The Air Quality Monitor "Benzene" Anomaly: Ground Testing and On-going Effects

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The International Space Station (ISS) Air Quality Monitors (AQMs) have provided targeted in-flight analysis of volatile organic compounds (VOCs) in the ISS atmosphere since early 2013. During their initial half decade of use (which included multiple sets of units), the AQMs performed well, meeting their validation criteria and showing excellent accuracy compared to archival samples. In addition to routine environmental monitoring, the AQMs have also been used during a number of contingency situations and investigations related to Environmental Control and Life Support Systems (ECLSS). These include a potential ammonia leak, increases in atmospheric ethanol, and efforts to locate potential sources of polydimethylsiloxanes that lead to the production of dimethylsilanediol (DMSD) in the US Water Processor Assembly (WPA). As the fleet of AQMs has aged, several issues have arisen. These have ranged from pervasive problems on electronics boards to loss of sensitivity due to operating in an elevated CO_2 environment. The most notable issue encountered during on-orbit operations was incorrect identification of compounds. This initially occurred in mid-2020, when AQM1 reported the presence of benzene. While the AQM team questioned the validity of these results, the concentration of the "benzene" continued to increase and eventually exceeded the 30- and 180-day Spacecraft Maximum Allowable Concentration (SMAC). This led to wide-ranging efforts by a number of groups aimed at understanding the situation and identifying the source of the "benzene." AQM1 failed after being relocated to the Russian Segment as part of the investigation, and the unit was returned for evaluation. When archive samples collected while the AQM was measuring elevated benzene showed no detectable benzene, the focus of the investigation shifted to determining the cause of the false positive readings. Here, we will discuss the results of this nvestigation by the AQM team, potential causes of the interference, and subsequent reporting of AQM1 results.

Nomenclature

AQM	=	Air Quality Monitor
BFE	=	Bacteria Filter Element
C_V	=	Compensation Voltage

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DMCPS	=	Decamethylcyclopentasiloxane
DMS	=	Differential Mobility Spectrometry
DMSD	=	Dimethylsilanediol
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
HMCTS	=	Hexamethylcyclotrisiloxane
ISS	=	International Space Station
JSC	=	Johnson Space Center
MART	=	Multilateral Anomaly Resolution Team
NESC	=	NASA Engineering and Safety Center
OMCTS	=	Octamethylcyclotetrasiloxane
PDMS	=	Polydimethylsiloxane
PPE	=	Personal Protective Equipment
RHS	=	Reactor Health Sensor
RIP	=	Reactant Ion Peak
RS	=	Russian Segment
SM	=	Service Module (Russian)
SMAC	=	Spacecraft Maximum Allowable Concentration
SVT	=	Science Verification Testing
TMS	=	Trimethylsilanol
TOC	=	Total Organic Carbon
USOS	=	United States Operating Segment
VCB	=	Vehicle Control Board
VOA	=	Volatile Organic Analyzer
VOC	=	Volatile Organic Compound
WPA	=	Water Processor Assembly

I. Introduction

As a semi-closed environment, it is necessary to monitor the air and water of spacecraft for chemical contaminants to ensure the safety of both the crew and spacecraft systems, with the type of required sampling generally being a function of the mission length. For short missions (up to a few weeks), archival samples are generally sufficient, while longer missions (months to years) require a combination of archival and in-flight monitoring due to the substantial timeframes that can occur between archival sample collection and ground-based analysis. Environmental monitoring techniques through the first 15 years of the ISS have been described previously.[1]

In early March 2013, the Air Quality Monitors (AQMs) were activated on the ISS. These instruments had been selected by the ISS Program[2] to replace the legacy Volatile Organic Analyzer (VOA) following a successful technology demonstration.[3-6] As part of the check out of these instruments, they underwent a 9-month validation to determine if results provided by the AQMs were accurate in comparison to the “gold standard” archival samples.[7, 8] This validation was successful, and these AQMs began to be used, in combination with other data, to make operational decisions. During the first several years of AQM use, they were used in a number of contingency operations where they were able to provide data that could be used by Mission Control and Subject Matter Experts to make operational decisions.

On January 14, 2015, an alarm indicated an ammonia leak near Node 2 of the ISS. As part of the emergency procedures, the US crew evacuated to the safe haven of the Russian Service Module (SM). There continued to be pressure fluctuations in the US Lab indicative of an ammonia leak, but the crew did not smell ammonia or experience any symptoms of high ammonia exposure. While the Environmental Control and Life Support Systems (ECLSS) team suspected a false alarm after reviewing downlinked data, there were still only two options to verify: 1) send the crew, with personal protective equipment (PPE), into the unknown US Lab atmosphere to perform measurements using Dräger tubes or 2) command the AQM from the ground to analyze the atmosphere and downlink the data. While the

AQM was originally meant to monitor ammonia in the 1-10 ppm range, ingestion of larger concentrations would lead to a large shift in the reactive ion peak (RIP), thereby providing a "yes/no" answer regarding the presence of ammonia. Following activation of the AQM, the results shown in **Figure 1A** were obtained (with a pre-flight ammonia calibration shown in **Figure 1B**). In **Figure 1A**, the RIP is present at a compensation voltage of ~ -10 V, which is the standard position during nominal operations. In **Figure 1B**, it can be seen that exposure of the AQM to 4.4 ppm ammonia leads to the reduction of the nominal RIP and the onset of a second RIP, this one at ~ -14.5 V. Further increases in ammonia concentration during AQM preparation were observed to lead to an increase in the intensity of this new RIP. As such, this data showed that any ammonia on the ISS was present at low levels, thereby confirming the analysis of the ECLSS team. Given the seriousness of the situation, the crew was still required to perform further analysis (with PPE) using other techniques, but the AQM permitted them to enter with high confidence that they were not entering a harmful environment and were not putting themselves or their safe haven at risk.[9, 10]

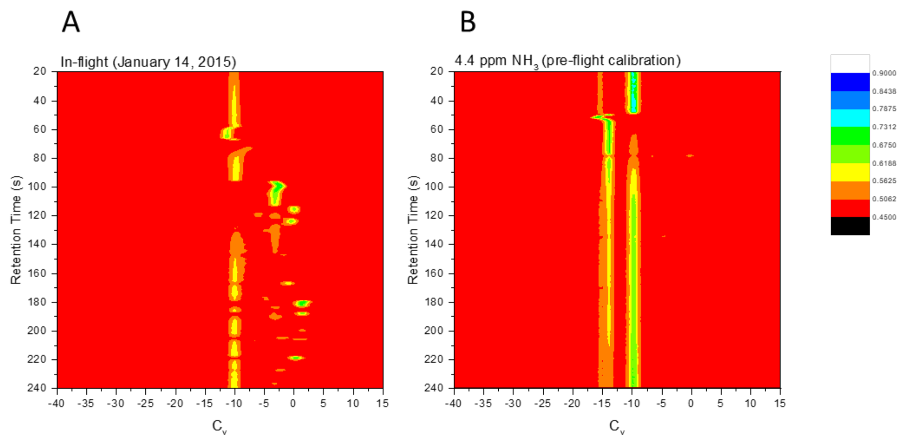

Figure 1: Scan runs obtained from AQM 1 (s/n 1004) during (A) in-flight operations in January 2015 and (B) pre-flight calibration. The additional RIP at a C_v of -14.5V in (B) shows the presence of ammonia. Note that this RIP is not present in (A), indicating that ammonia was not present in any quantity of concern.

A second off-nominal use of the AQMs occurred in the spring of 2015, when elevated conductivity was detected in the effluent of the US Water Processor Assembly (WPA). This elevated conductivity required extended reprocess cycles to allow the WPA to provide potable water.[11] Interestingly, after suitable conductivity was recovered, the addition of new condensate to the WPA led to additional conductivity increases, while the addition of urine distillate did not. This, combined with the observation of higher-than-normal levels of several alcohols in a November 2014 humidity condensate sample, suggested that it was the presence of elevated levels of volatile organics in the condensate leading the conductivity and reprocessing trends. Unsurprisingly, the AQM had been reporting elevated levels of ethanol in the ISS atmosphere for approximately a year, though the levels had begun to increase further in early 2015.[12] While the new levels being reported (~12 mg/m^3) were well below the Spacecraft Maximum Allowable Concentration (SMAC) for human health (2000 mg/m^3),[13] they were above the general < 5 mg/m^3 alcohol guideline developed to protect the WPA. The AQM team worked closely with ECLSS engineers during this time to provide up-to-date information on concentrations as a Multilateral Anomaly Resolution Team (MART) began a search for possible sources of ethanol. Eventually, the atmospheric ethanol levels decreased, though cycles of increasing and decreasing concentration continued to be observed over the next few years; as these were generally not to the same extent as the spring 2015 excursion, further RHS increases did not occur, and there was no root cause discovered for the elevated ethanol concentrations.

A third use of the AQM for off-nominal situations occurred in May 2016 and was related to the presence of dimethylsilanediol (DMSD) in humidity condensate and product water produced by the WPA. Following the discovery of DMSD as the source of elevated total organic carbon (TOC) in 2010,[14] efforts began to eliminate DMSD in the condensate by reducing atmospheric precursors, known to be polydimethylsiloxanes (PDMS) and trimethylsilanol (TMS).[15, 16] As part of these efforts, the ECLSS team replaced four of the Bacteria Filter Elements (BFEs) in Node 1 of the ISS with scrubbers containing activated charcoal.[17] Based on the results from the AQM,

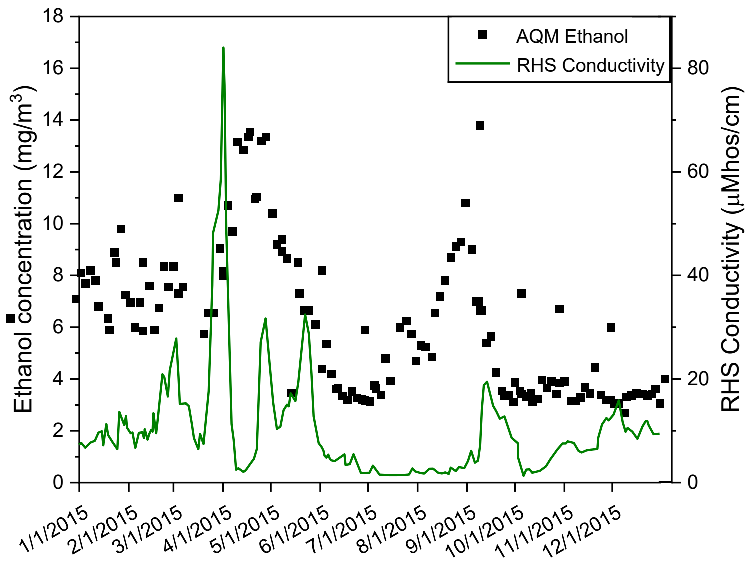

Figure 2: Correlation between atmospheric ethanol as measured by the AQM and conductivity in water (measured by the Reactor Health Sensor - RHS) entering the catalytic reactor of the WPA in 2015. During this period, the TOC of the humidity condensate was also elevated.

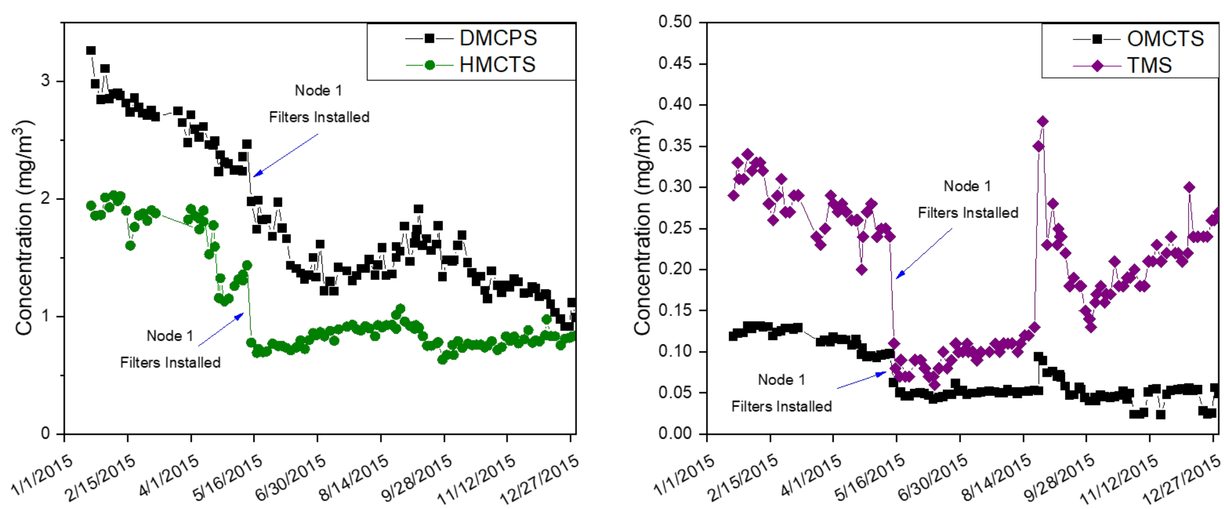

Figure 3: Concentrations of polydimethylsiloxanes and trimethylsilanol in the ISS atmosphere during 2015. Note the substantial concentration drop following the installation of charcoal filters in Node 1 in May. DMCPS – decamethylcyclopentasiloxane; OMCTS – octamethylcyclotetrasiloxane; HMCTS – hexamethylcyclotrisiloxane.

the scrubbers were indeed successful at reducing the levels of PDMS and TMS (**Figure 3**), but there was no corresponding decrease in the concentration of DMSD in the condensate.

A theory regarding this apparent inconsistency suggested that perhaps there were transient higher levels of siloxanes in Node 3 near the condensing heat exchanger and that the levels reported by the AQMs in the US Lab were not a true representation of what was reaching the Node 3 heat exchanger. In order to test this theory, an AQM was positioned in Node 3 to monitor siloxane levels during condensate collection following a routine 30-day dryout. **Figure 4** shows that, not only was the siloxane data from 2 different AQMs very similar, the data from the Lab unit matched the Node 3 unit extremely well (note that AQM 1005 was not calibrated for TMS due to coelution with other

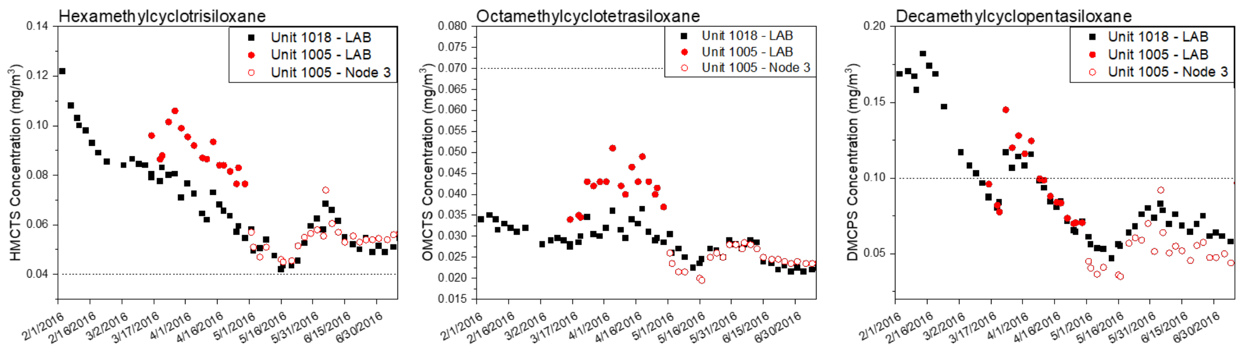

Figure 4: Atmospheric concentrations of 3 PDMSs as measured by the AQM in early-to-mid 2016. The open markers show the concentrations while AQM s/n 1005 was relocated to Node 3 to support an ECLSS investigation into transient PDMS concentrations.

target compounds). Therefore, while the AQMs were not able to provide a cause for the elevated condensate DMSD, they allowed the ECLSS team to move on to other theories for DMSD mitigation.

The events described above point to the benefits of having a small, portable analyzer with remote operation capabilities. However, as the AQM fleet has aged, some unexpected problems have arisen. The first of these was observed in 2019 with the docking of SpaceX-Demo1, when the AQM reported extremely high levels of isopropanol in the atmosphere.[18] An investigation showed that, while elevated isopropanol had been present (and was present again during Northrup-Grumman-11), the concentrations reported by the AQM were excessively high, a situation resulting in part to legacy methods of calibration and verification in the face of unexpected, non-transient levels of individual compounds; these methods did not account for the potential accumulation of high levels of individual compounds in the recirculation loop of the AQM. Regardless, the effects of potentially high levels of isopropanol on the WPA could be mitigated by using less (or no) condensate for processing operations. More recent events, however, led to much greater concerns.

Beginning on April 13, 2020, AQM s/n 1011 began to report the presence of benzene in the ISS atmosphere. While the AQM team was skeptical regarding the presence of benzene, largely based on experience during the technology demonstration of the GC-DMS instrument,[6] a review of the available data did not suggest that something other than benzene was being detected. Concentrations continued to rise in early May and remained at that level until May 12th.[19] Though the AQM team was still working through potential causes for the benzene concentrations, available time in the crew schedule led to the internal AQM sieve packs being replaced early as part of nominal 6-month maintentance procedures. This introduced a new variable and complicated the investigation. When issues arose immediately with the new sieve cartridges, a second set was installed on May 14th. Over the next several weeks, the benzene concentrations being reported by the AQM began to increase further and exceeded both the 180-day (0.2 mg/m^3) and 30-day (0.3 mg/m^3) SMACs.[13] As these limits were associated with long-term exposure to benzene, brief exceedances of these SMACs have previously been deemed acceptable by JSC Toxicology and flight surgeons, but the continued increases triggered a number of actions aimed at reducing the benzene concentration and determining the potential sources. These actions were largely captured in a JSC Knowledge Capture case study.[20] While this case study aims to show the massive efforts made to understand the purported presence of benzene, it points to some issues with bringing in stakeholders largely unfamiliar with certain technology or spaceflight conditions. These include: 1) stakeholders need to be aware of what is happening, but they may not have the technical expertise to provide meaningful input, 2) a continually-growing team slows progress as new team members need to be continually educated on processes and conditions, and 3) while outside experts are an important resource, their lack of understanding of spaceflight conditions and history can impair their ability to provide relevant assistance. However, the institutional heft of a NASA Tiger Team, including individuals from other NASA centers, members of the NASA Engineering and Safety Center (NESC), and outside experts, pushed certain efforts that may not previously have been possible.

In an attempt to gain further insight into the alleged benzene, split atmosphere operations between the Russian Segement (RS) and US Operating Segment (USOS) were initiated on June 11, 2020, and AQM 1011 was relocated to the RS for the first time (the AQM had not previously been certified for operations in the RS). During these operations, in which multiple autorun sequences were performed, the reported benzene concentration was very similar to the results seen in the USOS prior to the move, suggesting that the source of the benzene was not in the RS. Unfortunately, upon being returned to the USOS, AQM 1011 failed upon power-up. This unit was returned on SpaceX-Demo2 to support a benzene source investigation. At the same time, GSCs were returned and analyzed in the JSC Environmental Chemistry Laboratory (ECL). In agreement with other methods that had been brought to bear on the ISS, these samples showed no detectable benzene in the ISS atmosphere. As such, the investigation of AQM 1011 shifted to determining what had caused the false positive benzene readings. Following the repair of AQM 1011 by Human Health and Performance Contract (HHPC) Engineering personnel, the unit was transferred to the ECL for ground testing.

II. AQM Ground Testing Design

The details of the operational AQM and its use on the ISS have been described previously.[2, 7] 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 a purge through a separate port as part of their instrument methods.

As described previously,[18] it had been determined that the legacy methods of preparing and verifying the AQMs (the so-called Science Verification Testing [SVT] setup) would not necessarily provide accurate results under abnormal conditions due to the purge inlet not being exposed to test compounds. For the testing described here, the improved "Kintek" setup was used; this not only allowed both the sample and purge inlets to be exposed to the test gases but also allowed for increased testing durations through the use of clean house air (zero air) and larger cylinders of test mixtures as opposed to single 6 L canisters.

The test plan approved by the ISS Vehicle Control Board (VCB) on August 24, 2020 aimed at understanding if:

1. The AQM was operating nominally.
2. The AQM could still detect benzene.
3. There was carryover from previous benzene exposures.
4. The AQM was responding correctly to other target analytes.
5. There was carryover from previous target exposures.
6. Other compounds detected in GSCs could be responsible for the benzene responses.

To answer these questions, the following steps were planned for testing:

1. Both the sample and purge ports would be exposed to clean air, and a series of autorun scripts would be performed to check for the presence of contamination in the system.
2. Both the sample and purge ports would be exposed to standards with known concentrations of benzene, and a series of autoruns would be performed (1) to confirm that the AQM could still detect benzene and (2) to check for accumulation in the system.
3. Both the sample and purge ports would be exposed to clean air, and a series of autoruns would be performed to check for carryover from the previous benzene exposures.
4. Both the sample and purge ports would be exposed to known concentrations of other target analytes, and a series of autoruns would be performed to confirm that the AQM could still detect all target analytes.
5. Both the sample and purge ports would be exposed to clean air, and a series of autoruns would be performed to check for carryover from the previous target compound exposures.
6. Both the sample and purge ports would be exposed to known concentrations of potentially-interfering compounds identified in the GSCs returned on SpaceX-Demo2, and a series of autoruns would be performed to check for false positive benzene readings.

III. Ground Testing of AQM 1011

Chromatograms from no sample runs from the final in-flight sampling session, during the 1st clean air exposure on the ground, and during the 5th clean air exposure on the ground are shown in **Figure 5**. Here, the benzene retention time is marked with an asterisk in the in-flight chromatogram. As can be seen, this peak is not present in the clean air runs performed on the ground, showing that there was no evidence of contaminantion from benzene or an interfering compound. As such, AQM 1011 appeared to be operating nominally following its return and repair.

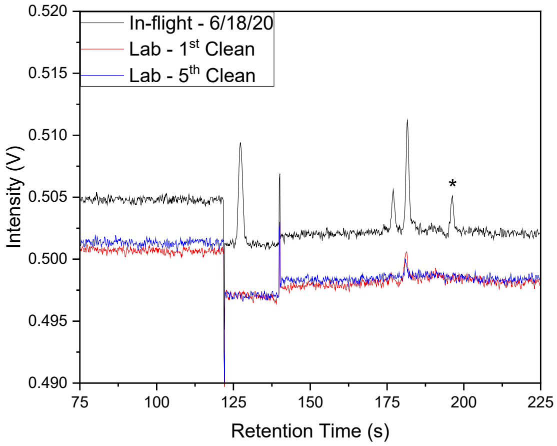

Figure 5: Chromatograms showing clean runs on AQM 1011 performed in the ECL following its return and repair compared to the final in-flight sample run. The peak in the benzene GC window is marked with an asterisk.

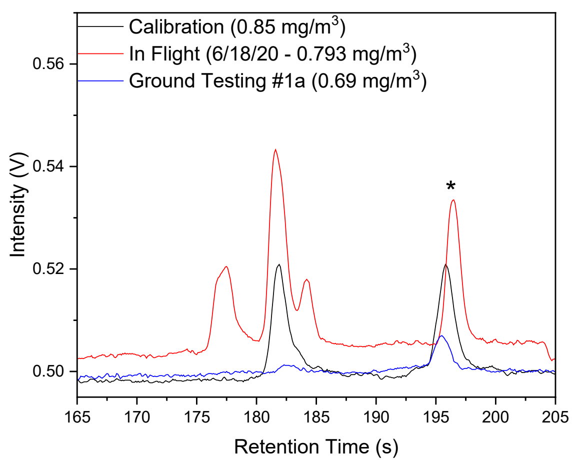

Figure 6: Chromatograms showing the changes in benzene response (*) between initial calibration of AQM 1011 in 2018 (black), the final in-flight sample run (red), and a sample run as a similar concentration performed following the return and repair of the instrument in 2020. Note the peak shift in the benzene region between the in-flight and ground runs.

Figure 6 shows chromatograms from the final in-flight sampling session, the first ground benzene exposure (0.69 mg/m^3), and a pre-flight calibration exposure of 0.85 mg/m^3 benzene. The difference between the intensity of the benzene peak is obvious in the 3 separate runs, particularly for the in-flight sample. However, more notable is the difference in intensity between the ground-based runs. Even though the benzene concentrations are relatively similar, the post-flight run is significantly less intense; a calculation of the concentration from this run using the pre-flight calibration showed it to be approximately one tenth of the expected response. Subsequent testing showed that increasing the flow rate in the updated (Kintek) test stand led to an increase in the benzene response, but the response was still ~ 30% of the expected concentration. This was further confirmed on the legacy (SVT) test stand.

In order to confirm the degraded AQM performance, a standard collection of compounds at concentrations used for SVT were exposed to the unit using both the SVT and Kintek setups. As can be seen in **Figure 7**, similar recoveries were obtained for all of the target compounds tested (isopropanol and benzene were obtained in a separate run). However, a significant decrease in response/accuracy was observed for all compounds when compared to the results of SVT in 2018 during pre-flight preparation (**Table 1**). The most likely explanation for the loss of sensitivity is a degraded pre-concentrator in the AQM, which would affect the amount of analyte being introduced to the GC. It should be noted that this would not be unexpected for an instrument of this age (~7 years between delivery from Draper Labs and activation on the ISS).

As part of the autorun sequence testing benzene response, scan runs were also collected. A comparison of scan runs from the last in-flight analysis, the first benzene exposure on the ground, and pre-flight calibration are shown in **Figure 8 (A-C**, respectively**)**. In these graphs, the black rectangle represents the position where benzene would be expected to appear. With the loss of sensitivity described above, it is not a surprise that no peak is present in the first ground test (**8B**) when one considers the weak peak obtained during calibration (**8C**). However, a comparison of the calibration run with that from the last in-flight run (**8A**) shows a peak in the benzene window that, while at the correct C_v and retention time, is significantly different in shape and intensity, suggesting that this peak is the result of an interfering compound.

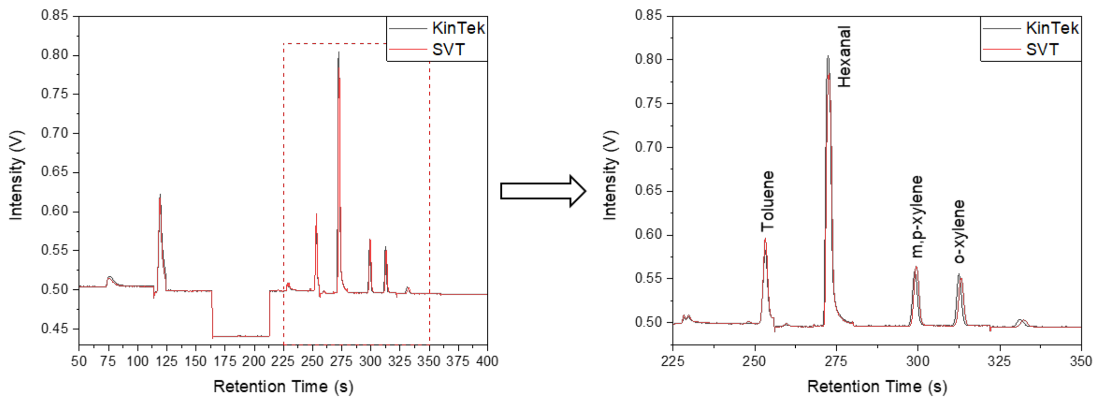

Figure 7: Long-run chromatograms for target compounds collected on two different ground testing setups. The retention times and responses for the targets are almost identical between the two testing setups.

Table 1: Accuracies of target compounds obtained during science verification testing in 2018 compared to 2020 after the return of AQM 1011 from the ISS.

	Accuracy (%)		
Compound	**2018 – Day 1**	**2018 – Day 2**	**2020**
Methanol	-19	-15	-75
Acetone	5	13	-44
Toluene	-18	-24	-61
Hexanal	-11	-3	-35
m,p-xylene	-13	-16	-74
o-xylene	-37	-35	-70
Isopropanol	-4	2	-50
Benzene	-27	-23	-78

During analysis of the GSCs returned on SpaceX-Demo2, three compounds were identified that could potentially interfere with AQM target analysis: isoprene (2-methyl-1,3-butadiene), isobutylene (2-methyl-1-propene), and acrylonitrile (2-propenenitrile). While these compounds were detected at trace levels by GC-MS (< 0.025 mg/m^3), the scan run data in **Figure 8** shows that the AQM is much more sensitive to the interfering compound. Even with the degraded sensitivity of AQM 1011, it was expected that an interfering compound would still appear in the chromatograms. **Figure 9** presents the chromatograms obtained following the introduction of each of these compounds using normal in-flight methods along with a chromatogram showing the benzene peak. Note that, under these methods, only isoprene appears in the spectra, and none of the compounds coelute with the benzene peak, indicating that none of these compounds are responsible for the elevated benzene readings seen in-flight.

IV. In-Flight Results of AQM 1007

With the failure of AQM 1011 in-flight, a new AQM (s/n 1007) was prepared for delivery. Initially, this instrument was only calibrated for benzene with the hope of delivery to the ISS on the (Russian) Progress-76 vehicle. When this attempt failed due to ground transfer issues in Russia, the calibration of AQM 1007 was completed for the remaining target compounds, and it was delivered to the ISS on Northrup Grumman-14. Following activation, it was found that AQM 1007 was also reporting elevated levels of benzene. An analysis of the chromatogram showed that a benzene peak was indeed present (**Figure 10A**), though much less intense than that seen on AQM 1011. Further analysis of the scan runs (**Figure 10B**) shows that, while a peak is indeed present in the benzene window, it is shifted from that seen both during calibration (**Figure 8C**) and the last in-flight runs of AQM 1011 (**Figure 8A**). This was further confirmation that the peak appearing in the chromatogram was not due to the presence of benzene. Even so, results for benzene were then reported as "matrix interference" due to the inability to distinguish between the interfering peak and actual benzene.

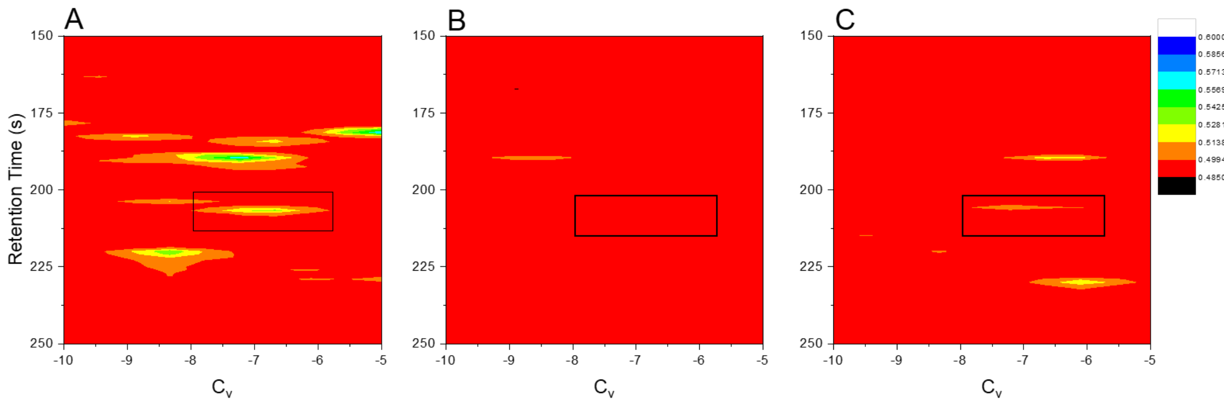

Figure 8: Scan runs from AQM 1011 showing the position of the benzene peak in (A) the final in-flight analysis, (B) the first exposure of benzene on the ground at levels similar to calibration, and (C) during pre-flight calibration. The black box designates the position expected for benzene.

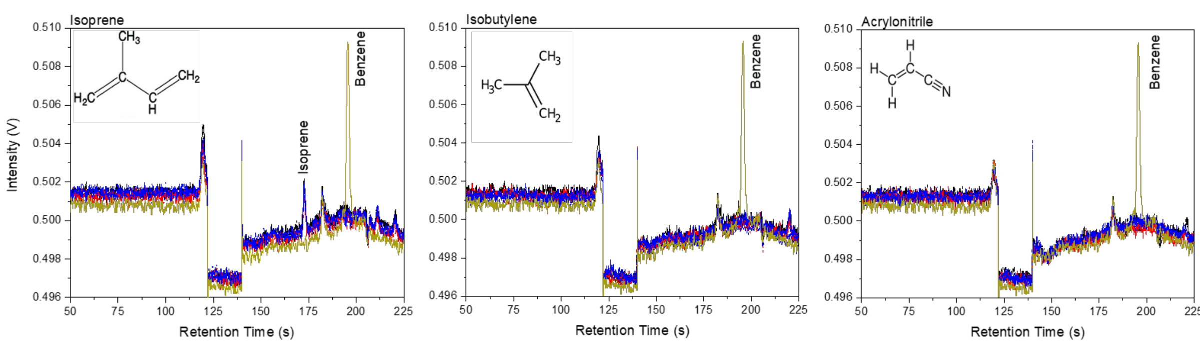

Figure 9: Chromatograms showing the effect of 3 potential interfering compounds on benzene detection. Under nominal methods, only isoprene appears in the spectrum, albeit at a significantly earlier retention time. None of the compounds appear to interfere with the benzene peak.

Though benzene has generally been reported as "matrix interference" or "non-detect" since AQM 1007 was deployed, the team has continued to monitor the data reported by the instrument both in the automated results as well as in the scan runs. In early April 2022, AQM 1007 again began to report the presence of elevated levels of benzene in the automated results. Analysis of scan runs obtained during this period (**Figure 11**) showed that this was again the result of an interfering peak and was not actually benzene. As can be seen in the figure, over a 3-week period, a peak appeared at the less-negative end of the C_v range for benzene and then moved towards the more-negative end of the range. Eventually, this peak moved completely out of the benzene window, again confirming that this unknown compound is not benzene.

With the knowledge that the benzene results provided by the AQM are not accurate, further efforts continue in order to gain a better understanding of the interfering peak. Simply analyzing the erroneous results produced by the AQMs provides an interesting pattern. As shown in **Figure 12**, where results are presented from both AQM 1011 (red circles - prior to its failure) and AQM 1007 (blue triangles), the "benzene" increases do not appear random. With the cyclical nature of the increases, the question arises as to if there are other activities or non-trace compounds that could be responsible. The first of these activities are shown in **Figure 12**, where the pink stars represent changes of the sieve packs in the AQMs. While some of the decreases appear generally tied to sieve pack changes (early 2021), other changes (2022, 2023) do not correlate as well. Concentrations of other non-trace compounds present in GSCs during this time (**Table 2**), including octafluoropropane, carbon dioxide, carbon monoxide, hydrogen, and methane, also did not appear to correlate with the pattern seen in the responses from the AQM.

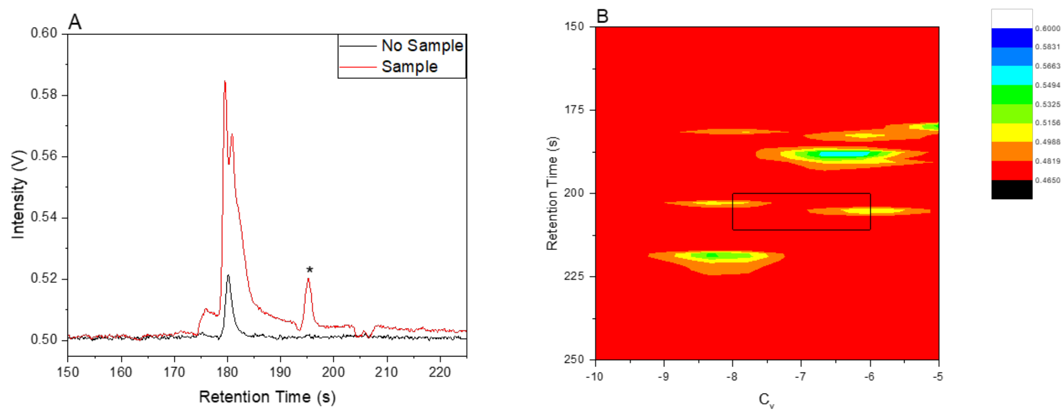

Figure 10: (A) Chromatogram showing the presence of a peak in the benzene window following the activation of AQM 1007 on the ISS in late-2020. (B) Scan run showing the presence of peaks in the appropriate benzene window during the same run session as (A). Note, however, that the peaks are shifted from those seen for AQM 1011, thereby providing further evidence that the "benzene" peak is actually a contaminant.

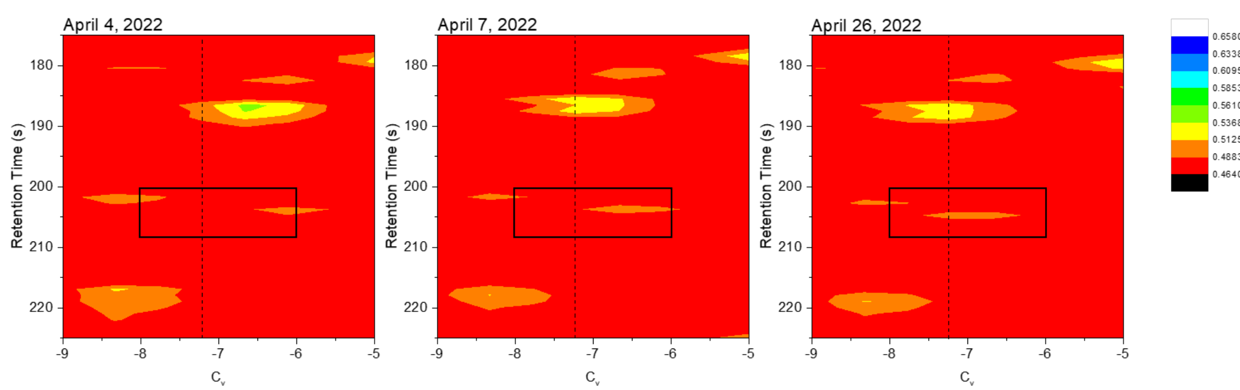

Figure 11: Scan runs obtained in April 2022 showing the movement of an interfering peak through the benzene window. While the presence of this peak led to an elevated benzene reading in the automated data analysis, its movement confirms that it is not benzene.

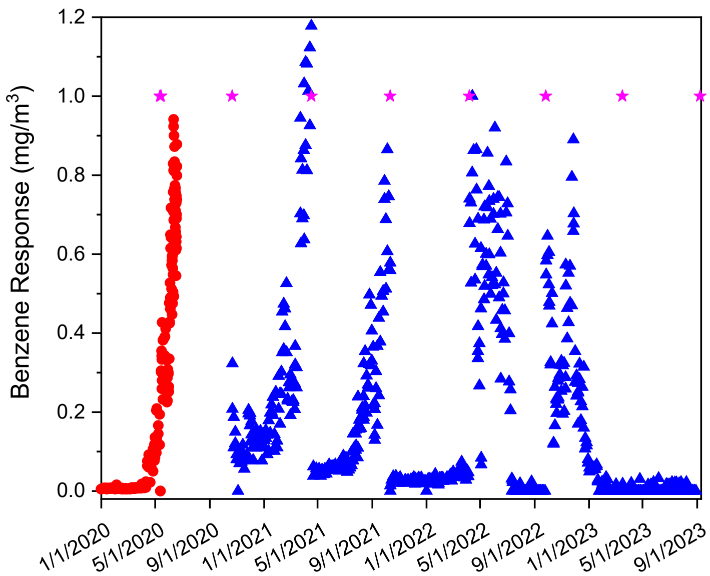

Figure 12: Automated benzene response from AQM 1011 (red circles) and AQM 1007 (blue triangles) since the original benzene anomaly in 2020. The changes in the recirculation sieve packs are shown in the pink stars. The benzene increases/decreases do not appear to be related to the sieve pack changes.

Table 2: Concentrations of selected non-trace compounds detected in archival samples collected in the US Lab since the onset of the original benzene anomaly in 2020.

Date	units	Octafluoropropane	Carbon Dioxide	Carbon Monoxide	Hydrogen	Methane
2/12/2020	mg/m³	140	2700	0.63	3.4	48
3/31/2020	mg/m³	130	3500	0.39	3.5	26
10/19/2020	mg/m³	199.9	7200	0.82	4.6	34
11/29/2020	mg/m³	215.3	6700	0.71	6.3	38
12/29/2020	mg/m³	192.2	6900	0.8	6	53
2/10/2021	mg/m³	138.4	5100	1.1	5.9	46
3/23/2021	mg/m³	184.6	5500	0.75	7.7	54
5/4/2021	mg/m³	192.2	6200	0.92	9.8	47
6/18/2021	mg/m³	215.3	6000	0.73	6.3	31
7/26/2021	mg/m³	238.4	5900	0.62	6.6	44
9/6/2021	mg/m³	223.0	5400	0.72	7.5	40
10/20/2021	mg/m³	5.7	4800	0.91	7.4	42
1/10/2022	mg/m³	9.9	5400	0.87	5.9	83
2/23/2022	mg/m³	13	4400	0.92	5.6	67
4/13/2022	mg/m³	5.9	5200	1.3	7.2	77
6/22/2022	mg/m³	1.5	3900	1.4	5	110
8/1/2022	mg/m³	8.4	4200	1.1	5.9	120
9/14/2022	mg/m³	1.9	3800	0.56	5.1	130
10/24/2022	mg/m³	7.9	4300	0.72	5.6	150
12/7/2022	mg/m³	5	3800	0.94	4.2	110
1/20/2023	mg/m³	4.4	3600	1	6.3	120
4/12/2023	mg/m³	10	3600	1.1	5.7	150
4/26/2023	mg/m³	4.4	4100	1.8	5.2	150
6/14/2023	mg/m³	5.6	4100	1.5	4.7	190
7/26/2023	mg/m³	2.5	4000	1.1	6	200

V. Summary

Since the initial deployment of the AQMs on the ISS in 2013, the instruments have successfully provided insight into the nominal composition of the ISS atmosphere and have also been used in off-nominal situations to provide assistance to the ECLSS community. However, the reporting of the presence of benzene in the ISS atmosphere by the AQM in Spring 2020, and the subsequent understanding that these readings were false, began to point to problems with the aging technology. Following the failure of AQM 1011 on orbit, the ISS Program determined that ground testing was needed to understand the cause of the false readings. After a repair of AQM 1011, ground testing showed that the instrument was operating nominally, there was no evidence of accumulation of an interfering compound, and that the AQM was still capable of detecting benzene and other target compounds, though a decrease in response from calibration pointed to a degraded preconcentration trap. Further testing showed that none of the potential interfering compounds detected in GSCs were responsible for the false benzene readings. Upon delivery of AQM 1007 to the ISS, the false benzene readings reappeared, leading to the decision to report benzene as "matrix interference" moving forward. To date, though efforts continue, there has been no identification of a cause of the interference seen in-flight.

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