52nd International Conference on Environmental Systems
16-20 July 2023, Calgary, Canada

ICES-2023-110

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

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technologies (e.g. ion chromatography, capillary electrophoresis) to flight-heritage technology such as ion-specific electrodes.

Nomenclature

BGE = Background Electrolyte
BTEX = Benzene-Toluene-Ethylbenzene-Xylene
CE = Capillary Electrophoresis
C^4D = Capacitively Coupled Contactless Conductivity Detection
DAI-GC = Direct Aqueous Injection Gas Chromatograph
GC = Gas Chromatograph
ECLSS = Environmental Control and Life Support System
EMILI = Europan Molecular Indicators of Life Investigation
ESI = Electrospray Ionization
HPLC = High Performance Liquid Chromatograph
IC = Ion Chromatograph
ICP-MS = Inductively-Coupled Plasma Mass Spectrometer
ILCESS = Ion Liquid Chromatograph for Solar System Exploration
ISE = Ion-Specific Electrode
ISS = International Space Station
LEO = Low Earth Orbit
LIBS = Laser-Induced Breakdown Spectroscopy
MS = Mass Spectrometer
MECA = Microscopy, Electrochemistry, and Conductivity Analyzer
MEMS = Micro-Electro-Mechanical Systems
MICA = Microfluidic Icy-World Chemistry Analyzer
μFID = micro-Flame Ionization Detector
miniTOCA = miniature-TOCA
NIR = Near-Infrared
OCEANS = Organic Capillary Electrophoresis ANalysis System
OTIC = Open Tubular IC
OWLS = Ocean Worlds Life Surveyor
OWM = Organic Water Module
QITMS = Quadrupole Ion Trap Mass Spectrometer
S.A.M. = Spacecraft Atmosphere Monitor
SBIR = Small Business Innovative Research
SIBS = Spark-Induced Breakdown Spectroscopy
STTR = Small Business Technology Transfer
SWIM = Spacecraft Water Impurity Monitor
TCD = Thermal Conductivity Detector
TOC = Total Organic Carbon
TOCA = Total Organic Carbon Analyzer
TDU = Technology Demonstration Unit
TMP = Turbo Molecular Pump
UV-Vis = Ultraviolet-Visible
VCAM = Vehicle Cabin Atmosphere Monitor
VOC = Volatile Organic Compound
WPA = Water Processor Assembly
WCL = Wet Chemistry Lab
WRS = Water Recovery System

I. Introduction

According to Limero 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 near-Earth sample strategy relies almost exclusively on sample archiving and return to ground for analysis. However, once traveling significant distances from Earth, Limero 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 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, total organic carbon (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 or quantifies the individual chemicals contributing to the TOC number. Nor does the TOC measurement begin to 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 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) managers to institute routine collection of water samples, and their subsequent return to earth for detailed laboratory analysis[3]. For exploration missions beyond low Earth orbit (LEO), the return of water samples to Earth for analysis (like for the ISS), whether for routine checks or for troubleshooting problems with the life support system, will be logistically challenging or impossible.

The Spacecraft Water Impurity Monitor (SWIM) is a collaboration between JSC and JPL to research and develop a modular instrument platform that will perform in-flight 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, because the state-of-the-art in water quality monitoring is a well-established discipline. It therefore makes sense to try and utilize many of the "gold standard" methods if possible. 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, 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 (GC) / mass spectrometer (MS) system, called the Organic Water Monitor (OWM), to detect and identify dissolved VOCs in drinking water supplies[6,7]. Liquid-injection GC/MS systems are the workhorses of analytical chemistry laboratories world-wide, and one of the gold standard techniques, but have not flown before for space applications. The MS for OWM, a Paul quadrupole ion trap (QIT) MS, does have ISS flight heritage; 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 programs. These technologies range from traditional liquid chromatography technologies, such as ion chromatography and capillary electrophoresis, to flight-heritage technology, such as ion-specific electrodes (e.g. next-generation Wet Chemistry Lab[10], originally part of the MECA instrument suite on the Phoenix spacecraft).

This paper is a progress report on technology development efforts for the organic and inorganic water modules of the Spacecraft Water Impurity Monitor.

II. Modular Architecture and Technology Matrix

The SWIM project aims to research, develop and (eventually) 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 LEO, where sample return is impractical[1,4,5]. Lunar Gateway, lunar surface, Mars transit, and Mars surface missions are all target end-users. 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 as well as 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 and an Inorganic Water Module 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 (if required) and detection modules.

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 NASA (e.g. HEOMD-AES, SMD-ROSES, SBIR/STTR,…) in order to try to leverage systems that might already have some flight development and/or pedigree. An overview of this 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 what would be considered the "gold" standard of analytical techniques used for drinking water worldwide, including 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].

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				
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

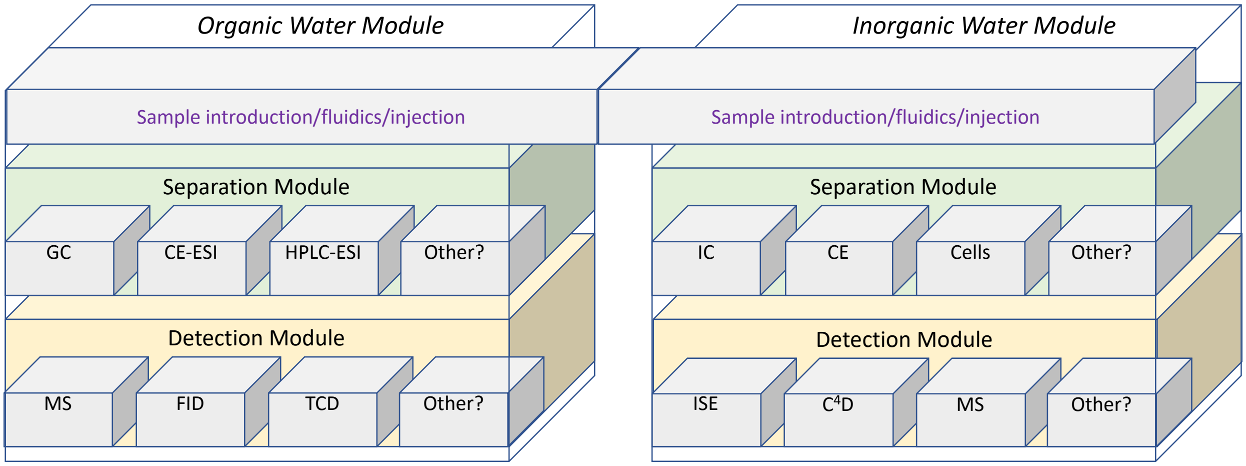


Figure 1. Modular approach to SWIM's architecture. *The configuration of SWIM is dependent on mission, spacecraft, customer needs, and size/mass/power constraints.*

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 gas chromatography thermal conductivity detector (DAI-GC-TCD) detection. Efforts continue toward the eventual goal of GC-TCD-MS detection of organics, 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 C^{4}D detection of candidate target mixtures and TRL advancement of C^{4}D detector electronics and hardware.

III. Organic Water Module

Organic contaminants in spacecraft cabin air and water present a unique 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, whether in the atmosphere or water, these contaminants can undergo chemical transformations and reactions, widening the scope of potential species. Fortunately, we know from experience that by the time contaminants make it into potable (WRS product) water, they usually are relatively small and simple molecules, making them volatile or semi-volatile. Candidate molecules for detection targets include acetone, methanol, ethanol, methyl-ethyl-ketone, dichloromethane, acetic acid, dimethylsilanediol, ethylene and propylene glycol, and trimethylsilanol, among others; all of these fit the "small molecule" description and can easily be analyzed by gas chromatography.

The SWIM team at JSC have been developing a liquid-injection gas chromatograph (GC) / mass spectrometer (MS) system, historically called the Organic Water Monitor (OWM). Liquid-injection GC/MS systems are the workhorses of analytical chemistry laboratories world-wide but have not flown before for space applications. Although the liquid-injection gas chromatograph being developed for spacecraft applications is of a new design, the mass spectrometer for OWM, a Paul quadrupole ion trap mass spectrometer (QIT-MS), has ISS flight heritage; 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] – both of these systems were/are used for *in situ* organic detection and identification (of the cabin air) in a crewed space vehicle.

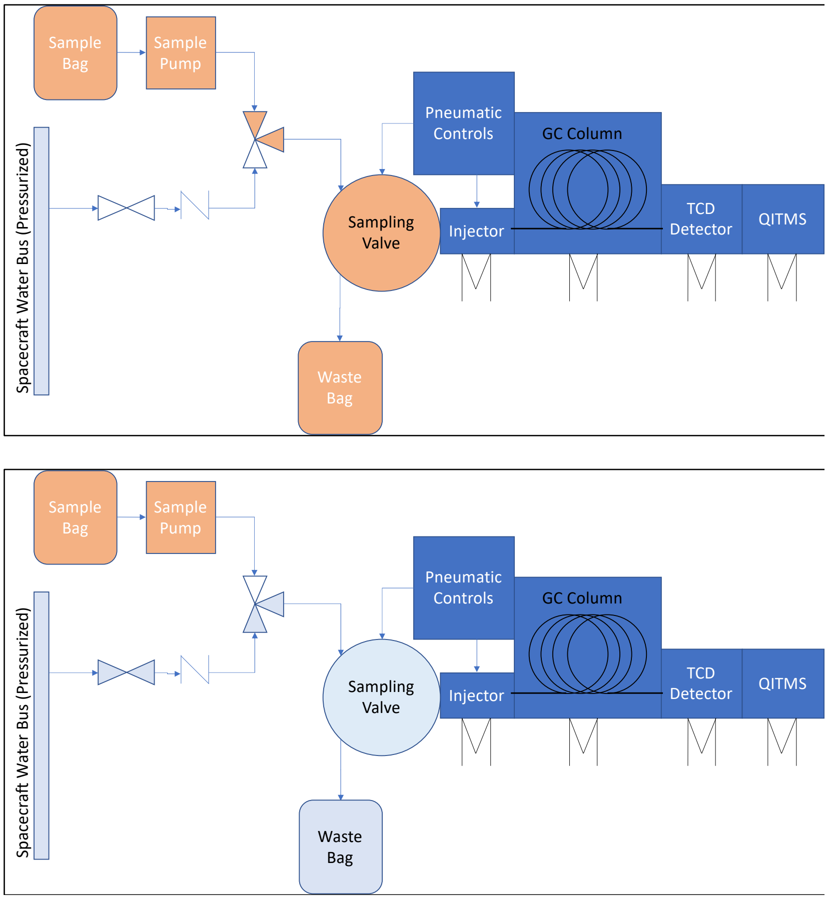
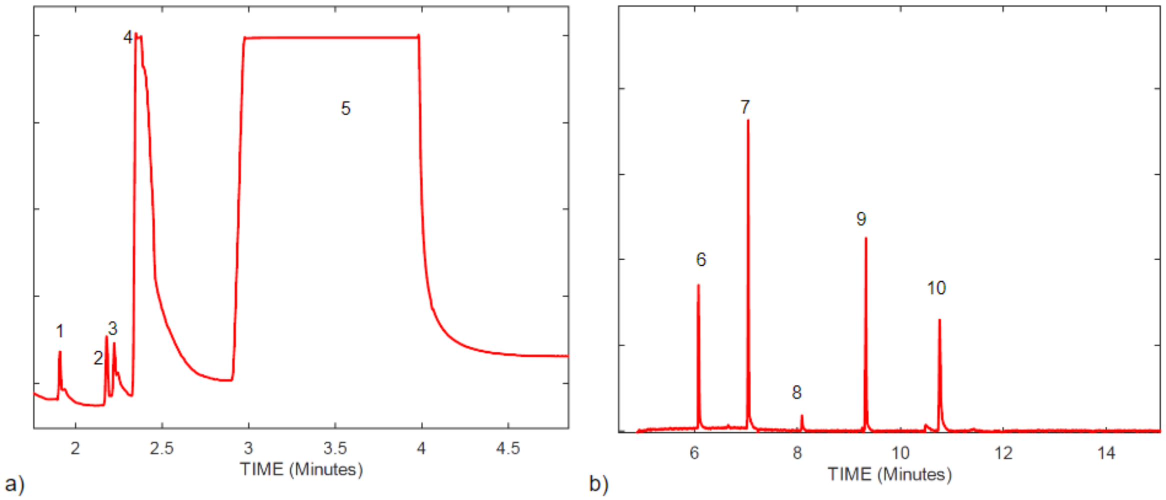


Figure 2. OWM's schematic for the liquid injection and gas chromatograph portion of the system. *Top, sampling mode. Bottom, injection/chromatography modes.*

A. Direct Aqueous Injection Gas Chromatograph (DAI-GC) and Thermal Conductivity Detector (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



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.*

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 by a thermal conductivity detector and eventually, the QIT-MS. The thermal conductivity detector is a useful device even when the QIT-MS 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 when the water is eluting from the column. 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-developed pneumatic controls and ground-station software. The Micro-Electro-Mechanical Systems (MEMS) thermal conductivity detector (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-GC-MS 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-GC-MS 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, if desired. The mass spectrometer sensor has already been identified as the flight design which will not change in the future SWIM implementation.

The sensor is a 3-D Paul 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 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.). 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. The QITMS detector assembly consists of a channel electron multiplier (CEM - 5901 Burle Magnum®, Photonis Inc.) and two protection meshes called grids.

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.

Due to the increased gas load expected from the liquid-injection GC, the QITMS is equipped with a Pfeiffer HiPace® 80 L/s turbomolecular pump (TMP) similar to what was flown on VCAM[22]. Keeping in-line with our modular approach to SWIM, if we have mass/power/size constraints, the QITMS can utilize S.A.M.'s ion-getter pump but at a lower duty cycle.

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 that consists of a micro-flame ionization detector (μFID) and a micro-gas chromatograph (μGC), which are integrated in a "lunch box" that has all the peripherals to operate micro-GC/FID without any external power and gas supply. Both micro-devices are now fabricated in JPL's Microdevices Laboratory using MEMS techniques. The μGC is now part of the preconcentrator/gas chromatograph subsystem of S.A.M.[24] and the μFID (see Figure 5) has been re-purposed as a potential detection module for OWM.

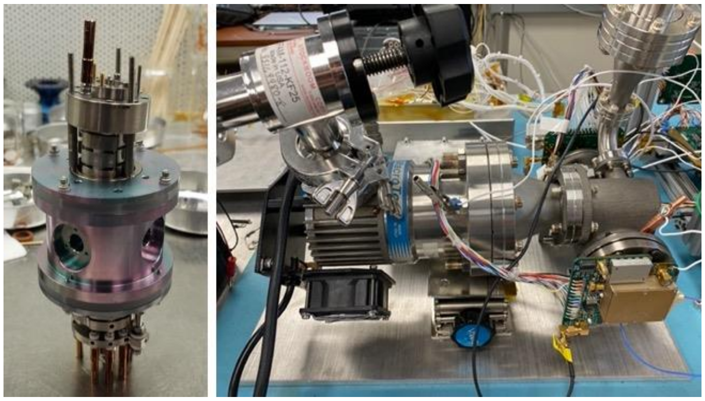


Figure 4. Flight-heritage quadrupole ion trap mass spectrometer. *The QITMS on the left is a duplicate of the S.A.M. QITMS. One the right panel shows the S.A.M. 3-D printed titanium vacuum chamber (with the ion trap inside) coupled to the VCAM-heritage turbo molecular pump.*

We made the microburner using a 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 Si wafer was used to make the burner structure. We made a silicon-on-insulator (SOI) wafer by fusion bonding of two 500 μm thickness wafers. Each wafer has 2 μm thickness of oxide.

Buried oxide serves as electrical isolation between two Si layers to avoid the short. After successful bonding of the two wafers, the same pattern as in the Macor® (a machinable glass ceramic made by Corning) 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 an Au melted profile by the flame on plane Au-sputtered Quartz plates. The same technique was used for the (a) metal electrode (Cr/Au = 100 Å/1000 Å) beneath the modified Macor® burner taking into consideration the flame's shape and location; and (b) two metal electrodes sandwiching the Macor® burner. The µFID features exceptional sensitivity over 40 mC/gC 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.

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 (Water Processing Assembly)[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 manned missions. These technologies range from traditional liquid chromatography technologies, such as ion chromatography and capillary electrophoresis, to flight-heritage technology such as ion-selective electrodes.

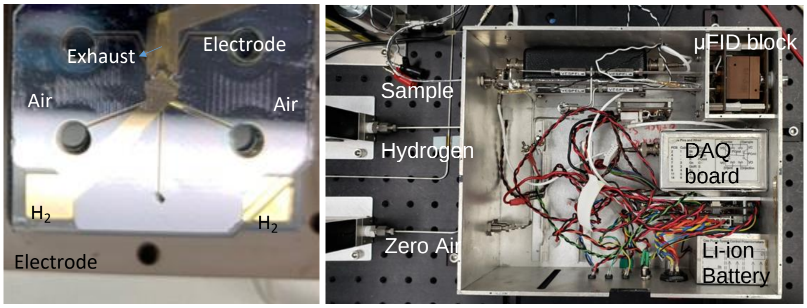


Figure 5. Micro-flame ionization detector. *Left, the µFID chip; on the right is the µFID module.*

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].

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 ≥100X, from 25 mL down to ≤250 µL. Additionally, MICA includes pH, 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 measured 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.

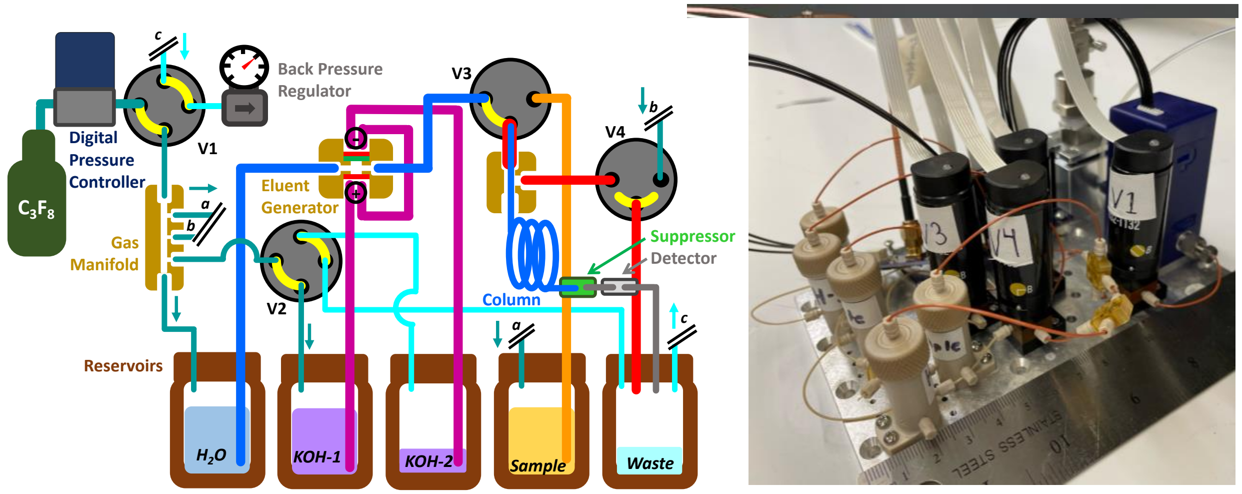


Figure 6. The ILCESS instrument. *Left: Schematic of the Ion Liquid Chromatograph for Solar System Exploration (ILCESS). Right: Prototype instrument photo (Courtesy of Professor Dasgupta, University of Texas, Arlington).*

control valves; (5) peristaltic pump; (6) fluid-in-channel feed-through (AC conductivity); (7) pressure sensor; (8) liquid connectors; (9) 48-electrode array.

B. Ion Chromatograph 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 6) 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].

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 7) of the Organic Capillary Electrophoresis ANalysis System (OCEANS)[15] has been developed and demonstrated as part of both the Europan 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 analyzers[42] 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 7. The CE-C^4D instrument. *Left, a table of inorganic species already demonstrated by the CE-C^4D system. Right, an image of the field portable CE-C^4D system with its cover off.*

V. Plan Forward

The Spacecraft Water Impurity Monitor is a collaboration between JSC and JPL to develop an instrument platform that will perform in-flight measurements, delivering 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 because there will be no ability to send water samples back to terrestrial labs for analysis. All analysis that is needed to determine water quality either for crew health purposes or for subsystem monitoring must be performed by an operational system on a given mission.

These capabilities 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-C^4D 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.

Acknowledgments

The research was carried out Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration (80NM0018D0004), at KBR as part of the Human Health and Performance Contract, HHPC (NNJ15HK11B), and at the NASA Johnson Space Center. Funding was also provided by the NASA Maturation of Instruments for Solar System Exploration (MatISSE) program and the Instrument Concepts for Europa Exploration 2 (ICEE-2) program. NASA JSC gratefully acknowledges funding from the NASA Exploration Capabilities Life Support Systems project. Trade names and trademarks and company names are used in this report for identification only. Their usage does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

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