National Aeronautics and Space Administration

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

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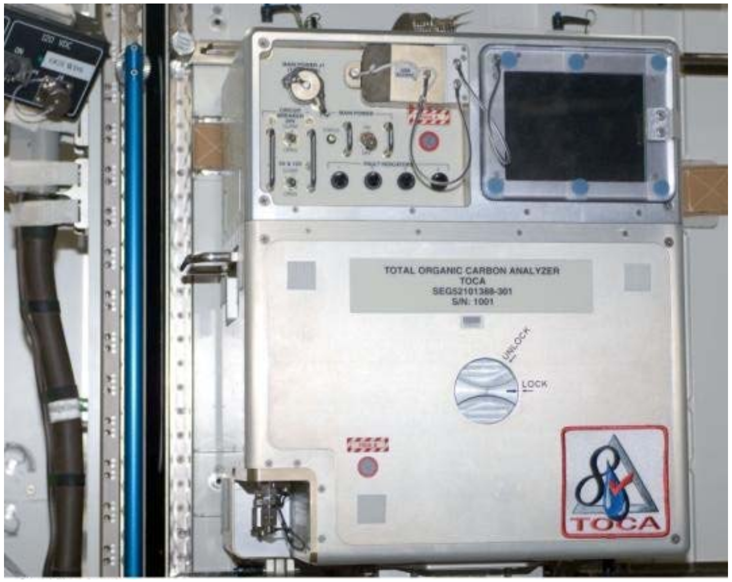
Need for Environmental Monitoring

- 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

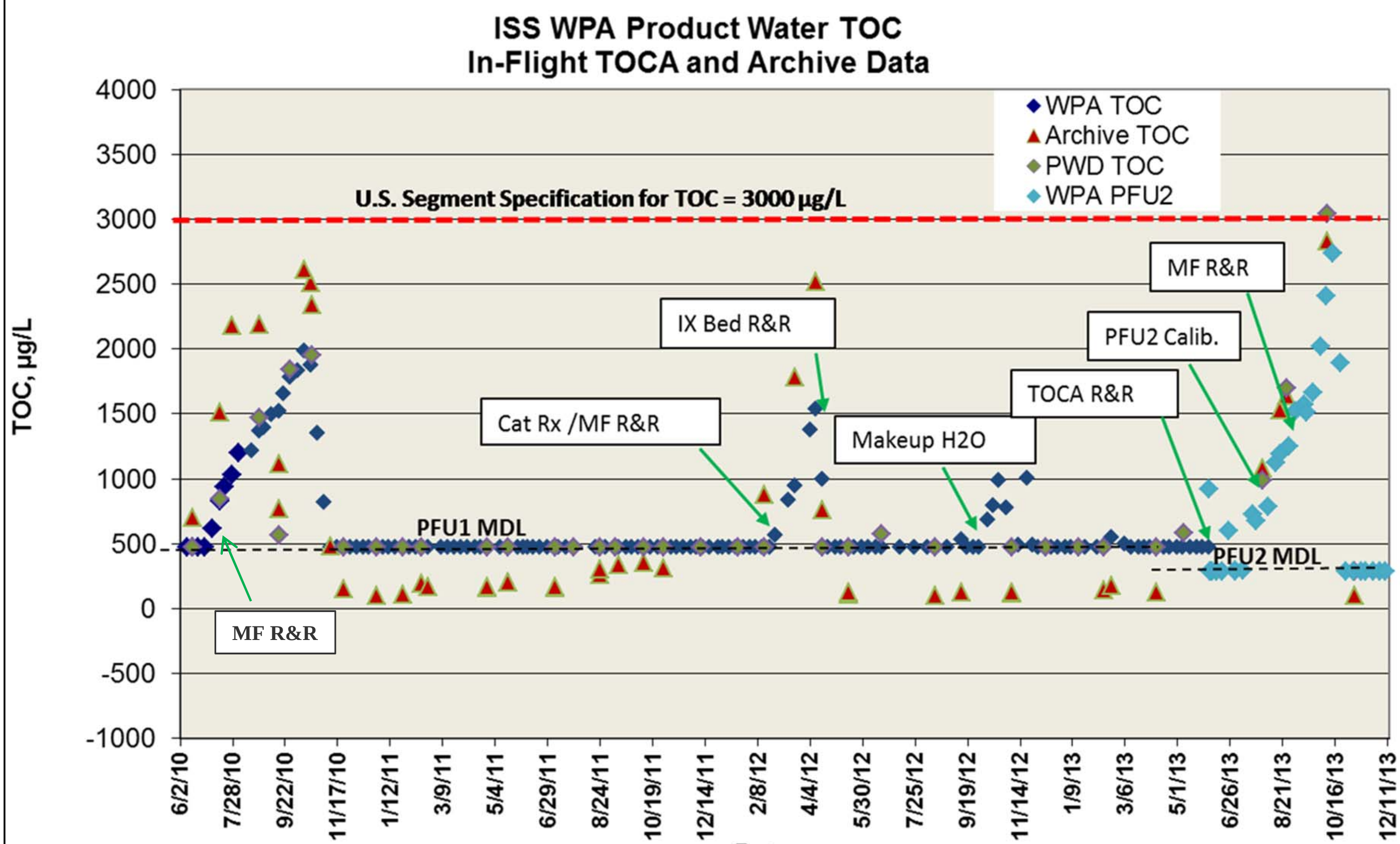


- TOCA (total organic carbon analyzer) – measures total organic carbon concentrations in ISS water
- CWQMK (colorimetric water quality monitoring kit) – measures biocide levels (Ag, I_2/total Iodine) in water
- Water Kit – archive sample collection, bacterial enumeration, and detection of coliform bacteria

Problem: no specificity for organic compounds!

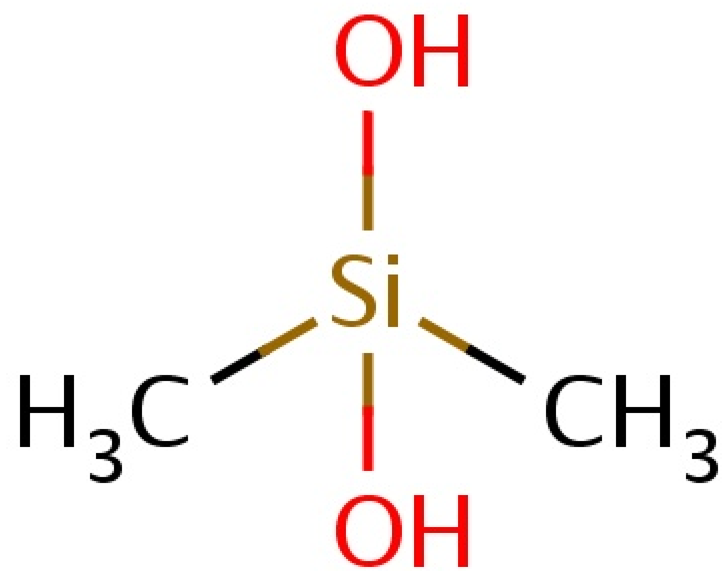
TOC Increases

- 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 Sin-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

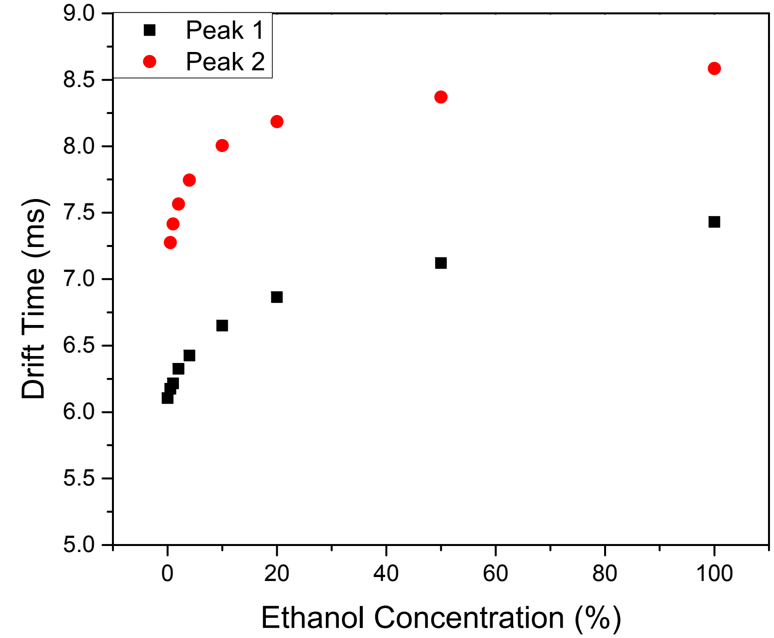


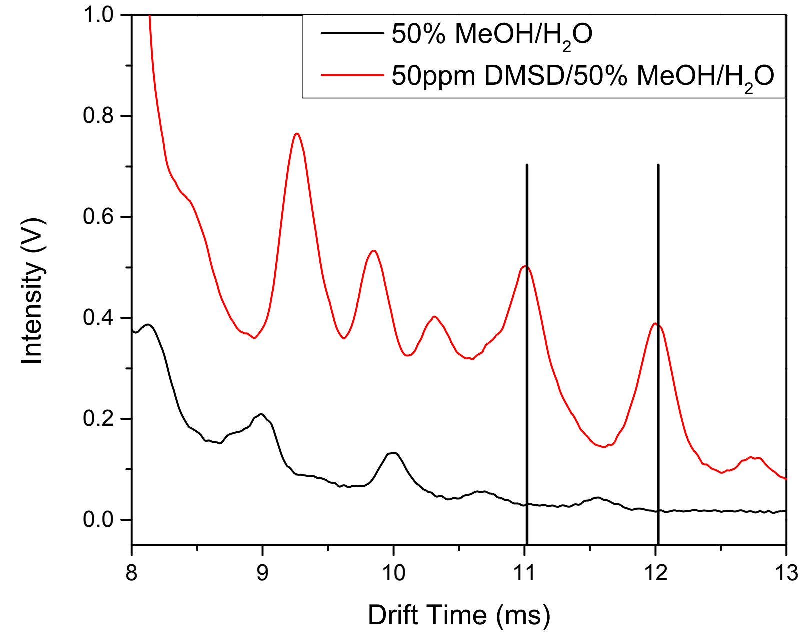
Needs

- 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

Previous Work

- 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 ≤ 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

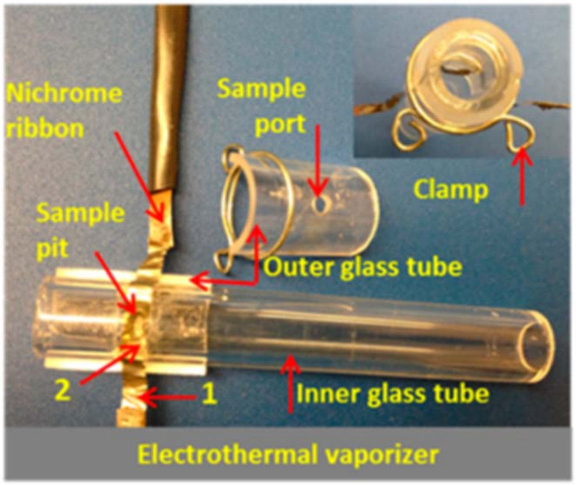


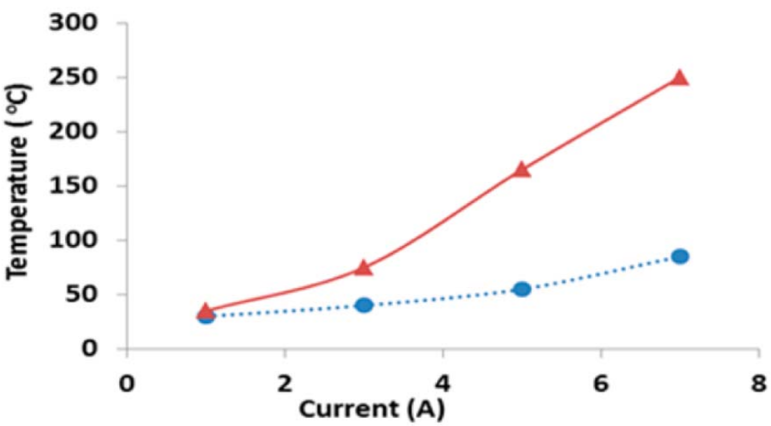


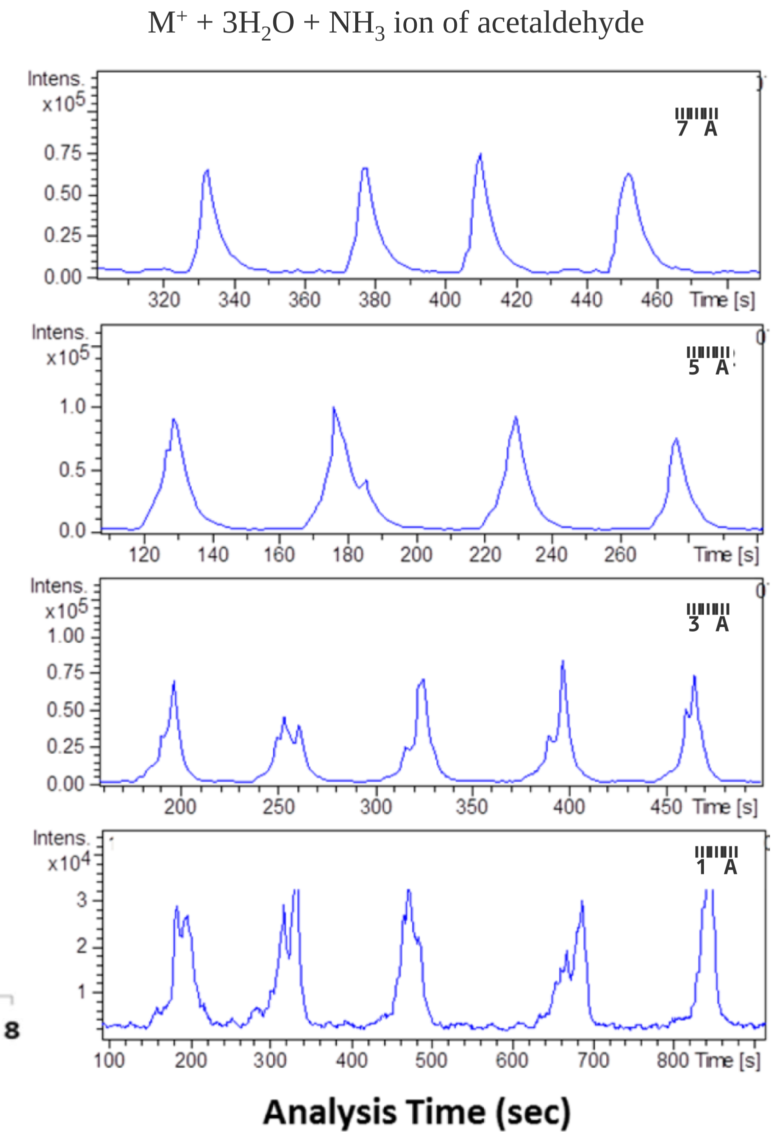
Path Forward

- 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)



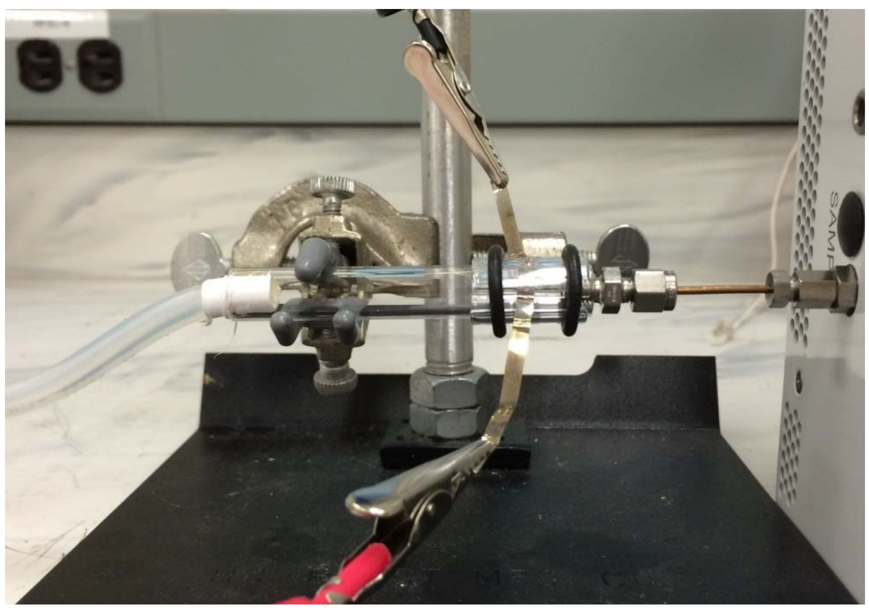


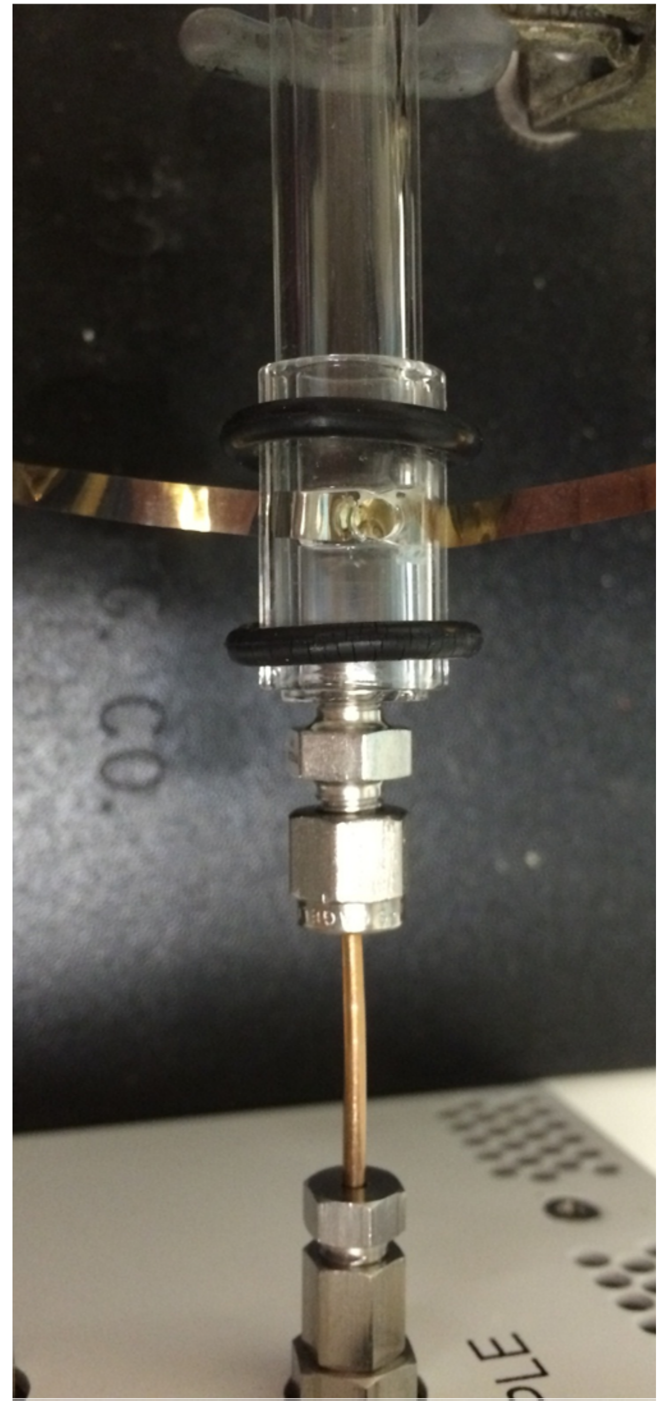


- ETV source placed in-line with DART-MS
- As current applied to nichrome ribbon containing sample, water solvent is vaporized and target analytes are volatilized and entrained in DART gas flow

Dwivedi et al., *Anal. Chem.* **85** (2013) 9898-9906.

ETV-AQM

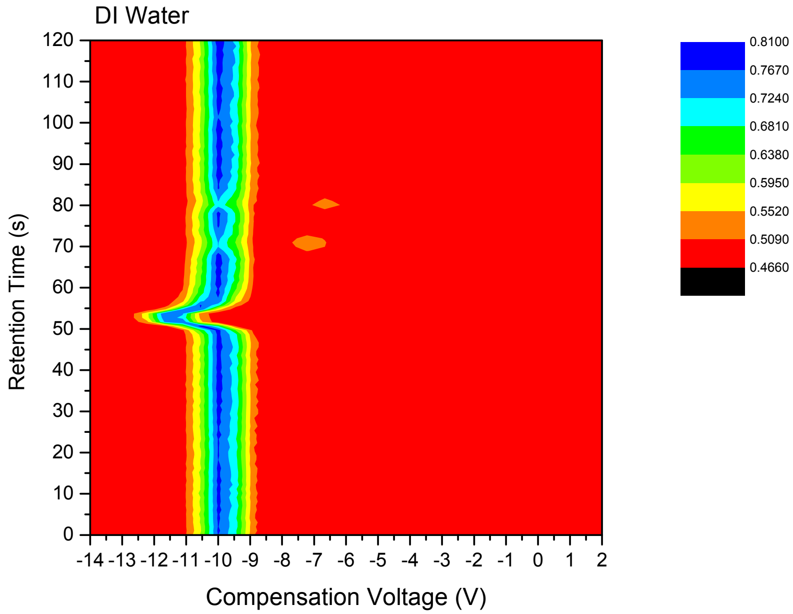


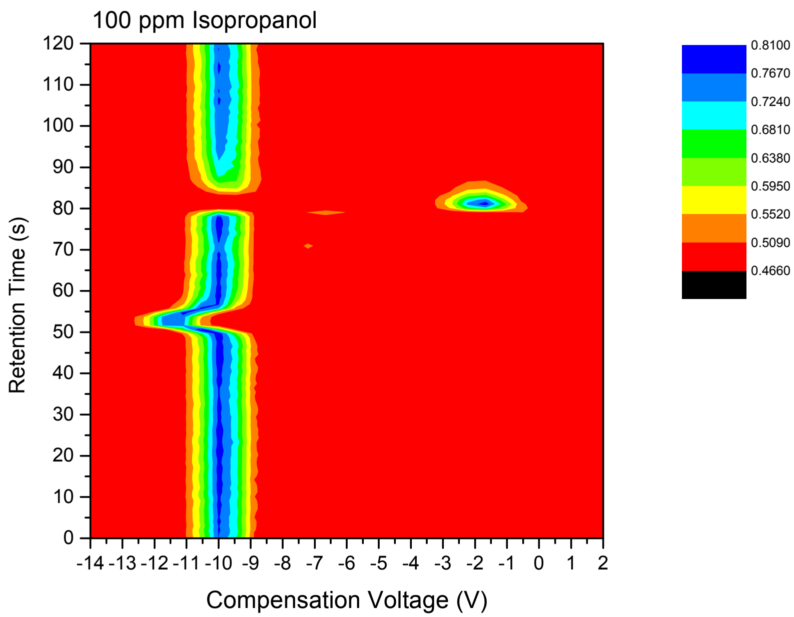


- DART-MS experiments show that ETV holds promise for sample introduction into air monitor

- 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

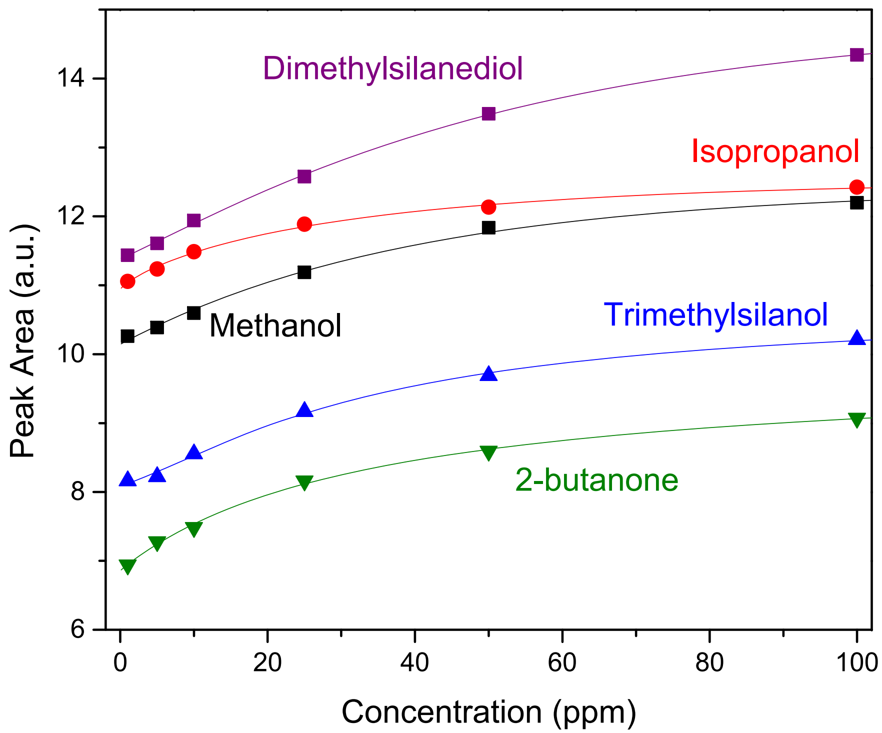


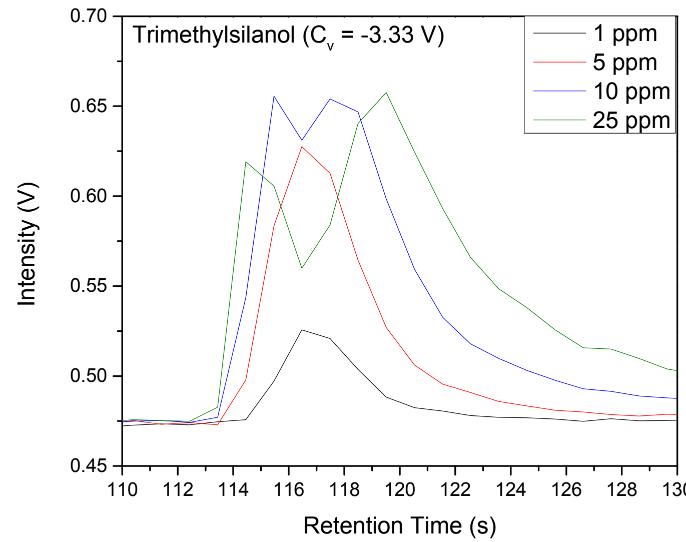


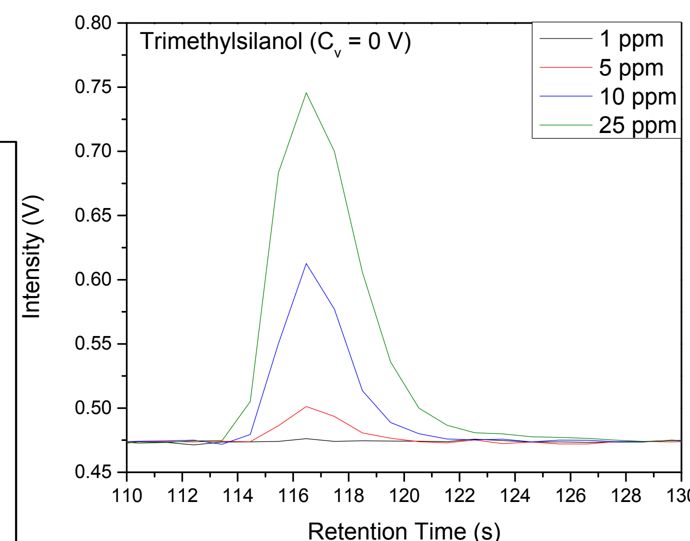
- Testing conditions
  - DB-5ms column
  - 2 uL of test solution placed on ETV ribbon
  - 250 cc/min zero air through ETV
  - Heating cycle – started with AQM run sequence
    - Clearance of ambient compounds (10 sec, 0 A) – corresponds to AQM pump running without sample valve open
    - Desolvation (1 sec, 2 A)
    - Analyte vaporization (2 sec, 5 A)
    - Decontamination (2 sec, 6 A)
- Concentration Range
  - 1 – 100 ppm

		Compensation Voltage			
Compound (mode)	**RT**	**RF900**	**RF1000**	**RF1100**	**RF1200**
Methanol (p)	60.66	-8.33	-11.11	-15.56	-20
Ethanol (p)	71.78	-3.33	-4.44	-5.56	
Acetone (p)	82.9	-0.56	-0.56		
Isopropanol (p)	81.89	-1.11	-1.11	-1.11	
Trimethylsilanol (p)	117.28	1.11	1.67	1.67	2.78
DMSD (n)	103.12	-1.67	-2.22	-2.22	-6.11
2-butanone (p)	135.47	0.56	0.56	1.11	

Concentration Dependence of Individual Compounds

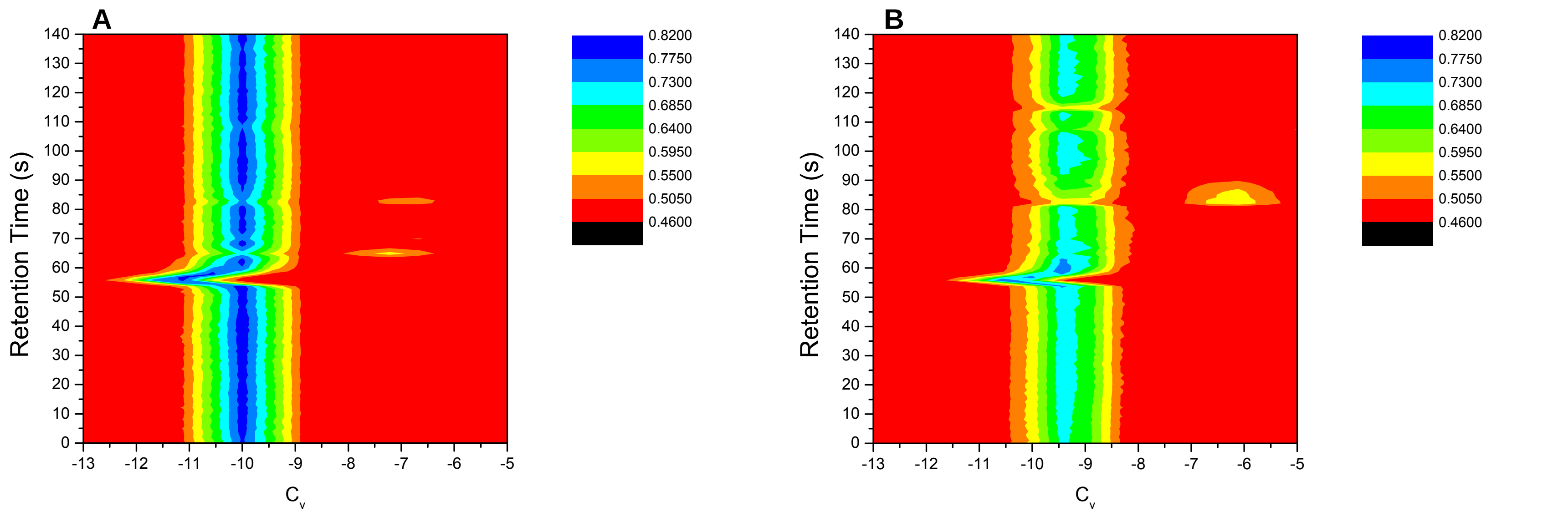




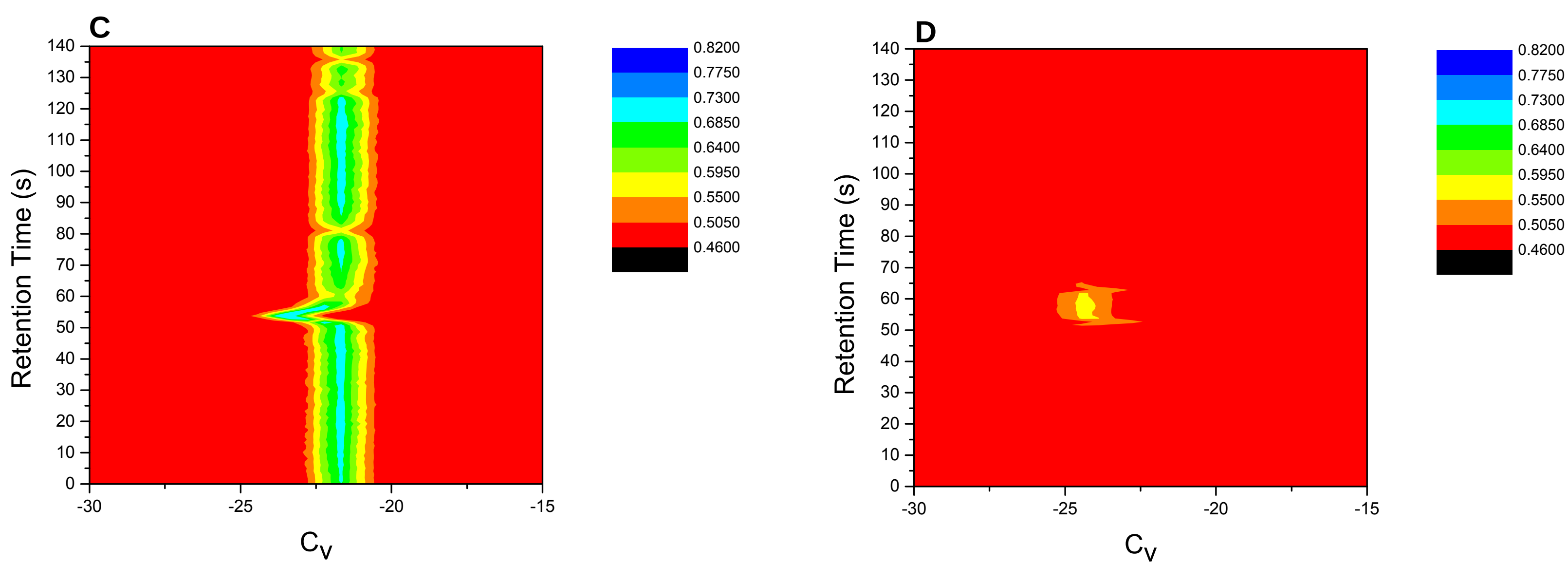


- Testing of TMS showed 2 peaks, causing difficulty in preparing calibration curve
  - Monomer peak gives better sensitivity
  - Dimer peak gives more dynamic range
- Concerns
  - What are the effects of using water samples?
  - What effect will mixtures have?
  - Can a GC method be prepared to use different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

Molecular Sieve Exhaustion

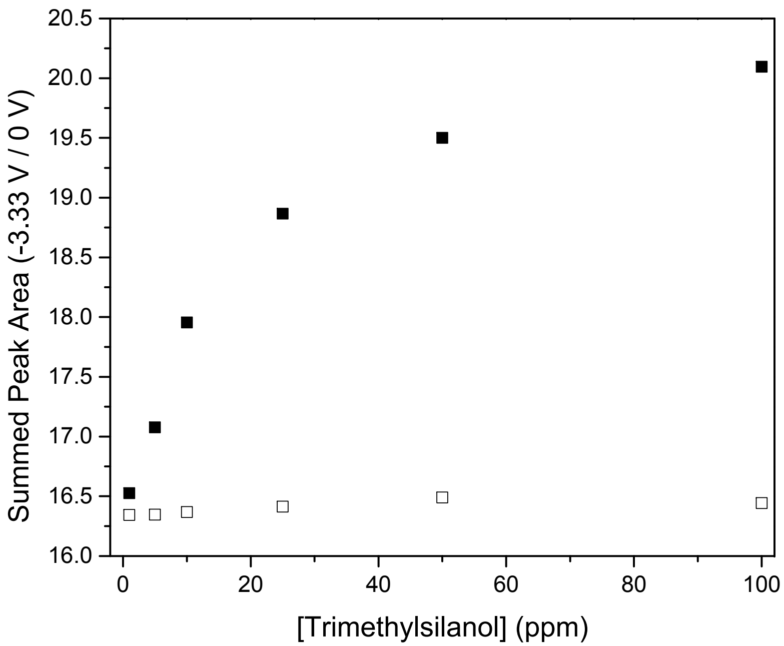


A: After 12 days of water testing (~ 98 runs with water), B: New sieve cartridges

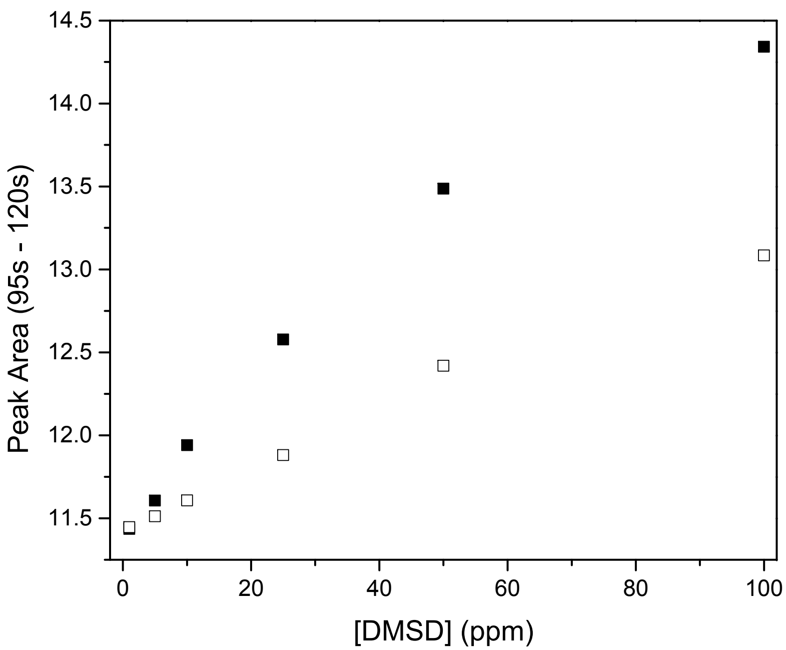


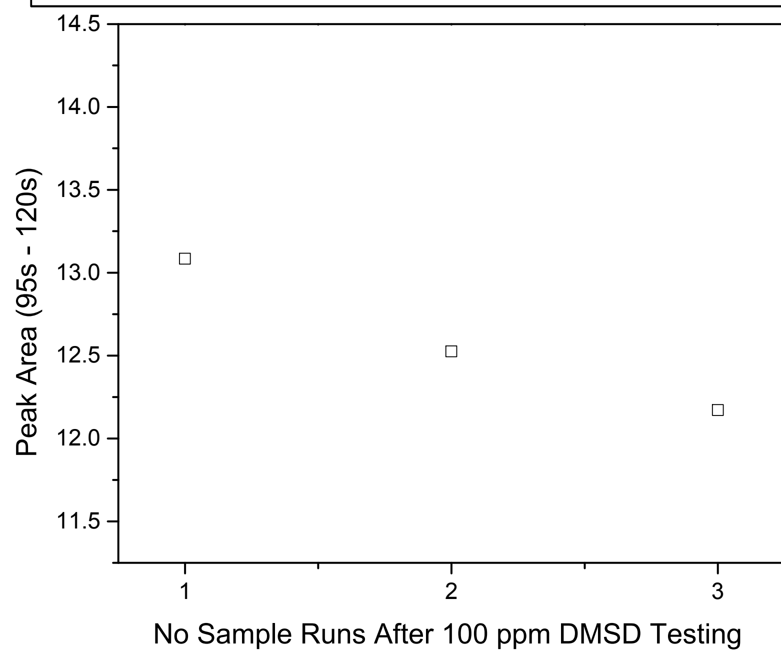
C: Blank run (no sample added to ribbon) after several weeks of water testing, D: Standard humidified air run

What About Carryover?

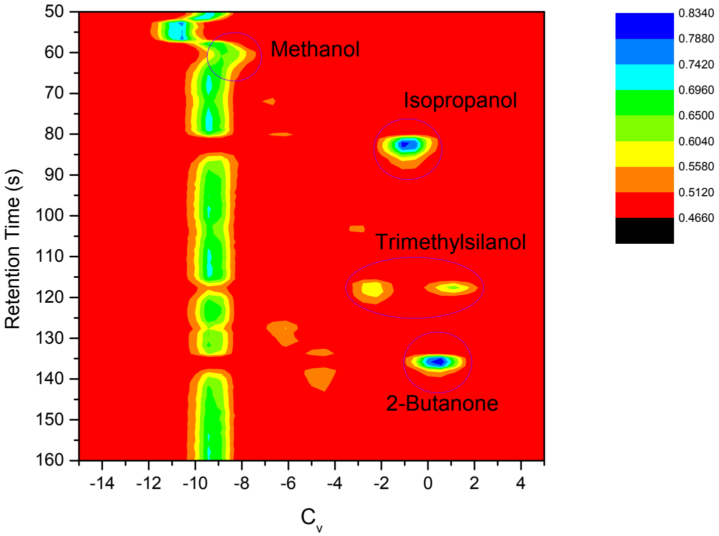


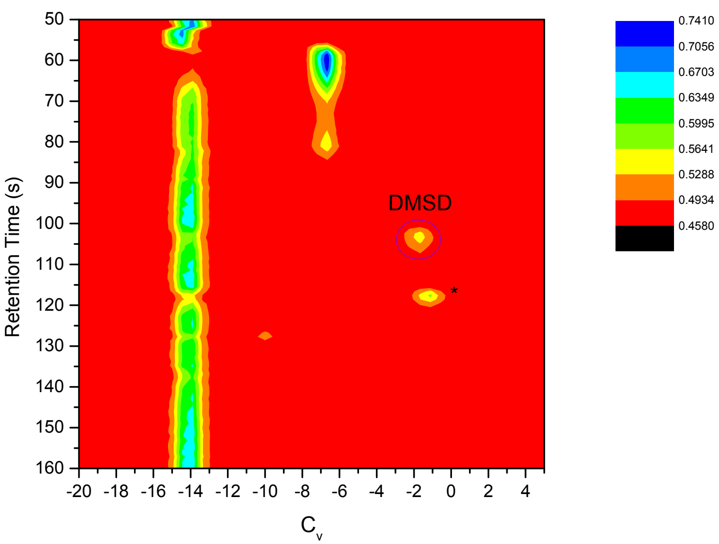
- Final step of heating sequence used to remove any remaining analyte
- Blank runs (no sample added) after sample runs show that decontamination step is sufficient for most compounds
- DMSD shows increasing intensity in blank runs correlating with sample concentration
- Multiple blank runs required to return intensity to pre-testing levels

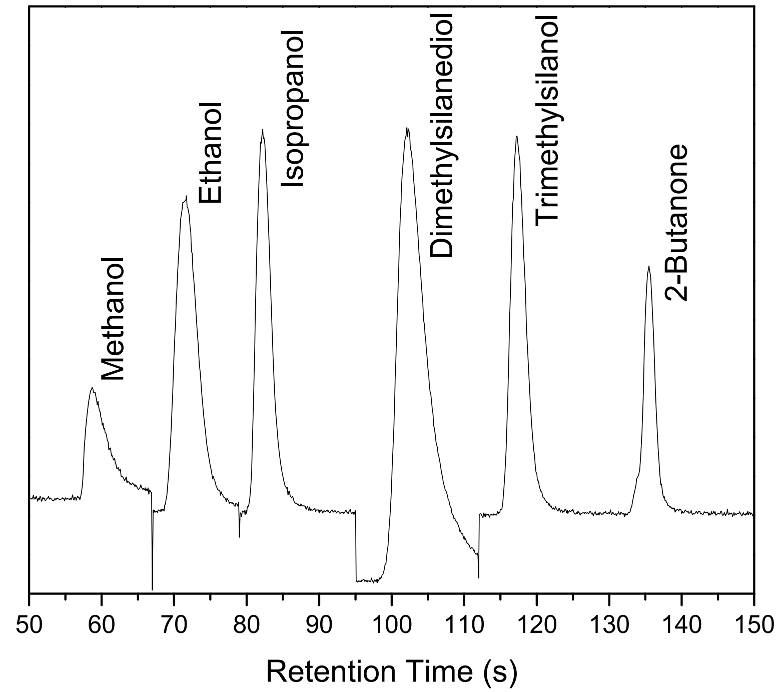




Testing of Mixtures and Preparation of GC Method

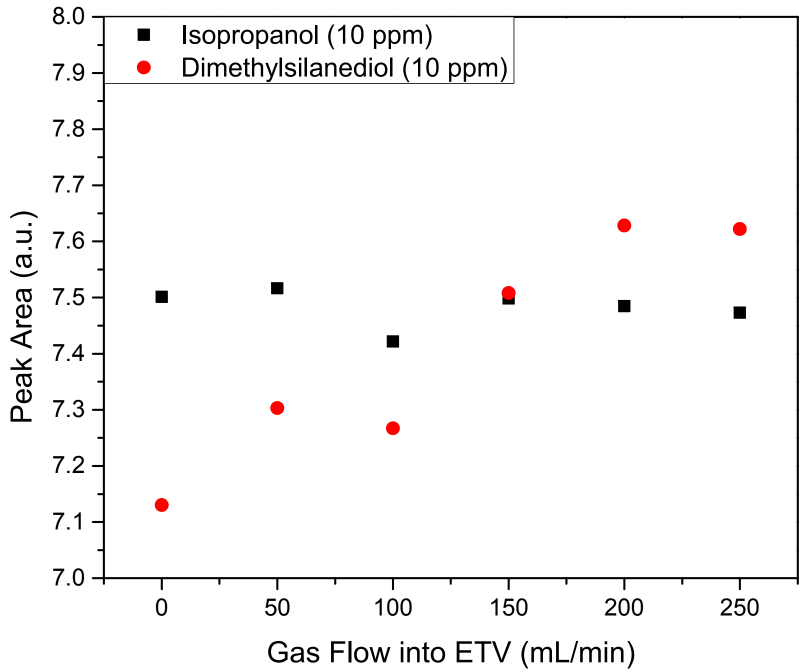


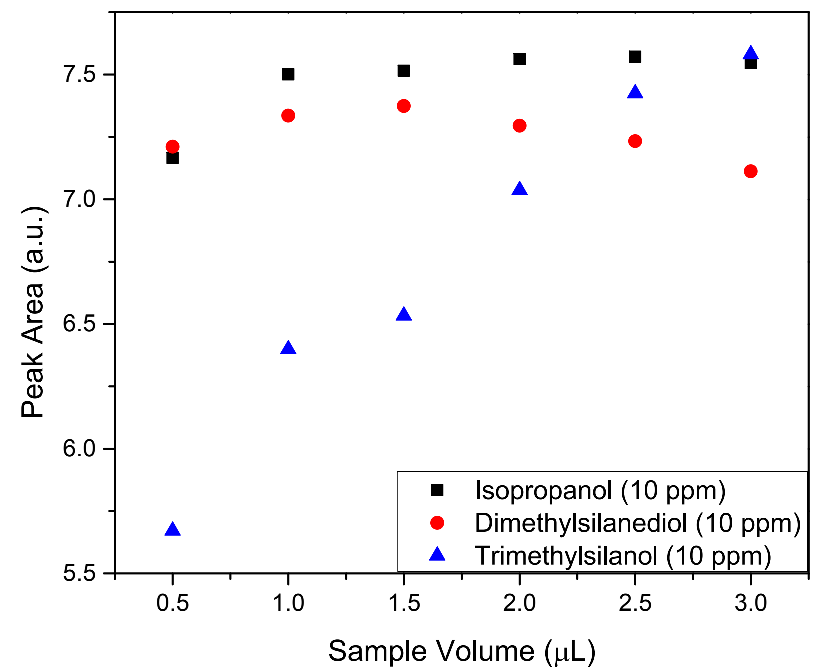




- Testing of mixture shows expected individual compounds
- GC method allows a single, short run (240 s) to be used for analysis of at least 6 compounds
- Coelution of acetone and IPA
    - Appropriate C_v allows IPA to be detected
- Without changes to AQM (cooling/dopant), different column needed for analysis of acetone

Effect of Flow Rate and Sample Volume

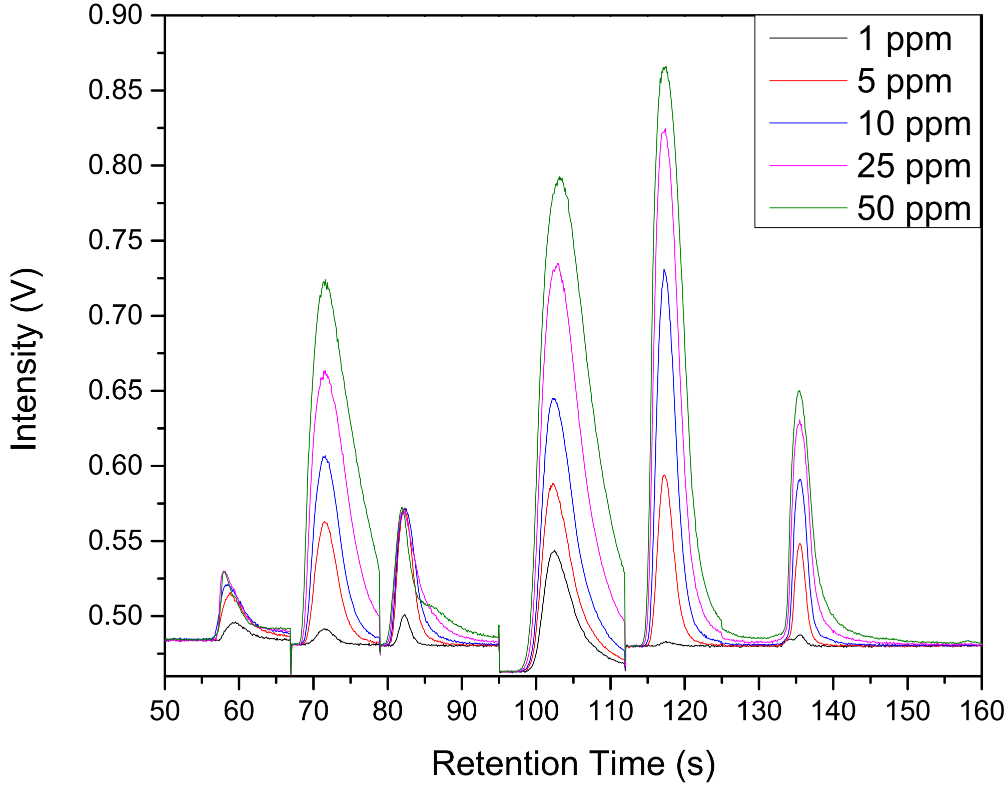


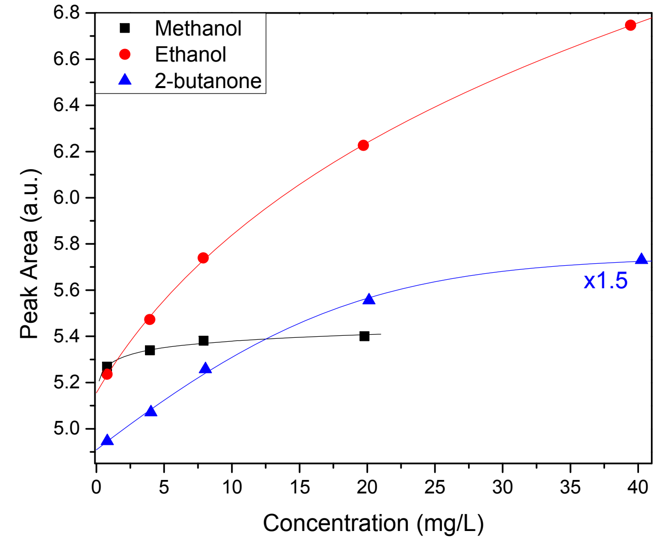


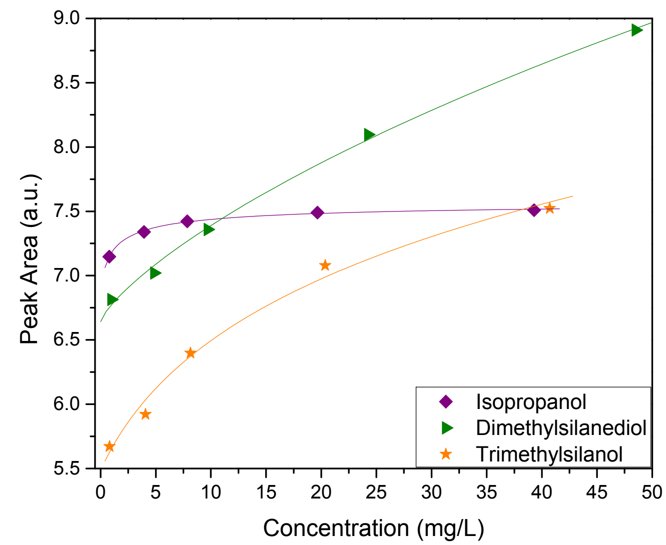
- Testing of DART-ETV-MS used flow through ETV of 3 L/min
    - Much too high for on-orbit operations
- Initial flows tested with ETV-AQM of 500 mL/min
- Further testing shows reproducible signals with *no* flow
- DMSD seems more susceptible to flow rates than IPA
- All further testing used 250 mL/min

- Testing with DART-ETV-MS used 0.5 – 2.0 µL sample volume
- Initial testing with ETV-AQM used 2.0 µL
- Reduced sample volume could improve sieve life and carryover
- Volume of 0.5 µL gives good signal for IPA/DMSD, but TMS not detectable

Calibration

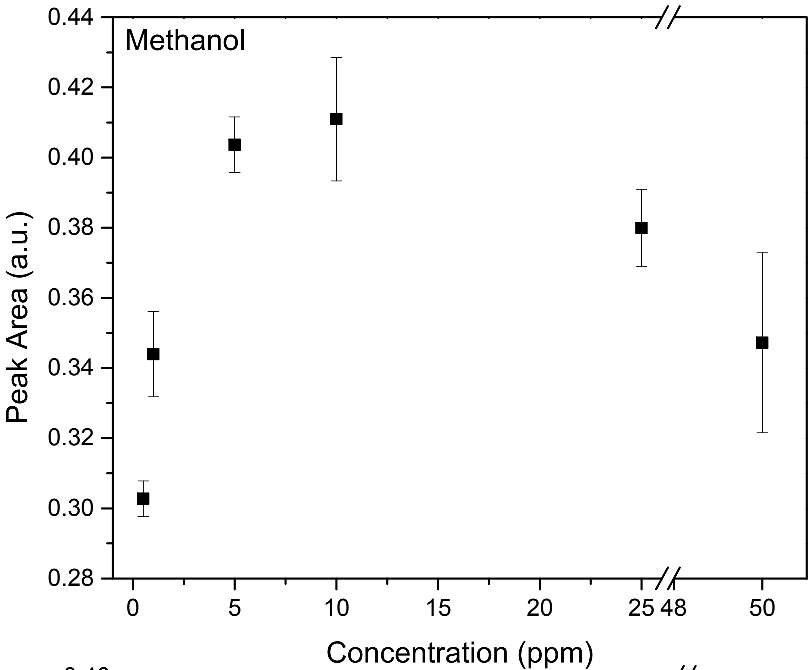


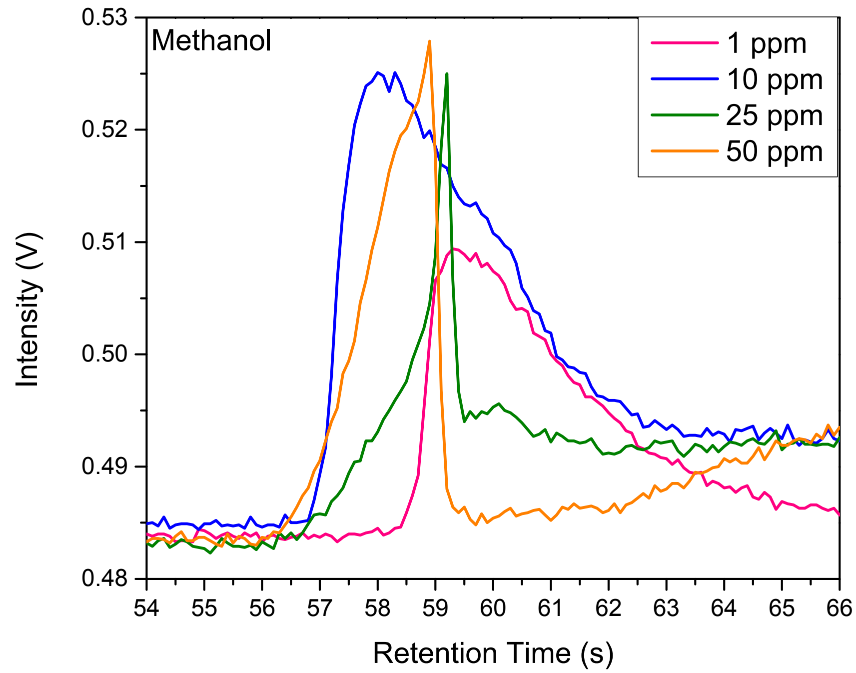


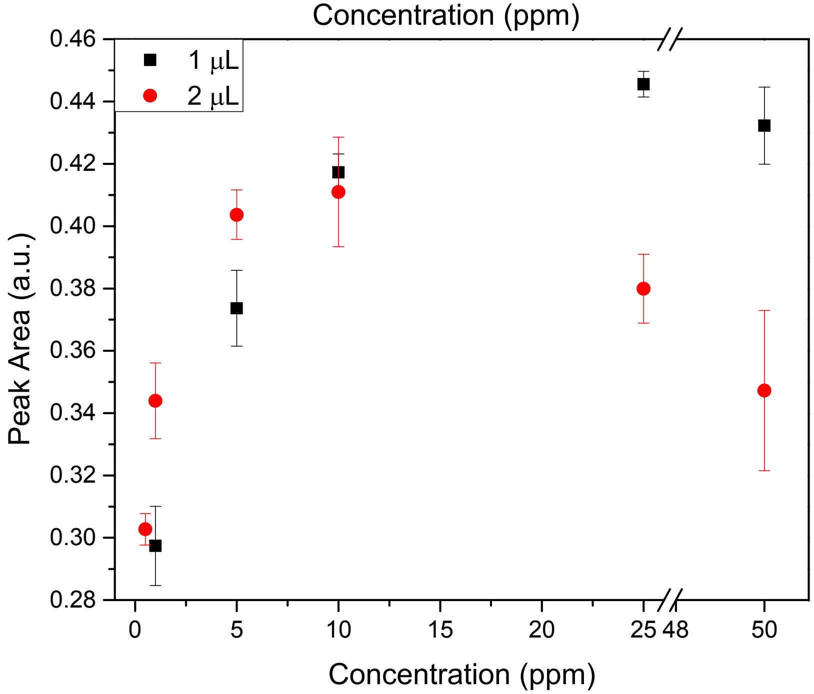


- Calibration of AQM using 7-compound mixtures to build calibration curves
- Calibration data used to check quality of curves
- Appropriate function chosen based on expected/historical concentrations
  - Quality of DMSD curve more important at > 10 ppm; quality of methanol curve more important < 10 ppm

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

		8/20/2013 Condensate		
Compound	Units	AQM	GC-MS / LC-RID	Percent Error
Methanol	µg/L	1305	5340	76
Ethanol	µg/L	33147	23800	39
Isopropanol	µg/L	756	405	87
Dimethylsilanediol	µg/L	26544	24000	11
Trimethylsilanol	µg/L	1223	500	145
2-butanone	µg/L	436	64	581

		9/10/2012 Condensate		
Compound	Units	AQM	GC-MS / LC-RID	Percent Error
Methanol	µg/L	1230	5480	78
Ethanol	µg/L	45409	49100	8
Isopropanol	µg/L	825	708	16
Dimethylsilanediol	µg/L	47124	44000	7
Trimethylsilanol	µg/L	1154	408	183
2-butanone	µg/L	354	68	421

- 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

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