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

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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, I₂/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 dimethysilanediol (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 Excellim GA2100

- Decrease in concentration of small polar molecules led to a peak shift; overlapping with water peak at relevant concentrations
  - DMSD not seen at ≤ 50 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

M⁺ + 3H₂O + NH₃ 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>
<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>
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<tr>
<td>Ethanol (p)</td>
<td>71.78</td>
<td>-3.33</td>
<td>-4.44</td>
<td>-5.56</td>
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<tr>
<td>Acetone (p)</td>
<td>82.9</td>
<td>-0.56</td>
<td>-0.56</td>
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<td></td>
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<tr>
<td>Isopropanol (p)</td>
<td>81.89</td>
<td>-1.11</td>
<td>-1.11</td>
<td>-1.11</td>
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<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>
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<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-butanone (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 Mixtures and Preparation of GC Method

- 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

- 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 uL 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>Methanol</td>
<td>µg/L</td>
<td>1305 5340 76</td>
<td>1230 5480 78</td>
</tr>
<tr>
<td>Ethanol</td>
<td>µg/L</td>
<td>33147 23800 39</td>
<td>45409 49100 8</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>µg/L</td>
<td>756 405 87</td>
<td>825 708 16</td>
</tr>
<tr>
<td>Dimethylsilanediol</td>
<td>µg/L</td>
<td>26544 24000 11</td>
<td>47124 44000 7</td>
</tr>
<tr>
<td>Trimethylsilanol</td>
<td>µg/L</td>
<td>1223 500 145</td>
<td>1154 408 183</td>
</tr>
<tr>
<td>2-butanone</td>
<td>µg/L</td>
<td>436 64 581</td>
<td>354 68 421</td>
</tr>
</tbody>
</table>

### Observations

- **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
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.
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