ENVIE CHEMI E. Spe Pt Toxicology C NAS	ICOLOGY AND RONMENTAL STRY GROUP Incer Williams, and Environmental Chemistry SA JSC/SK4 on, TX 77058		Memorandum Number TOX-SW-2020-05 Voice: (281) 483-8921 Fax: (281) 483-3058 edward.s.williams@nasa.gov		
DATE:	December 11, 2020				
SUBJECT:	Benzene in ISS Air, April 13 – August 2, 2020 (Increment 62-63)				
SUMMARY:	Benzene was reported at detectable levels by NASA's Air Quality Monitor Unit 1 from April until June 2020, when the unit failed on orbit. Subsequent measurements performed in-flight and on the ground indicated that these readings were erroneous and were likely due to the presence of an interfering compound that is not yet identified.				

NASA's Air Quality Monitor Unit 1 (AQM1) first detected a reportable level of benzene (0.07 mg/m<sup>3</sup>) on April 13, 2020. Concentrations rose in early May to approximately 0.15 mg/m<sup>3</sup> and remained near that level until May 12. On May 12, the sieve cartridges on AQM1 were replaced per routine on-orbit maintenance procedures. Data from the initial analysis run after the sieve replacement indicated that there was an issue with the new cartridges, so a second set of cartridges were installed on May 14. Following installation of the second set of cartridges, reported benzene concentrations on AQM1 had risen to 0.3-0.35 mg/m<sup>3</sup>. Benzene was monitored at a similar level through the rest of May until levels began to rise again on June 4. From this date, the reported benzene concentration rose to approximately 0.5 - 0.75 mg/m<sup>3</sup>.

NASA's 7-day and 30-day Spaceflight Maximum Allowable Concentration (SMAC) values for benzene are 1.5 and 0.3 mg/m<sup>3</sup>, respectively. These values are predicated on toxicological studies in which laboratory mice exposed to benzene experienced a reduction in white blood cells and increased susceptibility to infection. NASA's 180-d SMAC (0.2 mg/m<sup>3</sup>) is based on the likelihood of developing leukemia due to long-term exposures. Given that these outcomes were associated with long-term exposure to benzene, brief exceedances of these SMACs were deemed acceptable by JSC Toxicology and flight surgeons, but the data triggered actions to identify the potential source of benzene on orbit and to reduce exposure levels as soon as possible.

In order to locate and identify the potential benzene source, AQM1 was moved to the Russian segment (RS), and inter-module ventilation (IMV) between the RS and the US segment (USOS) was terminated on June 11 (i.e., split atmosphere). Approximately 4 hours after initiation of split atmosphere, the benzene concentration in the RS was measured at 0.93 mg/m<sup>3</sup>. The A $\phi$ OT scrubber on the RS was activated remotely 2 hours later, and the reported concentration was reduced to 0.69 mg/m<sup>3</sup>.

A second split atmosphere operation was performed on June 18. The measured benzene concentration in the RS during split atmosphere operations was  $0.81 \text{ mg/m}^3$ . One of the objectives for the second split atmosphere period was to capture measurements on both the USOS and RS in hopes that the source could be isolated to one segment. Unfortunately, AQM1 failed on June 18 after it was relocated back to the USOS. The data acquired by AQM1 from April 13 – June 18 are plotted in Figure 1.



Figure 1. AQM1 data for benzene on ISS, April 7 – June 18, 2020

During the time when elevated benzene levels were being detected with AQM1, NASA and International Partners (IPs) collaborated closely to identify potential sources of benzene on ISS. JSC Toxicology and specialists from IBMP conducted a thorough review of the on-orbit chemical databases for the USOS and RS, respectively. As expected, no obvious sources of benzene were identified in either segment.

Following the loss of AQM1, additional scrubbing hardware was deployed in the USOS. A carbon bed assembly (CBA) was connected to the IMV fan in Node 3 on July 7. Also, the combined charcoal/HEPA filters (CHIPS) in Node 1 were replaced with fresh charcoal beds.

NASA attempted to deliver a replacement AQM calibrated for benzene on 76P but was unsuccessful due to issues with radiation licenses. However, two Dräger Chip Measurement System (CMS) readers were delivered for launch on this flight along with numerous benzene-specific chips. The CMS readers delivered on 76P are identical to the CMS reader that is part of the ammonia monitoring kit (AMK) on ISS. Based on experience with the reader in the AMK, the operational plan for the new CMS readers was to conduct an on-orbit comparison to assess variability between the instruments. After designating one of the readers (S/N 1001) as the prime unit, a series of duplicate readings were taken in the US Lab and Russian Service Module (SM) between July 24 and August 5, 2020.

The performance of the Dräger CMS reader and the low-level benzene chips were evaluated in the TEC Laboratory at Johnson Space Center before launch. The published detection limit (DL) for the chips is 50 ppb; however, testing in the laboratory indicated that half of readings taken using an 80 ppb standard registered below the DL (<50 ppb). The minimum concentration where the chip would consistently produce concentrations above the DL was 100 ppb. While higher than the published value, this concentration (100 ppb/0.32 mg/m<sup>3</sup>) is well below the levels detected in the final analyses run on AQM1. Despite having a DL below the expected on-orbit concentration, no benzene was detected in any of the CMS readings (Table 1).

Sample Location	Sample Date	Sample Time	Benzene (mg/m <sup>3</sup> )
US Lab*	7/24/2020	17:21	ND
US Lab*	7/24/2020	17:48	ND
SM*	7/24/2020	18:16	ND
US Lab*	7/25/2020	10:30	ND
SM*	7/25/2020	10:30	ND
US Lab*	7/25/2020	12:30	ND
SM	7/25/2020	12:55	ND
SM	7/25/2020	13:05	ND
US Lab	7/25/2020	15:41	ND
US Lab	7/25/2020	15:53	ND
SM	7/25/2020	16:05	ND
SM	7/25/2020	16:17	ND
US Lab	7/25/2020	18:43	ND
US Lab	7/25/2020	18:53	ND
SM	7/25/2020	19:05	ND
SM	7/25/2020	19:20	ND
US Lab	7/27/2020	UNK	ND
SM	7/27/2020	UNK	ND
US Lab*	7/30/2020	8:55	ND
US Lab*	8/5/2020	16:19	ND

Table 1. Atmospheric readings for benzene conducted using Dräger CMS

\* duplicate readings were taken at this time in this location. ND: not detected, DL approximately 80 ppb or 0.26 mg/m<sup>3</sup>

In addition to the AQM readings and the CMS readings, eight contingency air samples and four routine archive air samples were collected in mini grab sample containers (mGSCs) between May 11 to June 24, 2020. This sampling methodology and the analytical techniques used to analyze these samples in the TEC laboratory are considered the standard for atmospheric monitoring during crewed spaceflight. All twelve of the mGSCs were returned on SpaceX Demo-2, which splashed down on August 2, 2020. By August 5, 2020, preliminary results from the analysis of 8 of these samples indicated that benzene was not present in the ISS air samples. Analysis of the remaining samples confirmed that **none of the samples returned on SpaceX Demo-2 contained reportable levels of benzene** (Table 2). In light of the preliminary data, the decision was made to discontinue in-flight benzene monitoring with the CMS chips.

The results from the archive air samples support the conclusion that benzene was not present on ISS during this period. Three of the contingency samples and two routine samples were taken while AQM1 was operating; the remainder were collected after the unit failed. Four of the samples were collected within ~2 hours of an AQM1 data point, and the sample collected on May 11, 2020 was collected ~14 hours after an AQM run. The consistency between these samples and the samples collected after AQM1 failed strongly suggests that benzene was never present at reportable levels in ISS air.

Return Flight	Sample	Sample	Benzene
Keturn Fight	Location	Date	$(mg/m^3)$
SpX Demo-2	Lab Bay 4	5/11/2020	ND
SpX Demo-2	US Lab*	5/20/2020	ND
SpX Demo-2	SM*	5/20/2020	ND
SpX Demo-2	US Lab	6/8/2020	ND
SpX Demo-2	SM	6/11/2020	ND
SpX Demo-2	US Lab	6/20/2020	ND
SpX Demo-2	US Lab	6/21/2020	ND
SpX Demo-2	US Lab*	6/29/2020	ND
SpX Demo-2	JPM*	6/29/2020	ND
SpX Demo-2	74P	7/7/2020	ND
SpX Demo-2	US Lab	7/9/2020	ND
SpX Demo-2	US Lab	7/24/2020	ND
180-d SMAC			0.2

Table 2: Analytical results from contingency and routine mGSC samples for benzene

\* Routine archive samples

ND: not detected

The replacement AQM unit that did not make the 76P launch was returned to the TEC laboratory where it was fully calibrated for all target analytes prior to delivery for launch on NG-14 (October 5, 2020). This unit was deployed and activated on October 21, 2020. The initial analysis run on the replacement AQM indicated the presence of benzene at 0.26 mg/m<sup>3</sup>. Initially, this result was surprising as data from all other in-flight and ground analyses showed no reportable benzene in the ISS atmosphere. However, this result probably should have been expected. The most likely explanation for the positive benzene readings is that there is an unidentified compound present in the ISS atmosphere that is interfering with the benzene measurement on the AQMs. As of early December 2020, AQM1 on ISS continues to report measurable levels of benzene. Considering that the additional scrubbing hardware that was deployed to reduce the benzene levels was deactivated once the archive samples showed no benzene was present, it is not surprising that the compound that caused the false positive readings on the previous AQM is producing the same effect on the new AQM. While the compound that is interfering with the benzene measurement on the AQMs are that no compounds were detected in the archive air samples at levels of concern for crew health.

The failed AQM1 unit was returned on SpaceX Demo-2 and repaired. Ground testing was initiated to identify the compound that is interfering with the on-orbit benzene measurements, and results from this testing will be reported separately.

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