Volatile Organic Analyzer (VOA) in 2006: Repair, Revalidation, and Restart of Elektron Event

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INTRODUCTION

The Volatile Organic Analyzer (VOA) was launched to the International Space Station (ISS) in August 2001 and was the first instrument to provide near real-time measurement of volatile organic compounds in a spacecraft atmosphere. The VOA performed an analysis of the ISS air approximately twice a month for most of its operation through May 2003. This intermittent operation, caused by a software interface issue with the ISS communication bus, slowed the validation of the VOA. However, operational validation was completed in 2003 when analysis of air samples collected in grab sample containers (GSCs) compared favorably with simultaneous VOA runs (1).

The VOA has two channels that provide redundant function, albeit at slightly reduced performance, when only one channel is operating (2). Most target compounds can be detected on both channels. In January 2003, the VOA identified a malfunction in the channel 2 preconcentrator and it shut down that channel. The anomaly profile suggested that a fuse might have failed, but the root cause could not be determined. In May 2003, channel 1 was shut down when the detector's elevated temperature could not longer be maintained. Since both VOA channels were now deactivated, VOA operations ended until an in-flight repair could be planned and executed.

This paper describes the process to repair the VOA and to revalidate it for operations, and then an account is given of the VOA's contribution following a contingency event on ISS.

EXPERIMENTAL

ON-ORBIT DIAGNOSTICS

The error messages displayed for the failures of the channel 2 preconcentrator and the channel 1 ion mobility Spectrometer (IMS) detector indicated the same problem: an inability to maintain the component temperature. This fault could have been caused by any of three elements: heater, heater drive board, or thermal fuse. The temperature sensors properly followed the declining temperature of the two affected units; therefore they were not considered to be the problem. The VOA is a complex instrument; therefore detailed procedures to isolate and test each suspect element were developed on an identical VOA ground unit.

The crew took the VOA out of the Crew Health Care System rack and removed covers to access the components to be tested. Crew inspections of the preconcentrator and IMS heater boards showed them to be free of damage. Next, the crew checked the preconcentrator and IMS fuse-heater circuits to determine if they or the boards had failed. These tests revealed that the channel 2 preconcentrator and channel 1 IMS circuits were open. The question remained whether the heaters or the fuses had failed on each channel. The thermal fuses for both components (Figure 1) were located and tested. The tests showed blown fuses on both components and a check of the heater circuit confirmed the heaters were operating properly.

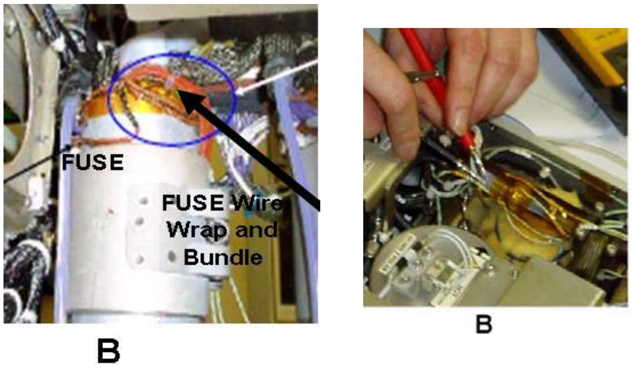

Figure 1 Fuse position and testing A) IMS cell B) preconcentrator

INFLIGHT MAINTENANCE

The diagnosis of failed fuses meant that the VOA could be repaired on orbit. These parts were not intended to be replaceable; therefore, nine months were required to create the procedure and arrange the crew time (almost 24 h) to perform the in-flight maintenance (IFM).

As before, a significant period of time was required for the crew to gain access to the components. The preconcentrator fuses were easily accessible and so they were the first to be replaced. The old fuses were removed by cutting the wire on each side, but leaving sufficient wire to connect the new fuse with a crimp connector. Replacing fuses on the IMS cells could easily introduce noise to the detector signal, unless the crew adhered exactly to the directions for removal of the old fuse and placement of the new fuse and associated wiring.

Some VOA parts (i.e. scrubbers and pumps) were orbital replacement units (ORUs), which are parts designed to be replaced at regular intervals. It was important that these be replaced after the IFM, because their operational life had expired.

DISCUSSION

VOA RESTART AND FUNCTION CHECK

VOA repairs were completed and the unit was restarted in December 2005. A functional check of the VOA was necessary because digging deep into a complex, sensitive instrument during a repair always poses a risk of damaging other components. Furthermore, the VOA had been idle for 2.5 years, during which time offgas products and contaminants from the cabin had accumulated in the VOA's preconcentrators, gas chromatograph (GC) columns, and IMS detectors.

The channel 2 positive and negative mode reactant ion peaks (RIP) for the early calibration runs (no sample acquired) are plotted in the Figure 2. In both modes the RIP was barely visible in the first few calibrant runs, but by the 6th run the RIPs were apparent. The VOA was in standby for nearly month and in this state the VOA can self-clean, since carrier gas flows through the GC, the detector is maintained at elevated temperatures, and a recirculated gas flow scrubs the detector. The cumulative effect of almost a month in standby translated into the substantial RIP peak heights seen in both modes for the 7th calibrant run in January 2006. The RIPs from this calibrant run compared to those of the December 2002 run (known good RIPs) showed similar peak height and position, thus affirming the VOA operational readiness.

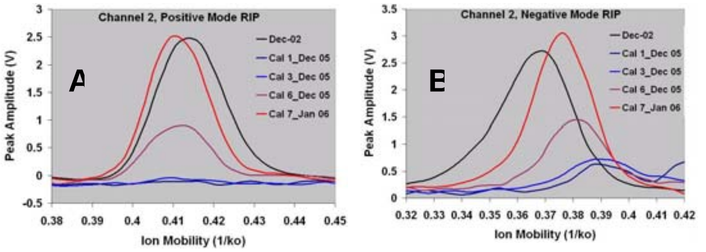

Figure 2 Channel 2 runs for December 2005 and the first run in January 2006 A) Positive RIP and B) Negative RIP

Although the channel 1 RIP plots (Figure 3) appeared similar to that of the channel 2 RIP, in this case the RIP in both modes was significantly displaced to the right of the December 2002 peak. Accurate ion mobility is crucial to proper compound identification. The ion's mobility is normalized for pressure, temperature, and electric field strength. It was determined that the channel 1 pressure sensor, used for normalizing the ion mobility, had drifted slightly from its calibration. All ions, not just the RIP, exhibited this offset. Fortunately, the pressure sensor remained stable and the problem was easily corrected by modifying the identification database to reflect the pressure sensor offset.

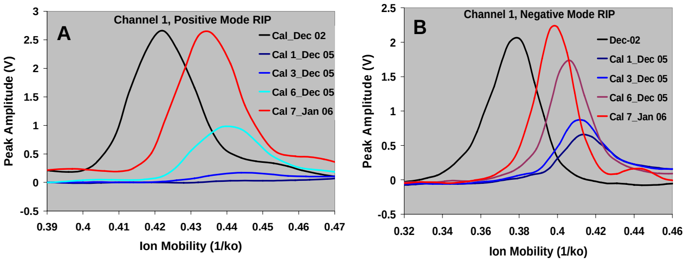

Figure 3 Channel 1 runs for December 2005 and the first run in January 2006 A) Positive RIP and B) Negative RIP

VOA REVALIDATION

The VOA was clean and functioning, so the next task was to determine if it could accurately identify and quantify the target compounds typically in the ISS atmosphere.

The VOA was calibrated for the required target compounds (3) and its performance and calibration were verified by challenge mixture runs prior to its launch in 2001. The VOA was operationally validated in flight during 200-2003. The revalidation of the VOA in 2006 mirrored the previous validation method (4). In this method the VOA analyses were compared with the ground-based analyses of several simultaneously acquired grab sample containers (GSC) samples. For compounds detected above trace levels, the VOA had to identify and quantify these compounds within +/-50% of the GSC analysis.

Figures 4 and 5 show the 2006 concentration data for the four compounds consistently detected above trace levels in the VOA and GSC samples. All 2006 VOA runs are shown, in addition to the VOA/GSC coordinated runs, to construct the temporal variation in the compound concentration. Channel 1 data were plotted only to June 2006 because at that time this detector was shut down, most likely because of a failed fuse.

VOA data for ethanol and 2-propanol (IPA) are presented in Figure 4. Only VOA/GSC matched data are shown for ethanol on Channel 1 because the data was extrapolated using a limited data set, thus limiting accuracy. The channel 1 GC column does not separate 2-propanol from other compounds; therefore detection and quantification used only channel 2 data.

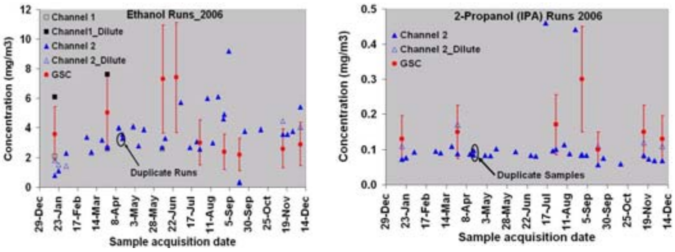

Figure 4 Plots of 2006 VOA data for ethanol and 2-propanol, plus matched GSC samples

It can be seen that compound concentrations for most of the VOA/GSC-matched samples were within the stated

+/-50%. The reproducibility of the VOA is illustrated by the tight values for consecutive runs in April.

The graphs of acetone and n-butanol (Figure 5) demonstrated a less variable pattern than seen for the alcohols in Figure 4. This might be explained by the fact that the main sources for these compounds are offgassing and human metabolism, whereas ethanol and 2-propanol are related to episodic onboard activities such as medical experiments. Again, most results met the acceptance criteria, but the success rate was poorer for acetone.

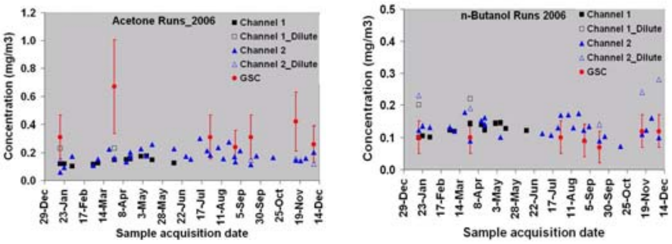

Figure 5 Plots of 2006 VOA data for acetone and n-butanol

Data produced by the VOA runs and the GSC samples are compared in Table 1 for compounds detected above trace levels. Acetaldehyde is adequately separated only on the channel 1 GC; therefore, acetaldehyde quantitation was lost when the VOA's channel 1 was disabled in June 2006. Results were excellent for acetaldehyde, 2-propanol, and n-butanol, with the last two having only one outlier in the 7 samples. Acetone had three points outside the ± 50% criterion, but one point was only slightly (52%) above the requirement. Ethanol concentrations were consistently beyond the VOA calibration curve, which necessitated extrapolation and this led to larger errors.

When compared with analysis of GSC samples, the VOA correctly identified compounds at trace concentrations and just as importantly, it did not detect compounds that were not present in the ISS atmosphere. Discrepancies in trace levels of a few compounds occurred because the detection limit for the analytical methods of the VOA IMS) and the GSC (gas chromatography/mass spectrometry) are different for some compounds.

Table 1 Comparison of VOA and GSC analytical results reported as % error. Shaded cells value did not meet the ± 50% requirement. *The 9/18 data point (52%) is included in the last column total.

Target Compound	01/18/06	03/28/06	07/28/06	08/29/06	09/18/06	11/14/06	12/07/06	Met Criteria (Total 7)
Ethanol	-42	-44	-13	104	-83	38	40	5
Acetone	-26	-66	-41	-44	-52	-62	-22	5*
2-Propanol	18	13	-40	-71	10	-20	-15	6
n-Butanol	1	-10	69	2	29	-8	-17	6
Acetaldehyde	-28	-32						2 of 2

In spite of these data, the VOA's age and the 6-year interval since its last calibration have led to a cautious approach called "quantitative trending." This allows the data to have a larger error band (>± 50%), but the data are still of sufficient quality for operational decision-making in ISS contingency scenarios.

RESULTS

The VOA plays an important role during contingency events on ISS, even with the restriction of "quantitative trending". The timeline in Figure 6 details the actions taken during the September 2006 Elektron incident. This event will be used to illustrate how the VOA data is interpreted and used for decision-making in these scenarios.

The Russian Elektron produces oxygen for ISS via water electrolysis and the oxygen then enters the ISS after passing through several filters. In September 2006, the crew had been working for several hours to restart the Elektron, but once it began operating the crew noticed a white smoke being released from the unit. Initially thinking it was a fire, the crew enacted the ISS fire protocol, which led to the quick deactivation of the intermodular ventilation (IMV).

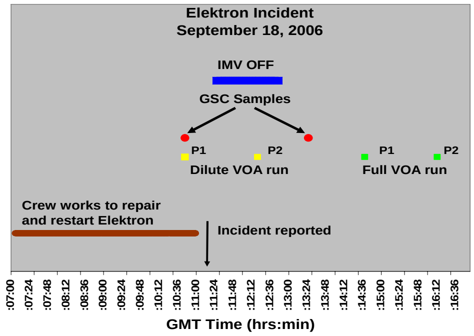

Figure 6 Elektron incident timeline of events related to air quality. P1 and P2 refer to Part 1 and Part 2 of the VOA runs.

Fortunately, a routine VOA sample session occurred during the time of the incident. The protocol required a dilute sample run (10 ml sample), which was coordinated with a GSC sample, followed by a full sample run (40 ml) about 3 hours later. It is important to note that the VOA is located in the U.S. LAB and the Elektron is in the Russian Service Module (SM). Normally, there is good mixing of the air between the two modules, but it can be seen in Figure 6 that the IMV was deactivated during the peak of the incident. The first GSC was acquired in the LAB next to the VOA, but this was prior to the event's major release. The other GSC, acquired in the SM, wasn't coordinated with the VOA run in proximity or time.

The positive-mode compounds will be the focus of the discussion, because they were the contaminants of most interest for this event. Positive-mode compounds are detected only in the sample acquisition for the VOA's Part 2 of the run ("P2" in Fig 6), since channel 1 has been disabled.

In Figure 7, the xylene mobility ($1/k_o=0.499$) is plotted as a function of GC retention time (GCRT) for VOA runs during the Elektron incident and nominal ISS runs (Sept

4 and Nov 14). The most striking observation was that a peak not found in nominal ISS runs had appeared at a GCRT of 2180 seconds. The unknown peak is very large in the dilute run, especially given that its sample volume was one-fourth of a full run. Important clues to this compound's identity were that its mobility was the same as the xylenes and the GCRT was slightly shorter than m/p-xylene. Additionally, toluene (GCRT=1884 sec, $1/k_o$= 0.463), another aromatic, was also detected at significantly elevated levels in the full sample run. The unknown was most likely ethylbenzene based upon the aforementioned information. Strengthening ethylbenzene's case was its identical molecular weight to xylene and a boiling point (bp) that was slightly lower than m/p-xylene. That ethylbenzene and toluene had identical molecular weights and similar molecular structure would account for the like $1/k_o$s. Ethylbenzene's lower bp explains its elution from the GC column (apolar) slightly before m/p-xylene. By contrast, toluene elutes from the GC column much earlier and has a faster drift time than the xylenes, which is sensible given toluene's smaller molecular weight and lower bp. Although confident the peak's identity was ethylbenzene, it wasn't until the return of the GSC samples that this was verified.

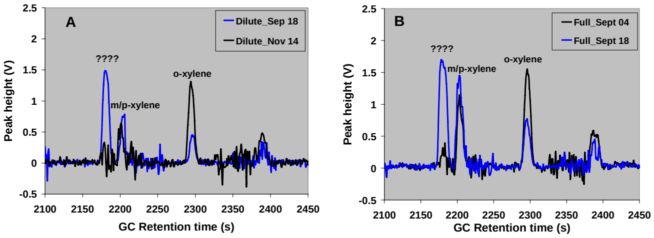

Figure 7 Xylene mobility ($1/k_o$= 0.499) plotted as a function of GC retention time. A) Dilute run, B) full run

Another important compound detected by the VOA was benzene, albeit just above the VOA's detection limit. The mobility spectra for this compound are shown in Figure 8. The calibration standards plotted in the graph illustrate the VOA's weak response for this compound.

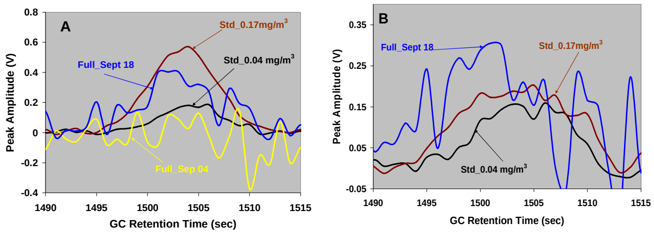

Figure 8 Benzene mobility for standard mixtures and Elektron sample: A) $1/k_o$ =0.424 and B) $1/k_o$ = 0.481

However, the sensitivity is actually better than expected because the drift gas is kept fairly dry. Although the September run is noisy, it is clear that benzene is present. The graph in Figure 8B is of a second peak always detected when benzene is present, but it has never been determined if this is a compound created by a reaction of benzene in the heated preconcentrator or a benzene adduct.

A comparison of results from the VOA and the GSC samples is depicted in Figure 9 along with the event timeline and sample location. The GSC sample (10:45) acquired in the LAB prior to the Elektron event shows only trace concentrations (detected, but below method quantitation limit) of the aromatic compounds detected at high concentrations in later samples. The trace levels for these compounds matches the profile of a nominal ISS sample run completed on September 4. The 1st GSC was coordinated with Part 1 of the VOA run. Unfortunately, the event began after the acquisition of the Part 1sample, but in any case the compounds released (aromatics) during the event were those detected in Part 2. The VOA Part 2 sample was acquired approximately 90 minutes after the Part 1 sample and 1 hour after the reported Elektron incident. The Part 2 data clearly illustrated a significant increase in the aromatic compounds. The VOA was never calibrated for ethylbenzene or dilute runs, so this data had to be extrapolated. Nevertheless, the detector response showed an unmistakable concentration increase for these aromatics. Noting that the IMV was active for only 5 minutes after the incident, it was concluded that the levels of aromatics in the VOA dilute sample came from a much earlier "unseen" release of these compounds. In fact these compounds were likely released in the initial attempts to restart the Elektron at lower amperage.

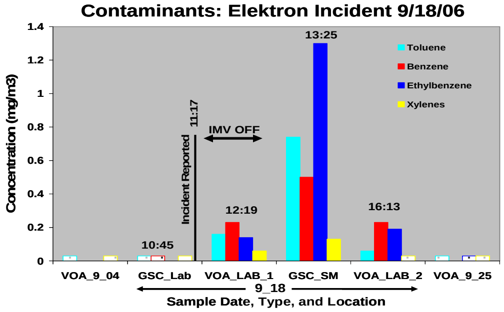

Figure 9 Results from VOA and GSC samples during the Elektron incident. Columns with dotted pattern represent trace concentration.

The IMV was restarted about 12:46 and at 13:03 the crew reported fewer odors in the SM. Although the 2nd GSC acquired a SM sample 30 minutes after the crew reported less odor, the concentrations of the aromatics were still quite high. The 2nd VOA run, an hour after the GSC sample, demonstrated that the air quality was being restored, but there were still higher than normal concentrations of the aromatics in the atmosphere.

The combination of GSC and VOA samples created a consistent picture of the air quality over the entire timeline. Prior to the event the initial GSC sample showed a nominal atmosphere; however the VOA data revealed that air quality degradation had begun, unbeknownst to the crew. Although peak concentrations in the SM were unknown, the later GSC sample and VOA run depicted a quickly improving atmosphere once the IMV was re-activated. The VOA sample on 9/25 showed the ISS air quality had returned to normal. Also, it is interesting to note that the xylene increases in both the GSC and VOA data are smaller compared to the other target aromatics. Given the temporal and spatial difference in VOA and GSC samples, the uniformity of the results is quite remarkable.

The GSC data wasn't available until months after the event, but the VOA data was used immediately to help assess any potential impact on the crew. Additionally, the VOA showed that the atmosphere was back to nominal by the next scheduled VOA run.

The data provided two other important pieces of information. First, data pointed to the fact that the incident began as much 60-90 minutes before the crew observed the problem. Secondly, the cause of the event could have been a release of organics from one of the filters. An offgas report showed that a Russian sealant released the compounds observed in this event and in approximately the same concentration ratio; therefore it was speculated that the overheating of a sealant in the Elektron produced the compounds released.

CONCLUSION

The data in this paper has shown the process required to diagnosis, repair, and re-activate the VOA after being idle for 2.5 years. The value of the VOA was demonstrated by the wealth of real-time information it provided during and after the Elektron event on ISS. The VOA data enabled insight into the source of the problem, the propagation of the problem, and the data helped in assessment of the incident and the impact to the crew. The GSC samples, analyzed much later on the ground, corroborated the conclusions from the VOA data.

ACKNOWLEDGEMENTS

Iona Dy-Liacco, a Wyle Laboratories biomedical engineer, was crucial to the success of this work because she helped develop the step-by-step activity and then she transformed it into a procedure that the crew followed. William McArthur performed this IFM with great enthusiasm and care. Finally, NASA's Dr. Bonnie Dunbar, Dr. Nigel Packham, and John Feighery, as well as James Breach from SmithsDetection, contributed tremendously to developing the procedures and ensuring the activity was scheduled.

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