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Effects of Ambient Alcohol Levels on the Real-time Monitoring of the Atmosphere of the International Space Station

William T. Wallace[1] and Thomas F. Limero[2]
KBR, 2400 NASA Pkwy., Houston, TX 77058

Kenneth W. Clark[3] and Edgar K. Hudson, Jr.[4]
JES Tech, 16870 Royal Crest Dr., Houston, TX 77058

and

Daniel B. Gazda[5]
NASA Lyndon B. Johnson Space Center, 2101 NASA Pkwy., Houston, TX 77058

Monitoring of the spacecraft environment is required to ensure the health of the crew and the vehicle systems. For the ISS atmosphere, routine volatile organic compound (VOC) monitoring has been performed for almost a decade by Air Quality Monitors (AQMs). The target compounds measured by the AQMs include three types of chemicals: 1) those compounds that would be harmful to crew, 2) those compounds that have been detected regularly in archival samples, and 3) compounds that, while not necessarily harmful to crew health, could present problems for Environmental Control and Life Support Systems (ECLSS).

Following the docking of SpaceX-Demo1 (SpX-DM1), the AQMs began to report high levels of isopropanol (IPA). While elevated IPA is routinely observed with visiting vehicles, the level measured by the AQM, and its continued presence following multiple days of scrubbing, caused concerns regarding the U.S. Water Recovery System. Following the departure of SpX-DM1, the IPA levels decreased to nominal levels, allowing the team to investigate the cause of the elevated measurements. Based on the changes in the shape of the gas chromatograph (GC) traces in the IPA region during docked operations, it appeared that an unknown coeluting species was causing problems with quantification. However, with the docking of Northrup-Grumman-11 (NG-11), the elevated IPA returned, as well as the changes in GC traces. In contrast to the SpX-DM1 results, the AQM IPA results did not return to nominal levels following the departure of NG-11, suggesting that the changes could not be tied directly to the visiting vehicle.

In this paper, we will discuss a number of potential causes for both the genuine (measured in archival samples) increases in IPA as well as the much higher levels measured by the AQM. Additionally, we will discuss methods being explored to decrease the potential for a reoccurrence in the future.

Nomenclature

AGA = Anomaly Gas Analyzer
AQM = Air Quality Monitor
CHIPS = Charcoal HEPA Integrated Particle Scrubbers
CSA-CP = Compound Specific Analyzer-Combustion Products

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[1] Task Order Manager, Environmental Sciences, KBR, 2400 NASA Pkwy., Houston, TX 77058.

[2] Subject Matter Expert-Chemistry (retired), Environmental Chemistry Laboratory, KBR, 2400 NASA Pkwy., Houston, TX 77058.

[3] Analytical Chemist, Environmental Chemistry Laboratory, JES Tech, 16870 Royal Crest, Houston, TX 77058.

[4] Laboratory Lead, Environmental Chemistry Laboratory, JES Tech, 16870 Royal Crest, Houston, TX 77058.

[5] Chief, Environmental Sciences Branch, Biomedical Research and Environmental Sciences Division, NASA Johnson Space Center, 2101 NASA Pkwy., Houston, TX 77058

C_V = Compensation Voltage
DMS = Differential Mobility Spectrometry
ECL = Environmental Chemistry Laboratory
ECLSS = Environmental Control and Life Support Systems
GC = Gas Chromatograph
GC-DMS = Gas Chromatograph-Differential Mobility Spectrometer
GC-MS = Gas Chromatograph-Mass Spectrometer
GSC = Grab Sample Container
HHPC = Human Health and Performance Contract
IMS = Ion Mobility Spectrometry
IPA = Isopropanol (Isopropyl alcohol)
ISS = International Space Station
JSC = Johnson Space Center
MCA = Major Constituent Analyzer
MDL = Minimum Detection Limit
MGM = Multi Gas Monitor
NG-11 = Northrup-Grumman-11 mission
SAM = Spacecraft Atmosphere Monitor
SMAC = Spacecraft Maximum Allowable Concentration
SpX = SpaceX
SpX-DM1 = SpaceX-Demo1 mission
SVT = Science Verification Testing
TAS = Thermal Amine Scrubber
TDLS = Tunable diode laser spectroscopy
USOS = United States Operating Segment
VOA = Volatile Organic Analyzer
VOC = Volatile Organic Compound
WRS = Water Recovery System

I. Introduction

Monitoring of the spacecraft environment is required to ensure the safety of the crew and the health of the vehicle systems. In the case of the spacecraft atmosphere, this monitoring has relied for many years on the collection of archival samples (grab sample containers – GSCs) and their return to Earth for analysis.[1,2] For short duration missions, such as those of Mercury, Gemini, Apollo, or the Space Shuttle, this type of monitoring was sufficient. However, with expeditions on the International Space Station (ISS) lasting up to (or surpassing) a year, it became necessary to develop real-time methods for determining the concentrations of major constituents (O_2, CO_2, N_2, etc.), trace contaminants (e.g. volatile organic compounds - VOCs), and combustion products (HCl, HF, HCN). A recent review has summarized some of this real-time monitoring on the ISS.[3] Currently, in the U.S. Operating Segment (USOS) of the ISS, the major constituent concentrations are measured using a magnetic sector mass spectrometer, the Major Constituent Analyzer (MCA).[4,5] Combustion products are monitored by the Compound Specific Analyzer-Combustion Products (CSA-CP), a handheld, electrochemical sensor-based device.[3] In addition to these operational instruments, a number of payloads have focused on further refining real-time atmospheric monitoring. For instance, the Multi-Gas Monitor (MGM) was launched to demonstrate the capabilities of tunable diode laser spectroscopy (TDLS) to monitor atmospheric constituents.[6,7] For the initial technology demonstration, oxygen, carbon dioxide, and water vapor concentrations were measured and compared to the values obtained from the MCA, showing excellent accuracy.[6] The success of that technology demonstration has led to the development of the Anomaly Gas Analyzer (AGA), which will be used on both the ISS and Orion (exploration) vehicles and will add combustion products analysis to the gases analyzed by the MGM.[8,9] A current technology demonstration is testing the performance of the Spacecraft Atmosphere Monitor (SAM), a gas chromatograph-mass spectrometer (GC-MS), for measurement of major constituents in the ISS atmosphere. SAM is also an option on the Environmental Control and Life Support Systems (ECLSS) technology roadmap for trace gas analysis for future missions.[9-11]

During the early years of the ISS, VOCs were monitored in real time using the Volatile Organic Analyzer (VOA), a large, rack-based instrument that combined gas chromatography (GC) for analyte separation with ion mobility spectrometry (IMS) for detection.[12-17] This instrument was exceedingly successful, working for 8 years and providing insight into several on-orbit issues in situations where the delay in archival sample return and analysis was unacceptable.[18] However, one of the lessons learned from the on-orbit VOA experience was that the size of the instrument [9.2 x 10^4 cm^3, 44.5 kg] eliminated the option of replacement, and the complexity of the instrument precluded easy on-orbit maintenance.[18] Additionally, it was found that the dependence of the VOA on some ISS resources (e.g. N_2 for the IMS carrier gas, rack airflow) made it unsuitable for longer-term use on the ISS and for future exploration missions.

One of the options for a future real-time VOC monitor was a gas chromatograph-differential mobility spectrometer (GC-DMS) designed by Sionex.[19,20] This device was approximately 1/10th the volume and mass of the VOA, did not depend on ISS gas supply for carrier gas, and could be moved to different positions in the stack. Following delivery to the ISS as a technology demonstration (experiment) in 2009, this device performed extremely well at its task of quantifying a targeted list of VOCs, and NASA determined that this performance warranted the development of an operational version of the instrument.[21]

The operational version of the GC-DMS, known as the Air Quality Monitor (AQM) and now produced by Draper Labs (Cambridge, MA), incorporated some lessons learned from the experimental version. The development of the AQM has been described in detail previously,[22-28] so only a brief description of the improvements will be given here. First, during the technology demonstration, some non-target compounds were found to coelute with the target compounds. For the operational version of the hardware, this issue was minimized by providing 2 instruments with different GC column chemistries: one non-polar (DB5ms) and one semi-polar (VF-624). The second issue was a loss of sensitivity in the negative mode of the instrument (affecting the ionization of some analytes).[22,23] This issue was eventually tracked to the ingestion of the higher CO_2 levels of the ISS into the recirculation loop of the instrument and a subsequent change in negative mode chemistry. It was thought that the negative mode sensitivity issue would be alleviated by the addition of larger sieve cartridges in the recirculation system to remove CO_2; however, the negative mode continues to cause issues with analysis.[27] The final issue to be resolved was the presence of water on the preconcentrator of the instrument.[29] It was found that this water would coelute with several of the lower molecular weight alcohols/aldehydes and, depending on the overall water vapor levels, could hinder the quantification of these compounds. The operational version of the AQM added a “purge” feature that would flow clean, dry air over the preconcentrator following sample acquisition in order to remove co-adsorbed water.

The target compounds measured by the AQM (22 compounds) are a subset of the target compounds measured in archival samples (> 120 compounds). The selection of AQM target compounds was based on 3 criteria: 1) compounds routinely detected in the ISS atmosphere at measureable concentrations, 2) compounds that would represent a significant hazard if detected, and 3) compounds that could potentially affect ECLSS. Examples of these classes are 1) acetone, xylenes, and 2-butanone, 2) benzene and acrolein, and 3) ethanol, 2-propanol, and cyclic siloxanes. The current target list, and the unit on which the individual compounds are measured, is shown in **Table 1**. The atmosphere of the ISS is generally very clean, and the potentially toxic compounds are present, if at all, at extremely low concentrations. However, some compounds, those with effects on ECLSS, are often present at elevated levels. Historically, alcohols have accounted for almost 80% of the non-methane VOC concentrations measured in the ISS, with ethanol typically far greater that 70% of the total alcohol concentration.[30] To deal with these higher excursions in ethanol concentrations, the calibration levels for ethanol were raised from those required by the science requirements levied on the AQM.[31] As the concentrations of the other alcohols appeared to remain stable, though, no calibration changes were made for these compounds.

Automatic run sequences (AutoRuns) are scheduled to run on the AQMs every 73 hours. These sequences include a series of maintenance and diagnostic runs as well as the actual analytical runs. In addition to the raw data files, the AQM software also provides concentrations for the target compounds via look-up tables prepared during calibration. The AutoRuns are supplemeted with analyses that can be manually started from the Johnson Space Center (JSC) Mission Control Center in Houston, TX to coincide with nominal archive sampling (approximately every 45 days), to support contingencies, or during first ingress of visiting vehicles berthing to the USOS of the ISS. This final usage is particularly helpful, as the AQM can provide additional insight into any potential off-gas products that may have accumulated between hatch closure on the ground and docking.[32]

During initial docking of the first SpaceX Crew Dragon vehicle (SpX-DM1, uncrewed during this first flight) on March 3rd, 2019, AQM runs were initiated within 30 minutes of hatch opening as occurs with other visiting vehicles. Due to the report of an odor present in the ISS atmosphere following the docking, a request was made for the AQM data to be analyzed immediately by JSC Environmental Chemistry Laboratory (ECL) personnel. These results indicated that the isopropanol (IPA) concentration collected from AQM1 (s/n 1011) was greater than 5.9 mg/m^3 (the

Table 1. Instrument-specific compound measured on the AQM. The compounds in red are those measured quantitatively on both instruments. *Ammonia is trending-only.

AQM1 (VF-624 column)	AQM2 (DB5ms column)
Methanol	Acetaldehyde
Acetone	Ethanol
2-Propanol (IPA)	n-Butanol
Hexane	Ethyl acetate
Benzene	Dichloromethane
Hexanal	2-Butanone (MEK)
Propenal (Acrolein)	Trimethylsilanol
1,2-Dichloroethane	
Toluene	**Toluene**
Xylenes (m,p)	**Xylenes (m,p)**
Xylene (o)	**Xylene (o)**
Hexamethylcyclotrisiloxane (HMCTS)	**Hexamethylcyclotrisiloxane (HMCTS)**
Octamethycyclotetrasiloxane (OMCTS)	**Octamethycyclotetrasiloxane (OMCTS)**
Decamethylcyclopentasiloxane (DMCPS)	**Decamethylcyclopentasiloxane (DMCPS)**
Ammonia*	**Ammonia***

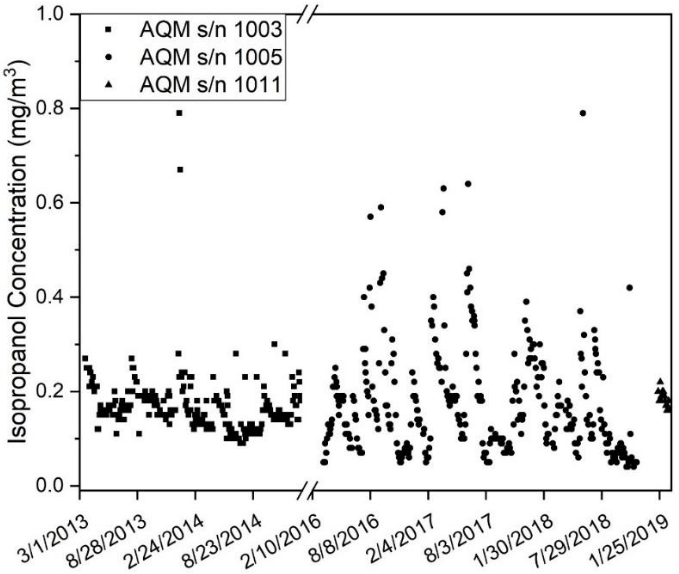

Figure 1. Isopropanol concentrations measured by the AQM on the ISS between the initial deployment in 2013 and the beginning of March 2019. The increases in isopropanol concentrations are generally associated with the docking of visiting vehicles.

upper limit of the IPA calibration curve). During docking of visiting vehicles, IPA concentrations are often seen to increase due to off-gassing during flight,[32] but throughout the time of AQM deployment on the ISS, the IPA concentration had never risen above 0.8 mg/m^3 (**Figure 1**). Based on off-gas tests performed on the SpX-DM1 vehicle prior to launch, IPA was expected to be present at first ingress, but not at such high levels. While the measured concentration was much lower than the 7-day/180-day Spacecraft Maximum Allowable Concentration (SMAC)[33] of 150 mg/m^3, it was greater than the 5 mg/m^3 total alcohol guideline that was developed to protect the U.S. Water

Recovery System (WRS). As a result of this unexpectedly high IPA concentration, Mission Control requested daily AQM analyses to monitor the IPA concentration during docked operations of SpX-DM1. During the analysis on March 4th, the IPA concentration dropped to 2.2 mg/m^3, suggesting that the elevated levels measured during first ingress could be attributed to vehicle offgassing, and the decrease was the result of ISS trace contaminant scrubbing. However, all subsequent AQM analyses over the next several days showed that the IPA concentrations were again greater than 5.9 mg/m^3, while other target analyte concentrations were normal (**Table 2**). This continued until the hatch closure and undocking of the vehicle on March 8th, at which point the IPA concentration in the US Lab returned to nominal levels (~ 0.2 mg/m^3).

With IPA concentrations stabilizing following the departure of the SpX-DM1 vehicle, efforts focused on determining the cause of the elevated levels measured by the AQM. GSCs collected during the docked operations were returned on SpX-DM1 and analyzed in the ECL at JSC. These analyses confirmed that there was a source of IPA aboard the SpX-DM1 vehicle (**Table 3**), and there were no other major discrepancies between the AQM and GSC data. The source of the elevated IPA eventually was determined to be a product of ground processing, in which the charcoal in the MegaHEPA filter used to scrub the air in SpX-DM1 had adsorbed IPA, and the IPA was subsequently

Table 2. Concentrations of target compounds in the US Lab reported by the AQMs in the time period bracketing the docking/undocking of SpX-DM1. DMCPS – decamethylcyclopentasiloxane, HMCTS – hexamethylcyclotrisiloxane, OMCTS – octamethylcyclotetrasiloxane; * - below reporting (quantification) limits

	Concentration (mg/m^3)										
	2/25/19	**3/1/19**	**3/3/19**	**3/4/19**	**3/5/19**	**3/6/19**	**3/7/19**	**3/8/19**	**3/11/19**	**3/12/19**	**3/15/19**
Acetaldehyde	0.55	0.48	0.39	0.47	0.39	0.38	0.35	0.4	0.29	0.33	0.44
Acetone	0.16	0.16	0.15	0.17	0.15	0.18	0.21	0.18		0.16	0.21
Acrolein	*	*	*	*	*	*	*	*		*	*
Benzene	*	*	*	*	*	*	*	*		*	*
Butanol	0.05	0.08	0.06	0.07	0.06	*	*	*	0.06	0.05	0.06
Dichloroethane	*	*	*	*	*	*	*	*	*		*
Dichloromethane	*	*	*	*	*	*	*	*	*	*	*
DMCPS	0.44	0.43	0.43	0.46	0.45	0.53	0.42	0.54		0.59	0.55
Ethanol	2.3	4.02	2.68	2.83	2.64	2.53	2.31	2.65	2.34	2.4	2.01
Ethyl acetate	*	*	*	*	*	*	*	*	*	*	*
Isopropanol	0.16	0.17	>5.90	2.2	>5.90	>5.90	>5.90	3.21		0.31	0.19
Hexanal	*	*	*	*	*	*	*	*		*	*
Hexane	*	*	*	*	*	*	*	*		*	*
HMCTS	0.19	0.18	0.18	0.2	0.17	0.14	0.14	0.18		0.2	0.21
Methanol	0.21	0.21	0.22	0.21	0.22	0.21	0.21	0.21		0.21	0.21
Methyl ethyl ketone	*	*	*	*	*	*	*	*	*	*	*
m,p-xylene	*	*	*	*	*	*	*	*		*	*
OMCTS	*	*	*	*	*	*	*	*		*	*
o-xylene	*	*	*	*	*	*	*	*		*	0.05
Toluene	0.03	0.03	0.03	0.03	0.03	0.03	0.05	*		0.04	0.05
Trimethylsilanol	0.09	0.08	0.08	0.09	0.07	0.05	0.07	0.09	0.09	0.1	0.11

Table 3. Isopropanol concentrations determined post-flight from GSCs returned on the SpX-DM1 vehicle

	Concentration (mg/m^3)			
	SpX-DM1 Ingress (3/3/19)	**SpX-DM1 Egress 1 Contingency (3/7/19)**	**SpX-DM1 Egress 2 (3/7/19)**	**SpX-DM1 After Splashdown (3/10/19)**
Isopropanol	5.2	0.81	2.3	1.2

released during flight. However, even though the concentrations in SpX-DM1 were elevated, they were not a credible source of the levels measured by the AQM. For example, while the first ingress GSC showed an IPA concentration of 5.2 mg/m^3, the concentration measured by the AQM should have been much lower as the SpX-DM1 vehicle concentration became diluted following diffusion through the ISS to the U.S. Lab, where the AQMs are located.

During this time, analysis of the AQM data continued in an attempt to understand the results from the SpX-DM1 docked operations. The changes in the gas chromatograms in the time before SpX-DM1 and during docked operations are striking. As seen in **Figure 2A**, prior to SpX-DM1, IPA appeared in the chromatogram as a very symmetric peak centered around a retention time of 128 seconds. Upon hatch opening, however, the peak height and width increased dramatically, and a shoulder appeared on the trailing edge, suggesting the presence of some unknown species (**Figure 2B**). These changes were also seen in the non-specific scan runs (used for manual analysis) of the AQM, as well.

In the 5 weeks following the departure of SpX-DM1, the IPA concentration on the ISS averaged ~ 0.16 mg/m^3, consistent with what had nominally been found via archival sampling throughout the life of the ISS. Additionally, the chromatographic peak shapes returned to normal (**Figure 3A**). However, with the docking of another visiting vehicle on April 19th (Northrup Grumman-11, NG-11), the IPA concentration measured by the AQM once again increased dramatically, and the unknown contaminant and changes in the GC spectra also returned (**Figure 3B**). Subsequent ground analysis of GSCs confirmed an elevated IPA concentration during ingress of the vehicle, but, as with SpX-DM1, the AQM concentration was significantly higher than expected due to off-gassing of the vehicle and the diffusion of the elevated IPA through the stack. Other nominal GSCs also continued to show elevated IPA.

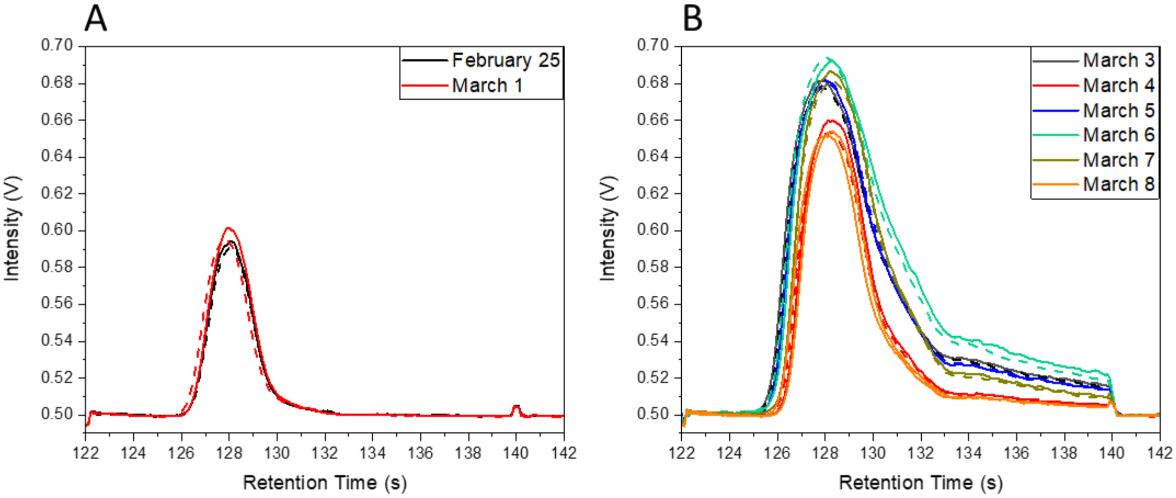

Figure 2. Changes in gas chromatogram traces for IPA from before (A) and after (B) docking of SpX-DM1 to the ISS. The dotted lines represent the second run of each day.

The question of why the AQM was providing incorrect, high-biased IPA readings was now joined by the question of the cause of elevated IPA in archival samples. AQM analysis of compounds detected at trace levels in both SpX-DM1 and NG-11 in GSCs (R-134a, isobutane, and 1-propanol) did not show effects on the IPA spectrum. Additionally, during NG-11 docked operations, there were no significant IPA releases reported, and there were no payloads containing large quantities of IPA delivered or operating in this timeframe. However, two pieces of hardware were delivered on NG-11 that were identified as potential sources of elevated IPA: Charcoal HEPA Integrated Particle Scrubbers (CHIPS)[34] and the Thermal Amine Scrubber (TAS).[35,36] The CHIPS filters were installed to aid in the reduction of airborne chemical and microbial contaminants. However, the vendor confirmed that these filters were processed in a facility that uses IPA, and final cleaning of the assemblies was performed with IPA. It was hypothesized that, similarly to the SpX-DM1 MegaHEPA filter, the charcoal in the CHIPS filter was adsorbing IPA and then releasing it into the atmosphere after being displaced by more strongly-bound species. The TAS is a carbon dioxide removal technology demonstration for which data from ground testing had shown elevated levels of IPA and acrylonitrile in some samples. GSCs collected around TAS operations on the ISS were also found to contain traces of acrylonitrile in addition to the elevated IPA.

While the CHIPS filters and TAS operations offer a plausible explanation for overall elevated IPA levels, there remained the question of the incorrect AQM readings. Here, we will detail our attempts to account for these extraordinarily high readings. The results will show that the "purge" feature of the AQM (included in almost all runs) could potentially be overloading the system by ingesting excess IPA, resulting in carryover from run-to-run.

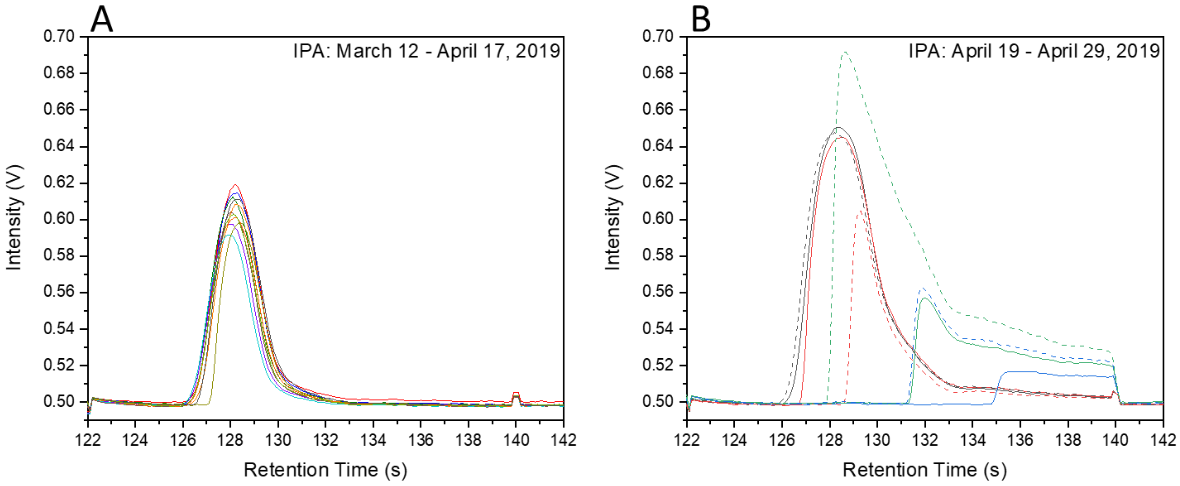

Figure 3. Gas chromatogram traces for IPA in the period (A) between SpX-DM1 undock and NG-11 docking and (B) following the docking of NG-11. The dotted lines represent the second run of each day.

II. Experimental

The details of the operational AQM and its use on the ISS have been described previously.[24,25] The methods loaded on the AQM prior to delivery to the ISS are the same used in the current work. The basic methods consist of "instrument" methods that define the temperature of the preconcentrator and GC column as a function of time and "GC" methods that define the compound-specific windows (retention time window, dispersion voltage, and compensation voltage [C_V]) during the run. For automated on-orbit performance, scripts detailing specific method combinations are available. These are started from Mission Control and allow the AQM to run without any further input from the ground. These scripts contain a number of clean runs interspersed with sample and no sample (blank) runs using GC methods as well as sample/no sample "scan" runs, in which all C_Vs are scanned during a single run. This type of run provides information on the presence of potential unknown compounds and instrument health but does not have the same sensitivity of regular "GC" runs. Additionally, it should be noted that the vast majority of runs include the purge as part of their instrument methods.

III. Results and Discussion

In June of 2019, a failure of AQM2 (s/n 1019) occurred on orbit, and the ECL was tasked with preparing a replacement unit. Following calibration and science verification testing, this unit (s/n 1010) was transferred off-site to the Human Health and Performance Contract (HHPC) flight hardware team for final flight preparation. As part of this preparation, an AutoRun of the unit is performed to ensure that the automated script works without any issues. Upon analysis of the data from these runs, it was discovered that an analyte peak in the acetone/IPA region (these compounds coelute on AQM2) had appeared (**Figure 4**). Interestingly, this peak appeared in the no sample scan run completed *before* any sample runs had occurred. This suggested the presence of contamination in the system, but no contamination was seen in the ECL during calibration and science verification. While VOC usage is tightly controlled in the ECL in order to reduce interference with the analytical instruments, no such controls are generally in place in the HHPC flight hardware labs. In these labs, IPA is commonly used to clean hardware prior to flight. As such, a source of the contamination had been located, but it is unclear as to why it was showing up in runs where no samples had been collected. To better understand this issue, ground testing was performed in the ECL with a non-flight unit. Initial testing included (*Test 1*) powering on the AQM with no IPA present, (*Test 2*) powering on the AQM in an atmosphere containing IPA but then removing the IPA source prior to performing any runs, and (*Test 3*) powering on the AQM in an atmosphere containing IPA and maintaining the source while runs were performed. *Test 1* showed no presence of IPA in the initial data runs. The results of *Tests 2* and *3* are shown in **Figures 5** and **6**. In both figures, it can be seen that, when the AQM is powered on in a background containing IPA, a peak corresponding to IPA can be seen in the very first run performed (a high temperature clean run). In **Figure 5**, when the IPA source is removed prior to the initiation of the run sequence, the IPA contaminant is no longer present by the second clean run. In **Figure 6**, though, when the IPA source remains present, the IPA contaminant grows larger with each run, even when these runs do not include sample collection. These results suggest the following:

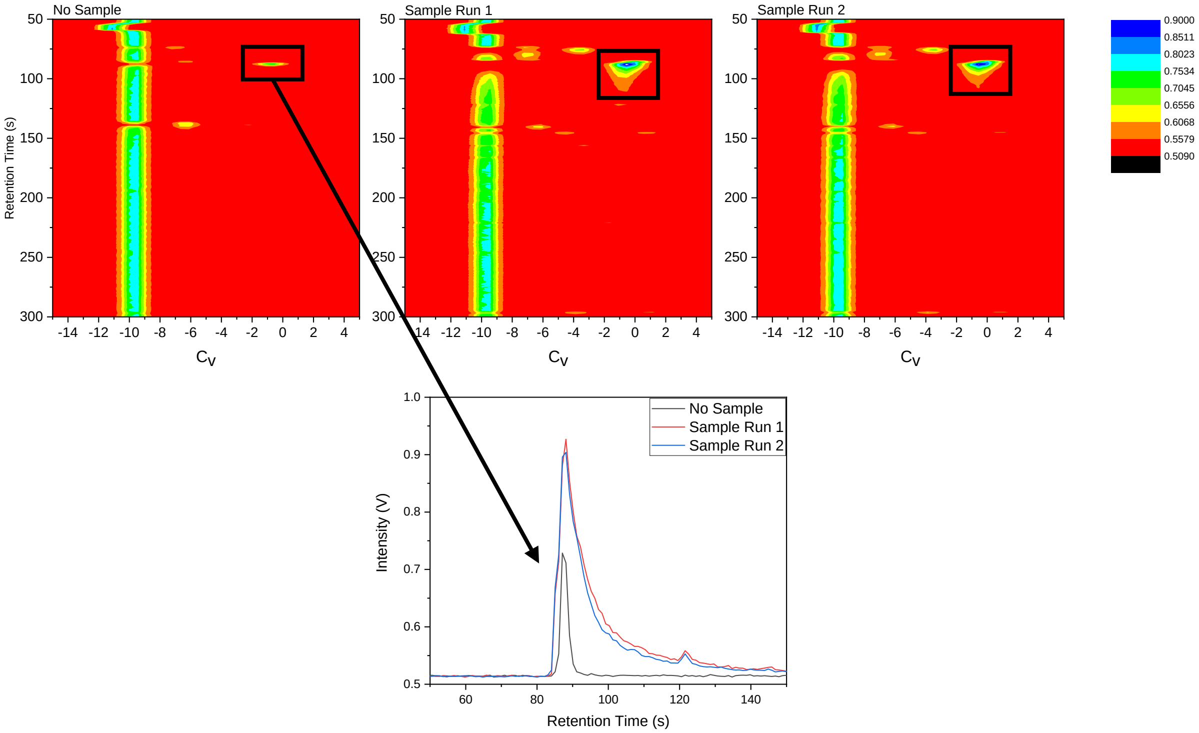

Figure 4. Scan runs showing the presence of IPA in no sample and sample scan runs during an AutoRun initiated during final flight processing when no IPA should be present. A GC trace at the appropriate IPA C_V is plotted to show the overall change.

- *Test 1*: If the AQM is powered on in a background containing low (or no) IPA, there will be no contamination in the initial non-sample runs
- *Test 2*: If the AQM is powered on in an atmosphere containing IPA, and that source is removed prior to the commencement of any runs, then the IPA contaminant will be removed by the sieve cartridges and initial clean runs

- *Test 3*: If the AQM is powered on in an atmosphere containing IPA, and that source remains, then IPA accumulates in the system during the initial non-sample runs, regardless of the scrubbing provided by the sieve cartridges

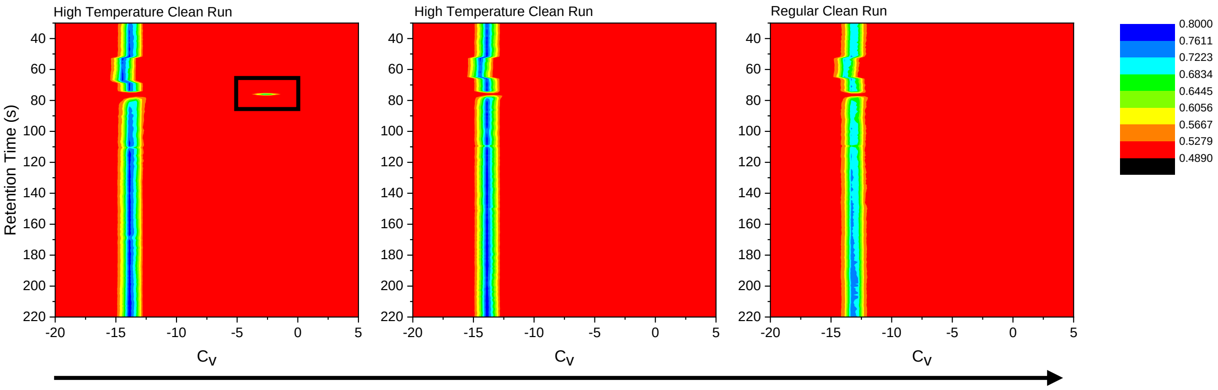

Figure 5. Scan runs performed as part of *Test 2* immediately following power-up of the AQM in an atmosphere containing IPA. The IPA was removed before starting the run sequence.

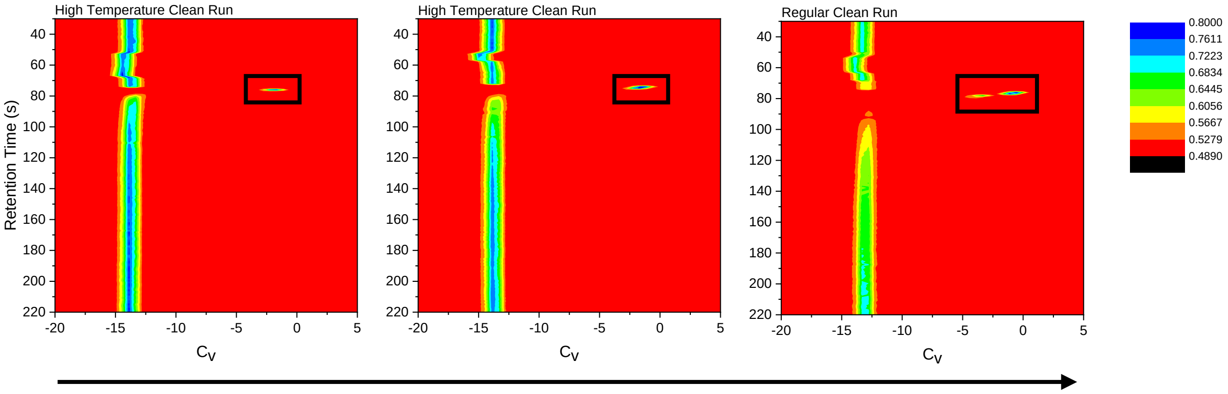

Figure 6. Scan runs performed as part of *Test 3* immediately following power-up of the AQM in an atmosphere containing IPA. The IPA source remained as the run sequence was begun.

The results of **Figures 5** and **6** show the effects of background IPA upon the spectra obtained from the AQM following start-up procedures. However, the effects of high transient and/or sustained IPA concentrations are still a concern. The assumption throughout the life cycle of the AQMs has been that high transient concentrations (such as those seen when testing at the top of the calibration range) do not lead to long-term carryover, as subsequent clean and no sample runs will cause any remaining species to be trapped in the absorbent materials of the sieve cartridges. **Figure 7** shows that this is indeed the case. In this test, neat IPA was held to the sample inlet of the AQM as the instrument collected a sample and began the run. Following sample collection, the IPA was removed. The figure shows a large peak arising from IPA in the sample run. Following this run, multiple clean runs were performed to understand the longevity of the contaminant. As can be seen, a peak arising from IPA is present even after 5 clean

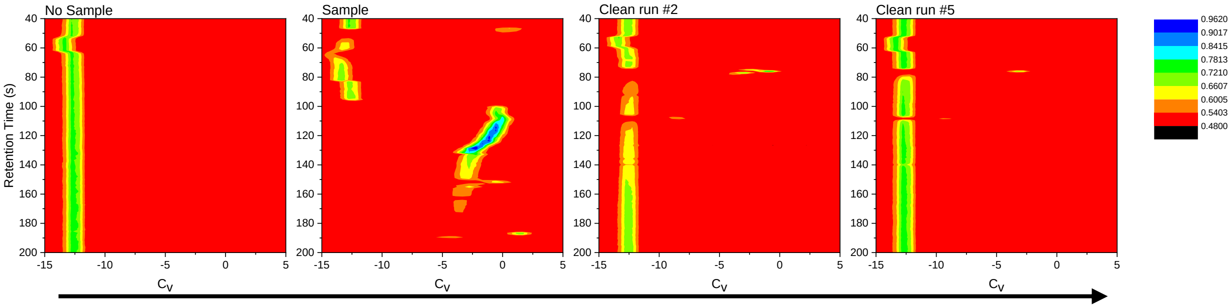

Figure 7. Scan runs showing the effects of high transient IPA concentrations on the spectra obtained from the AQM. Carryover of the IPA is present even following 5 clean runs but was removed after the subsequent clean run. The retention time change of IPA between sample and clean runs are due to different GC heating profiles.

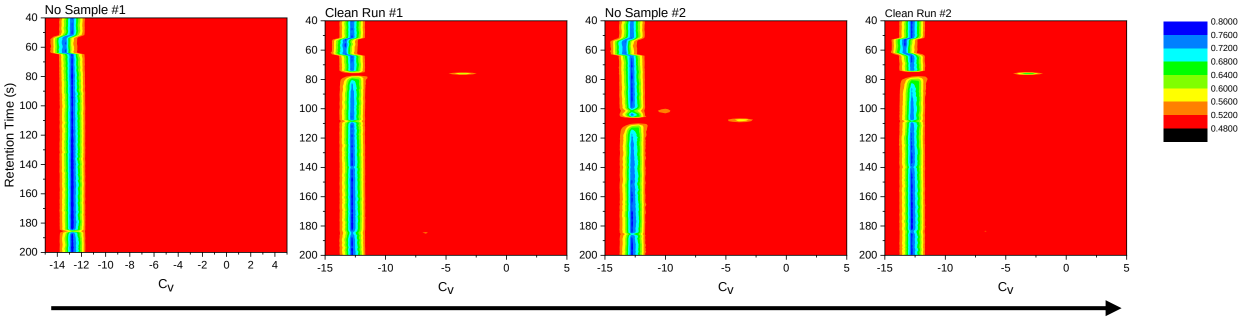

Figure 8. Scan runs showing the effect of exposure of elevated IPA to the AQM purge inlet during non-sample runs (beginning with Clean Run #1).

runs; a subsequent clean run showed no evidence of the IPA. Note that this IPA concentration is abnormal, and even the highest concentrations tested during calibration do not require this level of cleaning.

The final attempt to understand the effects of background IPA involved the exposure of the purge inlet to IPA during non-sample runs. **Figure 8** shows the build-up of IPA in the system occurring over a number of runs. Here, during the first no sample run, the AQM was simply exposed to laboratory air, and a clean spectrum was obtained. For the next run (Clean #1), neat IPA was held to the purge inlet, and this was repeated in alternating clean and no sample runs. This exposure resulted in the appearance of an IPA peak, and this peak grew larger with each subsequent run. With the removal of the IPA from the area of the purge inlet, a single clean run removed the contamination. These results clearly prove that continued operation of the AQM in the presence of elevated IPA (or, presumably, any other compound), could lead to interference in nominal target compound measurements.

While it is important that these results confirmed the theory that the elevated IPA reported by the AQM during SpX-DM1 and following NG-11 docking could be traced to the overall elevated levels on the ISS, another question arises. Namely, is the method of calibration used for the AQM since the first deployment actually appropriate? The current/legacy calibration methods utilize a “slip-stream” approach, in which the AQM collects sample split from a main, faster flow of mixture. With this method, the purge inlet is exposed to laboratory air, so there is no extra buildup of VOCs arising from the purges that are included with almost every run. The assumption accompanying this method, and one that was valid based on years of ISS data, is that there is no *consistent* elevated concentration of any particular compound in-flight.

Following an on-orbit failure, AQM s/n 1011 (AQM1) was returned to ground and repaired. As part of a separate investigation aimed at determining if the sensitivity towards benzene had decreased, this AQM was connected to the same sample introduction setup used during pre-flight verification testing (i.e. the "SVT" setup, **Figure 9**), and the same procedures were performed. As can be seen in **Table 4**, the average IPA concentration reported by the AQM during this testing was approximately half of the actual concentration measured by the ground-based ECL instrumentation (GC and GC-MS), showing that significant sensitivity had indeed been lost. Note that the results from the no sample runs performed as part of this testing were "not detected," indicating that the integrated area reported by the instrument did not meet the threshold for a numerical result. However, looking at the GC traces for the no sample runs (**Figure 10**; the sample traces are included for reference) provide a little more information. Here, we can see that, although the chromatograms for the sample runs are relatively consistent, successive no sample runs begin to show evidence of IPA in the chromatograms. This behavior had been seen previously, but, with the peaks being small and with no resultant output above the minimum detection limit (MDL), no action was taken to understand their presence.

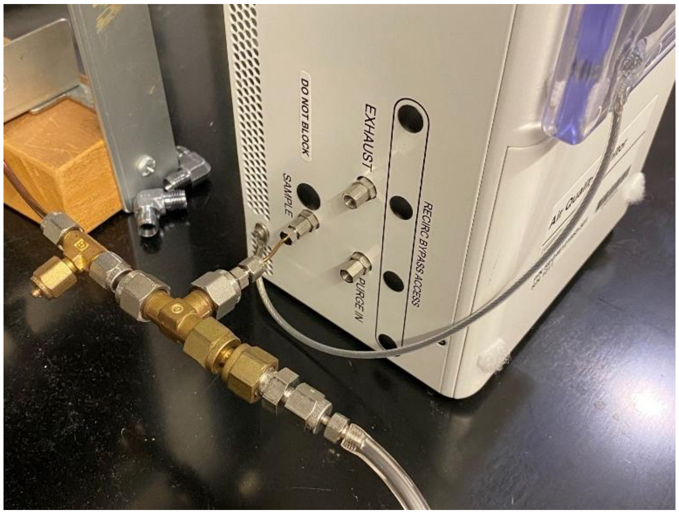

Figure 9. Science Verification Testing (SVT) setup, in which the test mixtures are sampled by the AQM in a slip-stream approach. In this configuration, the purge inlet pulls from the the laboratory air, which is at a lower concentration than the elevated transient concentrations experienced by the sample inlet.

Table 4. IPA concentrations (mg/m^3) measured during testing of AQM s/n 1011 following its return/repair from the ISS using the standard SVT setup. ND – Not Detected.

	Run 1	Run 2	Run 3	Run 4	Average AQM Concentration	Actual Concentration
Sample	0.7	0.72	0.65	0.63	0.68	1.35
No Sample	ND	ND	ND	ND	ND	

Following testing using the SVT setup, the AQM was placed into a separate test setup that allowed both the sample and purge inlets to pull from the same atmosphere (the “Kin-tek” setup, **Figure 11**), as they would do in flight. When the instrument was exposed to the same IPA concentration as used during the SVT testing, the results were quite different (**Table 5**). Here, the overall concentration is ~ 13% higher than the results from the SVT testing. More importantly, the no sample runs were now showing reportable results from the beginning of the tests. This can be seen more clearly in the GC traces of **Figure 12**. In these chromatograms, the peak height of the IPA is noticeably higher than in the SVT testing. Additionally, starting with the first run, the no sample chromatograms are well above the baseline, reinforcing the conclusions from the earlier tests that the purge inlet is responsible for the increase in IPA seen when there is an extended increase in concentration.

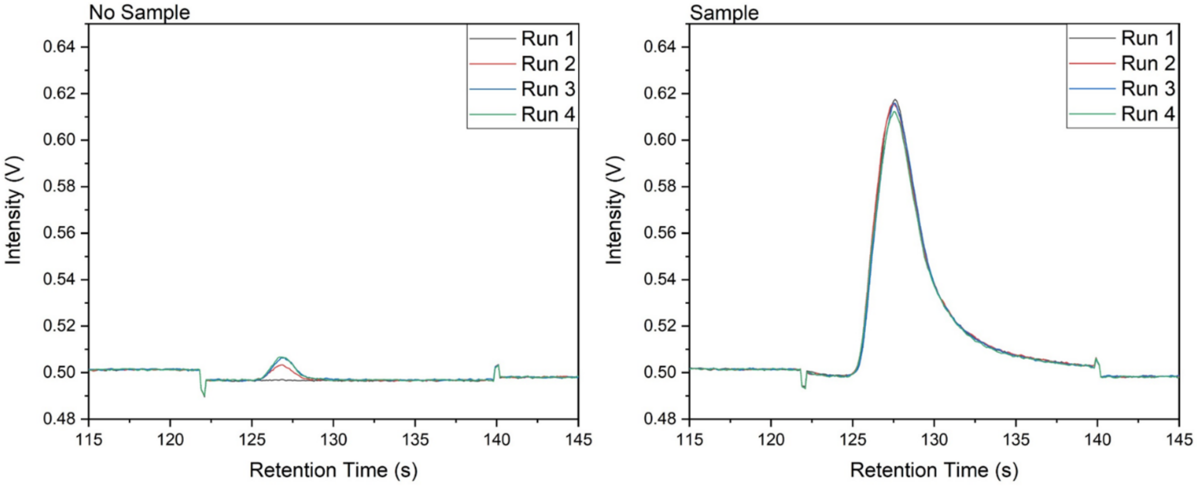

Figure 10. GC traces of IPA peak obtained during failure investigation of AQM s/n 1011 using the SVT setup. Note that, while the sample peak is consistent over multiple runs, the no sample peak increases with successive runs.

Table 5. IPA concentrations (mg/m^3) measured during testing of AQM s/n 1011 following its return/repair from the ISS using the Kin-tek setup, in which both the sample and purge inlets are exposed to the test gas. Note that the actual concentration of the test gas was 1.35 mg/m^3.

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Sample	0.74	0.87	0.74	0.77	0.62	0.91
No Sample	0.06	0.06	0.06	0.06	0.06	0.06

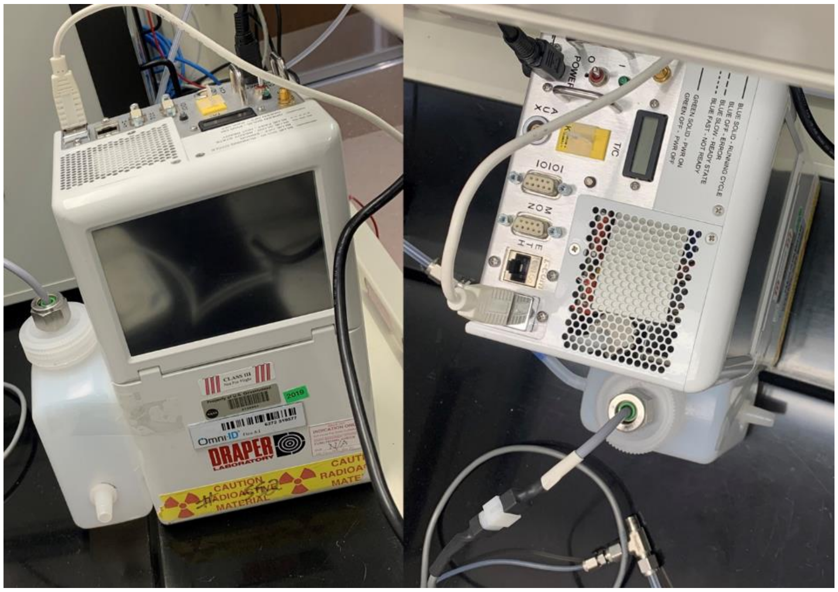

Figure 11. Kintek setup, in which the test mixture is exposed to both the sample and purge inlets at the same time. This configuration more closely accounts for the potential of consistent elevated concentrations of VOCs in the ISS atmosphere.

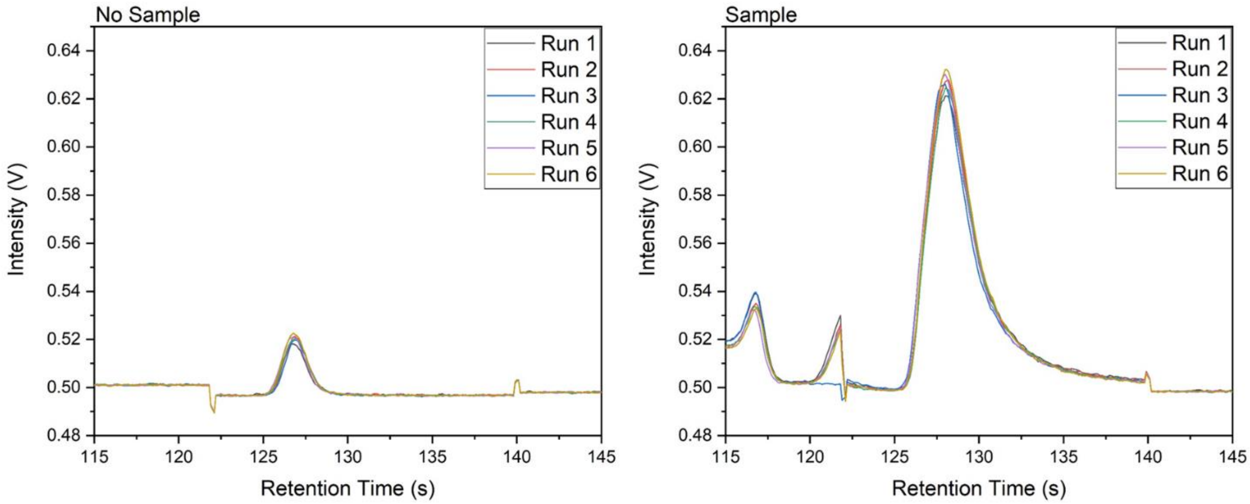

Figure 12. GC traces of IPA peak obtained during failure investigation of AQM s/n 1011 using the Kin-tek setup. Here, the no sample peak is consistently above the baseline.

IV. Conclusion

For almost a decade, the calibration and testing of the ISS Air Quality Monitor has been performed using methods that allow the purge option of the instrument to pull from the ambient lab air, while the sample port is exposed to calibration standards. While this method was based on long-term experience with the spacecraft atmosphere, in which most VOC excursions are short term, it does not account for extended elevated analyte concentrations. An assessment of the data provided by the AQM following saturation of the unit with IPA during the SpX-DM1 mission, during the NG-11 mission, and following the NG-11 mission shows that the standard calibration and testing method may no longer be acceptable, and future efforts to prepare AQMs for flight will need to take into account the additional sample provided by the purge while ensuring that any calibration changes do not affect the ability of the AQM to perform in more nominal environments.

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