Progress on the Organic and Inorganic Modules of the Spacecraft Water Impurity Monitor, a Next Generation Complete Water Analysis System for Crewed Vehicles

Stuart Pensinger and Mike Callahan, NASA

Evan Neidholdt, KBR HHPC (presenting)

Aaron Noell, Nathan Oborny, Byunghoon Bae, Valeria Lopez, Bruce Hancock, Marianne Gonzales, Margie Homer, Stojan Madzunkov, Murray Darrach, Richard Kidd; Jet Propulsion Laboratory, California Institute of Technology (JPL)

ICES-2023-110

Presenter name

Background

- The need for development of in-flight water quality monitoring beyond total organic carbon (TOC) is captured in NASA technology roadmaps.

- TOC is an important metric for spacecraft water quality, but only provides the *total* quantity of organic chemicals present in a water sample, it does not identify or quantify each chemical specifically.

- For exploration missions, the return of water samples to Earth for laboratory analysis to identify the chemicals responsible for the TOC number will be challenging or impossible, depending on the destination.

- **The Spacecraft Water Impurity Monitor (SWIM) will seek to provide the enhanced analytical capability that enables NASA to confidently send astronauts on distant missions without the possibility of returned water samples, due to new capabilities of both identification and quantitation for any water impurities.**

Need for monitoring beyond TOC

The need for development of in-flight water quality monitoring beyond TOC is captured in NASA Technology Roadmap:

- TA 6.4.1, Sensors: Air, Water, Microbial, and Acoustic.
- Specifically, 6.4.1.5 - water quality sensor to identify and quantify target organic and inorganic chemical species in the water of manned spacecraft **without any reliance on ground analysis**.

Unable to send samples back for lab analysis – must take lab with you!

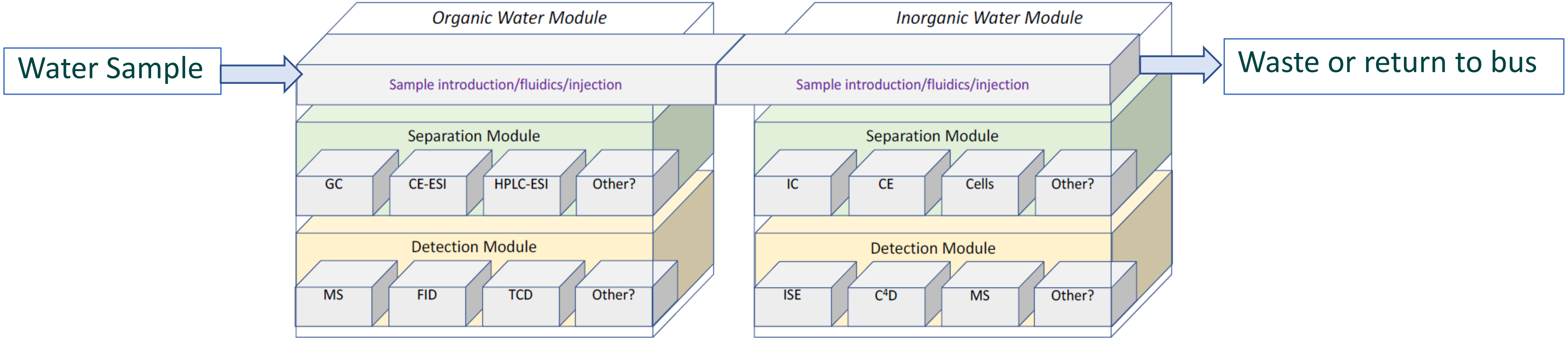
Customers:

- 1° - Habitat(s) System Management – ECLSS
- SK Health
- Lunar EVA
- Lunar ISRU
- Crop Food Production Research Area
- Martian EVA
- Martian ISRU
- JAXA
- Commercial
- SMD

SWIM Overview

- The SWIM system will comprise an organic water module (OWM) and an inorganic water module (IWM).
- The OWM subsystem currently comprises a liquid injection gas chromatograph mass spectrometer (GCMS) apparatus.
  - Liquid injection GCMS is one common technique in analytical chemistry laboratories for potable water analysis and is among one of many techniques utilized by the JSC Toxicology laboratory for analysis of returned water samples.
- The IWM subsystem team is investigating a number of technologies including:
  - Ion chromatography (IC)
  - capillary electrophoresis (CE)
  - ion specific electrodes (ISEs)
- **This presentation will report on technology development for the organic and inorganic water modules of SWIM.**

SWIM Modular Architecture



CE	=	Capillary Electrophoresis
C^4D	=	Capacitively Coupled Contactless Conductivity Detection
GC	=	Gas Chromatograph
ESI	=	Electrospray Ionization
HPLC	=	High Performance Liquid Chromatograph
IC	=	Ion Chromatograph

ICP-MS	=	Inductively-Coupled Plasma Mass Spectrometer
ISE	=	Ion-Specific Electrode
MS	=	Mass Spectrometer
FID	=	Flame Ionization Detector
TCD	=	Thermal Conductivity Detector

- The initial approach for development of SWIM has led to a modular approach.
  - The OWM and IWM are separate modules.
  - Each module could be broken down into injection, separation, and detection modules.
- The Organic Water Module and Inorganic Water Module can be independent of one another for analytical purposes.
- Each module could share sampling, data processing, or waste streams if desired.

SWIM Technology Matrix

- OWM has been emphasizing method development and demonstration of detection for some target compounds using direct aqueous injection (DAI) gas chromatography thermal conductivity detector (GC-TCD) detection.
- Efforts continue toward the eventual goal of GC-TCD detection of organics using a mass spectrometer (MS) for the final detection stage, which should provide both high sensitivity and excellent specificity for organic water impurities, with the ability to identify an unknown impurity by examining the mass spectrum of the chemical.
- IWM has been emphasizing Capacitively Coupled Contactless Conductivity Detection (C4D) of candidate target mixtures and TRL advancement of C4D detector electronics and hardware.

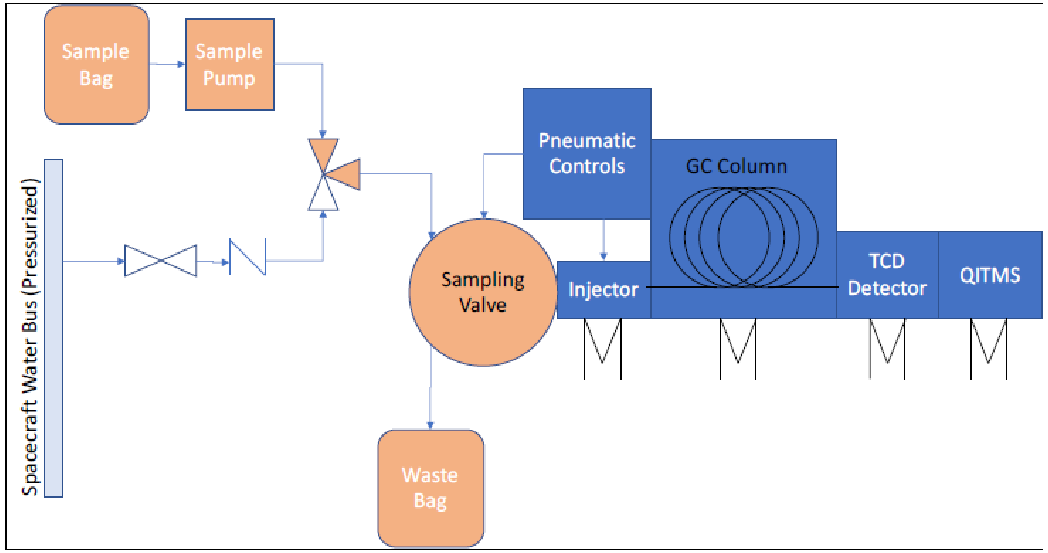
Organic Water Module				
Separation	*Detection*	*Instrument Name(s)*	*NASA-funded*	*TRL*
Gas Chromatograph (GC)	**Flame Ionization Detector (FID)**	OWM	Yes	3-4
	Thermal Conductivity Detector (TCD)	OWM	Yes	3
	Mass Spectrometer (MS)	OWM/S.A.M.[9,21]	Yes	4-5
Capillary Electrophoresis (CE)	Electrospray Ionization (ESI)-MS	EMILI[14]	Yes	4-5
	Conductivity	OCEANS[15]	Yes	5
High Performance Liquid Chromatograph (HPLC)	UV-Vis or fluorescence	–	No	2
	ESI-MS	–	No	2
Inorganic Water Module				
Separation	*Detection*	*Instrument Name(s)*	*NASA-funded*	*TRL*
–	Ion-Specific Electrodes (ISEs)	MICA[16]/OWLS[17,18]	Yes	5
Ion Chromatograph (IC)	Capacitively Coupled Contactless Conductivity Detection (C^4D)	ILCESS[19,20]	Yes	4
Capillary Electrophoresis (CE)	**C^4D**	OWLS	Yes	5
Inductively-Coupled Plasma (ICP)	Mass Spectrometer (MS)	–	No	2
Laser-Induced Breakdown Spectroscopy (LIBS)	Near-Infrared (NIR) Spectrometer	–	Yes, SBIR	3
Spark-Induced Breakdown Spectroscopy (SIBS)	NIR Spectrometer	–	Yes, SBIR	2

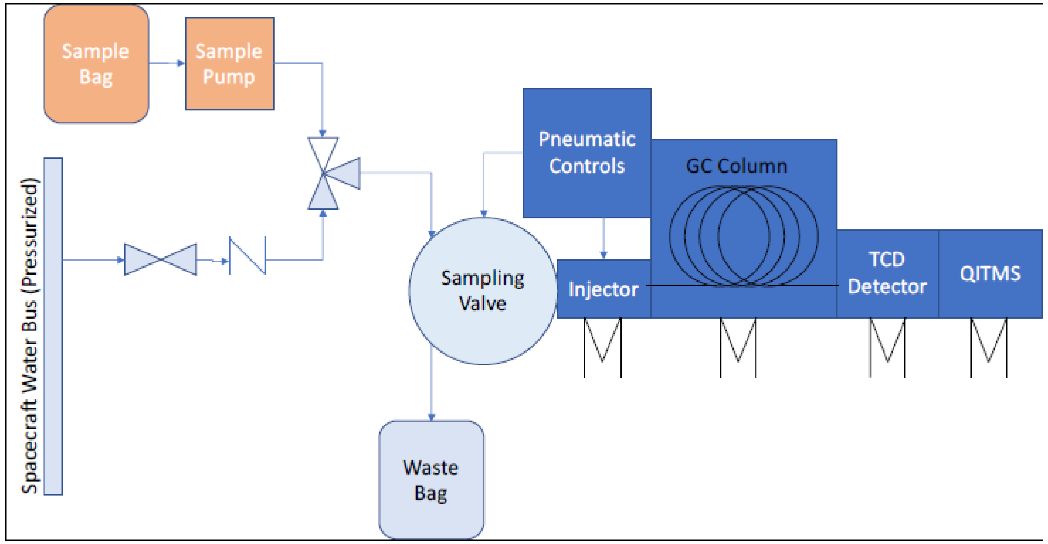
Organic Water Module

- Organic contaminants that appear in potable water are sourced from equipment, crew hygiene products, and the crew themselves (metabolic products).
- Once in the water, the organic contaminants are typical volatile small molecules such as
  - Acetone, methanol, MEK, ethanol, dicholoromethane, acetic acid, DMSD, DMS, ethylene glycol, propylene glycol, trimethylsilanol among others
- Direct Aqueous Injection GCMS is an excellent technique for analyzing volatile small molecules in water.

Organic Water Module

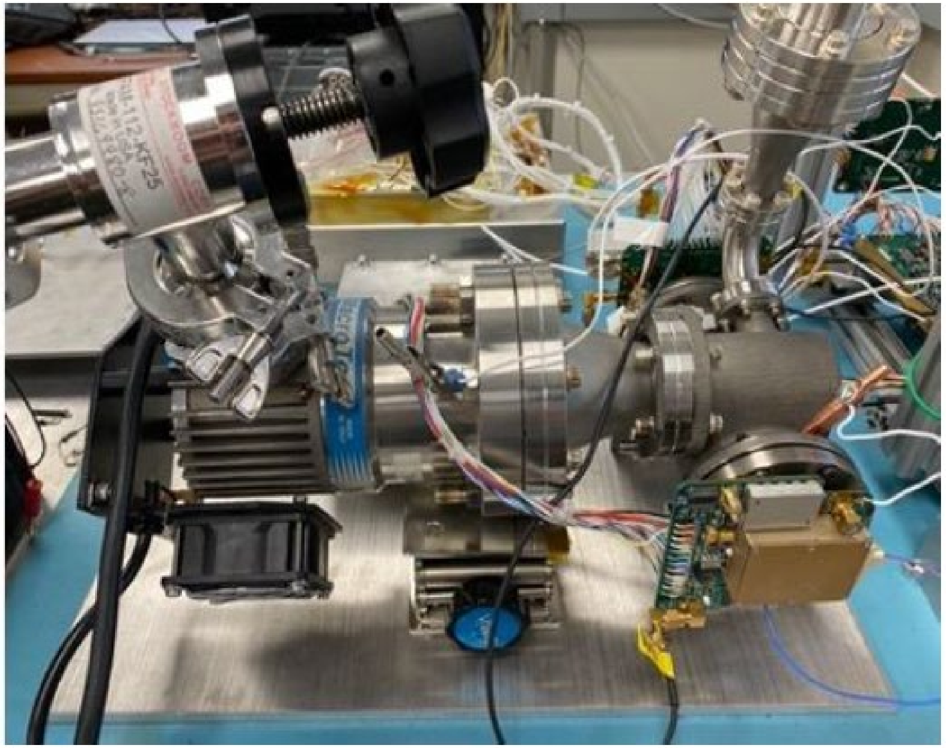
- Schematic of an OWM implementation which includes a thermal conductivity detector (TCD)
- Two sampling options are shown, bag samples or potable water bus
- Organic Water Module comprises pneumatic controls, injector, GC column, TCD detector and quadrupole ion trap mass spectrometer (QITMS)





Organic Water Module

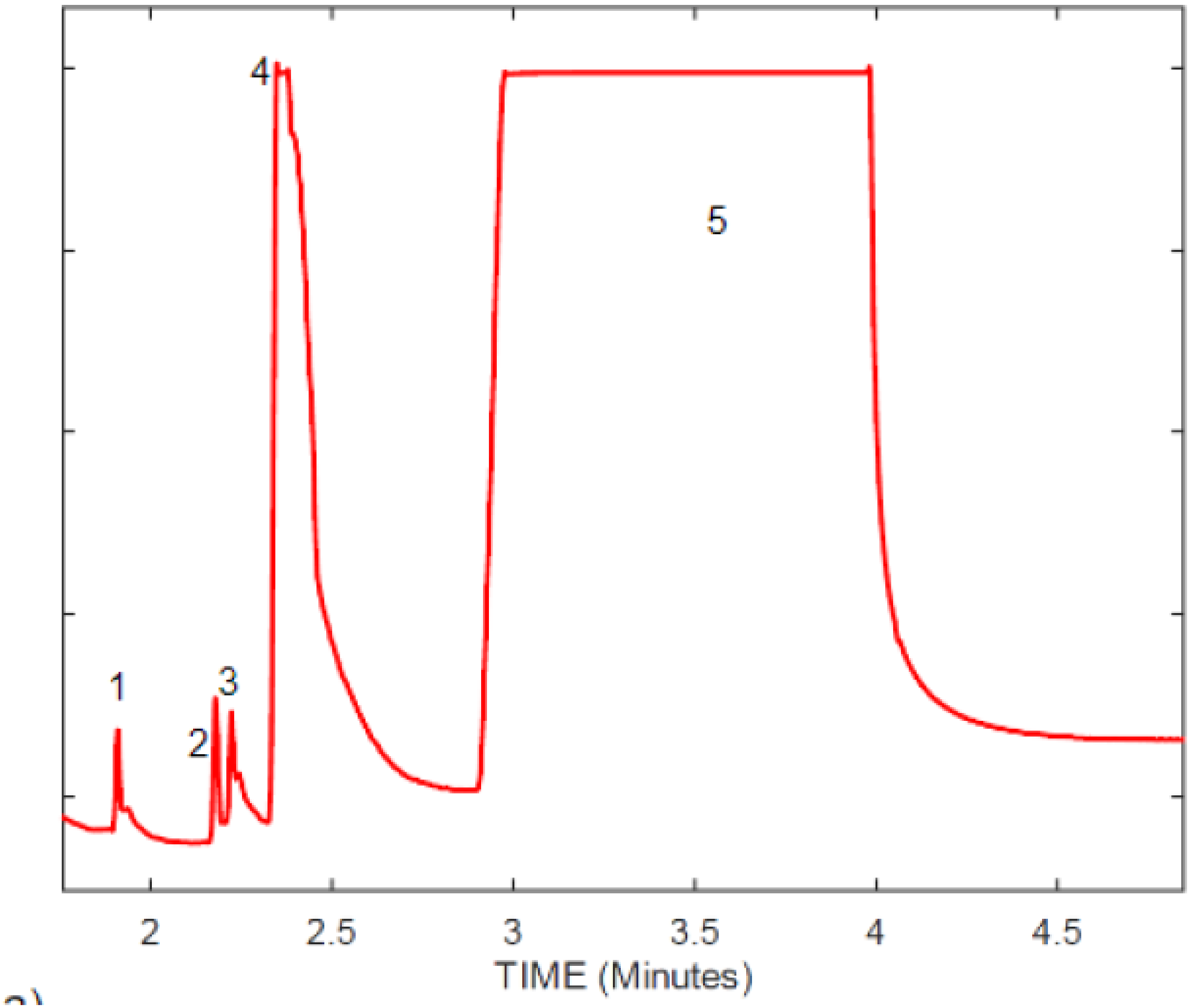
- QITMS – Quadrupole Ion Trap Mass Spectrometer
- Technology: 3d printed metal vacuum chamber, custom electron gun, SilcoGuard coated trap
- Same mass spectrometer that is used in Spacecraft Atmosphere Monitor (S.A.M.)
- Flight heritage S.A.M. on ISS (air monitoring)



- PM-Murray Darrach-JPL
- PI / DPM-Stojan Madzunkov-JPL

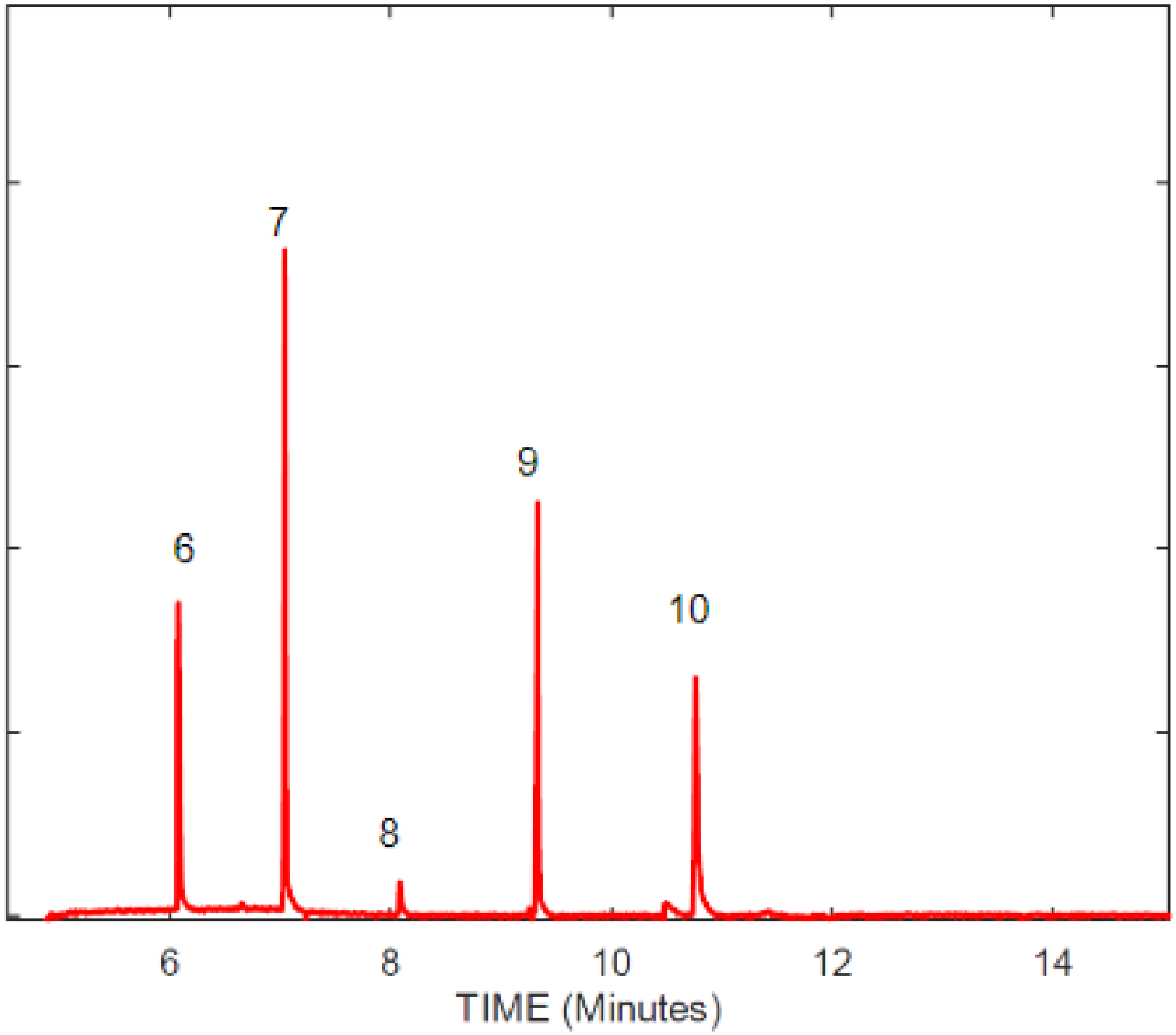
Organic Water Module-Example Results

- Separation and detection of
  - 1-acetone
  - 2-methanol
  - 3-methyl ethyl ketone (MEK)
  - 4-ethanol
  - 5-water (solvent for injection)
- Direct aqueous injection with TCD detection
- No sample pre-processing



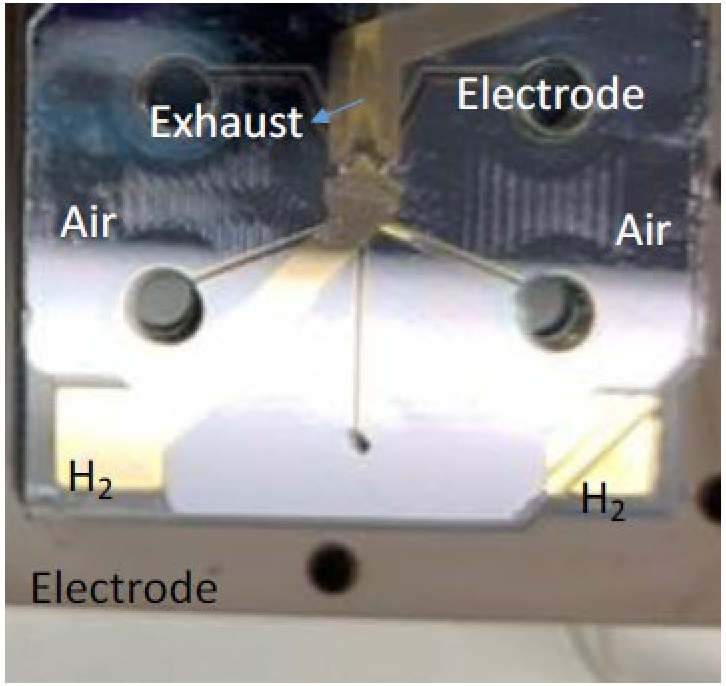
Organic Water Module-Example Results

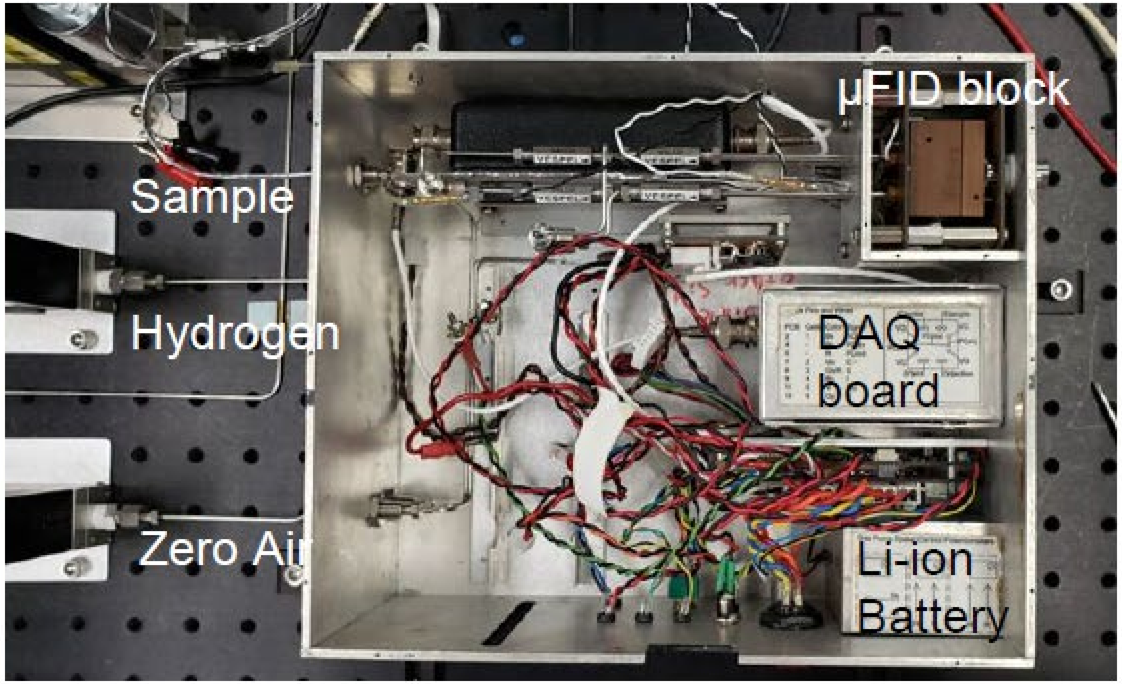
- Separation and detection of
  - 6-acetic acid
  - 7-propylene glycol
  - 8-DMSD
  - 9-dimethyl sulfone (DMS)
  - 10-o-phthalaldehyde (OPA)
- Direct aqueous injection with TCD detection
- No sample pre-processing



Organic Water Module-FID

- Micro Flame Ionization Detector (MicroFID)
- Flame ionization detector has been miniaturized and will be tested with the DAI-GC system of SWIM





PI: Byunghoon Bae (JPL)

Inorganic Water Module

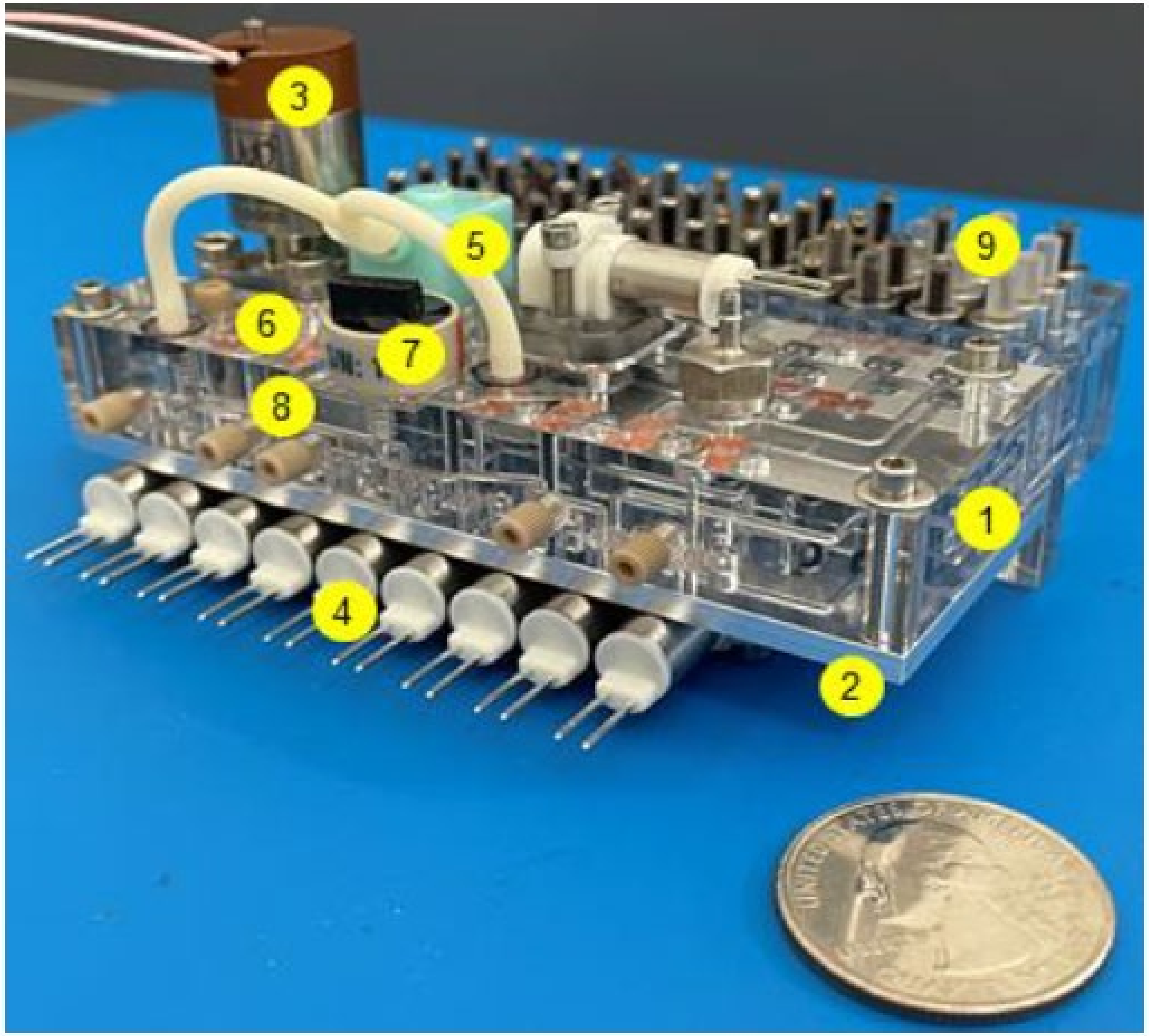
- The Inorganic Water Module will analyze the water for ions, metals, and other inorganic chemicals

- Techniques being investigated for SWIM include
  - Ion selective Electrodes (ISEs)
  - Ion chromatography with conductivity detection
  - Capillary electrophoresis with conductivity detection

- Previously funded work is being leveraged to evaluate technologies to take forward:
  - Microfluidic Icy World Chemical Analyzer **(MICA)** – Europa Lander proposed
  - Ion/Liquid Chromatograph for Exploration of the Solar System **(ILCESS)** – Mars exploration proposed
  - Organic Capillary Electrophoresis Analysis System **(OCEANS)** – proposed for EMILI and OWLS instrument suites

Inorganic Water Module

- Microfluidic Icy World Chemical Analyzer **(MICA)** – uses ion selective electrodes to analyze for Cl, Mg, Na, Ca, CO_3
- MICA also includes pH, electrical potential (Eh), conductivity, and voltammetry electrodes.



1-fused 3-layer manifold
2-thermomechanical backing plate
3-hermetic microvalve
4-fluid-control valves
5-peristaltic pump
6-fluid in-channel feed-through
7-pressure sensor
8-liquid connectors
9-48-electrode array

MICA

Science investigation:

- Measure soluble ions in samples to assess habitability, provide sample context, and look for potential metabolic redox couples.

Measurement targets and performance

- pH: 1 – 14, Eh: -1 – 1 V, Conductivity – 0.02 – 200 mS/cm
- Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+: 10 µM – 1 M
- Halides (Cl^-, Br^-, I^-): 10 µM – 1 M
- NO_3^-, ClO_4^-, SO_4^{2-}: 100 µM – 1 M
- Carbonate (CO_2, HCO_3^-, CO_3^{2-}): 100 µM – 1 M
- Reactive Oxidants (e.g. O_2, H_2O_2): 100 µM – 1M
- Reduced Sulfur species (H_2S, HS^-, S_2^-): 100 µM – 1M

SWIM POC: Aaron Noell

Measurement approach and technology

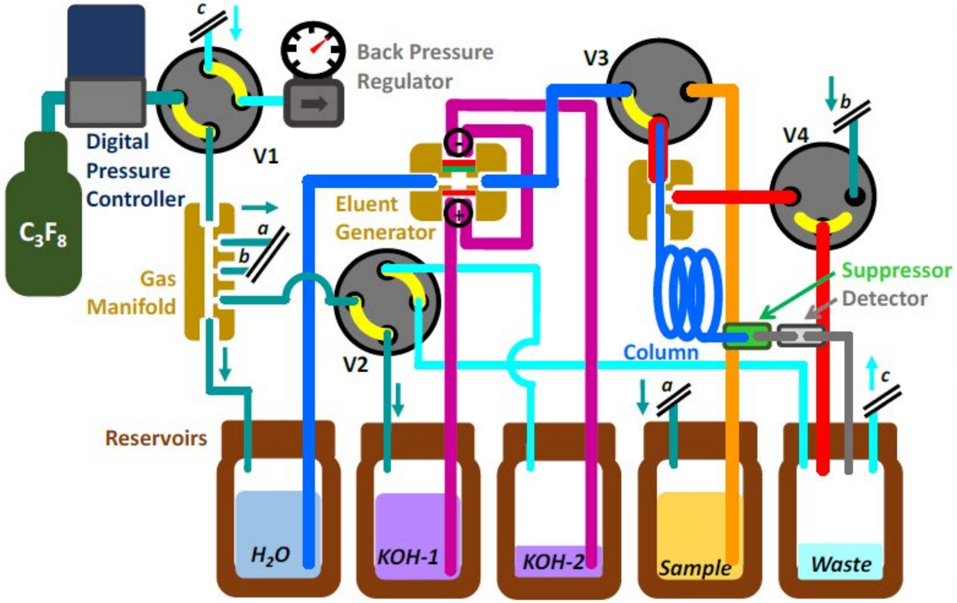
- MICA uses ion selective electrodes, cyclic voltammetry and chronopotentiometry to make electrochemical measurements in a microfluidic sensor array format. The sensor types were all originally used as part of the Wet Chemistry Lab on the Mars Phoenix Lander.

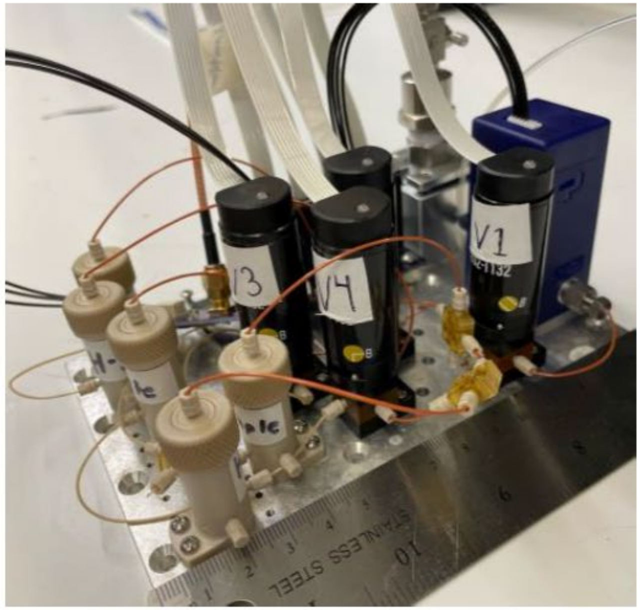
Water Monitoring Notes

- Silver team is working on an ISE approach for silver detection.
- Ni can be detected via titration and a Cu ISE.

Inorganic Water Module

- Ion/Liquid Chromatograph for Exploration of the Solar System (**ILCESS**)





- Chloride, chlorate, perchlorate, formate, acetate, benzoate

ILCESS

SWIM POC: Aaron Noell

Science investigation:

- Measure soluble anions in samples to assess habitability and look for potential metabolic redox couples including small organics.

Measurement targets and performance

- Inorganic anions: Cl^-, Br^-,F^-, NO_3^-,NO_2^-, ClO_4^-, ClO_3^-, SO_4^{2-}: 0.2 µM – 10 mM
- Organic anions: Formate, acetate, benzoate etc.: 0.2 µM – 10 mM
- As a chromatography technique, it allows discovery of unanticipated compounds as well once trained.

Measurement approach and technology

- ILCESS uses an open tubular chromatography approach to enable robust small sample volume separations. The open tubular column has functionalized walls, not packed resin, for ion exchange. Coupled with on demand eluent generation and suppressed conductivity detection, ILCESS provides unsurpassed anion sensitivity.

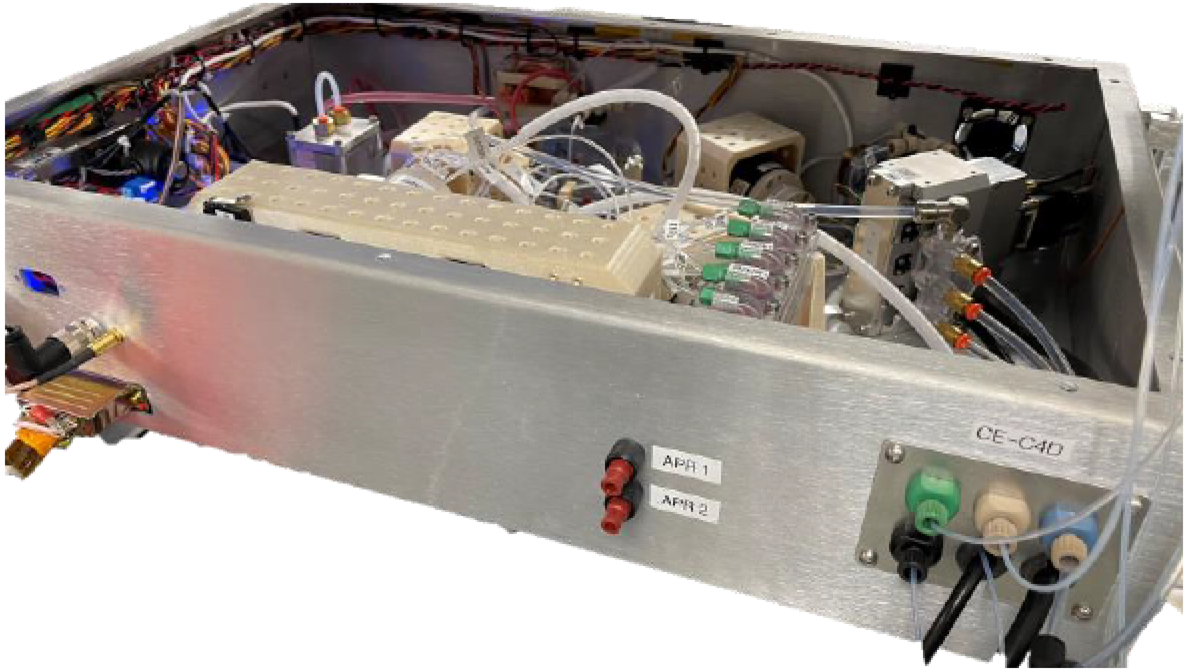
Water Monitoring Notes

- "Gold standard" EPA method for anions in water.
- Transition metals typically are detected by UV/Vis or ICP-MS after separation, but conductivity is possible.

Inorganic Water Module

- Organic Capillary Electrophoresis Analysis System **(OCEANS)**
- Capillary electrophoresis (CE) with capacitively-coupled contactless conductivity detection (C^4D)

Cations	Anions	Metals
Sodium	Chloride	Silver
Potassium	Nitrate	Nickel
Magnesium	Sulfate	Zinc
Calcium	Chlorate	
Lithium	Perchlorate	
Ammonium	Phosphate	



OCEANS

SWIM POC: Aaron Noell, Alt: Mauro Ferreira Santos

Science investigation:

- Measure soluble cations and anions in samples including inorganic and organic evidence of habitability and life.

Measurement targets and performance

- Inorganic anions/cations: Cl^-, Br^-, NO_3^-,NO_2^-, ClO_4^-, ClO_3^-, SO_4^{2-}, PO_4^{3-} Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+: 1 µM – 10 mM.
- Organic anions/cations: di- and tri-carboxylic acids (oxalate, malate, citrate etc.), short chain fatty acids (C1 – C10 monocarboxylics), amino acids: 10 µM – 10 mM.
- As a separation science technique, it allows discovery of unanticipated compounds.

Measurement approach and technology

- CE-C^4D uses the separation power of capillary electrophoresis coupled with the broad detection capability of conductivity in a contactless implementation. Anions and cations are detected with two different separation modes.

Water Monitoring Notes

- CE is attractive because method updates require the least amount of hardware changes, i.e., only reagents need to be swapped out.
- Have coupled to ESI-MS w/ GSFC (EMILE).

SWIM Plan Forward

- Organic Water Module
  - Demonstrate DAI-GC-MS
  - Test MicroFID detector with the SWIM GC methods
  - Continue to mature detailed design of subsystems
- Inorganic Water Module
  - Build and demonstrate a breadboard IWM system using CE sensors
  - Develop a metals preconcentrator breadboard to improve sensitivity of a CE system
  - Build and test miniature conductivity, pH, and specific ion electrochemical sensors in microfluidic arrays for continuous or near-continuous monitoring

Acknowledgements

Stuart J. Pensinger and Michael Callahan
NASA Johnson Space Center, Houston, TX 77058

Evan L. Neidholdt
KBR, Science & Space Business Unit, Houston, TX 77058

Aaron C. Noell, Nathan J. Oborny, Byunghoon Bae, Valeria Lopez, Bruce R. Hancock, Marianne P. Gonzales, Margie L. Homer, Stojan Madzunkov, Murray R. Darrach, Richard D. Kidd
Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109

Spacecraft Water Impurity Monitor (SWIM) gratefully acknowledges support and funding from the Exploration Capabilities Life Support Systems (EC-LSS) Project