of CO₂ and its hydrates,^{18,19} which would suggest that negative mode analytes should be more easily ionized when CO₂ is present. However, that would only be the case if no

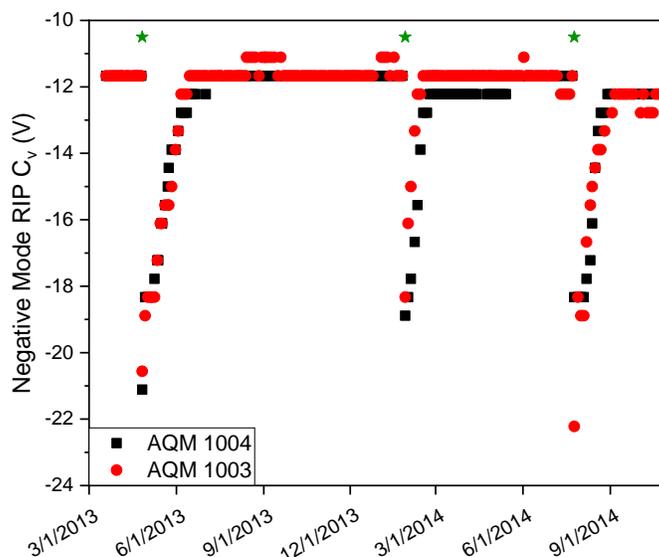


Figure 2 – Changes in the negative mode RIP (RF900) from March 2013 to November 2014 in the first AQM-GFE units delivered to the ISS. The green stars denote sieve pack changes in both units.

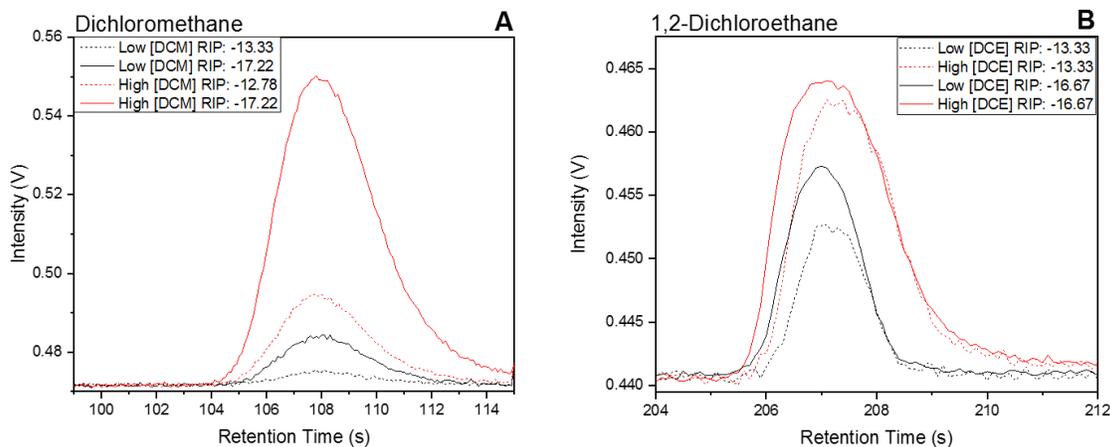


Figure 3 – Changes in automated dichloromethane (A) and 1,2-dichloroethane (B) response with changes in the negative mode RIP. After purging the sieve cartridges overnight with zero air, the RIP returns to a “cleaner” value, and the responses increase dramatically.

oxygen was present. The CO_4^- species arising from the simultaneous presence of O_2 and CO_2 may have a much higher EA than either of the individual molecules; unfortunately, there is no EA available for this ion.

While the effects of background CO_2 on the negative mode RIP are the major focus of this paper, the potential effects of CO_2 on positive-mode analytes is not negligible. On-orbit data has shown that there is a pronounced change in the C_V of the methanol peak over time following the installation of new sieve cartridges. **Figure 4** shows this change compared to the positive and negative mode RIPs. Note that, as expected, the installation of new sieve cartridges does not affect the positive RIP. However, the methanol C_V quickly begins to shift, mirroring that of the negative mode RIP change with increasing CO_2 (It is unclear what is responsible for the reversal in methanol C_V shift in September 2016, though this behavior has been seen repeatedly). This result would seemingly indicate that increased clustering with CO_2 is responsible for the shift.⁷ One would expect a shift to a more negative C_V to be due to an increased mobility due to the size (collision cross section) of the ion being smaller, which would not be the case if CO_2 was bound to a hydrated methanol ion, unless the CO_2 displaced multiple water molecules. However, the strong asymmetric electric fields in the DMS cell cause changes in ion temperature that affect clustering,²⁰ so it is possible that the presence of the CO_2 molecule also affects the ability of water molecules to bind to methanol, thereby leading to a smaller ion at the higher fields.

For DCM and methanol, the changes caused by excess CO_2 preclude the use of the automated analysis techniques generally preferred with the AQM, requiring manual analysis of “scan runs.”²¹ However, the ability to perform this type of analysis will be limited at best during exploration missions. As such, it is clear that continued efforts are necessary to determine methods by which the effects of CO_2 on the AQM can be minimized. Here, we describe testing in our lab to understand the effects of the current sieve pack materials on CO_2 scrubbing and test another potential sorbent, with the hope to potentially extend the lifetimes of sieve packs in-flight.

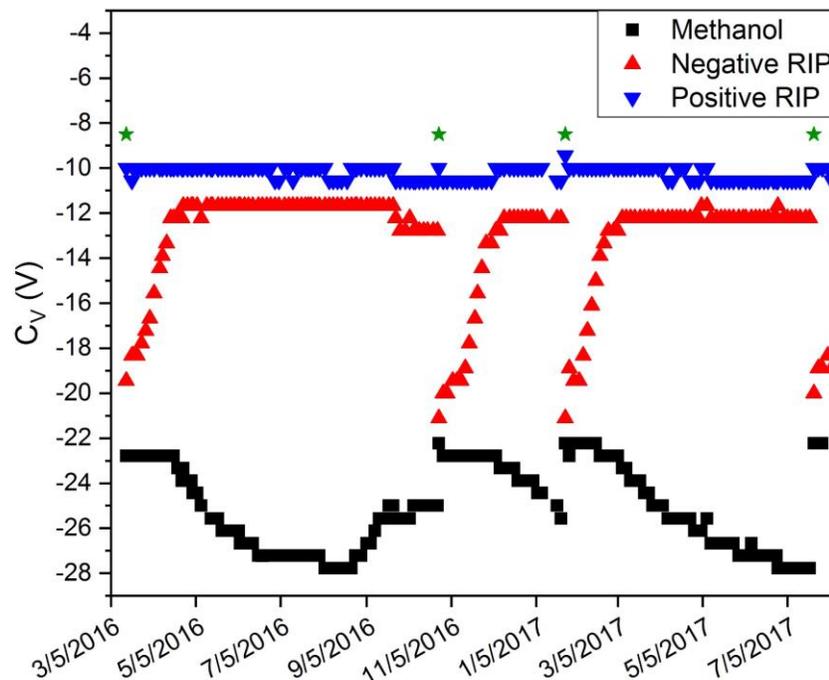


Figure 4 – Changes in methanol C_V (black) compared to the negative RIP (red) and the positive RIP (blue). The stars indicate sieve cartridge changes. While the methanol is detected in the positive mode, its behavior coincides more with the behavior of the negative RIP, suggesting that CO_2 is playing a role in its detection.

II. Experimental

A. Preparation of test cartridges

For testing of different sieve pack materials, a single, stainless steel, flight-like sieve cartridge was filled with the sorbent or sorbent combination of interest. For testing of Hydrocarbon and Moisture Trap Absorbent Media (HCRMS, Agilent), the entire sieve cartridge was filled with HCRMS. For testing of Carboxen 569/HCRMS, the cartridge was prepared as for flight, in which 8.0 +/- 0.5 g of Carboxen was placed into the cartridge, a small filter pad (Draper Laboratories) was placed on top of the Carboxen, and the remainder of the cartridge was filled with HCRMS. After filling each of these types of cartridges, the cartridge was wrapped with heat tape and heated slightly using a Variac, while flowing zero air passed through overnight at ~ 100 cc/min. Following each round of testing, the sieve packs were regenerated by heating and purging overnight. Cartridges containing a combination of lithium hydroxide (LiOH) and HCRMS were prepared by coarsely grinding a small amount (2.5-3.0 g) of LiOH with an alumina mortar and pestle, placing it in the cartridge, adding the pad, and filling the remainder with HCRMS. These cartridges were then heated and purged overnight. Regeneration of these cartridges after testing did not appear to provide the same results as when using new material, so all tests using LiOH were performed with fresh sample.

B. Testing of sorbent materials

Testing of sieve pack materials was performed using a Sionex SVAC-V (**Figure 5**), which allows test gases to be input to a temperature-controlled DMS cell without first flowing through a GC column.²⁰ Sionex Expert software was used to control the SVAC, and test gases were introduced through a bank of rotometers. Backing pressures were maintained at 30 psig, and the total flow of gases introduced into the SVAC was maintained at 300 cc/min. Each combination of sorbent materials was tested at least 3 times.

Initial testing of sieve cartridges with nominal ISS CO₂ concentrations led to changes in the C_v that were much too rapid. Therefore, it was decided to use 1000 ppm concentrations for the current testing. While this is much lower than the nominal on-orbit CO₂ concentration, it must be remembered that, upon deployment and activation, the AQM brings in only enough ambient air to build a sufficient head pressure on the GC column and to serve as the recirculated carrier gas and detector make up gas. These volumes are not sufficient to overwhelm the sieve material. However, in a continuous flow system as that described here, 1000 ppm CO₂ changes the DMS spectra in a convenient amount of time for study and comparison of different materials. A 0.1% CO₂ standard was diluted using the rotometers to achieve this final concentration while maintaining the total flow described above.

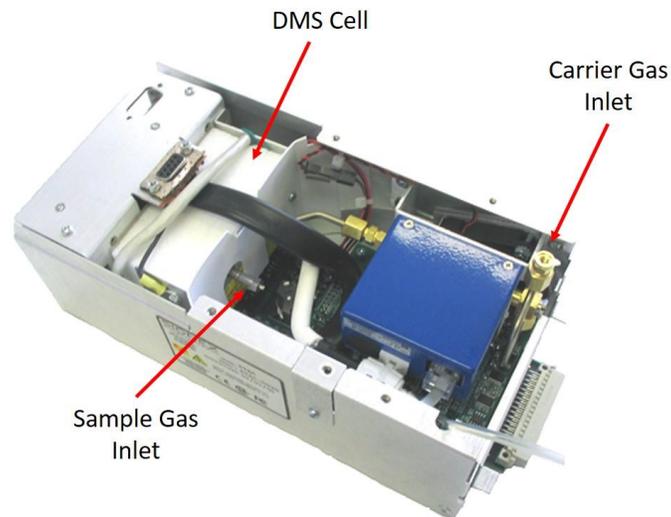


Figure 5 – Sionex SVAC-V differential mobility spectrometer

III. Results

A. GC-MS Analysis of Current Sorbent Materials

While it was clear from the earlier studies that high levels of CO₂ would lead to a shift in the negative mode RIP, previous observations in our lab had indicated that this shift would occur even under ambient conditions while running (~ 600 ppm) or when the AQM was turned off. This led to a question as to whether some material in the sieve packs (Carboxen or HCRMS) was off-gassing an unknown contaminant (It is known that SO₂ is present as a contaminant from Carboxen 1000, which is present in the AQM preconcentrator⁷). In order to test this possibility, a modified soil analysis method was performed using GC-MS. In this testing, samples of Carboxen and HCRMS (separately) were purged with He at a temperature of 70 °C, and the headspace was analyzed. This temperature represents that of the carrier gas flowing through the sieve packs during nominal operation. The results of this study showed only slightly increased concentrations of CO₂ and argon over a method blank and a small amount of propane in one sample. Neither the argon nor propane would account for changes in the negative mode RIP, verifying that the sorbent materials themselves are not responsible for the change in C_V.

B. DMS Analysis of Sorbent Materials Exposed to CO₂

The first sorbent material to be exposed to CO₂ and have the exhaust analyzed by DMS was HCRMS. To obtain a baseline, separate analyses of purified zero air and the 1000 ppm CO₂ were performed with no sieve cartridges in-line. The average C_V for zero air was -17.92 ± 0.26 V while the average C_V for the 1000 ppm CO₂ was -12.76 ± 0.15 V. Upon placing the sieve cartridge containing HCRMS in-line prior to the DMS, the C_V immediately began to become less negative, with the value approaching that of the unscrubbed 1000 ppm CO₂ within 30-40 minutes and continuing to alternate within ~ 0.5 V over the remainder of testing. This behavior is shown in **Figure 6** (black icons).

Following testing of HCRMS alone, testing of the “flight-like” sieve cartridges was performed (**Figure 6-red icons**). The baseline measurements provided C_Vs of -18.45 ± 0.48 V (zero air) and -12.93 ± 0.37 V (1000 ppm CO₂). In a change from the HCRMS testing, a time point was obtained at 1 minute following placement of the sieve pack in-line. This C_V at this time point was actually slightly *more* negative than that obtained for the purified zero air. However, even though the initial rate of C_V decay was less than that when only the HCRMS was present in-line, the C_V again reached the position of the unscrubbed CO₂ within 30-40 minutes, showing that any extra CO₂ scrubbing provided by the Carboxen is minimal.

The final set of sieve material testing consisted of replacing Carboxen with LiOH (**Figure 6 – blue icons**). Due to the need to grind this material prior to placing it in the sieve cartridge, as well as its potential to irritate, it was not as easy to add reproducible amounts when preparing the sieve cartridges. Additionally, as mentioned above, regeneration of these cartridges by heating and purging with zero air actually appeared to reduce their activity, so each test used fresh LiOH and HCRMS. The baseline values for this testing were -18.71 ± 0.27 V (zero air) and -13.28 ± 0.3 V (1000 ppm CO₂). As with the Carboxen/HCRMS cartridges, the initial test point showed that the C_V was more negative. However, this behavior continued, with an even more negative C_V being obtained at the 3-minute test point. The C_V eventually became less negative, but it reached an approximate steady state around -17 V, which is well within the nominal range for the AQM when new sieve cartridges are used.

IV. Discussion

While the negative mode of DMS has been used extensively as a detection method for various species (see, for instance, references [22-26]), little to no effort has focused on the effects of CO₂ on these measurements. This is largely due to the fact that these studies have been carried out under idealized conditions, in which pure carrier gases were used. As such, it is unlikely that shifts in the RIP, and the accompanying loss of sensitivity, would have occurred. However, the introduction by Sionex of the GC-DMS and its use of recirculated air as carrier gas necessitated the use of sorbent material to scrub VOCs and moisture.²⁷ Again, though, the effects of CO₂ do not appear to have presented a concern, likely due to the relatively low concentrations of CO₂ in ambient air (~ 600 ppm). The use of the GC-DMS on the ISS, however, has shown that CO₂ can present a major problem for the detection of atmospheric contaminants, particularly in the negative mode. The results presented here have confirmed that both HCRMS and Carboxen, which currently make up the contents of the AQM-GFE sieve cartridges, have extremely limited capacity for CO₂ scrubbing. Furthermore, it is clear that LiOH is a superior CO₂ scrubbing material for DMS. This is no surprise, as LiOH has a long history of use in spaceflight for this very purpose.²⁸ This

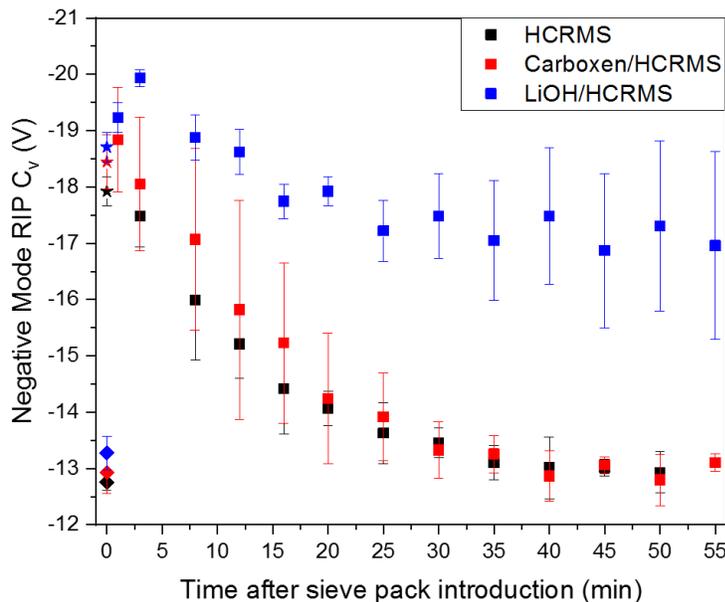


Figure 6 – Effect of different sorbent materials on maintaining the negative mode RIP upon exposure to 1000 ppm CO₂. Stars indicate the position of the RIP when no CO₂ is present and diamonds indicate the position when no sorbent is present. Note that the slight shifts in the baseline measurements are well within the expected variability of the test.

would seemingly suggest that LiOH should either replace one of the other materials in at least one sieve cartridge or be added to both of the recirculation cartridges. However, there are some concerns with the use of this material, not least of which is the possible effects on crew members. Lithium hydroxide is an irritant and has potential toxic effects if it is released into the cabin atmosphere.^{29,30} While the materials in the AQM sieve cartridges are contained, there could still be a concern regarding dusting from the cartridges if one of the internal pads is compromised. The other concern relates to the unknown effects that the LiOH could have on the detection of other compounds, though this is unlikely. Initial work has been performed using an AQM-GFE in an attempt to confirm this speculation.³¹ Future testing with the DMS-only configuration of the SVAC will aim to determine if DCM and methanol can be detected under high CO₂ conditions using LiOH/HCRMS scrubbing and if the use of LiOH will cause any difficulties in the detection of other compounds.

V. Conclusion

The AQM has successfully been used to monitor the atmosphere of ISS since early 2013. However, the high CO₂ levels continue to create difficulties related to the automated detection of some compounds, as they affect the composition of the RIP used for ionization in the negative mode and the composition of analyte clusters in the positive mode. Here, we have reviewed the known effects of CO₂ on AQM detection and described some initial testing aimed at understanding a potential method for removing CO₂ from the recirculating carrier gas. These results have shown that replacing one of the current sorbent materials used for scrubbing the carrier gas, Carboxen, with LiOH will prevent the movement of the negative mode RIP. It is unknown at this time, however, if the use of LiOH will solve the issues seen for DCM and methanol detection in high CO₂ atmospheres or if the use of LiOH could potentially change the makeup of the carrier gas in other ways that could affect VOC detection.

Acknowledgments

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