Performance Evaluation of the Operational Air Quality Monitor for Water Testing Aboard the International Space Station

William T. Wallace, Thomas F. Limero, and Daniel B. Gazda
Wyle Science, Technology, and Engineering Group, Houston, TX 77058

John M. Minton
University of Arkansas at Little Rock, Little Rock, AR 72204

Ariel V. Macatangay
NASA Johnson Space Center, Houston, TX 77058

Prabha Dwivedi and Facundo M. Fernández
Georgia Institute of Technology, Atlanta, GA 30332
Need for Environmental Monitoring

- In order to ensure astronaut health during spaceflight, air and water quality must be maintained.

- Time delay for return and analysis of archival samples precludes immediate mitigation of problems:
  - Return of samples can be > 6 months after collection

- Real-time monitoring becoming a priority, especially for future exploration missions:
  - Lack of ground support

- Air Quality Monitor (AQM) recently validated for real-time analysis of air quality

- Still a need for real-time water analysis
Current In-flight Water Quality Monitors

- TOCA (total organic carbon analyzer) – measures total organic carbon concentrations in ISS water
- CWQMK (colorimetric water quality monitoring kit) – measures biocide levels (Ag, I$_2$/total Iodine) in water
- Water Kit – archive sample collection, bacterial enumeration, and detection of coliform bacteria

Problem: no specificity for organic compounds!
June 2010: TOCA begins to see increase in TOC from Water Processor Assembly (WPA).

Late September 2010: First archival samples analyzed. Archival samples showed no individual organics at significant levels.

Interfering peak in glycols analysis traced to dimethylsilanediol (DMSD).
Dimethylsilanediol (DMSD)

- Degradation/hydrolysis product of other Si-based organics
- DMSD accounted for > 90% of TOC seen in WPA samples
- Low-to-moderate toxicological concern for oral exposure
- DMSD could mask the presence of other compounds that are of higher toxicological interest
Needs

- TOCA supplies excellent trending data regarding organics (and overall water quality) in ISS water.
- Rise attributable to DMSD shows that a single compound can skew the data.
- Compound-specific information needed to determine if drastic changes in TOCA require mitigation efforts or if water can still be safely used.
- Validated AQM shows ability to monitor trace organics in real time; many of target compounds are the same for water.
- Development of multifunctional monitor would improve current analysis and is a first step towards fulfilling the needs of future missions.
- IMS or DMS presents a potential starting point.
- Need to liberate organics from water matrix for analysis.
Electrospray ionization (ESI) – IMS provided first opportunity to test with liquids

Initial testing with alcohols and small molecules of interest using WSU instrument and then Excellims GA2100

- Decrease in concentration of small polar molecules led to a peak shift; overlapping with water peak at relevant concentrations
  - DMSD not seen at \( \leq 50 \text{ ppm} \)
  - Peaks arising from DMSD addition seen when using 50% methanol (ethanol) as solvent; no ID for multiple peaks
- No peak shift seen with decreasing DMSD concentration (down to 0.1 ppm)
- Testing of ISS archival samples showed that areas of DMSD peaks trended with DMSD concentrations determined using lab-based methods
  - Some variation in peak height/area day-to-day
Path Forward

- Relevant concentrations of trace polar organics are not sufficiently separated from water using ESI-IMS
  - Analysis of archive samples showed ability of ESI-IMS to qualitatively detect DMSD at ISS-relevant concentrations
  - Still need a method for identification and quantification of trace organics
Electrothermal Vaporization (ETV)

- ETV source placed in-line with DART-MS
- As current applied to nichrome ribbon containing sample, water solvent is vaporized and target analytes are volatilized and entrained in DART gas flow

\[ 	ext{M}^+ + 3\text{H}_2\text{O} + \text{NH}_3 \text{ ion of acetaldehyde} \]

ETV-AQM

• DART-MS experiments show that ETV holds promise for sample introduction into air monitor

• For spaceflight water monitoring, need to utilize current hardware and reduce reliance on ISS (e.g. power and carrier gas)
Initial Analysis of Individual Compounds

- **Testing conditions**
  - DB-5ms column
  - 2 uL of test solution placed on ETV ribbon
  - 250 cc/min zero air through ETV
  - Heating cycle – started with AQM run sequence
    - Clearance of ambient compounds (10 sec, 0 A) – corresponds to AQM pump running without sample valve open
    - Desolvation (1 sec, 2 A)
    - Analyte vaporization (2 sec, 5 A)
    - Decontamination (2 sec, 6 A)

- **Concentration Range**
  - 1 – 100 ppm

### Table: Compensation Voltage

<table>
<thead>
<tr>
<th>Compound (mode)</th>
<th>RT</th>
<th>RF900</th>
<th>RF1000</th>
<th>RF1100</th>
<th>RF1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol (p)</td>
<td>60.66</td>
<td>-8.33</td>
<td>-11.11</td>
<td>-15.56</td>
<td>-20</td>
</tr>
<tr>
<td>Ethanol (p)</td>
<td>71.78</td>
<td>-3.33</td>
<td>-4.44</td>
<td>-5.56</td>
<td></td>
</tr>
<tr>
<td>Acetone (p)</td>
<td>82.9</td>
<td>-0.56</td>
<td>-0.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isopropanol (p)</td>
<td>81.89</td>
<td>-1.11</td>
<td>-1.11</td>
<td>-1.11</td>
<td></td>
</tr>
<tr>
<td>Trimethylsilanol (p)</td>
<td>117.28</td>
<td>1.11</td>
<td>1.67</td>
<td>1.67</td>
<td>2.78</td>
</tr>
<tr>
<td>DMSD (n)</td>
<td>103.12</td>
<td>-1.67</td>
<td>-2.22</td>
<td>-2.22</td>
<td>-6.11</td>
</tr>
<tr>
<td>2-butaneone (p)</td>
<td>135.47</td>
<td>0.56</td>
<td>0.56</td>
<td>1.11</td>
<td></td>
</tr>
</tbody>
</table>
Concentration Dependence of Individual Compounds

- Testing of TMS showed 2 peaks, causing difficulty in preparing calibration curve
  - Monomer peak gives better sensitivity
  - Dimer peak gives more dynamic range
- Concerns
  - What are the effects of using water samples?
  - What effect will mixtures have?
  - Can a GC method be prepared to use different RF voltages in a single run?
Molecular Sieve Exhaustion

A: After 12 days of water testing (~98 runs with water), B: New sieve cartridges

C: Blank run (no sample added to ribbon) after several weeks of water testing, D: Standard humidified air run
What About Carryover?

- Final step of heating sequence used to remove any remaining analyte
- Blank runs (no sample added) after sample runs show that decontamination step is sufficient for most compounds
- DMSD shows increasing intensity in blank runs correlating with sample concentration
- Multiple blank runs required to return intensity to pre-testing levels
• Testing of mixture shows expected individual compounds
• GC method allows a single, short run (240 s) to be used for analysis of at least 6 compounds
• Coelution of acetone and IPA
  • Appropriate $C_v$ allows IPA to be detected
• Without changes to AQM (cooling/dopant), different column needed for analysis of acetone
Effect of Flow Rate and Sample Volume

- Testing of DART-ETV-MS used flow through ETV of 3 L/min
  - Much too high for on-orbit operations
  - Initial flows tested with ETV-AQM of 500 mL/min
  - Further testing shows reproducible signals with no flow
  - DMSD seems more susceptible to flow rates than IPA
  - All further testing used 250 mL/min

- Testing with DART-ETV-MS used 0.5 – 2.0 µL sample volume
  - Initial testing with ETV-AQM used 2.0 L
  - Reduced sample volume could improve sieve life and carryover
  - Volume of 0.5 L gives good signal for IPA/DMSD, but TMS not detectable
• Calibration of AQM using 7-compound mixtures to build calibration curves
• Calibration data used to check quality of curves
• Appropriate function chosen based on expected/historical concentrations
  • Quality of DMSD curve more important at > 10 ppm; quality of methanol curve more important < 10 ppm
Overloading of Trap during Calibration

- When using mixtures for calibration, methanol peak area turns over above 10 ppm
- Other compounds act as expected
- Previous studies with AQM have indicated that high concentrations of large molecules can push smaller molecules off of the trap
- Use of 1 μL removes problem up to 25 ppm
- Removal of 50 ppm point not important; well above any concentration expected on ISS
## Analysis of ISS Archival Samples

<table>
<thead>
<tr>
<th>Compound</th>
<th>Units</th>
<th>8/20/2013 Condensate</th>
<th>9/10/2012 Condensate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>AQM</td>
<td>GC-MS / LC-RID</td>
</tr>
<tr>
<td>Methanol</td>
<td>µg/L</td>
<td>1305</td>
<td>5340</td>
</tr>
<tr>
<td>Ethanol</td>
<td>µg/L</td>
<td>33147</td>
<td>23800</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>µg/L</td>
<td>756</td>
<td>405</td>
</tr>
<tr>
<td>Dimethylsilanediol</td>
<td>µg/L</td>
<td>26544</td>
<td>24000</td>
</tr>
<tr>
<td>Trimethylsilanol</td>
<td>µg/L</td>
<td>1223</td>
<td>500</td>
</tr>
<tr>
<td>2-butanone</td>
<td>µg/L</td>
<td>436</td>
<td>64</td>
</tr>
</tbody>
</table>

- DMSD – correlates well with laboratory-based methods
  - Low concentration archival samples still < 50% error
- Ethanol also within acceptable accuracy for in-flight monitor (based on current AQM air requirements)
- TMS / 2-butanone values determined by lab-based methods are below the lowest AQM calibration point
  - Reason for higher AQM values unclear
- Methanol – sampling issue?
  - Checking of calibration points gave excellent accuracy at concentrations relevant to present archival samples
- IPA – higher AQM values could indicate contribution of acetone
  - Acetone present at relatively high concentration based on GC-MS (~ 2300 µg/L)
  - Different column/unit potentially necessary for IPA/acetone analysis
- Lower concentration points needed
Summary

- Real-time environmental monitoring on ISS is necessary to provide data in a timely fashion and to help ensure astronaut health.

- Current real-time water TOC monitoring provides high-quality trending information, but compound-specific data is needed.
  - The combination of ETV with the AQM showed that compounds of interest could be liberated from water and analyzed in the same manner as air sampling.
  - Calibration of the AQM using water samples allowed for the quantitative analysis of ISS archival samples.
  - Some calibration issues remain, but the excellent accuracy of DMSD indicates that ETV holds promise for as a sample introduction method for water analysis in spaceflight.
Acknowledgements

- Funding: Bioastronautics Contract # NAS 9-02078
- Brian Hauck – Washington State Univ.
- Prof. Herb Hill – Washington State Univ.
- Dr. Ching Wu – Excellims Corp.
- Jeff Rutz – Wyle Environmental Chemistry Labs
- Debrah Plumlee – Wyle Environmental Chemistry Labs
- Dr. Mike Kuo – Wyle Environmental Chemistry Labs
- Office of the Chief Technologist at JSC