

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

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The Spacecraft Water Impurity Monitor (SWIM) is a joint collaboration to develop an instrument platform that will perform in-flight measurements and deliver a more complete picture of water quality to decision makers. For exploration missions, returned water samples will not be an option, so spacecraft and habitats will need to be equipped with advanced water monitoring capabilities. Eventually, missions to the moon, Mars, and beyond should be equipped with analytical capabilities roughly analogous to those found in terrestrial labs. Based on what we know about current and future spacecraft environments, SWIM will seek to provide enhanced analytical capability that enables NASA to confidently send astronauts on distant missions without the possibility of returned water samples. The SWIM architecture can be broken down in an Organic Water Module (OWM) and an Inorganic Water Module (IWM), independent of each other but can be flown together if desired; an integrated system may share some commonality, e.g., single sample injection, sampling consumables, waste, etc. Each of these main modules can be broken down further into separation (if required) and detection modules. And, each separation module can be paired with one or more detection module depending on mission, spacecraft, customer needs, and size/mass/power constraints. This paper discusses the research and development progress toward the goal of a total water analysis system. For OWM, one of the analysis technologies that the SWIM team have been developing is a liquid-injection gas chromatograph mass spectrometer system; these systems are the workhorses of analytical chemistry laboratories world-wide. For IWM, the team is exploring a number of technologies ranging from traditional liquid chromatography technologies (e.g., ion chromatography, capillary electrophoresis) to flight-heritage technology such as ion-specific electrodes.

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Nomenclature

<i>BGE</i>	= Background Electrolyte	<i>MEMS</i>	= Micro-Electro-Mechanical Systems
<i>BTEX</i>	= Benzene-Toluene-Ethylbenzene-Xylene	<i>MICA</i>	= Microfluidic Icy-World Chemistry Analyzer
<i>CE</i>	= Capillary Electrophoresis	<i>μFID</i>	= micro-Flame Ionization Detector
<i>C⁴D</i>	= Capacitively Coupled Contactless Conductivity Detection	<i>miniTOCA</i>	= miniature-TOCA
<i>DAI-GC</i>	= Direct Aqueous Injection Gas Chromatograph	<i>NIR</i>	= Near-Infrared
<i>GC</i>	= Gas Chromatograph	<i>OCEANS</i>	= Organic Capillary Electrophoresis ANalysis System
<i>GCMS</i>	= Gas Chromatograph Mass Spectrometer	<i>OTIC</i>	= Open Tubular IC
<i>ECLSS</i>	= Environmental Control and Life Support System	<i>OWLS</i>	= Ocean Worlds Life Surveyor
<i>EMILI</i>	= European Molecular Indicators of Life Investigation	<i>OWM</i>	= Organic Water Module
<i>ESI</i>	= Electrospray Ionization	<i>QITMS</i>	= Quadrupole Ion Trap Mass Spectrometer
<i>HPLC</i>	= High Performance Liquid Chromatograph	<i>S.A.M.</i>	= Spacecraft Atmosphere Monitor
<i>IC</i>	= Ion Chromatograph	<i>SBIR</i>	= Small Business Innovative Research
<i>ICP-MS</i>	= Inductively-Coupled Plasma Mass Spectrometer	<i>SIBS</i>	= Spark-Induced Breakdown Spectroscopy
<i>ILCESS</i>	= Ion Liquid Chromatograph for Solar System Exploration	<i>STTR</i>	= Small Business Technology Transfer
<i>ISE</i>	= Ion-Specific Electrode	<i>SWIM</i>	= Spacecraft Water Impurity Monitor
<i>ISS</i>	= International Space Station	<i>TCD</i>	= Thermal Conductivity Detector
<i>LEO</i>	= Low Earth Orbit	<i>TOC</i>	= Total Organic Carbon
<i>LIBS</i>	= Laser-Induced Breakdown Spectroscopy	<i>TOCA</i>	= Total Organic Carbon Analyzer
<i>MS</i>	= Mass Spectrometer	<i>TDU</i>	= Technology Demonstration Unit
<i>MECA</i>	= Microscopy, Electrochemistry, and Conductivity Analyzer	<i>TMP</i>	= Turbo Molecular Pump
		<i>UV-Vis</i>	= Ultraviolet-Visible
		<i>VCAM</i>	= Vehicle Cabin Atmosphere Monitor
		<i>VOC</i>	= Volatile Organic Compound
		<i>WPA</i>	= Water Processor Assembly
		<i>WCL</i>	= Wet Chemistry Lab
		<i>WRS</i>	= Water Recovery System

I. Introduction

According to Limeró et al. (2017),¹ ensuring the quality of potable water for crew during spaceflight missions is of "paramount" importance. This involves ensuring that the water contains limited amounts of organic, inorganic, and microbial contaminants. Although some on-orbit monitoring is available currently and implemented on the ISS, the monitoring strategy relies on sample archiving and subsequent return to ground for full analytical workup of water samples. Once mission profiles involve traveling significant distances from Earth, Limeró et al., suggest that the onus for water sampling and analysis must shift from sample collection and return to that of real-time on-board spacecraft monitoring.¹ The need for development of in-flight water quality monitoring beyond total organic carbon (TOC) is captured in NASA Technology Roadmap TA 6.4.1, Sensors: Air, Water, Microbial, and Acoustic,^{4,5} 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.

As an example of limited on-orbit analysis capability, TOC is currently measured on the International Space Station (ISS) using the Total Organic Carbon Analyzer (TOCA).² On-orbit analysis of the TOC content of recycled water has been an indispensable tool for monitoring the performance of the Water Recovery System (WRS) and for ensuring that water is fit for crew consumption. While TOC has been, and will continue to be, an important metric for spacecraft water quality it provides only limited insight into the total picture of water quality. As a measurement, TOC only provides a single "lump sum" quantity of all organic chemicals present in a water sample (as milligrams of carbon per liter of water); it neither identifies nor quantifies the *individual* chemicals contributing to the TOC number. The TOC measurement does not address inorganic constituents, be they undesired contaminants such as metals (e.g., nickel) resulting from corrosion of water system components, or an intentionally-dosed biocide such as silver or iodine. Because the ability to make more comprehensive in-flight measurements of water quality has not existed for ISS, it has been the practice of NASA toxicologists and Environmental Control and Life Support System (ECLSS) system managers to institute routine collection of water samples and subsequently return them to earth for detailed

laboratory analysis.³ For exploration missions beyond low Earth orbit (LEO), the return of water samples to Earth for analysis, whether for routine checks or for troubleshooting problems with the life support system, will be logistically challenging or impossible. A system is needed in the future to fill this role of water quality analyzer that will operate as part of the spacecraft system, precluding the need for returned water samples.

The Spacecraft Water Impurity Monitor (SWIM) will serve in this role and is a collaboration between JSC and JPL to research and develop a modular instrument platform that will perform in-flight water analysis measurements and deliver a more complete picture of water quality to decision makers. Eventually, missions to the moon, Mars, and beyond should be equipped with analytical capabilities analogous to those found in terrestrial labs, carefully selecting techniques which are feasible for flight instruments yet provide maximal information from a water sample. Whether it is the TOC measurement which makes the first step in determining the aggregate amount of and presence of organics in the water, or a conductivity sensor which can sense ions in the water but not what type they are, current total water analysis capabilities are limited. The ability to identify and quantify impurities is the critical capability missing. 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 quantification for any water impurities.

For organic impurity analysis, one of the analysis technologies that the SWIM team have been developing is a liquid-injection gas chromatograph mass spectrometer (GCMS) system, called the Organic Water Monitor, to detect and identify dissolved volatile organic compounds (VOCs) in drinking water supplies.^{6,7} Liquid-injection GCMS systems are the workhorses of analytical chemistry laboratories world-wide, but have not flown before for space applications. The mass spectrometer for OWM, a Paul quadrupole ion trap mass spectrometer (QITMS), has ISS flight heritage because it was first used in the Vehicle Cabin Atmosphere Monitor (VCAM)⁸ in 2010 and is currently in use in the Spacecraft Atmosphere Monitor (S.A.M.).⁹ For inorganic analysis, the team is exploring a number of technologies that are currently funded by NASA research and technology development programs. These technologies range from traditional liquid chromatography technologies, such as ion chromatography (IC) and capillary electrophoresis (CE), to flight-heritage technology such as ion-specific electrodes (ISEs) such as those from the next-generation Wet Chemistry Lab (WCL),¹⁰ originally part of the Microscopy, Electrochemistry, and Conductivity Analyzer (MECA) instrument suite on the Mars Phoenix Lander spacecraft.

This paper is a progress report on technology development efforts for the organic and inorganic water modules of SWIM.

II. Modular Architecture and Technology Matrix

The SWIM project aims to research, develop, and deliver an instrument for identification and quantification of organic and inorganic impurities in spacecraft water. This instrument is expected to play a vital role in NASA's human spaceflight missions beyond low earth orbit, where sample return is impractical.^{1,4,5} Lunar Gateway, lunar surface, Mars transit, and Mars surface missions are all target end-users of the instrument suite. The capability to identify organics and inorganics detected in water samples represents an enhanced capability for water analysis which should provide crew health and performance and system management decision makers with more pertinent information about the exact nature of the detected impurities.

The initial approach to SWIM development has led to a modular approach for SWIM and its subsystems (Figure 1), not dissimilar to commercially built analytical chemistry instrumentation used for liquid sample analysis. The SWIM architecture can be broken down in an Organic Water Module (OWM) and an Inorganic Water Module (IWM) which are independent of each other for analytical purposes yet can be combined later in an integrated system which may share some commonality, e.g., single sample injection, sampling consumables, waste, etc. The OWM and IWM can be broken down further into separation and detection modules.

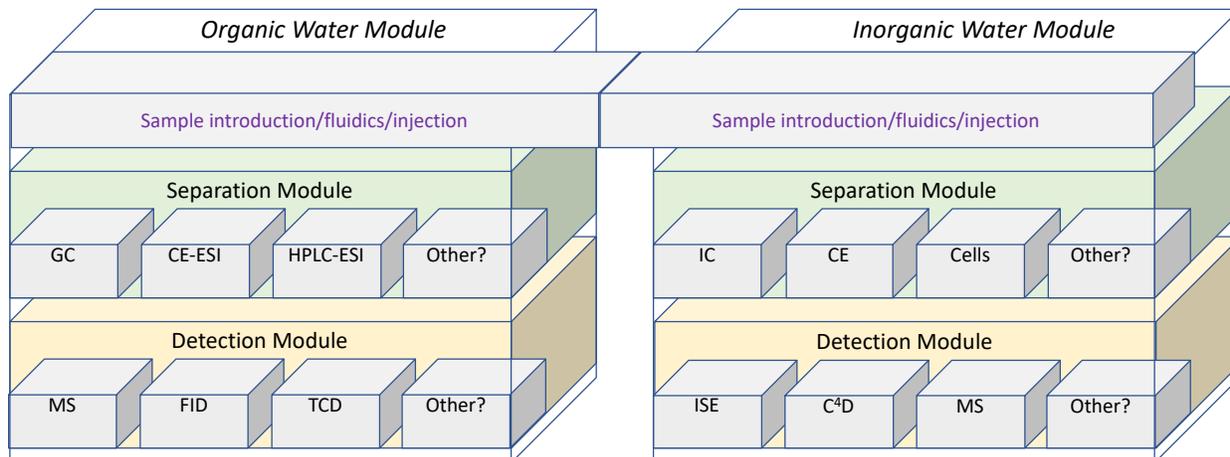


Figure 1. Modular approach to SWIM's architecture. The configuration of SWIM is dependent on mission, spacecraft, customer needs, and size / mass / power constraints.

The SWIM team has been assembling a technology matrix populated with analytical chemistry technology typically used for water analysis on Earth, but also with an emphasis on technologies currently funded through other NASA sources in order to leverage systems that might already have some flight development and/or pedigree. An overview of this technology matrix is shown in Table 1. What may be evident from the table is that many of the technologies currently under consideration are based on common laboratory analytical techniques used for drinking water analysis worldwide, including in the Environmental Sciences, Toxicology & Environmental Chemistry Laboratory at NASA's Johnson Space Center who performs analysis of the potable water return samples from the ISS.¹ The aim is to choose technologies which provide the most information from the water sample with minimal pre-processing or sample conditioning, and are possible to operate in a flight instrument due to feasible resource requirements. The flight readiness of a technology can be assessed using a technology readiness level (TRL), a rating from 1 to 9 which signifies what stage of development the technology is presently in for a given flight application. Specific details of each TRL level are not given here, but briefly, TRL 1 is a concept, not even implemented in a laboratory. TRL 3-4 is a laboratory experiment or instrument looking forward to a flight development, TRL 5 means some detailed engineering for a flight application has taken place, TRL 6 means fully form-fit-function packaged for a flight application, and TRL 9 is flown or full flight heritage.

Details of recent efforts in technology development for the OWM and IWM are described in sections following. 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.

III. Organic Water Module

Organic contaminants in spacecraft water present a unique analytical challenge due to the ubiquity of potential sources, and the diversity of their chemical composition, structure, and behavior. Sources include outgassing from equipment (e.g., plastics, rubbers, fabrics, coatings), crew hygiene products (e.g., deodorants, lotions, wipes), and metabolic byproducts from the crew themselves. Once in the cabin environment, these contaminants can undergo chemical transformations and reactions, widening the scope of potential speciation with eventual introduction into the spacecraft or habitation water systems. Fortunately, we know from experience that by the time contaminants make it into potable water, they are typically small and simple molecules, usually volatile or semi-volatile. Water system managers observing the ISS water systems over the years have developed a short list of candidate molecules for detection targets, examples of which include acetone, methanol, ethanol, methyl-ethyl-ketone, dichloromethane, acetic acid, dimethylsilanediol, dimethyl sulfone, ethylene, and propylene glycol, and trimethylsilanol. All of these fit into

Table 1. SWIM Top-level Technology Matrix. It is modular with some systems utilizing one or more NASA-funded modules. Instrument names are defined on pages 1-2. Technologies with current development emphasis on the SWIM project are noted in bold type.

Organic Water Module				
<i>Separation</i>	<i>Detection</i>	<i>Instrument Name(s)</i>	<i>NASA-funded</i>	<i>TRL</i>
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				
<i>Separation</i>	<i>Detection</i>	<i>Instrument Name(s)</i>	<i>NASA-funded</i>	<i>TRL</i>
–	Ion-Specific Electrodes (ISEs)	MICA ¹⁶ /OWLS ^{17,18}	Yes	5
Ion Chromatograph (IC)	Capacitively Coupled Contactless Conductivity Detection (C ⁴ D)	ILCESS ^{19,20}	Yes	4
Capillary Electrophoresis (CE)	C⁴D	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

the “small molecule” description and can easily be analyzed by DAI-GC without the need for sample preparation.

DAI-GCMS systems are the workhorses of analytical chemistry laboratories worldwide but have not flown before for space applications. The liquid injection system and gas chromatograph being developed for the OWM application are of a new design which has been under development at JSC. The GC methods being developed are intended to directly analyze water samples without the use of preconcentration or purge-and-trap pre-processing. The QITMS was selected as the mass spectrometer detector due to its flight heritage on ISS in VCAM and S.A.M. and because it has now been successfully demonstrated twice as a viable detector for environmental monitoring for organic compounds in spacecraft cabin environments. The logical extension of the application is detection of organics in water as part of SWIM.

A. DAI-GC-TCD

Under the current SWIM technology development program, the team has been developing a direct aqueous injection gas chromatograph (DAI-GC) system capable of analyzing many classes of compounds in a single GC run, including alcohols, glycols, and siloxanes. Figure 2 is a general schematic for the liquid injection and gas chromatograph portion of the system, with an example of the interface to the spacecraft. The water sample is injected using a multiport, internal sample loop valve. The spacecraft interface and sampling valve permits on-line analysis of the spacecraft water bus or a sample bag through the use of a sample pump. After injection, the sample is volatilized in the heated injector. The compounds are separated in the GC column in the usual manner, and are detected by a thermal conductivity detector and eventually, the QITMS. The thermal conductivity detector is a useful device even when the QITMS is present because it can aid in detecting when the water peak is eluting from the column. The system has the capability to isolate the mass spectrometer from the column flow to keep water out of the system and help maintain cleanliness. The configuration in Figure 2 is one of many possible candidates for the SWIM organics detection module, and technology development efforts over the coming years will help to finalize the organics detection architecture.

SWIM currently has breadboard-fidelity DAI-GC hardware running in the JSC Spacecraft Water Engineering Laboratory and has demonstrated the detection of both VOCs and heavier organics in a single GC run, using project-

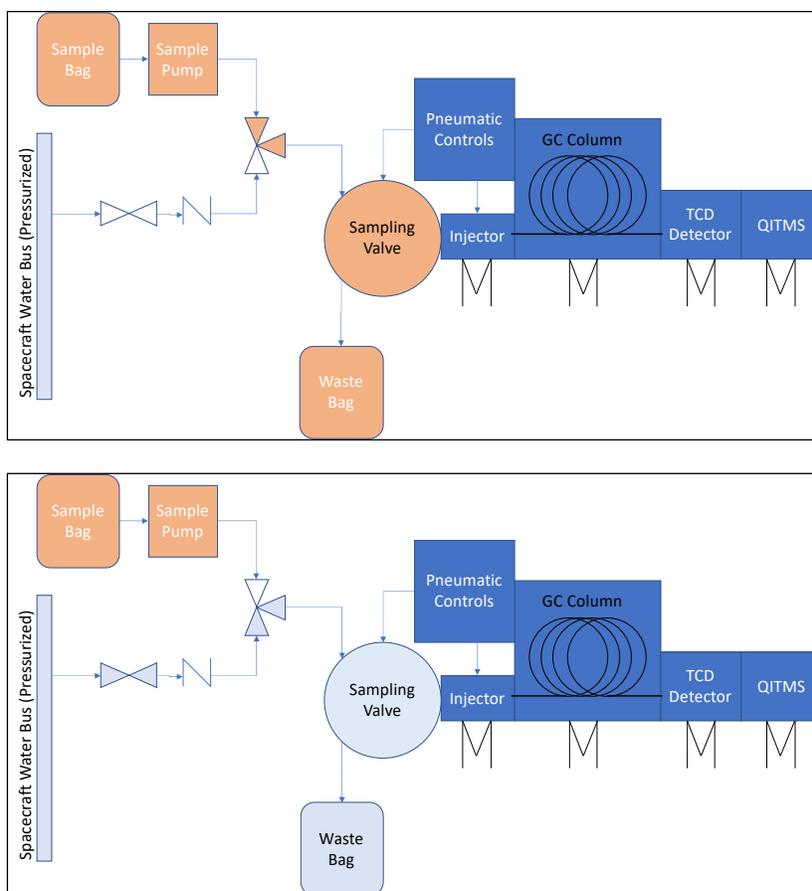


Figure 2. OWM's schematic for the liquid injection and gas chromatograph portion of the system. Top, sampling mode. Bottom, injection / chromatography mode.

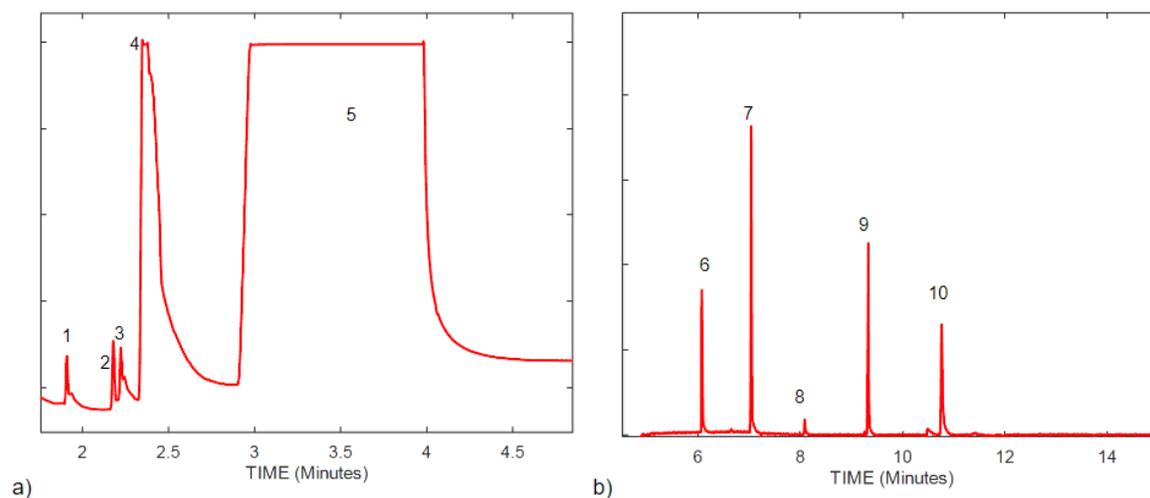
developed pneumatic controls and ground-station software. No pre-concentration or purge-and-trap pre-processing was used. The Micro-Electro-Mechanical Systems (MEMS) TCD control and readout electronics are also entirely project-developed, which allows for maximum future design flexibility. Progress has been made in the areas of development of reliable pneumatic controls using flight-heritage valves and components, miniaturized packaging for gas chromatography columns, and overall instrument control and monitoring hardware and software.

Figure 3 shows sample chromatograms from the GC-TCD system. Viewing the chromatogram in two sections aids in observing the full capability of separation for the OWM. The next step in SWIM development is interfacing the GC system with the QITMS, to build a DAI-GCMS system. The addition of the mass spectrometer will provide increased sensitivity versus a thermal conductivity detector, as well as positive identification of compounds observed in the chromatogram by correlating the mass spectrum with the observed retention times.

B. Quadrupole Ion Trap Mass Spectrometer

The mass spectrometer detector for the DAI-GCMS system that will analyze organics for SWIM will include the QITMS which is identical to that used in S.A.M.²¹ The S.A.M. technology development units (TDUs) for the detection of major constituents (TDU1) and organics (TDU2) in the ISS cabin atmosphere are now flight heritage designs which can be leveraged for future SWIM subsystem development. The mass spectrometer sensor from the S.A.M. instruments has already been identified as the flight design for SWIM.

Further details about the sensor are provided here. The sensor is a 3-D Paul ion trap with a 10 mm field radius and effective capacitance of 85 pF. The trap is nominally operated using an 800 kHz rf voltage up to 2 kV in amplitude provided by a series resonant inductor (SRL) to the central ring electrode. The top and bottom endcaps are nominally kept at ground but, if desired, can be driven with arbitrary rf (180° out-of-phase) to provide secular excitation profiles



Peak identification: 1-acetone; 2-methanol, 3-methyl ethyl ketone, 4-ethanol, 5-water, 6-acetic acid, 7-propylene glycol, 8-dimethylsilanediol (DMSD), 9-dimethylsulfone, 10-o-phthalaldehyde

Figure 3. Sample chromatogram. a) Section of chromatogram of OWM mixture solution, 80 ng on-column each component, focused on region for volatile organics. Signal for ethanol is off-scale due to the need for adding ethanol to enhance solubility of OPA. B) Section of chromatogram of OWM mixture solution, 80 ng on-column each component, focused on region for glycols, siloxanes, acids, and high-boiling organics.

to the trapped ions for further mass discrimination. These ion trapping parameters correspond to mass ranges up to 330 amu. At the center of both endcaps are two 1 mm OD x 2.5 mm long holes: one for the introduction of the electron beam and the second for the ejection of ions into the detector assembly. These small axial orifices have the added effect of transforming the trap volume into a pressure cell due the small 0.1 L/s effective conductance between the trap volume and the external vacuum chamber. Typical pumping speeds in the external chamber (~10 L/s) result in a 100-fold increase in pressure (and therefore ion count rates) in the QITMS trap volume. To prevent the creation of patch potentials due to the adhesion of trace organics on trap surfaces, the QIT is also coated with SilcoGuard[®] (SilicoTek Inc.) which helps to dissipate space charging and prevent adhesion of organic molecules to the bare metal electrode surface. To further maintain the cleanliness of trap surfaces, the QITMS is equipped with a 20 W halogen bulb which nominally heats the trap to above 200°C during bakeout operations. The QITMS detector assembly consists of a channel electron multiplier (CEM - 5901 Burle Magnum[®], Photonis Inc.) and two protection meshes called grids.

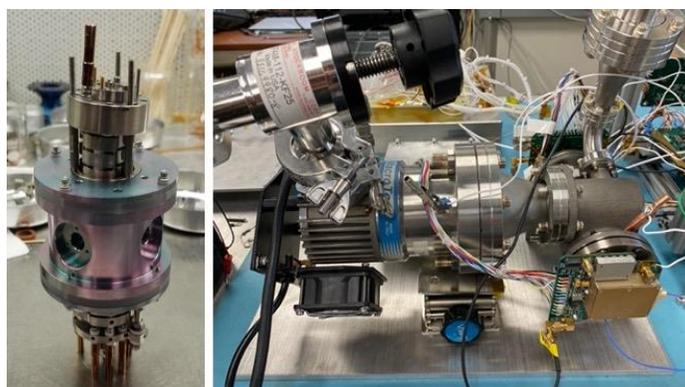


Figure 4. Flight-heritage quadrupole ion trap mass spectrometer. The QITMS on the left is a duplicate of the S.A.M. QITMS. One the right panel shows the S.A.M. 3-D printed titanium vacuum chamber (with the ion trap inside) coupled to the VCAM-heritage turbo molecular pump.

During the ionization period of the QITMS duty cycle, the two grids are elevated to -100 V and +100 V to prevent the negatively charged electron beam and positively charged ions from striking the CEM, which could otherwise result in decreased lifetimes due to oversaturation. During the q-scan rf ramp, both grids are lowered to ground allowing ejected ions to reach the CEM. Under nominal operation, the CEM is biased to -2.2 kV. Ion count rates are corrected for non-paralyzable dead times characteristic of this CEM type (~10 ns).

The QITMS assembly is housed in a 3D-printed titanium vacuum chamber (shown in Figure 4), which is intentionally designed to minimize the weight and footprint of the MS Sensor assembly. The additive manufacturing process (CalRAM[®], Carpenter Technology) includes a state-of-the-art laser sintering procedure followed by hot isostatic pressing that reduces the porosity of the titanium to minimize outgassing and to increase its durability. After printing, the chamber undergoes traditional machining to clean out the internal volume as well as to create the knife edges for Conflat[®] flange seals. Ultimately these custom QITMS chambers exhibit external leak rates less than 10^{-11} Torr L/s and base pressures less than 10^{-10} Torr following a typical 24-hour bakeout at 150°C. These rates are ultra-low, comparable to or better than traditional welded vacuum chambers with all-metal seals, and contribute to long mission lifetime of the sensor.

SWIM utilizes the QITMS in a unique application with increased gas input to the vacuum chamber relative to the S.A.M. implementation. In the SWIM system, the QITMS is equipped with a Pfeiffer HiPace[®] 80 L/s turbomolecular pump (TMP) similar to what was flown on VCAM²² to handle the large flows of helium carrier gas currently used in SWIM GC methods.

C. Micro-Flame Ionization Detector

A possible detector for the gas chromatograph which is quite sensitive is a micro flame ionization detector (micro-FID). The micro-FID for SWIM was originally an STTR project.²³ We have been developing a portable gas sensor system that consists of a micro-flame ionization detector (μ FID) and a micro-gas chromatograph (μ GC), which are integrated in a self-contained electronics unit that has all the peripherals to operate micro-GCFID without any external power and gas supply. Both micro-devices are fabricated in JPL's Microdevices Laboratory using MEMS techniques. The μ GC is now part of the preconcentrator/gas chromatograph subsystem of S.A.M.²⁴ and the μ FID (Figure 5) has been re-purposed as a potential detection module for OWM.

We made the FID microburner using a silicon (Si) wafer since smaller burner cavities can be more easily made using microfabrication technologies in Si than the normal machining needed for Macor[®], allowing easier manufacturing of smaller feature sizes with a lower tolerance, total cost reduction using batch process for mass production. A standard silicon wafer was used to make the burner structure. We made a silicon-on-insulator (SOI) wafer by fusion bonding of two 500 μ m thickness wafers. Each wafer has 2 μ m thickness of oxide.

Buried oxide serves as electrical isolation between two silicon layers to avoid an electrical short. After successful bonding of the two wafers, a microchannel was made and etched using inductively-coupled plasma deep reactive ion etching (ICP-DRIE). Finally, a thermal oxide was grown over the entire device for 13.5 hrs at 1100°C. To obtain the desired flame shape, we used a gold (Au) melted profile by the flame on plane Au-sputtered Quartz plates. The same technique was used for the metal electrode (Cr/Au = 100 Å/1000 Å) beneath the modified Macor[®] burner taking into consideration the flame's shape and location and two metal electrodes sandwiching the Macor[®] burner. The μ FID features exceptional sensitivity over 40 mC/(grams carbon) with a detection limit of less than 8 ng hexane. BTEX (benzene-toluene-ethylbenzene-xylene) and various hydrocarbon compounds at the level of nanograms were also separated and detected.

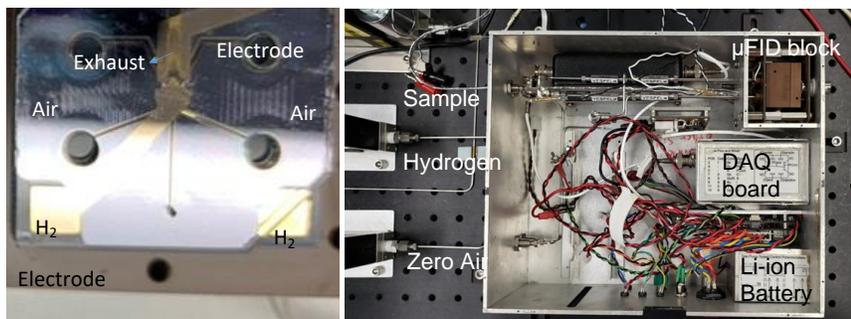


Figure 5. Micro-flame ionization detector. Left, the μ FID chip; on the right is the μ FID module.

IV. Inorganic Water Module

To date, the only technology deployed for inorganic monitoring of drinking water on the ISS is the Conductivity Sensor on the WPA.¹³ Therefore, for more detailed inorganic analysis, the team is exploring a number of technologies that are currently funded by NASA for planetary exploration that could also be applied for human spaceflight applications. These technologies range from traditional liquid chromatography technologies, such as ion chromatography and capillary electrophoresis, to flight-heritage technology such as ion-selective electrodes.

A. Ion-Selective Electrodes

Ion selective electrodes (ISEs) are a well-established tool of analytical chemistry most widely used in routine blood analysis.²⁵ NASA used them to measure the soluble properties of the Martian regolith on the Phoenix mission. ISEs were part of the Wet Chemistry Lab (WCL), one subsystem of the Microscopy, Electrochemistry, and Conductivity Analyzer (MECA) instrument.¹⁰ WCL made the most surprising discovery of the Phoenix mission when it found significant quantities of perchlorate salts in the regolith,²⁶ and demonstrated the power of ISEs for identifying unexpected compounds. Since Phoenix, NASA has continued to fund ISE sensors and sensor array instrument development work to further miniaturize the system and expand the list of measurable targets. One of the most recent efforts is the Microfluidic Icy World Chemical Analyzer (MICA) developed for inclusion on a potential Europa Lander mission (Figure 6).¹⁶

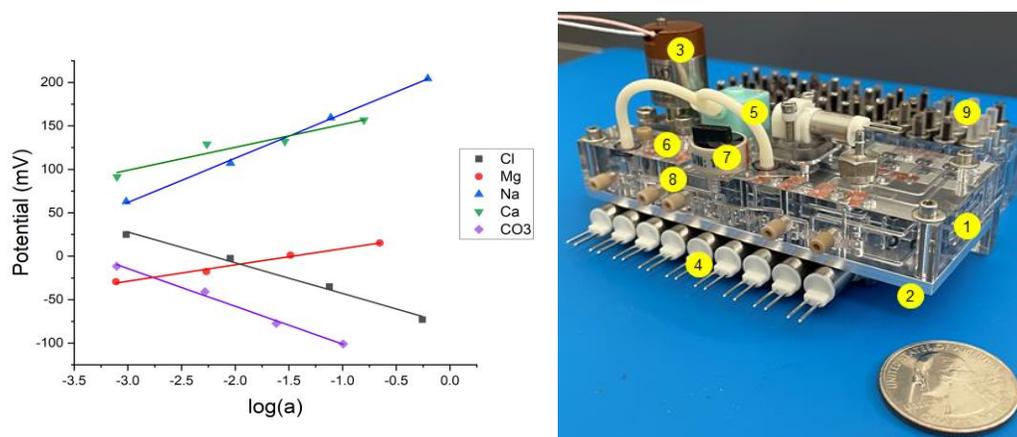


Figure 6. The MICA instrument. Left, calibration plots for a selection individual ISEs. Right, Photo of MICA fluidic system with: 1) fused 3-layer manifold; (2) thermomechanical backing plate; (3) hermetic microvalve; (4) fluid-control valves; (5) peristaltic pump; (6) fluid-in-channel feed-through (AC conductivity); (7) pressure sensor; (8) liquid connectors; (9) 48-electrode array.

MICA has taken the next step in ISE sensor technology by making use of nanocarbon based solid contact ISEs instead of the hydrogel-based sensors used in WCL.²⁷ This has allowed for a reduction in size of the sensors (and their arrays) as well as moving from a beaker style measurement to a fluidic channel. This reduces the volume needed for analysis by $\geq 100X$, from 25 mL down to $\leq 250 \mu\text{L}$. Additionally, MICA includes pH, electrical potential (Eh), conductivity, and voltammetry electrodes to measure other fundamental properties of the solution also relevant to SWIM. MICA also takes advantage of NASA's significant investment in microfluidics for space biology experiments, leveraging the miniaturized technology developed for multiple CubeSat missions.²⁸⁻³⁰ In general, the electrochemical sensor array approach has the benefit that it is easily scalable based on the number of targets desired. A minimal instrument that measures conductivity, as well as had ISEs for pH and silver concentrations, would require few resources. However, even MICA, a fully populated array capable of targeting a wide variety of anions and cations is compatible with a 2 – 3 U CubeSat-style form-factor.

B. Ion Chromatography with Conductivity Detection

Motivated by WCL's detection of perchlorate on Mars, development of more capable ion detection instruments followed the Phoenix mission as well. Ion chromatography (IC) is an industry standard for water quality monitoring of municipal systems as well as in the pharmaceutical and semiconductor industries.³¹ Traditional IC uses packed chromatography columns made up of functionalized resin/particles in the 2 – 25 μm size range. The disadvantages of packed chromatographic columns for space applications are that they require large high-pressure pumps needed to

generate flow through the small pores between the particles, and that temperature extremes or periods of dryness have the potential to disturb the packing of the column itself (channeling) leading to reduced performance.

To circumvent these challenges, open tubular IC (OTIC) approaches were funded by NASA. OTIC uses a narrow diameter capillary (10 – 30 μm) with a functionalized surface as the chromatographic column. This drastically reduces the pressure required for separations (~ 10 PSI) and makes the column more robust to different environmental and operational conditions. All of the critical functional components of an IC system including eluent generation, sample injection, the column, background suppression, and conductivity detection have been matured to allow commercial system level performance from an OTIC system.³²⁻³⁵ Currently, the Ion/Liquid Chromatograph for Exploration of the Solar System (ILCESS, Figure 7) project is working to mature the TRL of an OTIC system for planetary applications.

ILCESS has focused primarily on anion chromatography, motivated by the desire to unravel the chlorine speciation of Mars (chloride, chlorate, and perchlorate) as well as to look for relevant markers of habitability including nitrite/nitrate and small organic acids like formate, acetate, and benzoate. However, adaptation of the system to also measure cations via the inclusion of a cation column has been demonstrated in the literature.³⁶

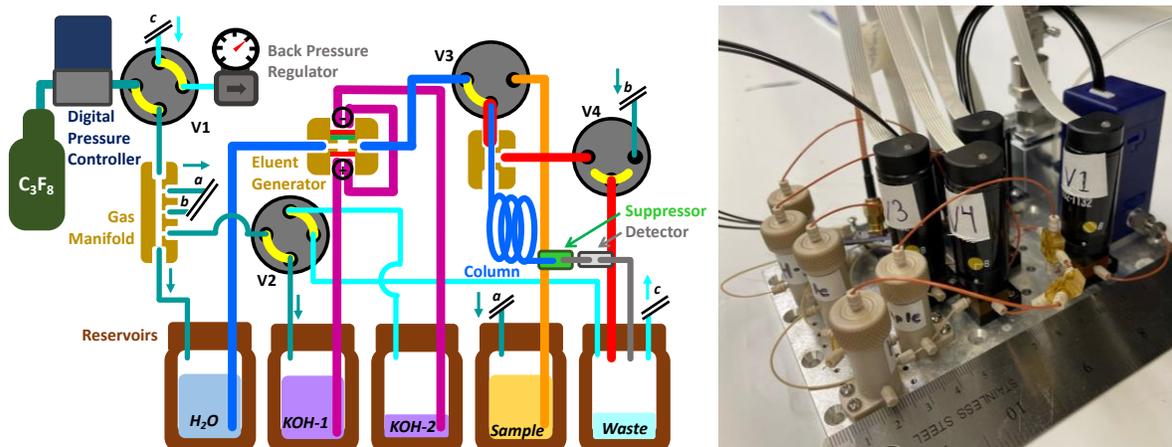


Figure 7. The ILCESS instrument. *Left: Schematic of the Ion Liquid Chromatograph for Solar System Exploration (ILCESS). Right: Prototype instrument photo (Courtesy of Professor Dasgupta, University of Texas, Arlington).*

C. Capillary Electrophoresis with Conductivity Detection

Capillary electrophoresis (CE) is another high efficiency separation method that is well established for small ion analysis.³⁷ NASA funded work initially focused on amino acids for life detection missions,³⁸ but has recently branched out into capacitively-coupled contactless conductivity detection (C^4D) as well with methods broadly applicable to both anions and cations of potential relevance to water systems.^{39,40} A method was even developed for the detection of silver and other metals at ISS relevant levels as a direct example of what type of performance a system like this could have as part of the SWIM architecture.⁴¹

CE is an attractive approach because of its simplicity and flexibility. Its simplicity is that it only requires a standard glass capillary filled with a conductive background electrolyte (BGE) to allow the establishment of an electrical circuit and electrophoretic separation of any charged species. Its flexibility is that by simply changing the BGE a wide variety of different methods targeting different compound classes can be achieved.

A complete prototype (Figure 8) of the Organic Capillary Electrophoresis Analysis System (OCEANS)¹⁵ has been developed and demonstrated as part of both the European Molecular Indicators of Life Investigation (EMILI)¹⁴ project and another life detection instrument suite, Ocean Worlds Life Surveyor (OWLS).^{17,18} The OCEANS prototype demonstrates performance identical to that of commercial analyzers⁴² using a number of different detectors including C^4D . Separately, a C^4D detector design that restricted itself to a flight migratable EEE parts selection, was also built and tested demonstrating equivalent performance to commercial detectors while also being suitable for flight.⁴³

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



Figure 8. The OCEANS CE-C⁴D instrument. Left, a table of inorganic species already demonstrated by the CE-C⁴D system. Right, an image of the field portable CE-C⁴D system with its cover off.

V. Plan Forward

The capabilities for SWIM must be developed and implemented in an incremental and strategic fashion, with emphasis placed on the most impactful measurements first. SWIM is currently in a research and development phase, primarily identifying technologies that could adequately analyze organic and inorganic components of an ECLSS-produced potable water and might have a path-to-flight. We will continue to leverage and combine NASA-funded and commercially available technologies to provide the broadest flexibility in future enhanced water-monitoring capabilities.

For the OWM, we will continue to mature the DAI-GC-MS system and include the thermal conductivity detector and micro-FID where appropriate in the system. Extensive testing of aqueous mixtures of target compounds will continue. For the IWM, we will continue to mature the CE-C⁴D instrumentation and verify capabilities to detect target ionic species. For the full SWIM system, we will continue to perform technology selection trades, architecture studies, and look for opportunities to include detection technologies that have not yet been considered for SWIM where it is advantageous to do so.

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