Evaluation of a Gas Chromatograph-Differential Mobility Spectrometer for Potential Water Monitoring on the International Space Station

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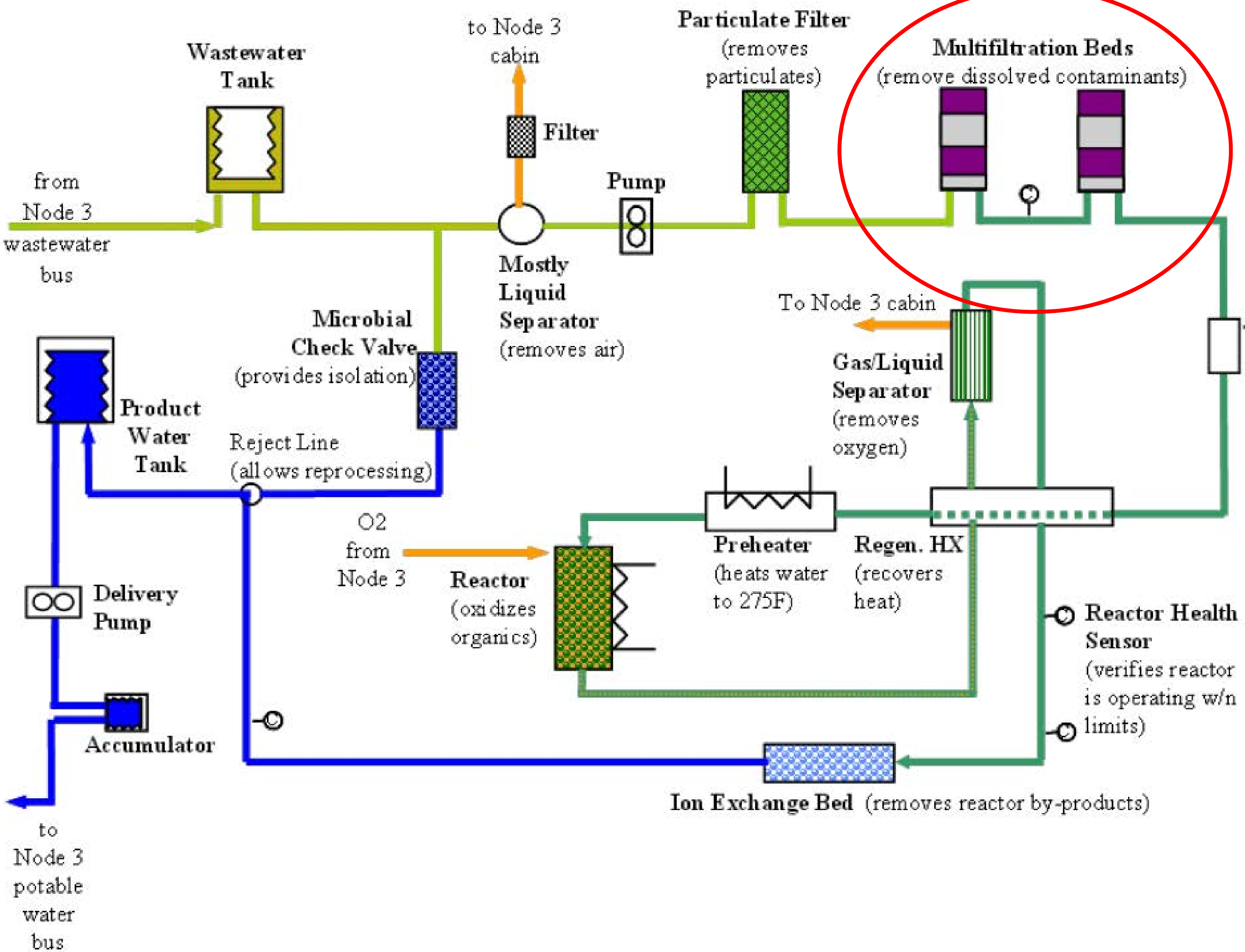
Water on the International Space Station

ISS Program established a water quality & monitoring program for regenerated and stored potable water

- Water Recovery System (WRS)
  - Urine Processor Assembly (UPA) processes pretreated urine by distillation and delivers distillate to a wastewater tank where it is combined with humidity condensate.
  - Water Processor Assembly (WPA) treats the wastewater using multifiltration and thermal catalytic oxidation, adds iodine biocide, and stores product water for delivery to the potable water bus.
- Potable Water Dispenser (PWD)
  - Receives WPA product water direct from the bus and dispenses either hot or ambient water after removing iodine at the point of use

WPA Schematic



Removes inorganics and non-volatile organics

Water Quality Monitoring on ISS

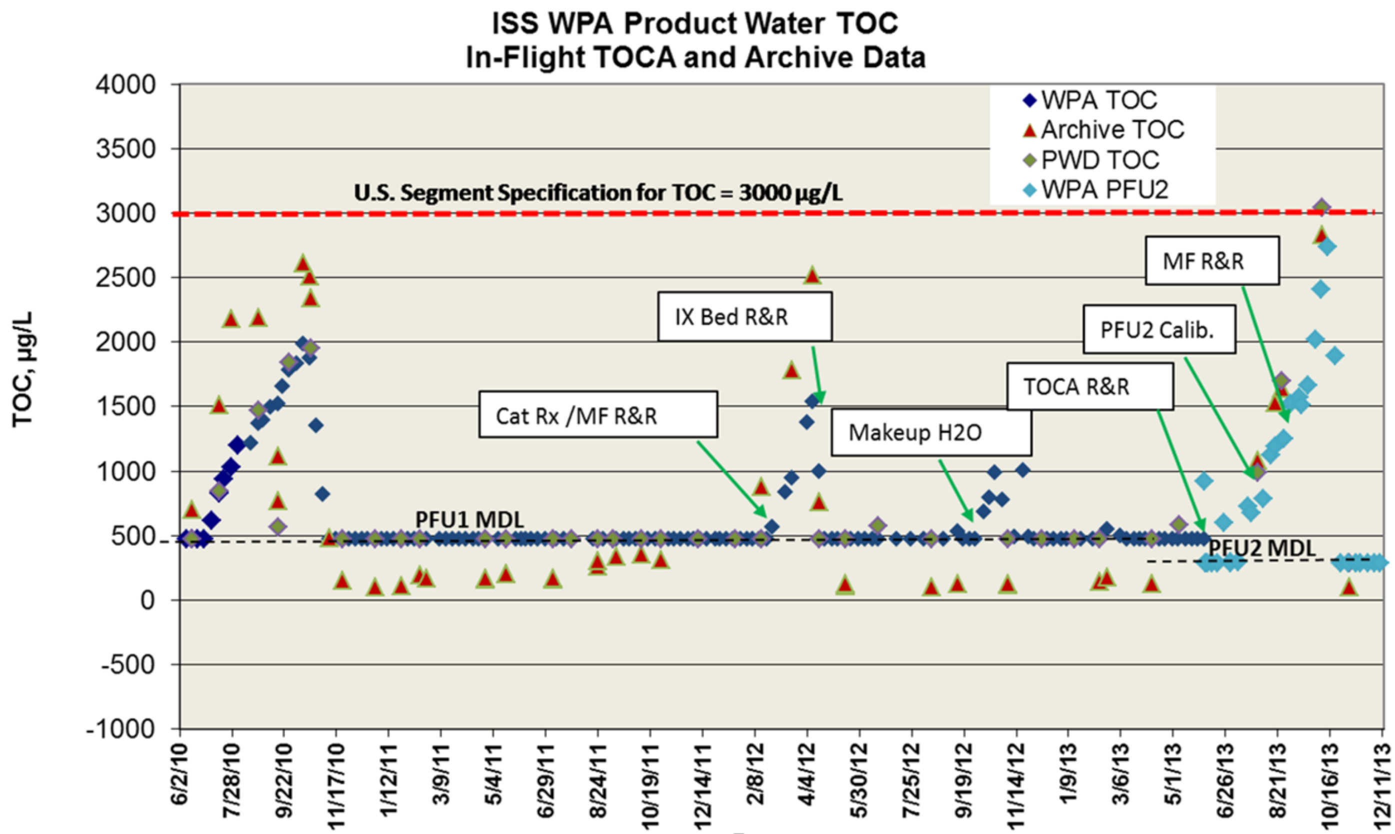
- Due to the relatively high purity of ISS potable water, the water quality monitoring strategy currently employs the following:
  - Monitor TOC (total organic carbon) with TOCA
  - Monitor biocide levels (iodine in US potable water) with CWQMK
  - Archival samples returned for ground analysis

TOCA (total organic carbon analyzer) – measures total organic carbon concentrations in ISS water using IR

CWQMK (colorimetric water quality monitoring kit) – measures biocide levels (Ag, I_2/total Iodine) in water using absorbance

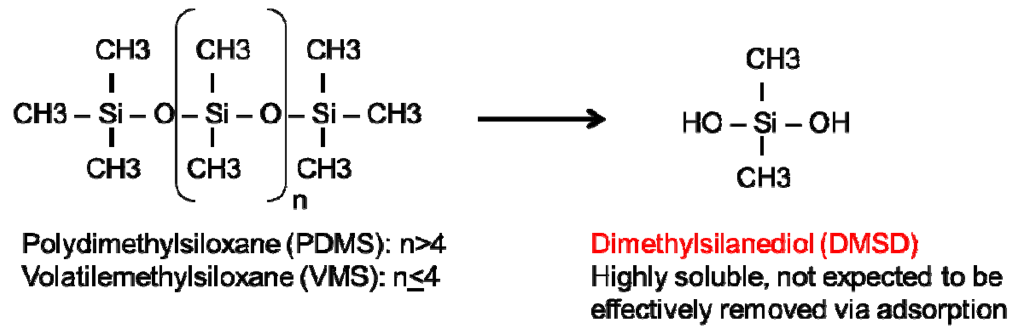
Water Quality Monitoring on ISS

- In 2010, crew observed increase in TOC, approaching the 3000 µg/L US Segment Specification for TOC; replacement of multi-filtration bed of WPA required



- Return samples and extensive ground analysis attributed rise of TOC (>90%) to presence of dimethylsilanediol (DMSD)

Water Quality Monitoring on ISS

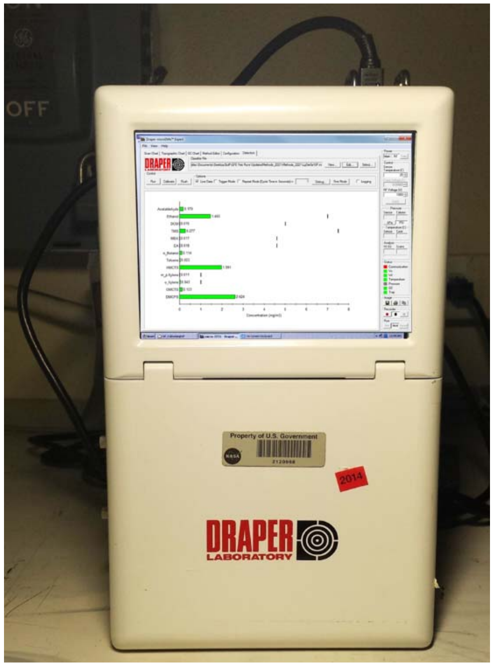


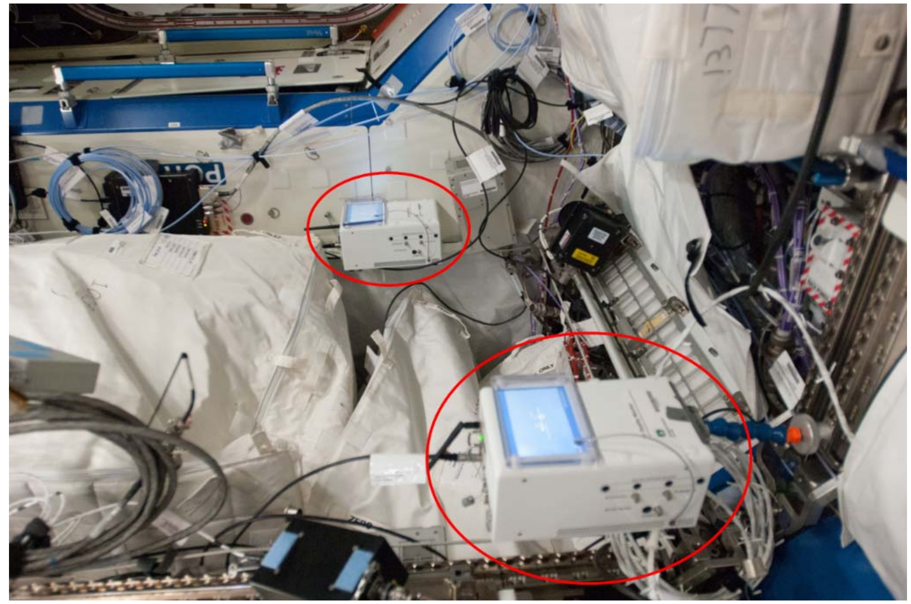
- DMSD not health concern below 35,000 µg/L (equivalent to a TOC of 9000 µg/L)
- ECLSS concern since DMSD shortens life of multi-filtration beds of WPA and impacts traffic model
- Increase in TOC continues to occur periodically
- Exposure to DMSD is low risk from crew health perspective, but its ability to increase background TOC has potential to hide other problems
  - Mask presence of more toxic compounds present at low concentrations
  - Mask indication that WPA performance is compromised, e.g., incomplete/partial oxidation of small organics due to problems with oxidation reactor
- *DMSD has effectively shed light on a hole in current ISS water quality monitoring strategy – ability to identify and quantify target species in ISS potable water in real time*

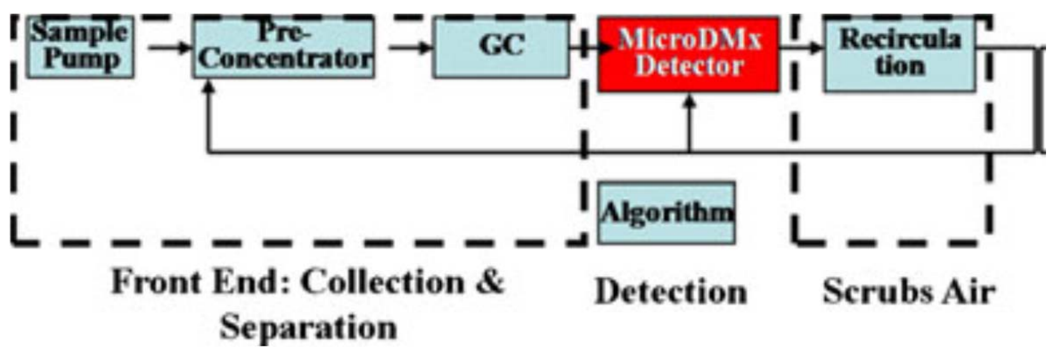
Need for Real-time Monitoring

- 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
- 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 of target species a priority, especially for future exploration missions
    - Lack of ground support
- Compound-specific information needed to determine if drastic changes in TOC require mitigation efforts or if water can still be safely used
- *Ground analysis of water samples typically involves same analytical hardware used in the ground analysis of air samples; only difference is method to separate the water from the compounds of interest*
- Air Quality Monitor (AQM) monitors trace volatile organics in real time; many of the target compounds in air are the same for water; presents a potential starting point
- Development of multifunctional monitor would improve current analysis and is a first step towards fulfilling the needs of future missions
- *Need to liberate organics from water matrix for analysis*

Air Quality Monitor (AQM)

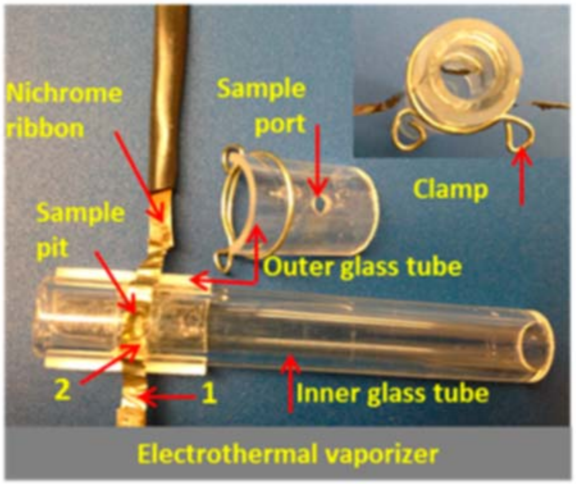


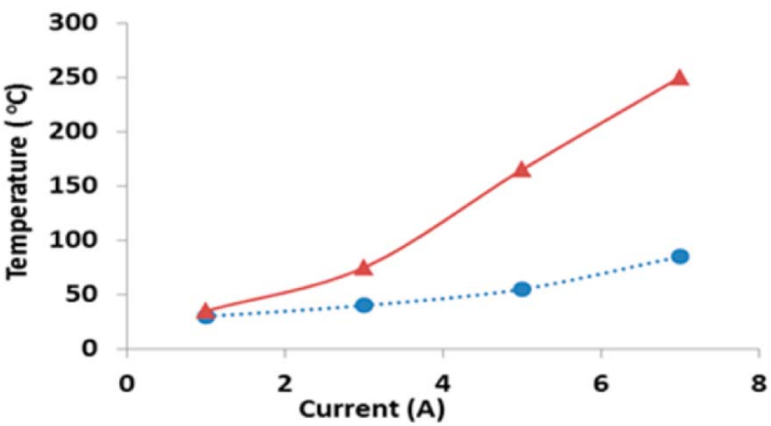


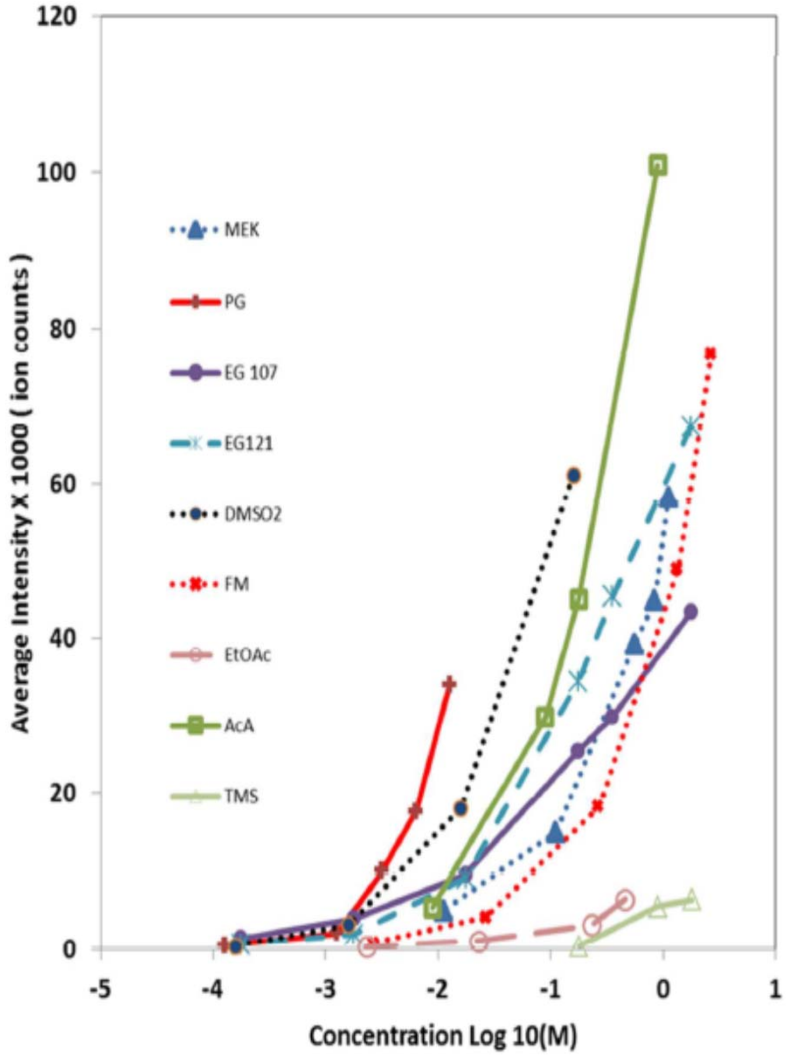


- AQM combines gas chromatography with differential mobility spectrometry
- 2 units currently on board the ISS; different GC columns
- Target list of 22 compounds detected using automated methods
    - Other compounds analyzed manually
- Sample purge available to remove moisture

Electrothermal Vaporization (ETV) Inlet





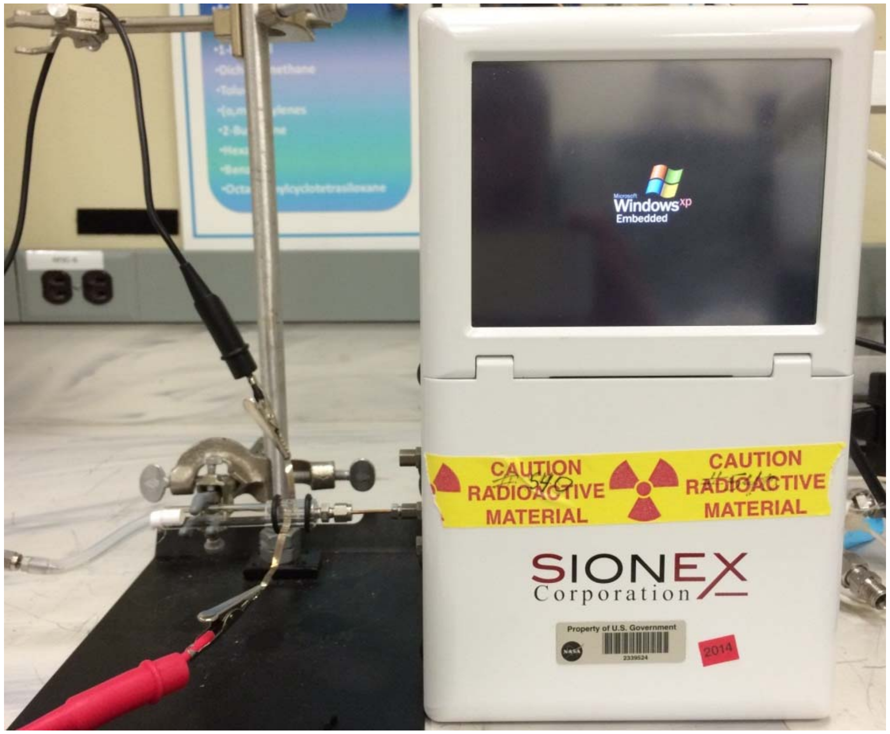


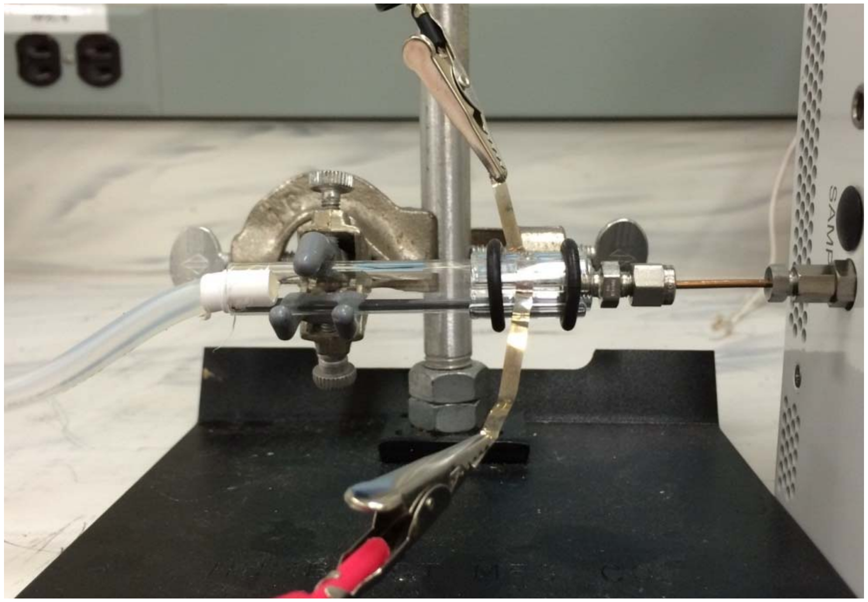
- ETV source placed in-line with atmospheric pressure ionization source (DART) coupled with mass spectrometer
- As current applied to nichrome ribbon containing sample, water solvent is vaporized and target analytes are volatilized and entrained in carrier gas

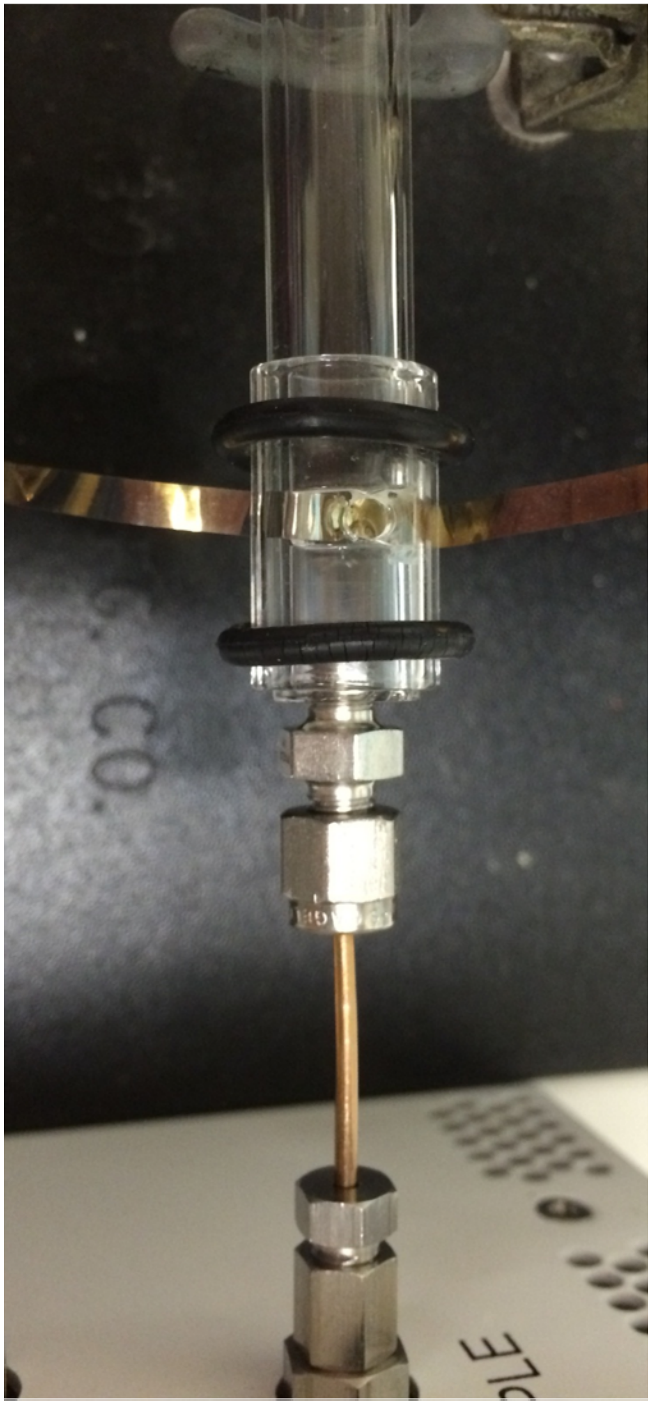
Dwivedi et al., *Anal. Chem.* **85** (2013) 9898-9906.

ETV-AQM

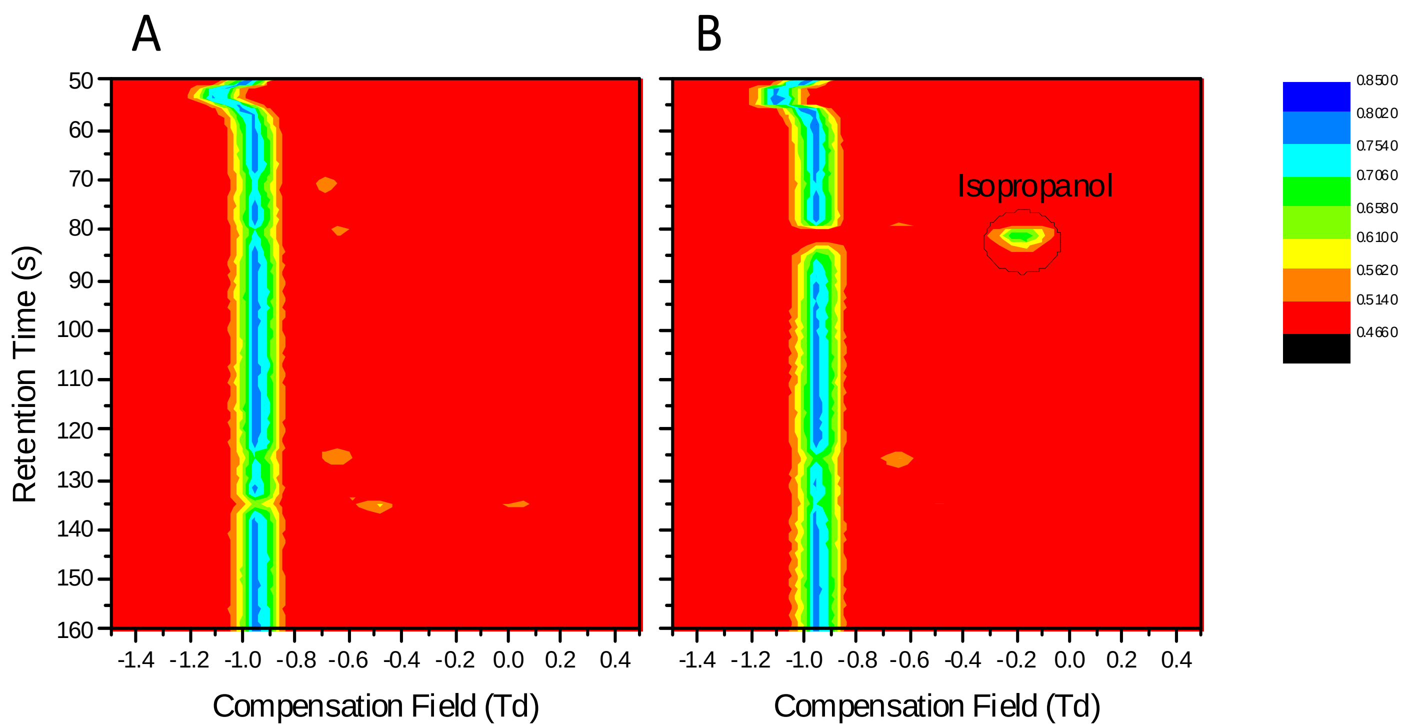
- DART-MS experiments show that ETV holds promise for sample introduction into air monitor
- For spaceflight water monitoring, need to utilize current hardware and reduce reliance on ISS (e.g. power and carrier gas)







Initial Analysis of Individual Compounds

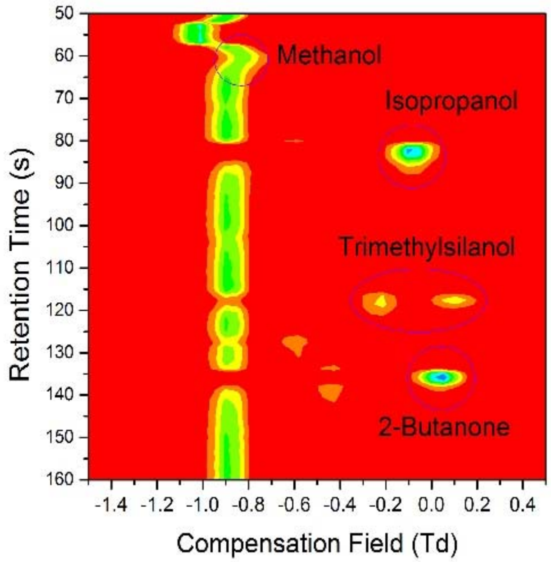


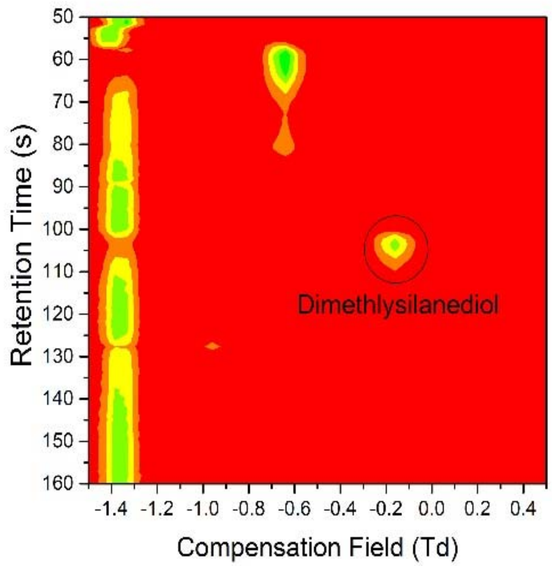
- Tested DI water (A) using ETV-AQM for control
- Added subset of target compounds (B) to determine retention time and DMS parameters
- Concentration Range
  - 1 – 100 mg/L

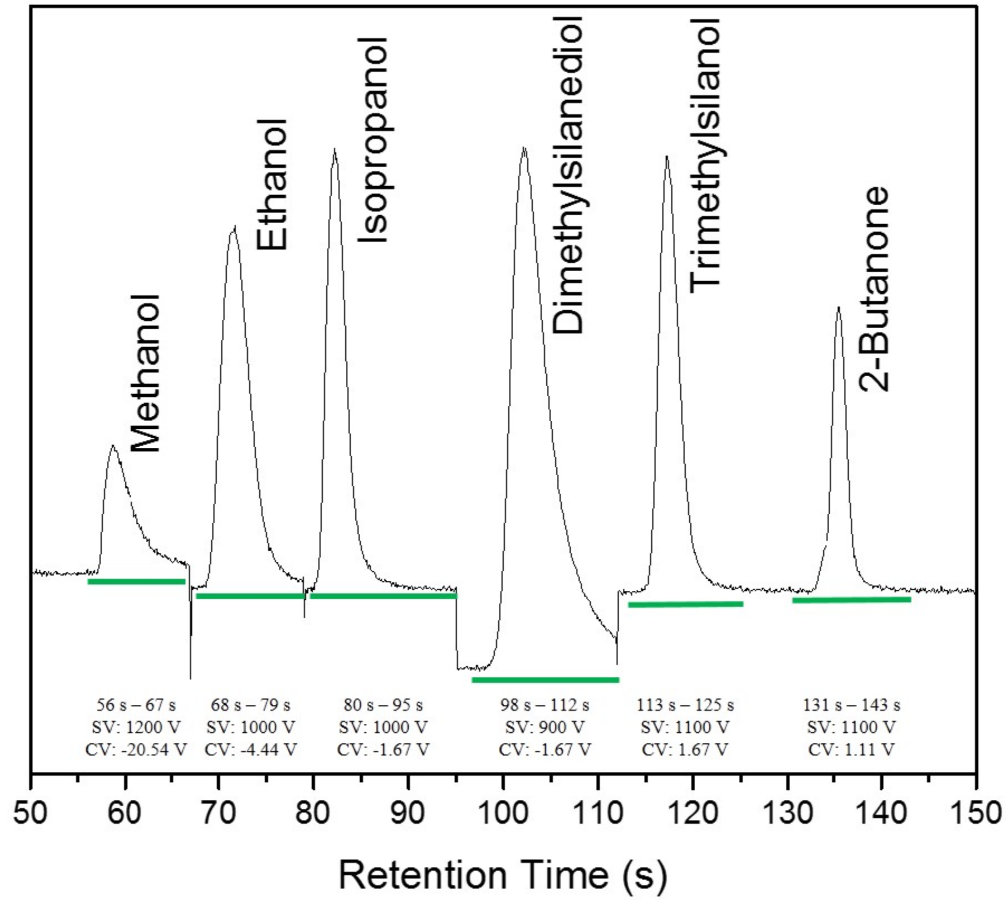
Wallace et al., *Anal. Chem.* (2015) submitted

		Separation Field				
Compound (mode)	**Retention Time (s)**	**87 Td**	**96 Td**	**106 Td**	**115 Td**	
Methanol (+)	60.7	-0.85	-1.12	-1.50	-1.92	**Compensation Field (Td)**
Ethanol (+)	71.8	-0.32	-0.43	-0.54		
Isopropanol (+)	81.9	-0.11	-0.11	-0.11		
Acetone (+)	82.9	-0.05	-0.05			
Dimethylsilanediol (-)	103.1	-0.16	-0.21	-0.21	-0.59	
Trimethylsilanol (+)	117.3	0.11	0.16	0.16	0.27	
2-Butanone (+)	135.5	0.05	0.05	0.11		

Testing of Mixtures and Preparation of GC Method

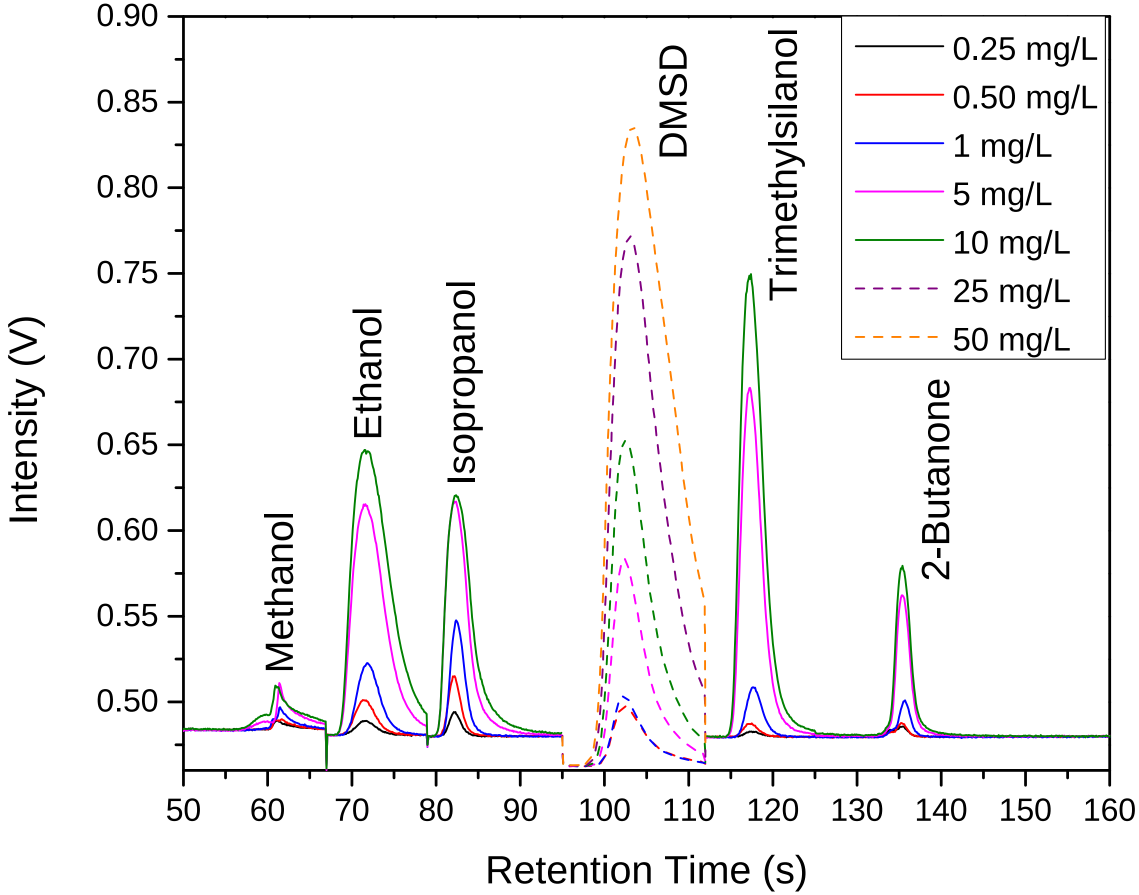


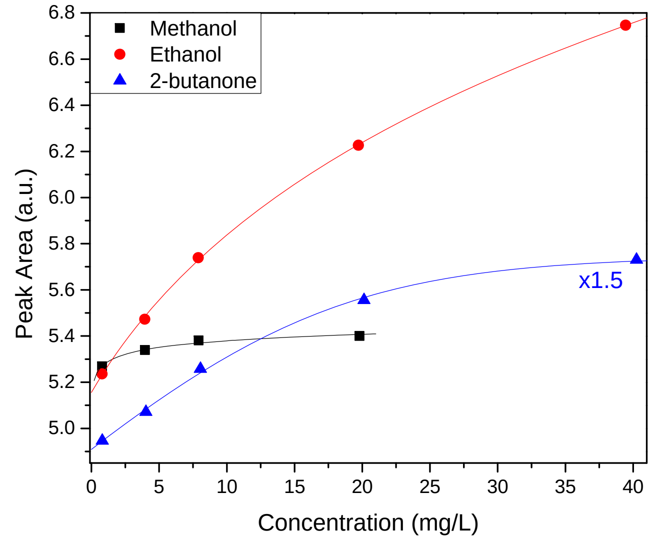


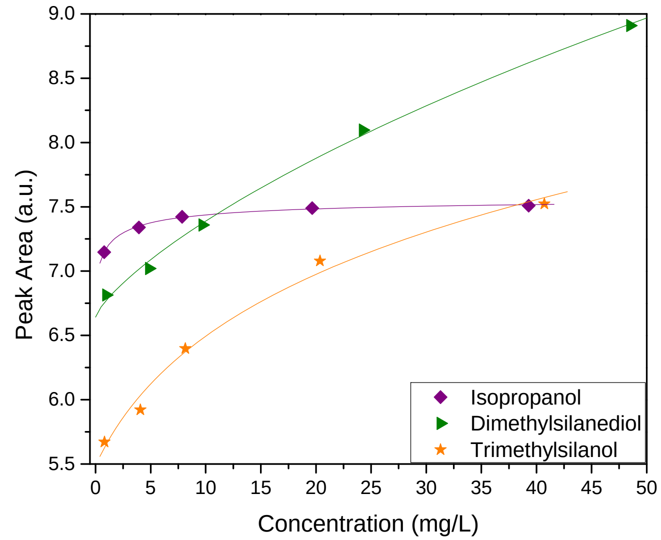


- Testing of mixture shows expected individual compounds
- Scan method does not provide automated, optimized information (i.e. concentration)
- GC method allows a single, short run (240 s) to be used for automated analysis of at least 6 compounds
- Coelution of acetone and IPA
  - Appropriate C_v allows IPA to be detected
- Without changes to AQM (cooling/dopant), different column needed for analysis of acetone

Calibration







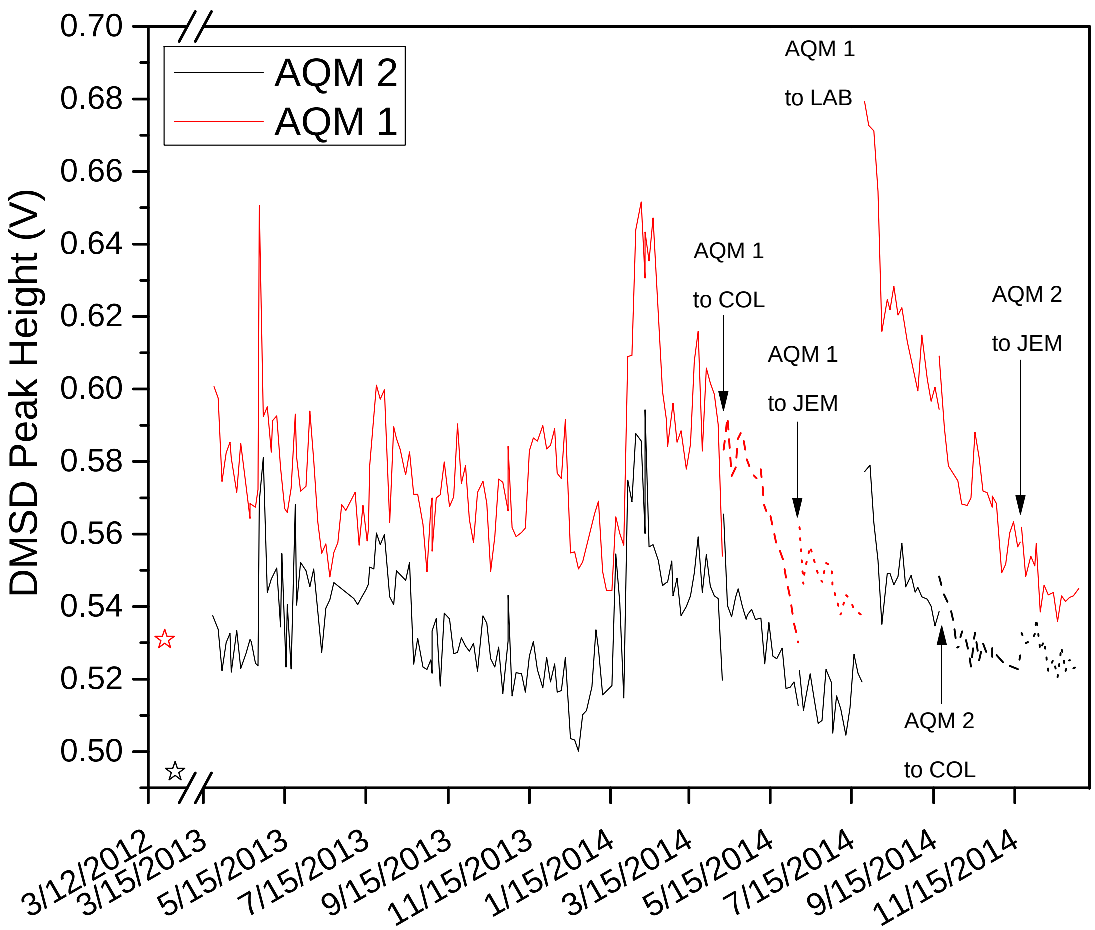
- Calibration of AQM using 7-compound mixtures to build calibration curves
- Appropriate function chosen based on expected/historical concentrations
- Calibration data used to check quality of curves

Analysis of ISS Archival Samples

		Potable Water Dispenser 7/30/2013		Product Water 8/19/2013	
Compound	**Units**	**ETV-AQM**	**GC-MS/LC-RID**	**ETV-AQM**	**GC-MS/LC-RID**
Methanol	$\mu g\ L^{-1}$	17.8	< 200	ND	< 200
Ethanol	$\mu g\ L^{-1}$	15.4	< 200	28.9	< 200
Isopropanol	$\mu g\ L^{-1}$	ND	< 200	ND	< 200
Dimethylsilanediol	$\mu g\ L^{-1}$	4390	3800	6830	5300
Trimethylsilanol	$\mu g\ L^{-1}$	403	ND	228	ND
2-butanone	$\mu g\ L^{-1}$	41.1	< 5	81.9	< 5

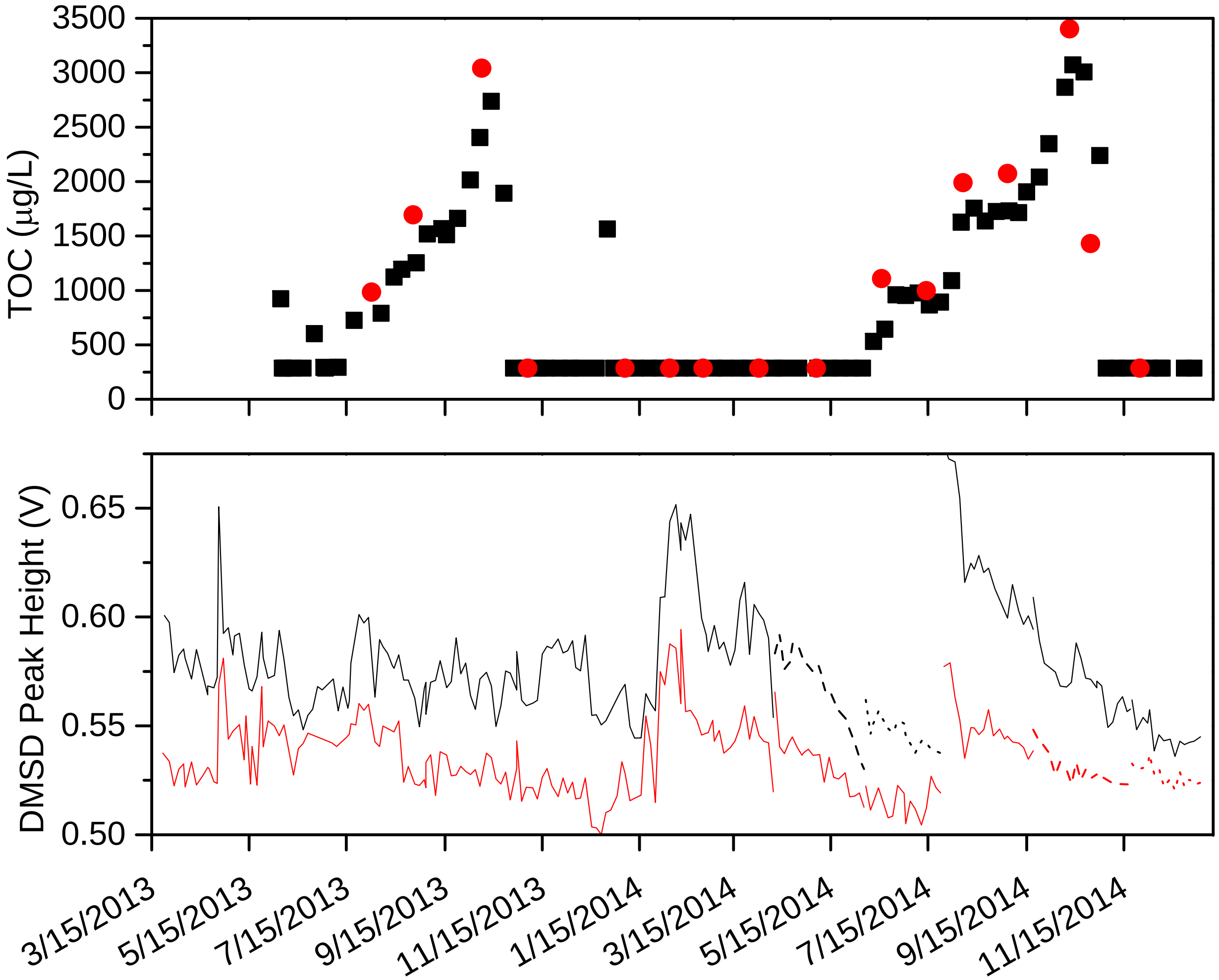
- DMSD, methanol, ethanol, and isopropanol – correlate well with laboratory-based methods
- TMS / 2-butanone values determined by lab-based methods are below the lowest AQM calibration point
    - Reason for higher AQM values unclear

Is DMSD Present in the Atmosphere?



- Vapor pressure of DMSD in solution is low; difficult/impossible to introduce samples into AQM
  - No way to determine analytical parameters (RT, C_V, +/-)
- Testing of ETV with MS gave first surprising information; *DMSD detected as negative ion*
- Integration of ETV with AQM provided other parameters
  - AQM parameters of other organics tested in water matched those tested in air
- Analysis of ground prep data and flight data shows marked increase in DMSD peak
- Presence of peak and similar trends on both instruments indicates not an artifact

Does the Atmospheric DMSD Correlate with the TOC Increases?



- No obvious correlation between TOCA readings and atmospheric DMSD
- DMSD in product water based on buildup and breakthrough of MF beds
  - Should not expect direct relationship
- Comparison with condensate samples would be interesting
  - Not enough points for comparison currently

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
- Analysis of atmospheric data shows presence of DMSD, but no direct correlation with TOC

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