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Membrane Inlet Mass Spectrometry for Ocean Worlds

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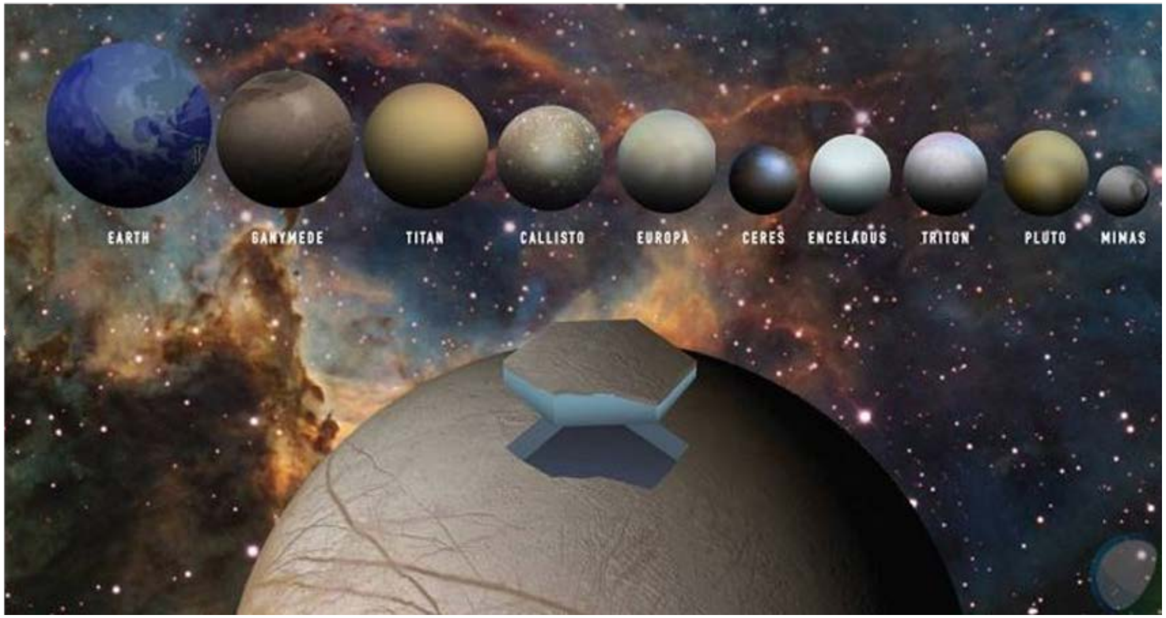
13th Workshop on Harsh Environment Mass Spectrometry
16-19 September 2019

Outline

- Exploration of Ocean Worlds
- NASA Membrane Extraction for Space Applications (MESA) Project
  - Project objectives
  - SRI static membrane interface probe design
  - Membrane inlet mass spectrometry (MIMS) data using static probe
  - Fabrication of custom membranes
  - GSFC gas processing system (GPS) and operation
  - Plan for integration of SRI static MIMS probe and GSFC GPS
  - Future concept for Europa
- Melt Probe with a Membrane Inlet Mass Spectrometer for Ocean Worlds (MeltMIMS) Concept
  - SRI underwater mass spectrometer
  - Integration with Honeybee Robotics melt probe
- Acknowledgments

Exploration of Ocean Worlds

- Worlds with subsurface oceans are worth exploring for detection of extant life and habitability assessment
- The moons Europa, Enceladus, and Titan are highest priority for further study
- The recent discovery of sub-ice water on Mars may provide a near-term opportunity for exploration
- If life is present, then so are the gaseous hydrocarbon byproducts

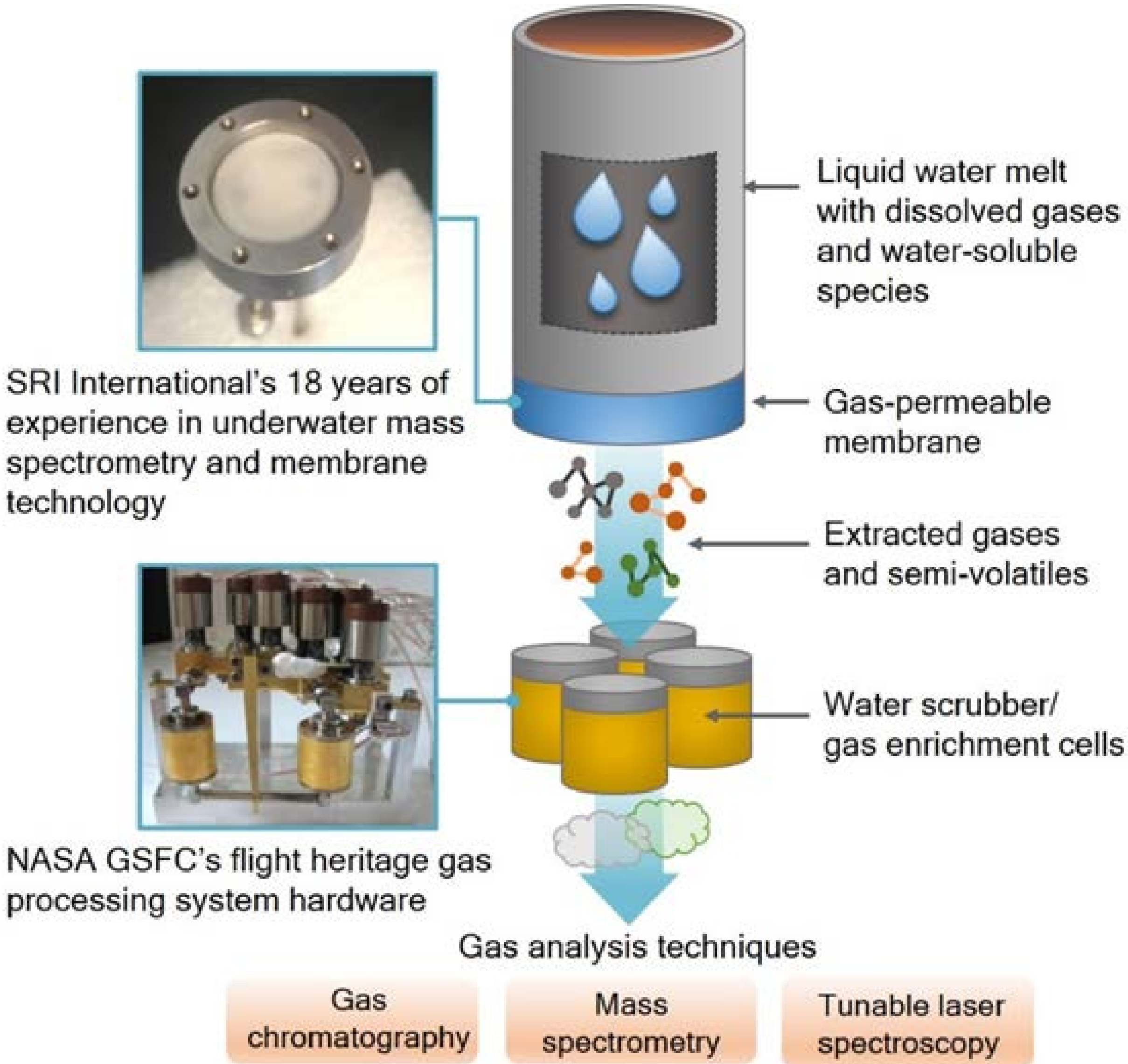


- *Many analytical methods for detection of signs of life target complex refractory biomolecules that have low abundance and are difficult to sample*
- *Gases are a more abundant, equally relevant set of analytes and include light hydrocarbons and volatile organic compounds (VOCs)*
- *These compounds can be extracted and concentrated from water and ice while keeping refractory molecules intact*

Membrane Extraction for Space Applications

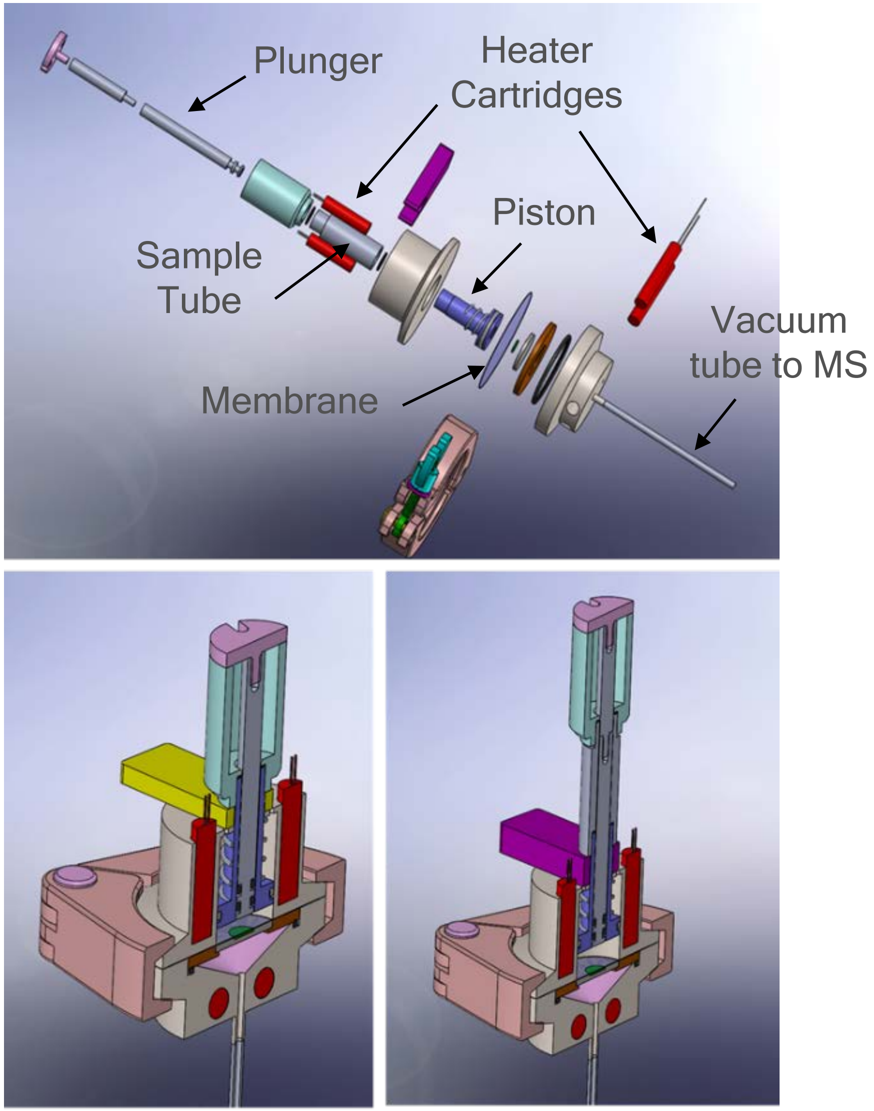
NASA PICASSO

- Extract and quantify dissolved atmospheric gases, biomarker gases, alkanes, and VOCs
- Combine static MIMS with scrubbers and enrichment cells
- Scrubbing water vapor reduces background MS interferences
- Enrichment cells concentrate analytes and release to MS in a sharp injection to improve sensitivity



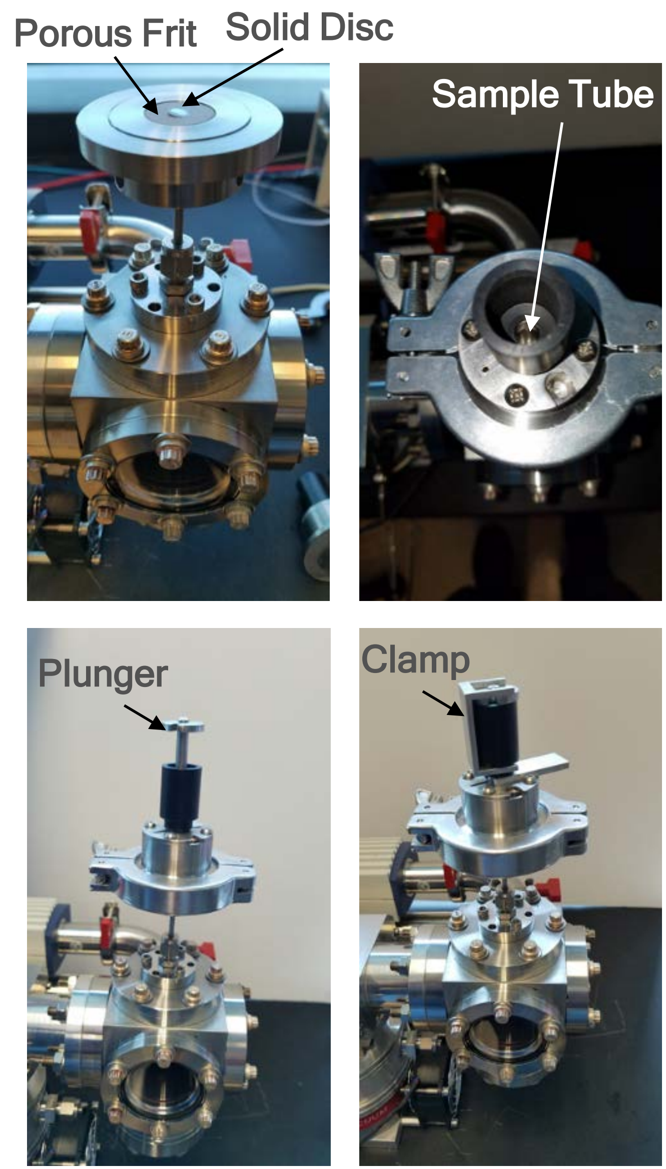
MESA Static Membrane Probe Design

- Goal: Design and test a low-power MIMS interface probe that will efficiently extract volatile analytes from a limited volume of water
- Static design obviates need for continuous sample pump to reduce power consumption
- Top of static probe accepts a fixed volume of water onto a polydimethylsiloxane (PDMS) sheet membrane
- Bottom of probe is connected to vacuum system of mass analyzer
- Modular design allows optimization of probe parameters (volume & membrane surface area/thickness)

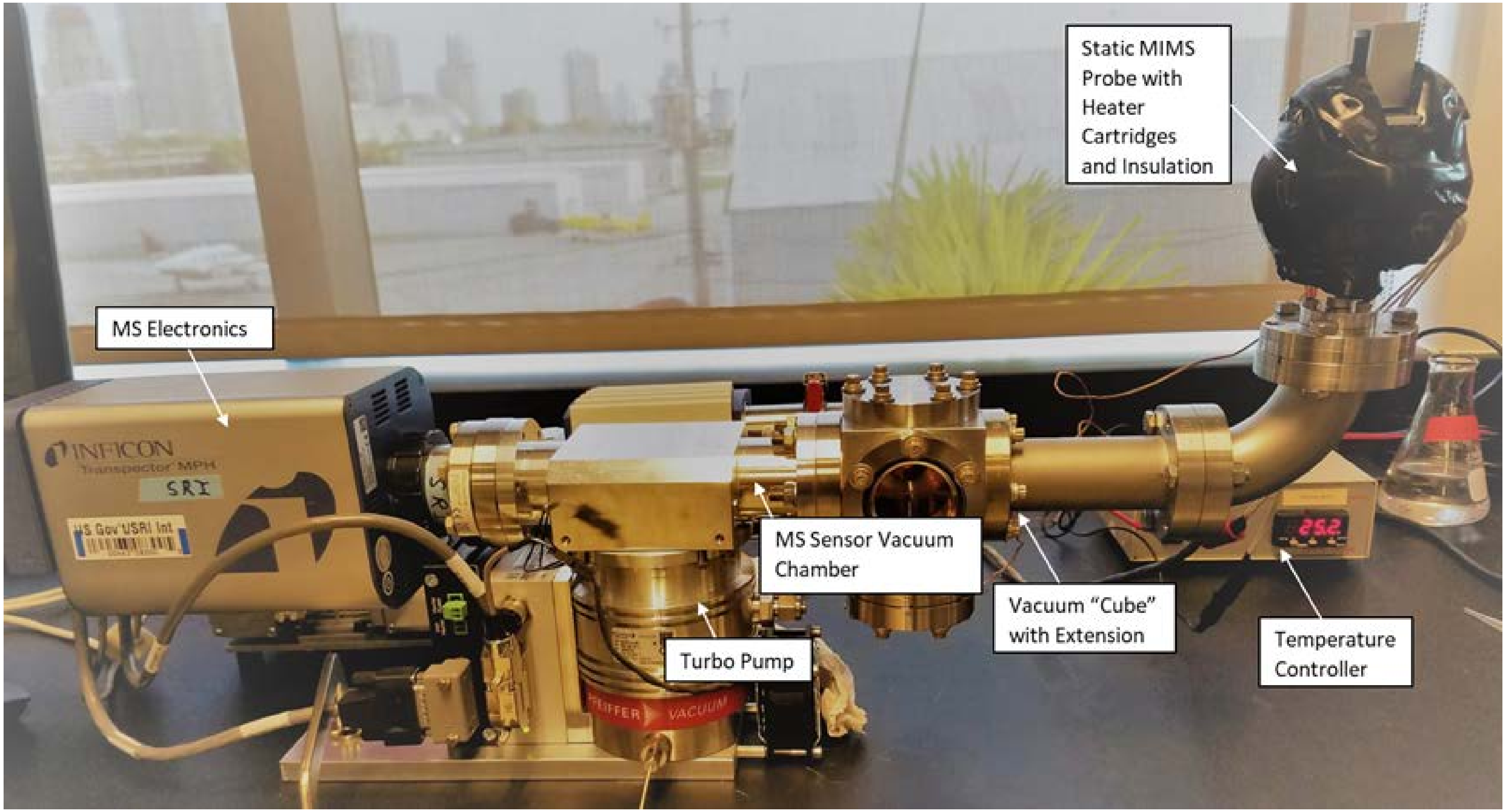


Static Membrane Probe Construction and Operation

- Porous stainless steel (SS) frit supports PDMS membrane
- Water sample introduced into sample tube above membrane
- Solid SS disc in middle of frit prevents volatile analytes from entering the MS vacuum system
- Plunger is inserted into sample tube, and a spring-loaded piston rises to allow sample to cover surface of membrane above frit
- Dissolved analytes immediately begin to diffuse through membrane into the MS vacuum system
- Plunger is clamped in place until analysis is complete



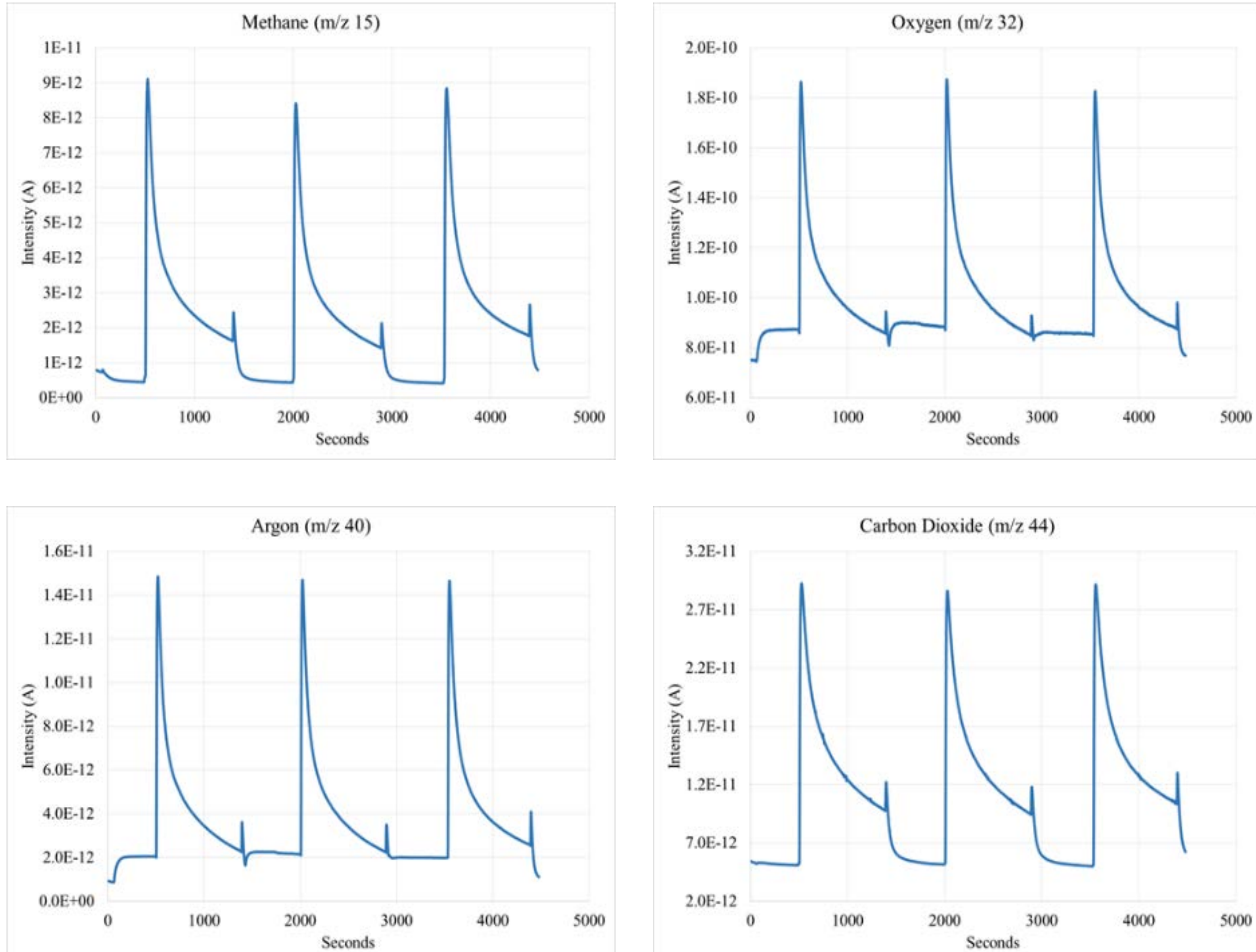
Static Membrane Probe Installed on MIMS Testbed



- MIMS testbed uses a 200-amu linear quadrupole mass filter for analysis
- Static probe is slightly heated (typically 25 ^{o}C) to maintain constant temperature (minimal power consumption)

Dissolved Gas Data from Static MIMS Experiments

- Optimal frit surface area and water volume determined to be 1 mL and 2.5 cm^2
- Commercial PDMS membranes with thickness of 127 and 254 µm tested
- Deionized water equilibrated with a mixture of major atmospheric gases and methane
- Samples injected into probe and removed after ~15 min of analysis

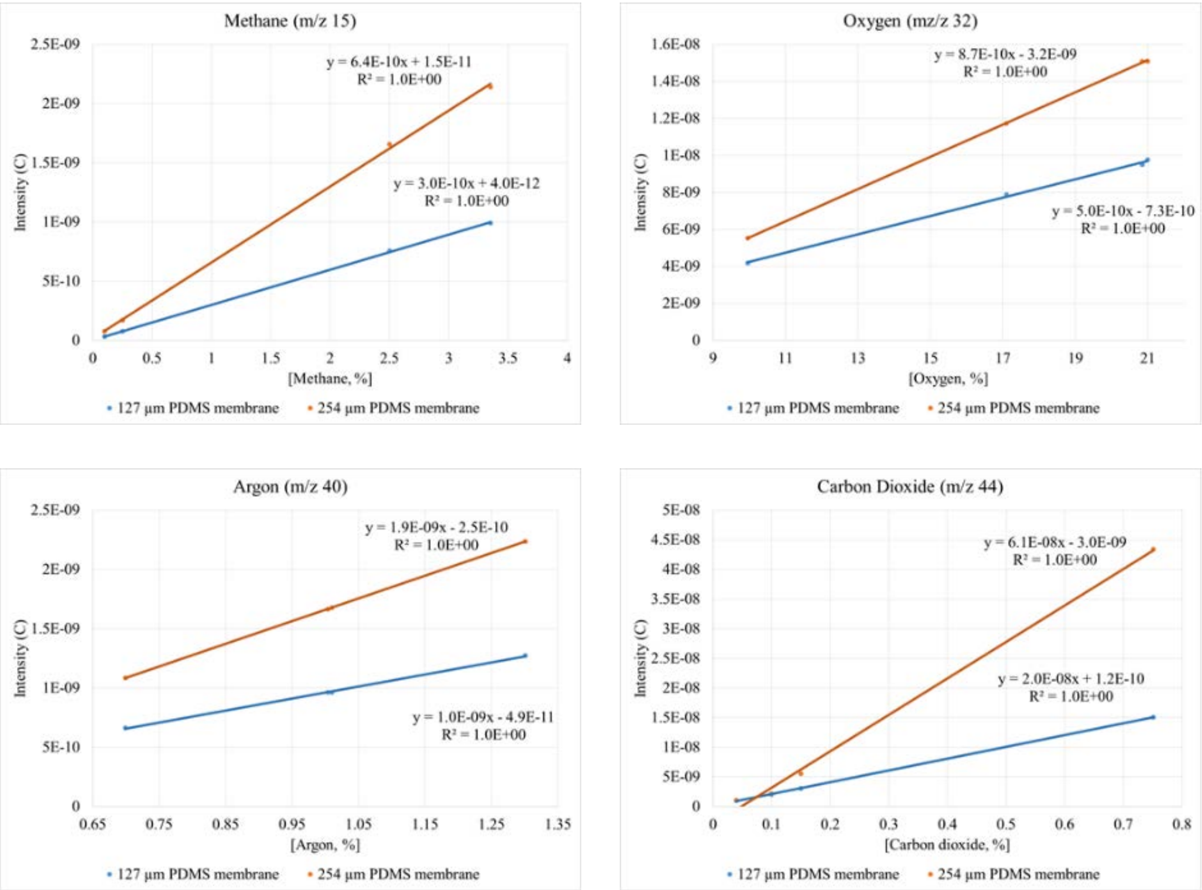


MIMS data from three replicate injections of 1-mL water samples show a sharp rise in signal when plunger is inserted and water delivered to membrane surface

Static MIMS Calibration Plots for Dissolved Gases

- Calibrations for analyses of DI water equilibrated with 4 gas mixtures (see table)
- Comparison of results using two different membranes (127 and 254-µm)
- Total pressure ~1.4x10^{-4} Torr with 127-µm membrane

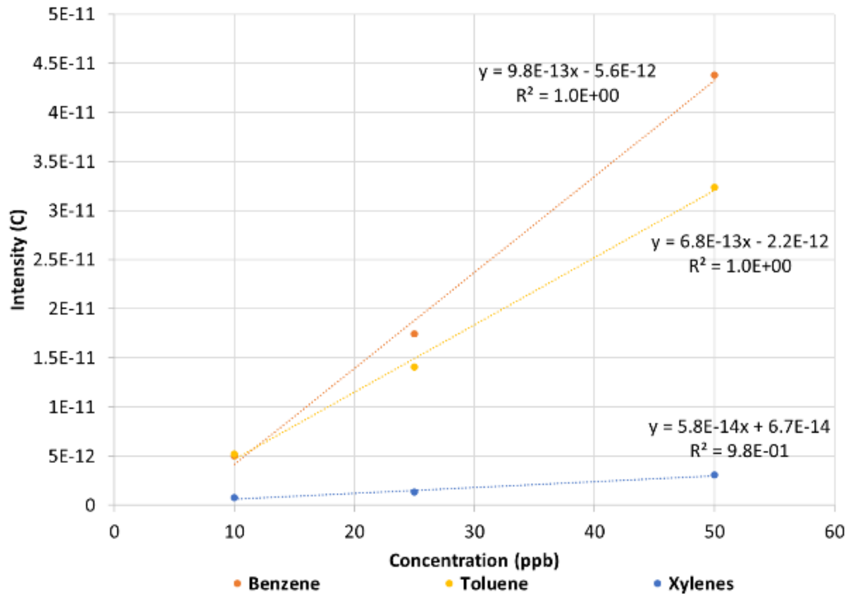
Analyte	1	2	3	4
Methane	0.1%	0.25%	2.5%	3.35%
Nitrogen	Bal	Bal	Bal	Bal
Oxygen	20.8%	21.0%	17.1%	9.96%
Argon	1.01%	1.3%	1.0%	0.7%
Carbon Dioxide	0.1%	0.75%	0.15%	0.04%

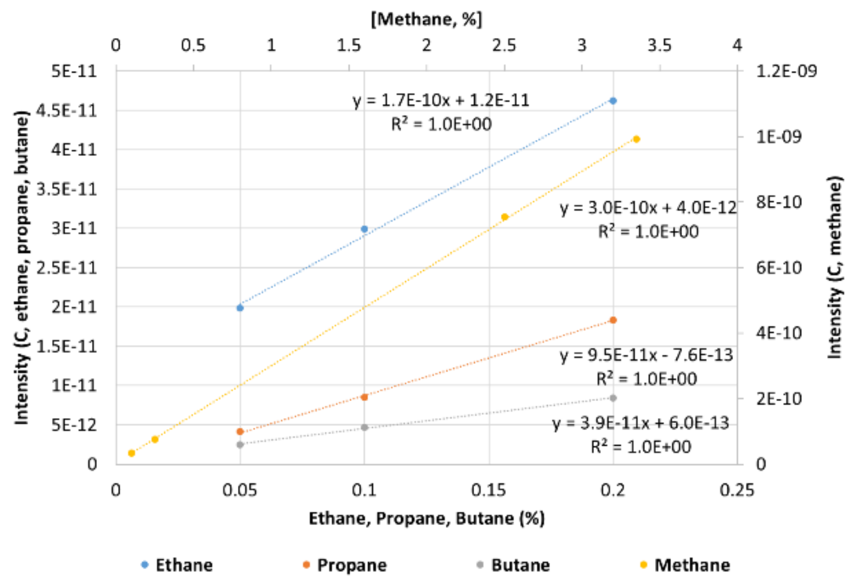


Linear calibration plots to relate MIMS response (average peak areas) for each gas as a function of dissolved gas partial pressure for two different thicknesses of commercial PDMS membranes

Static MIMS Calibration Plots for VOCs and Alkanes

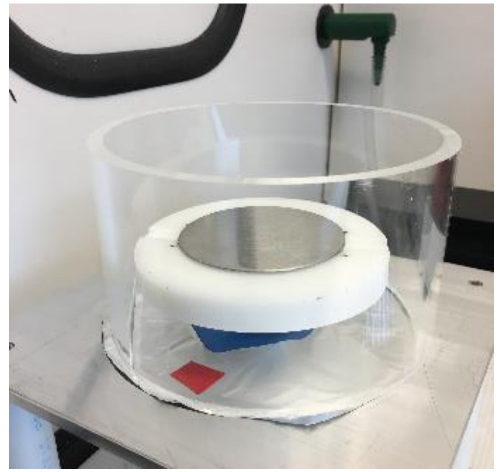
- Calibrations for VOCs and alkanes used 127-µm PDMS membrane
- Three different solutions of benzene, toluene, and xylene were created using serial dilution in DI water of stock solution in methanol
- Three different mixtures of methane, ethane, propane, and butane were equilibrated with DI water
- Plotted are average peak areas vs. concentration or partial pressure of each analyte
- Sensitivities decrease with increasing mass for both sets of analytes

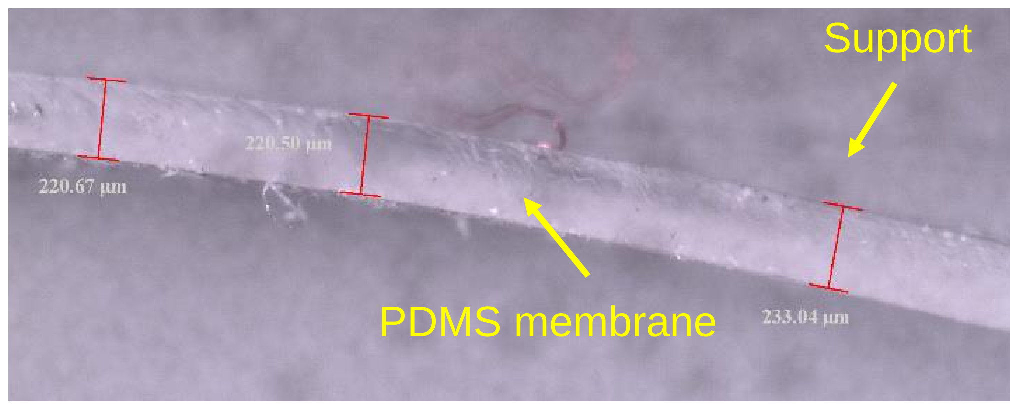




Development of Custom PDMS Membranes

- The goal is to produce PDMS membranes of a desired thicknesses for static MIMS separations
- PDMS membranes were spun using an in-house spinner and substrate
  - Dow SYLGARD™ 184
  - Spun for 20 s at 616 RPM
  - Baked in 100 °C oven for 40 minutes
  - Characterized using a Leica MZ16 stereo microscope with DFC290 camera

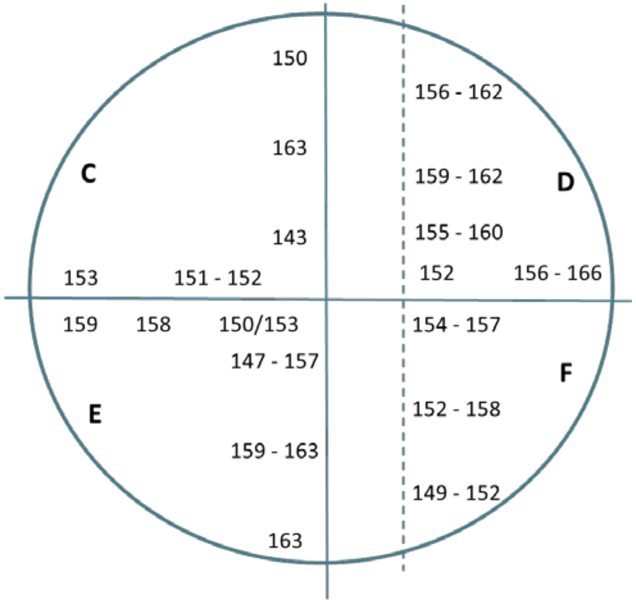


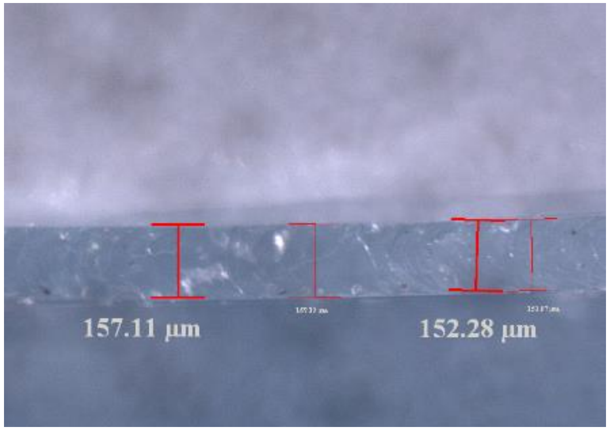


PDMS membrane with thickness varying from 220 µm to 233 µm

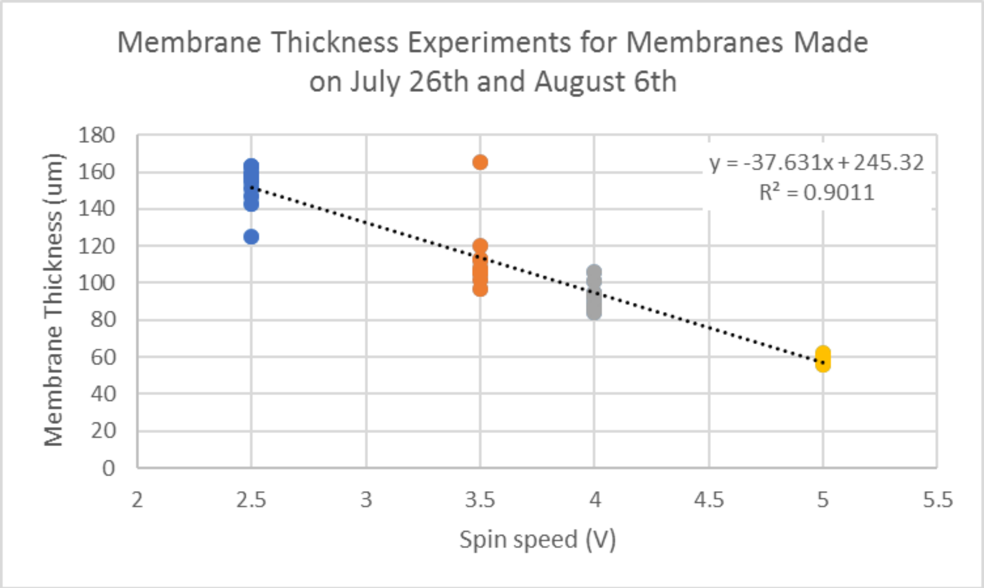
Evaluation of Spin Speed on Thickness of PDMS Membranes

- Membranes were cut into pieces and thicknesses measured using a microscope
- Thicknesses were found to be fairly uniform
- Several measurements per membrane were used to plot the trend in thickness vs. spin speed.



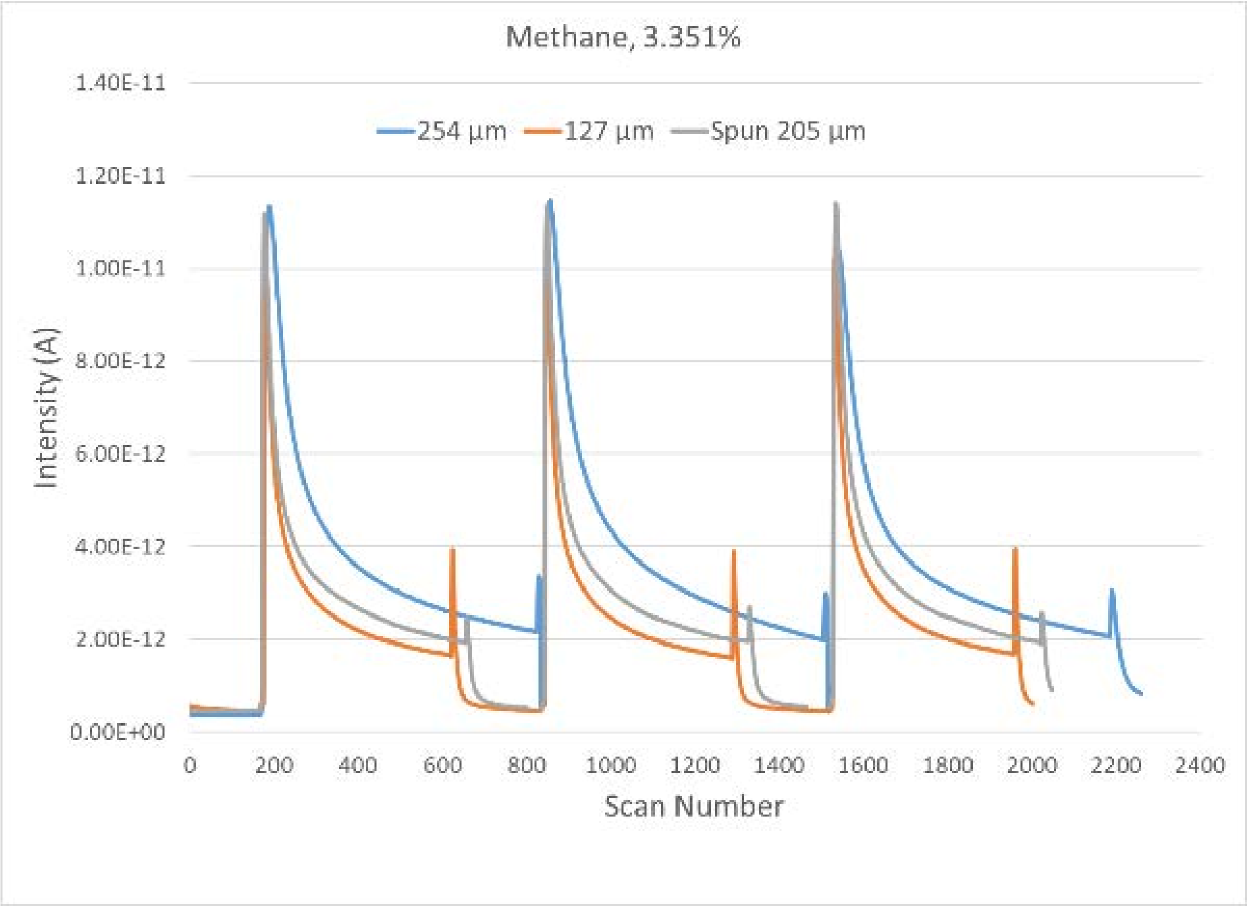


Spin speed of 673 RPM (2.5V), section F



MIMS Response Time vs. Membrane Thickness

- Three different thicknesses of PDMS membranes were tested:
  - 254-µm purchased
  - 127-µm purchased
  - 205-µm fabricated at SRI
- In all cases the response times (rise and decay) improved with decreasing thickness
- For most gases, the intensities (peak heights) were very similar



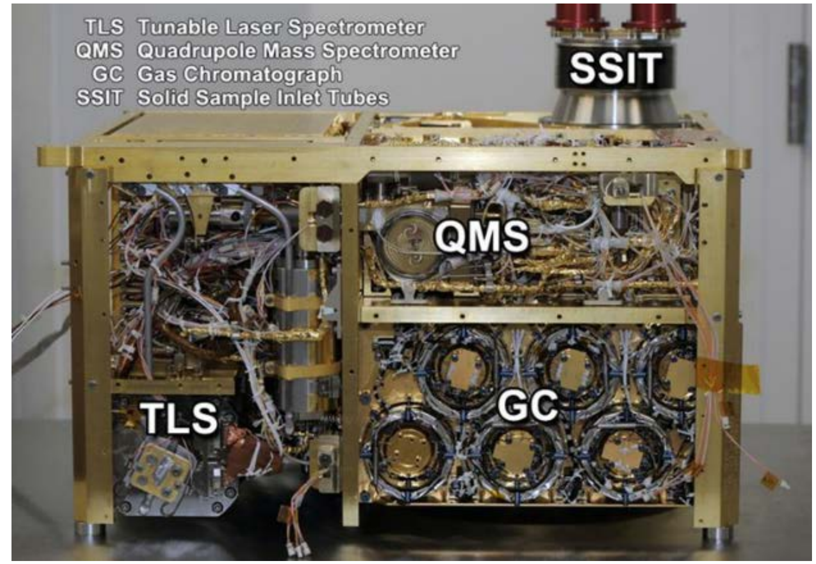
Limits of Detection (LODs) Determined for Static Probe

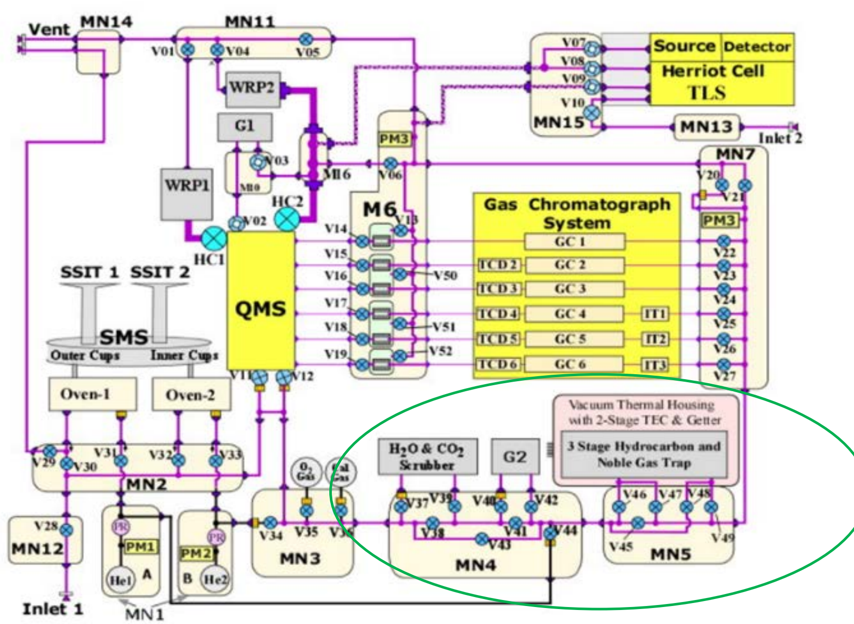
- LODs were determined for a suite of analytes
  - Atmospheric gases
  - Alkanes
  - VOCs
- Table shows results for the127-µm membrane
- LODs calculated by two methods
  - Sensitivity from calibrations and 3σ of background
  - Average from calculation for each concentration
- Oxygen LOD is high due to residual gas background

Analyte	Sensitivity (Int vs. Conc)	LOD (Slope)	LOD (Plot)
Oxygen	5.6E-12 (A/%)	620 ppm	620 ppm
Argon	1.1E-11 (A/%)	13 ppm	12 ppm
Carbon Dioxide	1.4E-10 (A/%)	1.2 ppm	1.0 ppm
Methane	2.9E-12 (A/%)	34 ppm	27 ppm
Ethane	2.4E-12 (A/%)	40 ppm	28 ppm
Propane	7.3E-13 (A/%)	160 ppm	130 ppm
Butane	3.9E-13 (A/%)	290 ppm	220 ppm
Benzene	2.9E-15 (A/ppb)	0.004 ppm	0.004 ppm
Toluene	1.3E-15 (A/ppb)	0.008 ppm	0.007 ppm
Xylene	N/A	N/A	0.038 ppm

MESA GPS is Based on Sample Analysis at Mars (SAM)

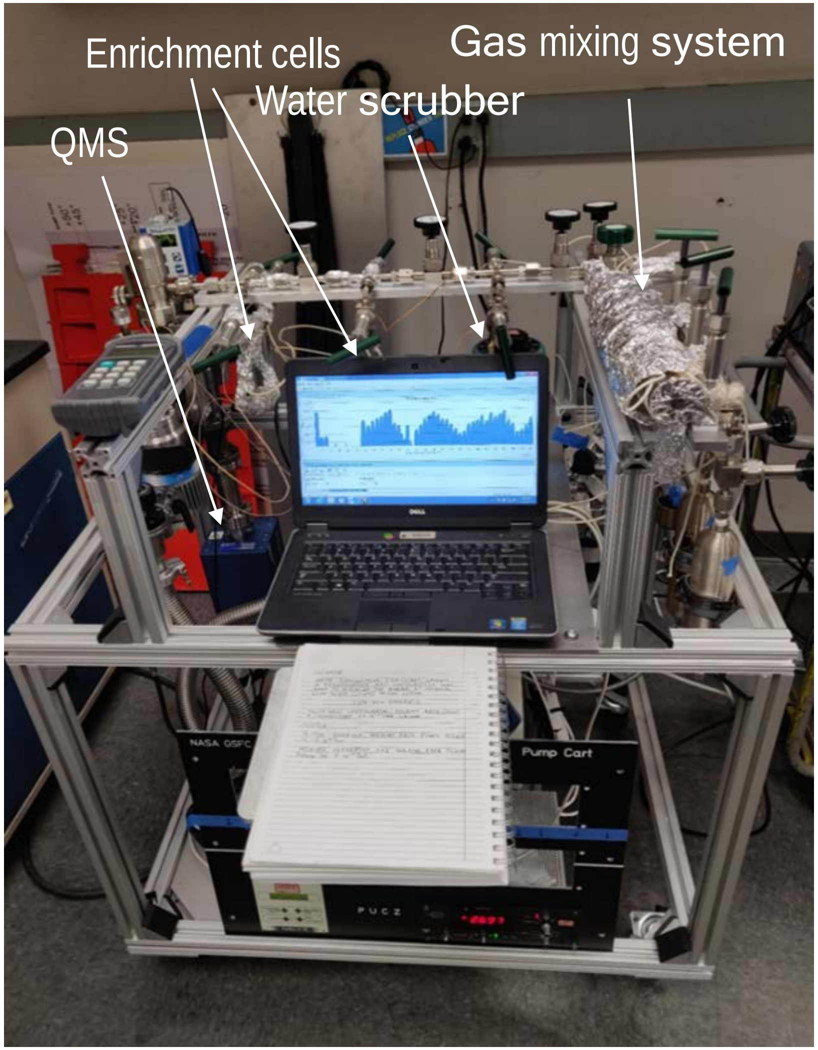
- SAM is currently operational on the Curiosity Rover on Mars
- SAM instruments include
  - Six gas chromatographs (GCs)
  - Quadrupole mass spectrometer (QMS)
  - Tunable laser spectrometer (TLS)
  - Solid sample inlet tubes (SSITs)
  - Gas processing system (GPS) – inside green ellipse on schematic
- SAM GPS includes
  - Water vapor and carbon dioxide scrubbers
  - Hydrocarbon and noble gas traps for concentration of analytes
- Concentrated analytes can be introduced into the GC, QMS, or TLS





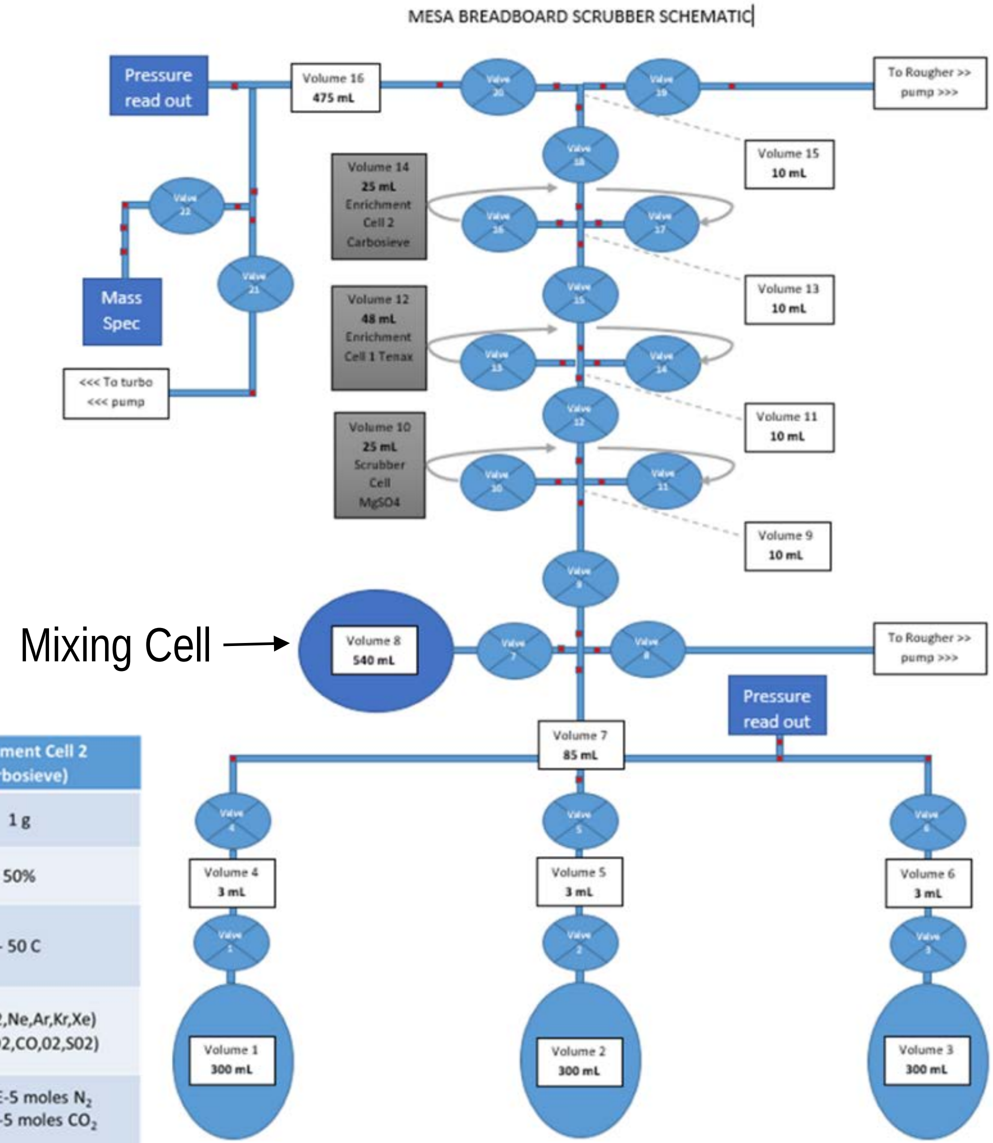
MESA Gas Processing System

- MESA breadboard GPS includes
  - Gas mixing system
  - One water scrubber cell ($MgSO_4$)
  - Two analyte enrichment cells (Tenax and Carbosieve)
  - Linear quadrupole mass spectrometer (QMS)
  - High-vacuum system for QMS and roughing pump for evacuating cells
- Scrubber and enrichment cells can be individually selected or bypassed
- Enrichment cells provide a sharp injection of concentrated analytes into MS to improve LODs



MESA Gas Processing System

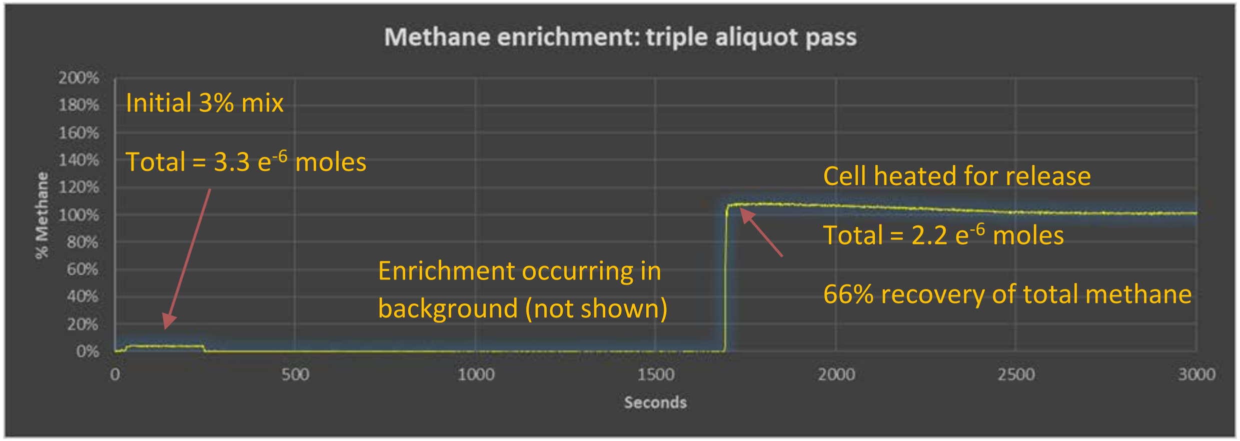
- Gas mixing system can be used to create mixtures of up to two analytes or water vapor
- Scrubber and enrichment cells are cooled during trapping and heated during release
- A needle valve is used to control gas flow to the QMS to maintain high vacuum levels

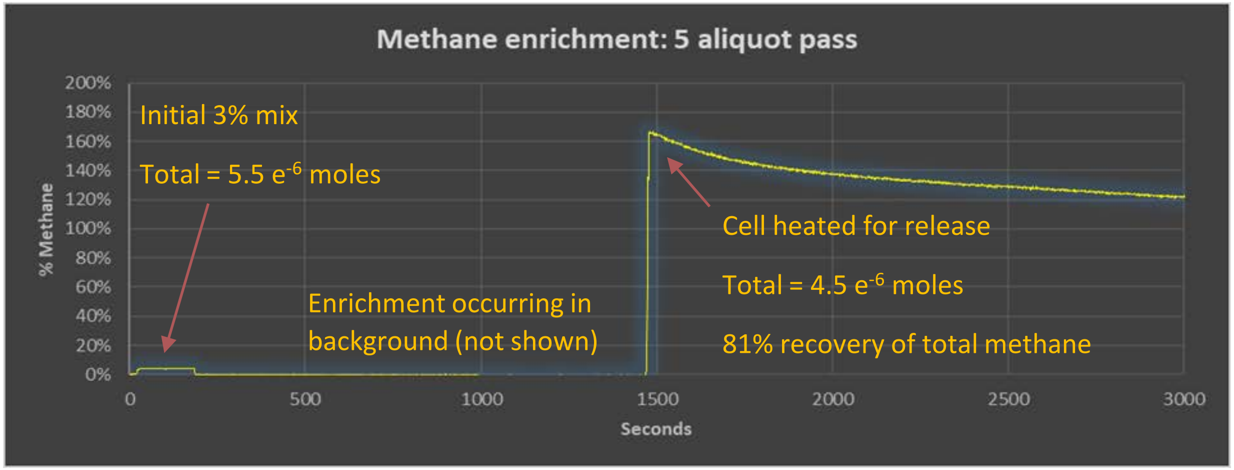


	Scrubber (MgSO4)	Enrichment Cell 1 (Tenax)	Enrichment Cell 2 (Carbosieve)
Cell Mass	1 g	1 g	1 g
Volume fill	25%	100%	50%
Optimal capture temperature	0 C	- 50 C	- 50 C
Optimal desorption temperature	350 C	150 C	<0C (N2,Ne,Ar,Kr,Xe) >0C (CO2,CO,02,S02)
Total capacity at operating pressure	0.05 grams H20	tbd	1.347 E-5 moles N_2 1.348 E-5 moles CO_2

Example Methane Concentration Experiments using GPS

- Aliquots of 3% methane in nitrogen were introduced into the GPS
- Initial MS measurements of the methane (m/z 15) signal intensity were made
- Carbosieve trap (cooled to -50°C) was exposed to each gas aliquot and adsorbed methane for 15 min
- Nitrogen was removed and carbosieve trap heated to 100°C and then opened to the MS

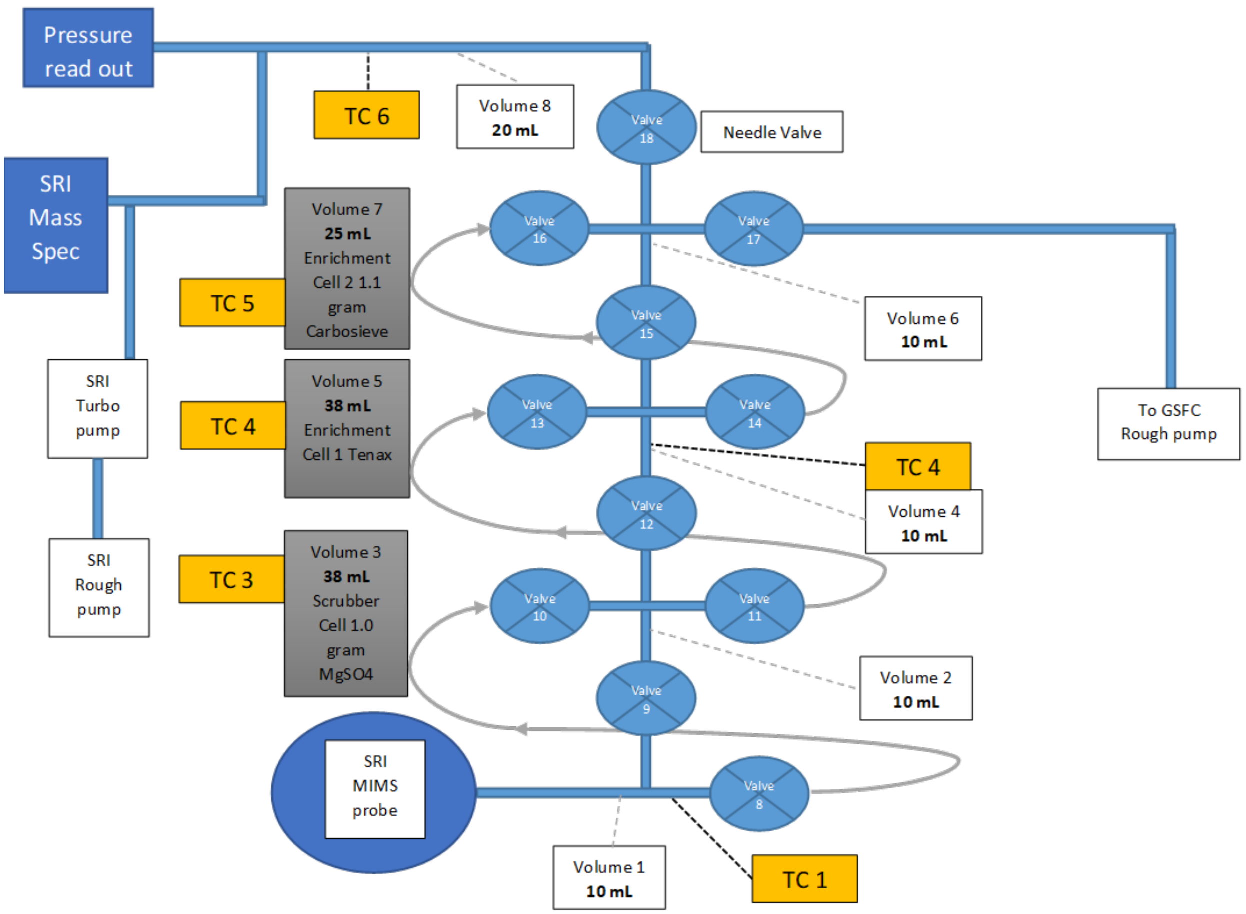




Improved enrichment demonstrated with exposure to increasing number of aliquots of methane-nitrogen mixture

MESA GPS Integrated with SRI MIMS (September 2019)

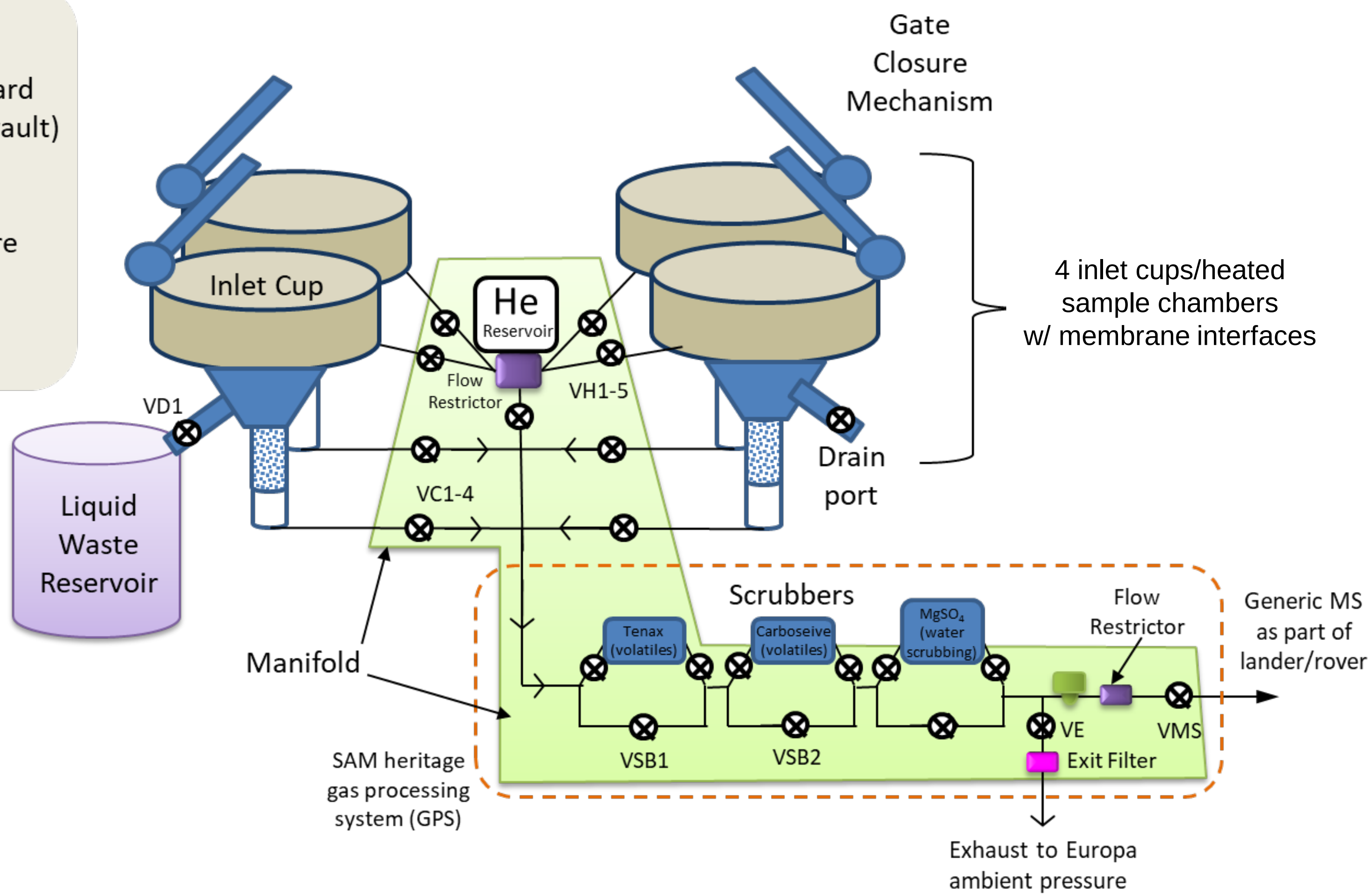
- GPS gas-mixing system will be replaced with static membrane probe
- MS and vacuum pumping system will be replaced with SRI MS system
- Experiments will be performed to concentrate a wider range of analytes of interest using different membranes
- Water scrubber will allow use of thinner membranes



Future Concept of MESA for Analysis of Ice Samples

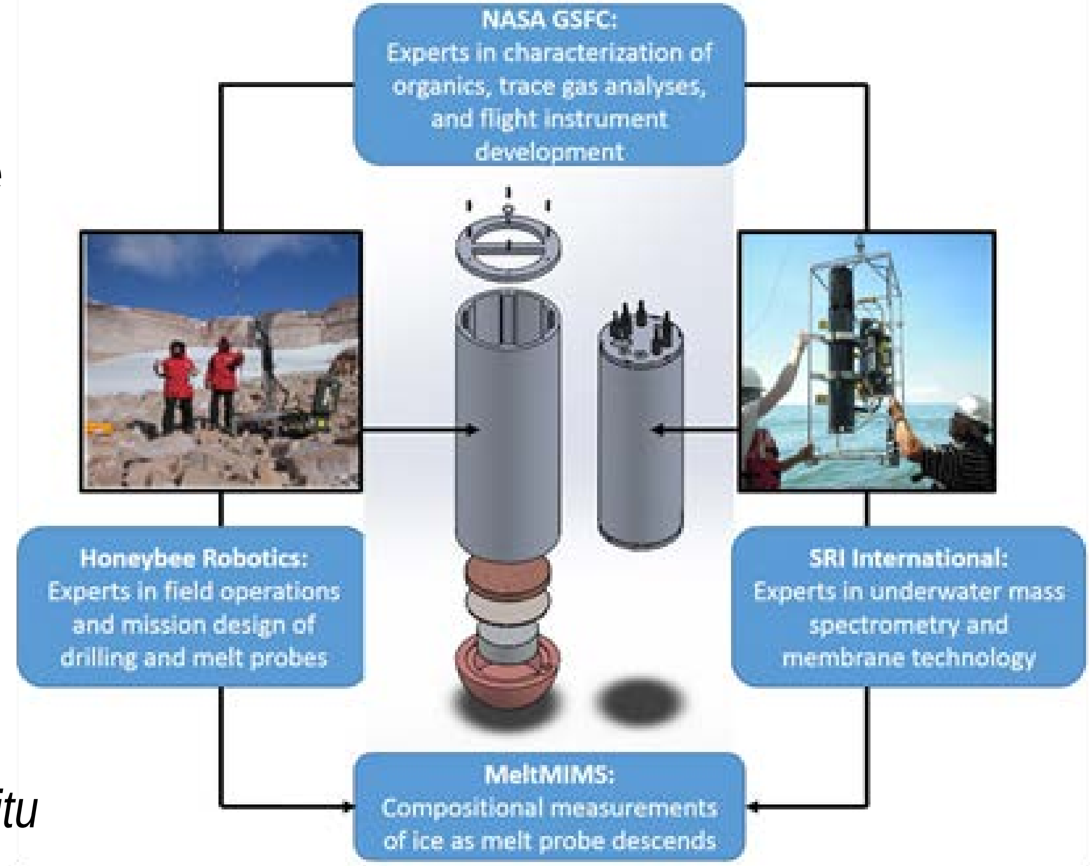
Other Hardware:

- Control Board (in lander vault)
- Pressure Sensors
- Temperature Sensors
- Heaters
- Harness



Concept developed for future lander mission to Europa

MeltMIMS: Melt Probe with a Membrane Inlet Mass Spectrometer for Ocean Worlds



Science:

- Identify volatile biomarkers and products of radiolysis to support life detection and explore habitability
- Develop MeltMIMS, an *in situ* system for extracting volatiles from icy planetary materials

Objectives:

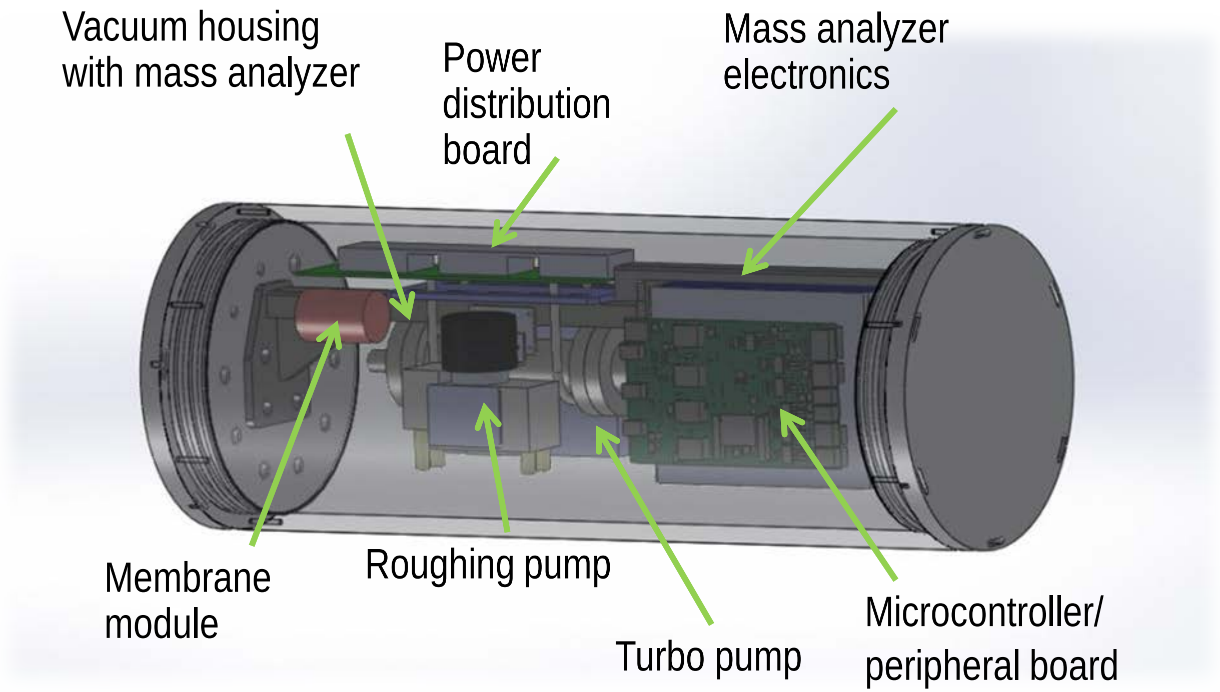
- Demonstrate the efficacy of MIMS for extremely cold environments
- Couple a ruggedized MIMS with a melt probe for proof of concept *in situ* analyses of target analytes in ice
- Create a breadboard instrument able to extract and analyze volatile species as a function of depth in ice

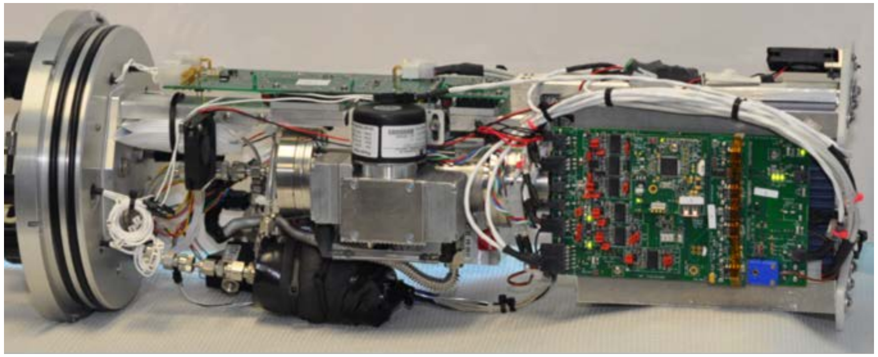
Targets: *Ocean worlds, icy moons: Mars, Europa and Enceladus (surface, subsurface)*

SRI's Underwater Membrane Inlet Mass Spectrometer

Specifications

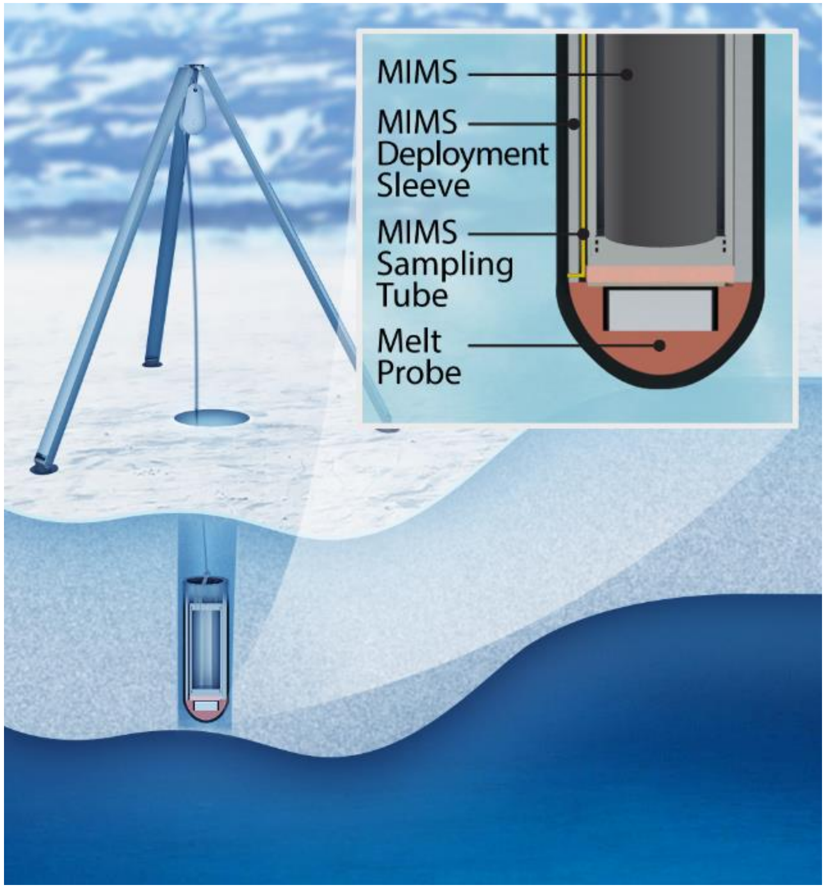
- Power: 60-80 W
- Voltage: 24 VDC
- Dimensions
  - Length: 64 cm
  - Diameter: 24 cm
- Weight
  - In air: 35 kg
  - In water: 5 kg neg.
- Depth rating: 2000 m

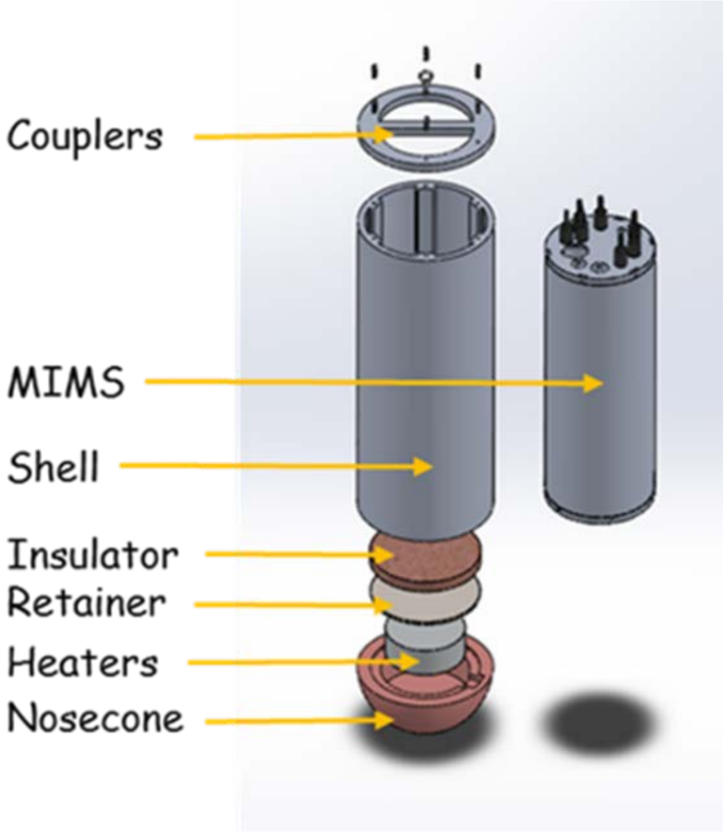




Underwater MIMS instrument without pressure housing

MeltMIMS: Underwater MIMS Instrument with Melt Probe

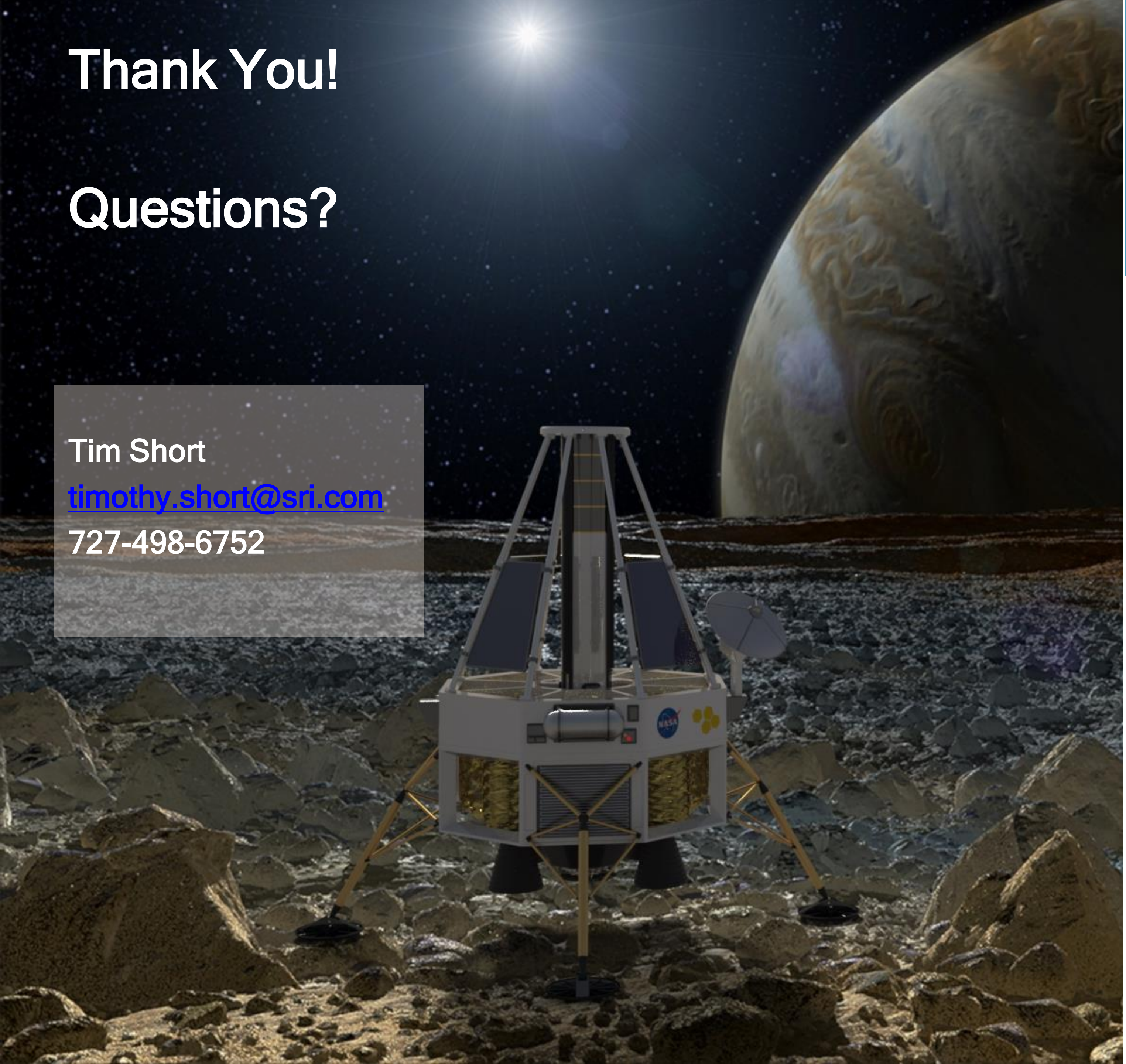




The MeltMIMS concept combines expertise and technologies from SRI, GSFC, and Honeybee Robotics to support in situ applications icy Ocean World missions

Acknowledgments

- The Membrane Extraction for Space Applications material is based on work supported by NASA under award 80NSSC17K0096 to SRI
- Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of NASA
- Mechanical engineering support for design of static membrane probe from Steve Untiedt at Cantel Technology Corporation (Parrish, FL)
- Machine shop support for fabrication of static membrane probe from JAG Machine and MFG (Pinellas Park, FL)
- GSFC Instrument Design Lab Team for development of future MESA Concept for Europa Lander mission



Thank You!

Questions?

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