Compact Quadrupole Ion Trap (QIT) Mass Spectrometers for Space Applications

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Development of Air Monitor for Human Space Explorations

- NASA instrument and JPL strategic funding for:
  - GC-QIT-MS for major constituent analyses (MCA) and trace gas analyses (TGA) for ISS cabin health monitoring
    - VCAM and S.A.M.
  - ESI-QIT-MS for exploring ocean worlds
- QIT-MS with applications driven by sample input
  - Significant reduction in mass, power, volume, and data rate over past decade
  - Focus on TRL enhancement for flight applications and transition to commercialization

Members of the Vehicle Cabin Atmosphere Monitor team, from left: Ara Chutjian, Dan Karmon, Jim Hofman, Benny Toomarian, Murray Darrach, John MacAskill, Stojan Madzunkov, Arvid Croonquist and Richard Kidd.

Vehicle Cabin Atmosphere Monitor (VCAM) ISS deployment in 2010

- Funded by NASA AEMC

MCA (Major Constituent Analysis) with 2 sec updates and fraction of a percent error (performance checkout underway)

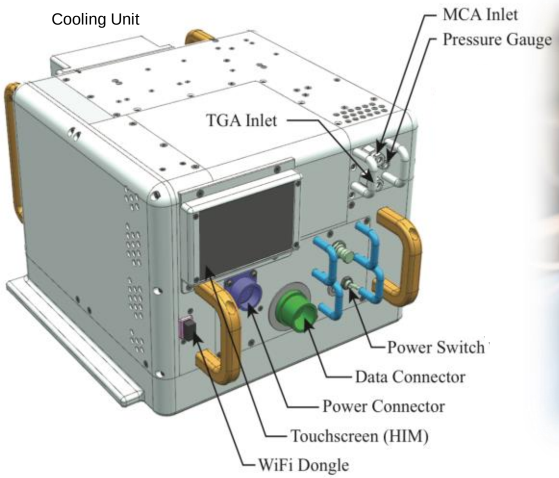
TGA (Trace Gas Analysis) with daily 20 minutes runs, down to 10-1000ppb Dynamic range TGA $3x10^4$

M. Darrach, S. Madzunkov, E. Diaz, B. Moore, R. Kidd, B. Bae, J. Simcic, S. Schowalter, R. Purcell, I. Cisneros, R. Schaefer, F. Cheung, K. Reichenbach, T. Loc, J. Lam, A. Oyake, D. Nikolic, R. Murdock

Spacecraft Atmosphere Monitor (S.A.M.) ISS power on in August 2019

- Funded by NASA AEMC & AES

Spacecraft Atmosphere Monitor (S.A.M.) Major Requirements



Technical Specifications	
Mass	9.55 kg
Dimensions	9.5” x 8.75” x 7.5”
Average Power	42 W (28 VDC, 1.5 A)
Startup Time	<2 min
Configuration	Rack-Mounted (EXPRESS), Aisle-Deployed
Communication	Wired or WiFi (aisle-deployed)
Compute Element	Xilinx Zynq FPGA (Red Pitaya)
Operating System	Linux

MCA Mode		
Report Cadence	2 s	
Data Integration Time	30 s	
Leak Description	1.5” x 2 μm ID microcapillary	
Leak Rate	5 x 10^{-8} Torr L/s	
QITMS Pressure	10^{-9} – 10^{-8} Torr	
Species	Measurement Range	Measurement Precision (for 30 s)
Nitrogen (N_2)	360 – 600 Torr (47-79%)	±0.60 Torr (±0.078%abs)
Oxygen (O_2)	130 – 160 Torr (17-21%)	±0.54 Torr (±0.071%abs)
Carbon Dioxide (CO_2)	3 – 7 Torr (0.4 – 1.0%)	±0.05 Torr (±0.007%abs)
Methane (CH_4)	0 – 7 Torr (0 – 1.0%)	±0.07 Torr (±0.009%abs)

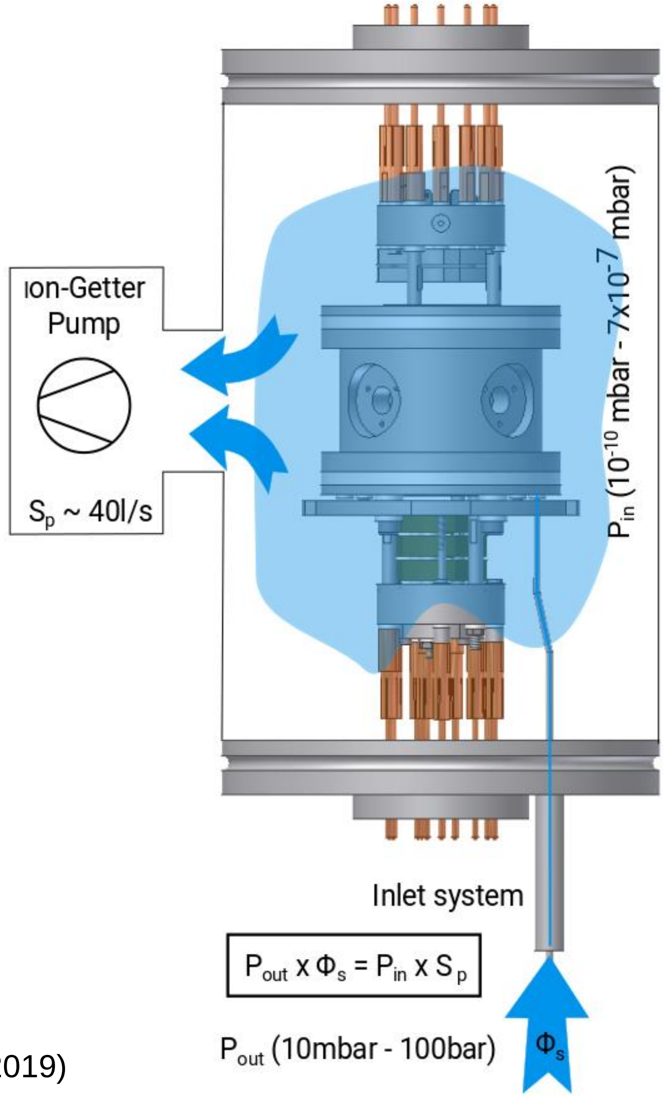
TGA Mode					
Frequency			1 per day (or on-demand)		
Run Time			10 – 20 minutes		
GC Carrier			H_2 (10 L metal hydride tank)		
GC Column			6 m x 86 μm ID microcolumn		
GC Flow rate			0.10 sccm H2		
PC Description			250 nL Carboxen 1000		
PC Heating			250 ºC for 5 s		
QITMS Pressure			10^{-6} – 10^{-5} Torr		
TGA Measurement Precision			40% relative		
Species	Low (PPM)*	High (PPM)*	Species	Low (PPM)*	High (PPM)*
Hexane	0.014	1.4	Dichloromethane	0.01	0.1
Propenal	0.004	0.04	Acetaldehyde	0.06	1.1
Ethanol	0.5	11	Perfluoropropane	13	130
2-Propanol	0.04	4	Methanol	0.1	4
1-Butanol	0.02	0.7	Octamethylcyclotetrasiloxane	0.02	0.2
Acetone	0.04	1.3	Hexamethylcyclotrisiloxane	0.02	0.2
Benzene	0.01	0.2	Decamethylcyclopentasiloxane	0.01	0.1
Toluene	0.03	0.3	Propylene glycol	TBD	TBD
o,m,p-Xylene	0.02	0.2	Trimethylsilanol	0.05	1

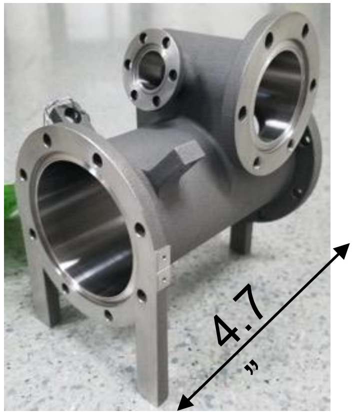
S.A.M. Status

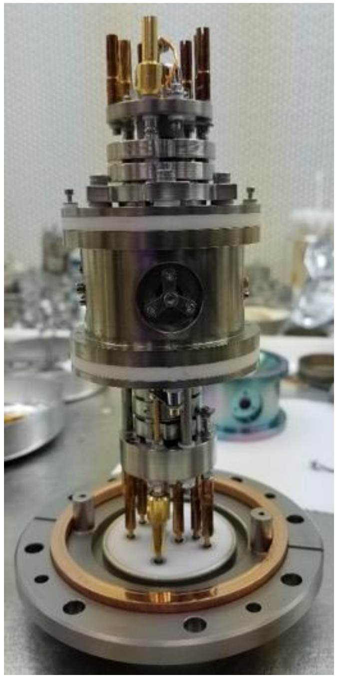
- TDU#1 in operation on ISS since Sep. 2019
- TDU#2 in development for planned delivery by the end of 2020 (depending on COVID19)

Main Component of QIT-MS

- QIT-MS base pressure high 10^{-11} torr
- **Operates without He buffer gas**
- Different modes of operation (dynamic, static, resonant ejection)
- S.A.M operating pressure starting at $1x10^{-5}$ (collision of N_2) but nominal $5x10^{-9}$ torr
- S.A.M. operating sensitivity $5x10^{12}$ cnts /torr/sec (dynamic)
- Inlet = fussed silica tube (single)
- Allows for MCA every 2 sec





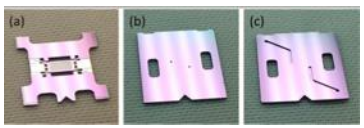


Notes
QIT-MS = Quadrupole Ion Trap Mass Spectrometer
S.A.M. = Spacecraft Atmosphere Monitor (launch 2019)

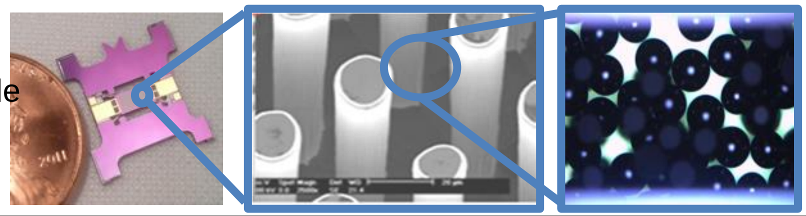
MEMS Gas Chromatography Components

For S.A.M. we developed a variety of chip-based gas chromatography components that can be mixed and matched to give complete systems (or coupled to mass spectrometers) for a variety of planetary and human applications

Pre-Concentrator (PC)

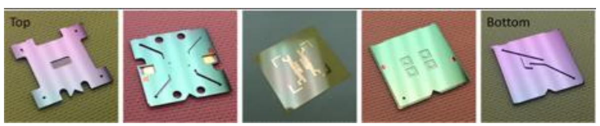


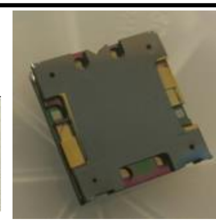
Heater/carboxen/inlet-outlet layers

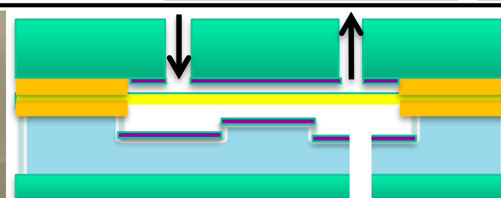


- Carboxen 1000
- ~200 µm particles
- ~10 Å pore diam.

Micro-Valve (MV)

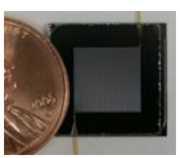


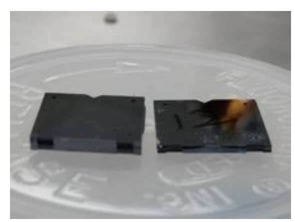




- Four microvalves are integrated in a chip: Sample, Vent, Carrier, and Injection.
- All the valves are electrostatic.

Gas Chromatograph (GC)





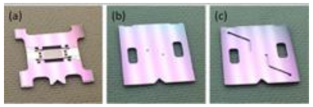
- 1 m length x 86 µm diameter chip dynamically coated.
- Serpentine column is superior to spiral design.
- A novel turn geometry to counteracts the dean vortices producing lower dispersion.
- Chips can be stacked to increase column length.

Other frontend developments in progress to support analyses of water and other liquids, aerosols, and capturing molecules under hypervelocity (˜10km/sec)

Miniaturization of trace gas analyzer inlet system by micromachining

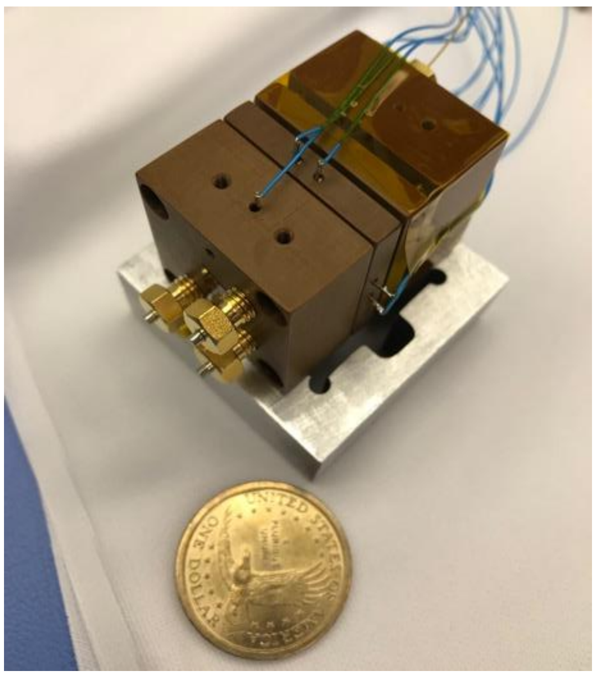
S.A.M. Spacecraft Atmosphere Monitor

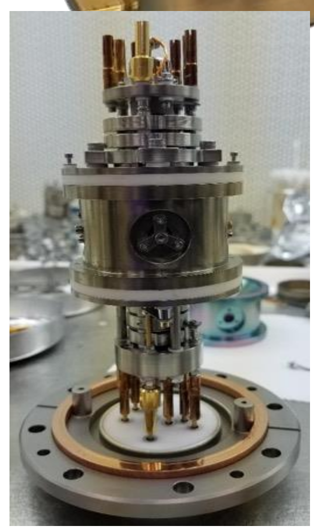
PC layer

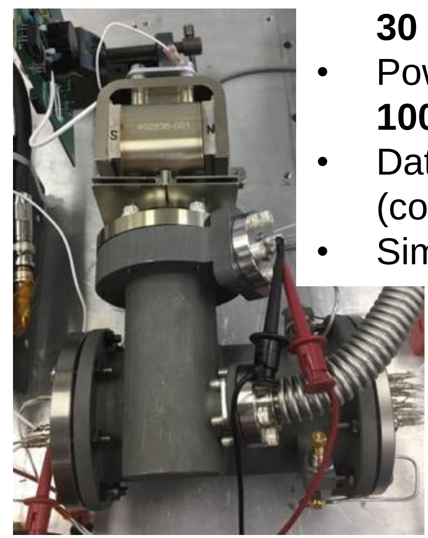


Valve layer

GC column



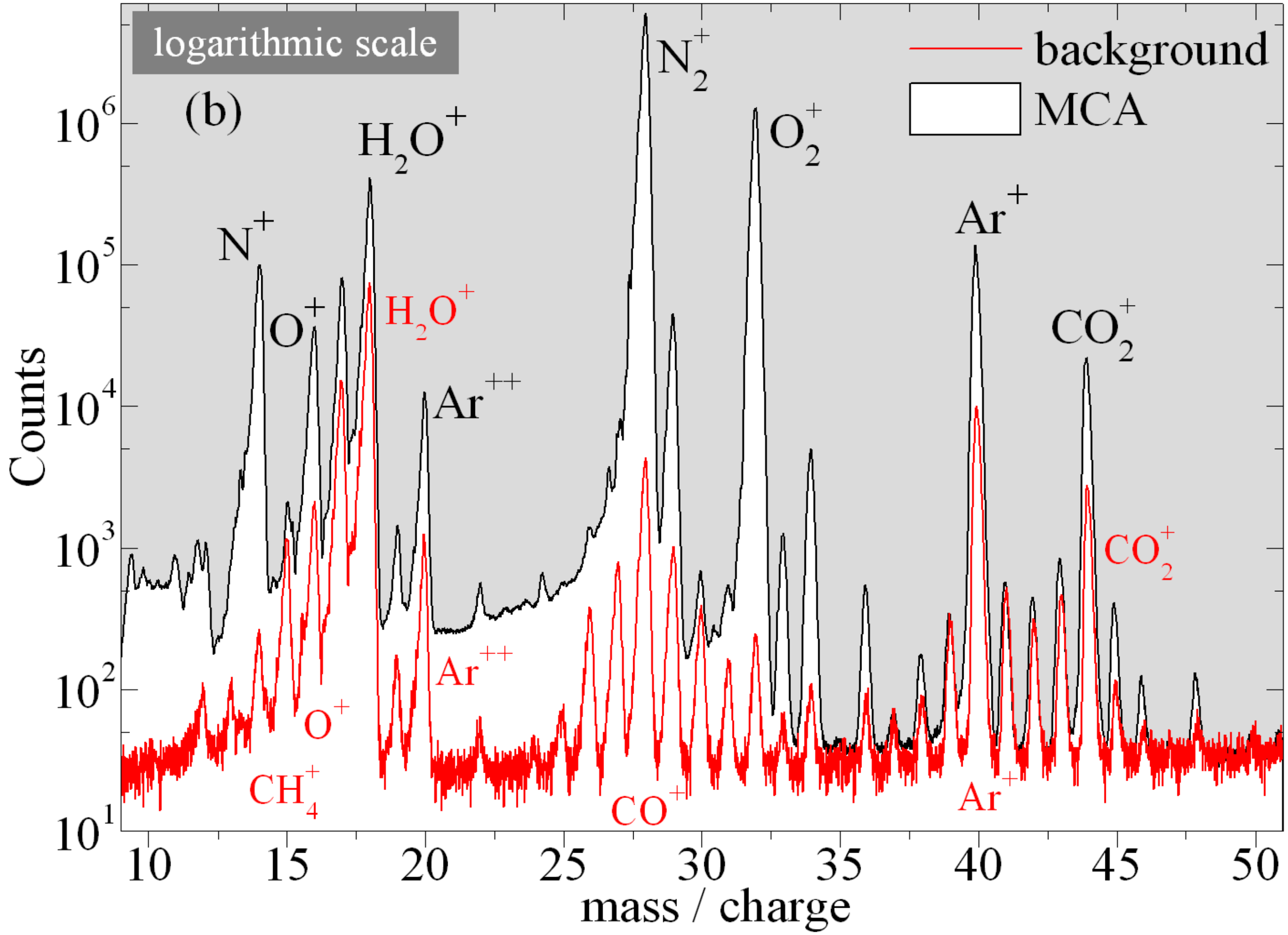




Flight:

- Mass: (2011, VCAM) **30 kg,** (2019) **7 kg**
- Power (2011, VCAM) **100 W,** (2019) **30 W**
- Data rate 3.2 kbits (compressed)
- Simple operation

S.A.M. TDU#1 MCA with underlying background (inlet closed)



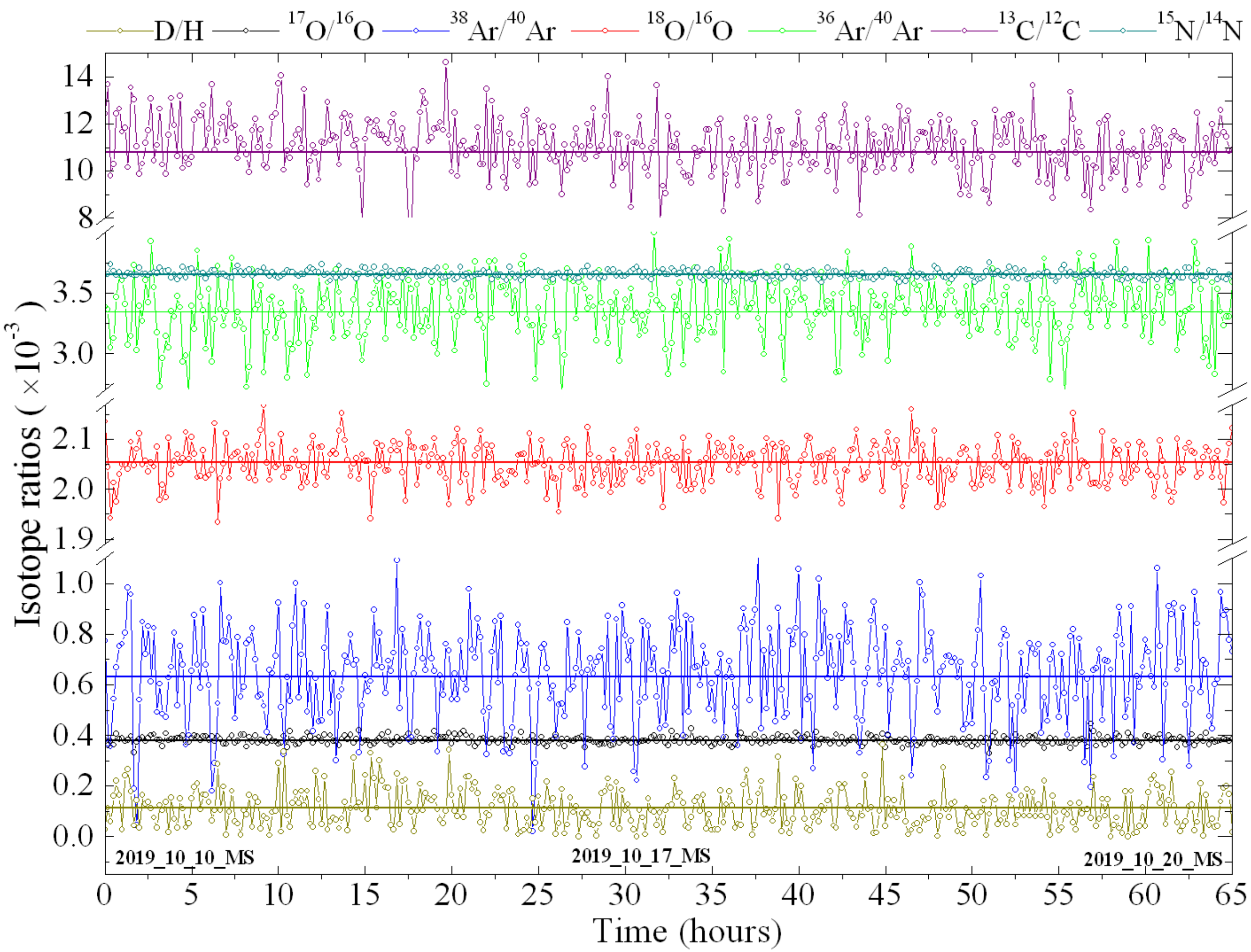
September 13, 2019

- **Earth's magnetic field observed with TDU#1**
- **TDU#2 will have magnetic shielding**
- **No impact on MCA measurements**

To be published, S. M. Madzunkov, D. Nikolić, A. Belousov, and M. R. Darrach, "Data Analysis and Isotopic Ratios Measured Onboard the Spacecraft Atmosphere Monitor," 50th International Conference on Environmental Systems ICES-2020-527, 12-16 July 2020, Lisbon, Portugal

Meeting measurement requirements despite sensitivity to Earth's magnetic field

Isotopic long term stability of S.A.M. data (adjusted to Earth reference values)



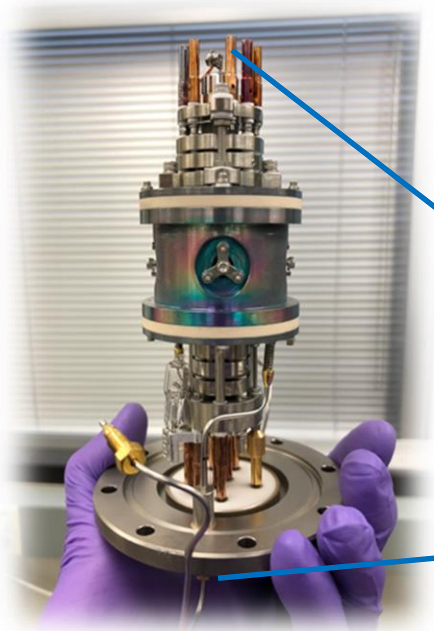
Results are comparable to magnetic-sector isotope-ratio mass spectrometers

To be published:
S. M. Madzunkov, D. Nikolić, A. Belousov, and M. R. Darrach, "Data Analysis and Isotopic Ratios Measured Onboard the Spacecraft Atmosphere Monitor," 50th International Conference on Environmental Systems ICES-2020-527 12-16 July 2020, Lisbon, Portugal

High stability of QIT-MS

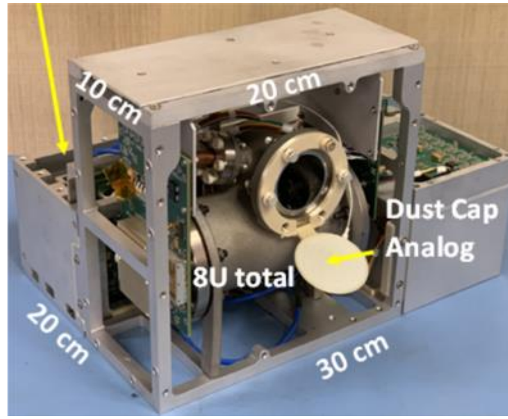
Lunar Effort

Compact QIT-Mass Spectrometer for Lunar and Planetary Applications

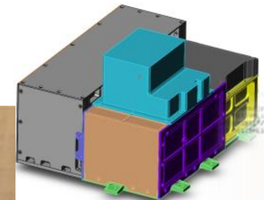


Sensor

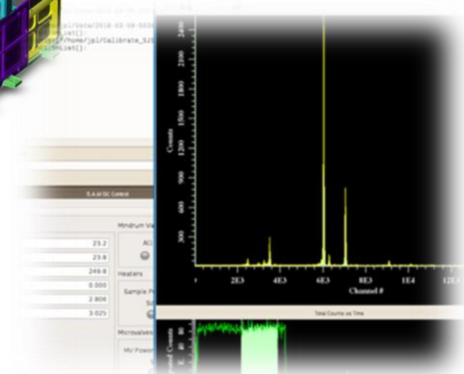
J. Simcic, et al. *Miniature Gas Chromatograph Mass Spectrometer (GCMS) For Planetary Atmospheres In Situ Studies*, 3rd International Workshop on Instrumentation for Planetary Missions, 2016



Prototype QIT-MS

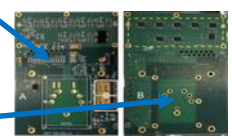


DALI package
(fab started)



Integrated Software

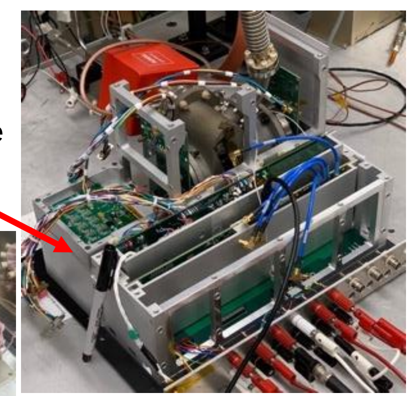
D. Nikolić, et al., *Mass Spectra Deconvolution of Gaseous Mixtures Containing Volatile Organic Compounds*, 48th International Conference on Environmental Systems, article 313, 6 pages (2018).



Cap electronics

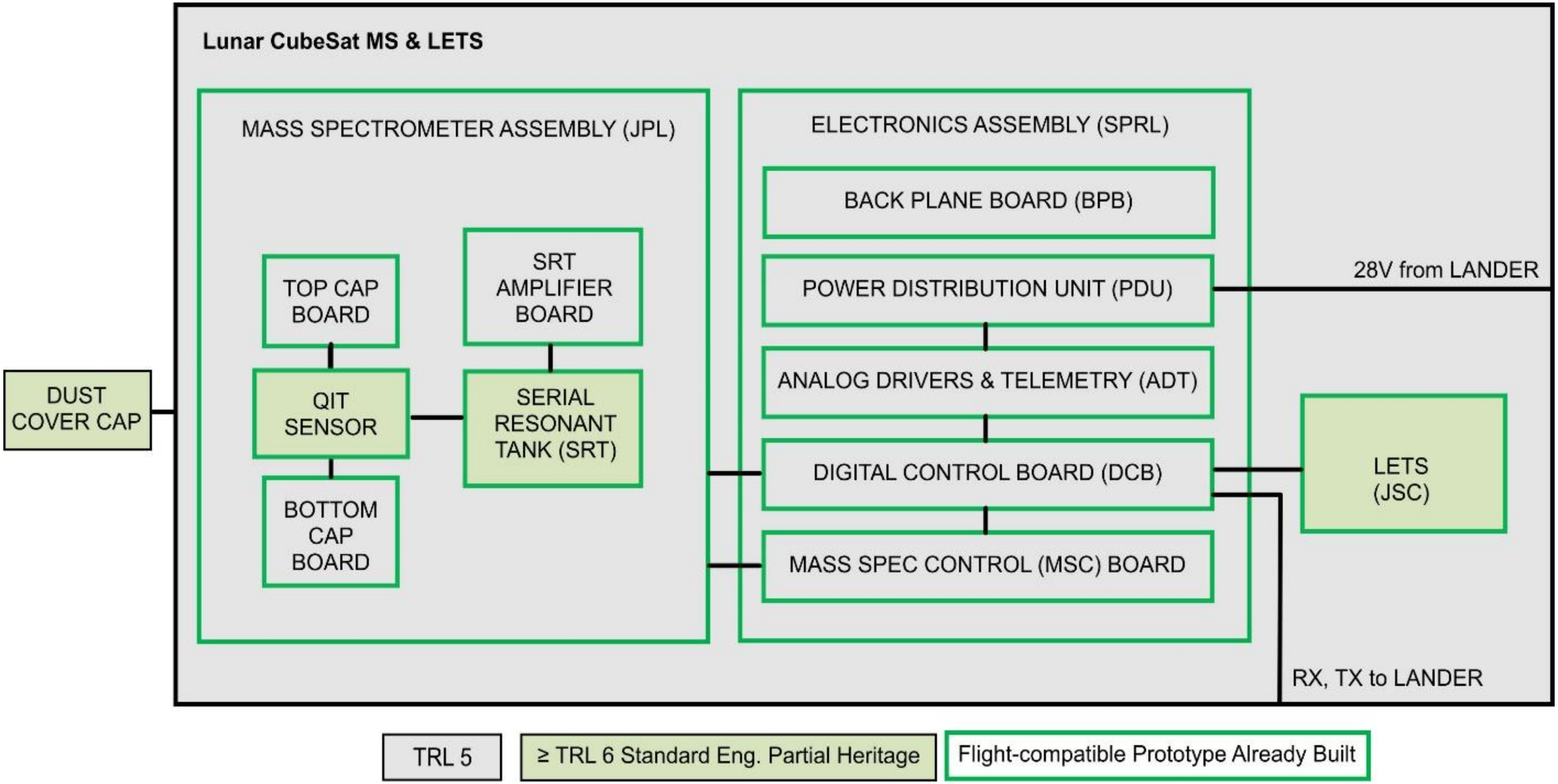
Power and CPU Electronics

High Q
diamond weave
Litz wire coil



Mechanical Integration

Readiness for Flight Implementation

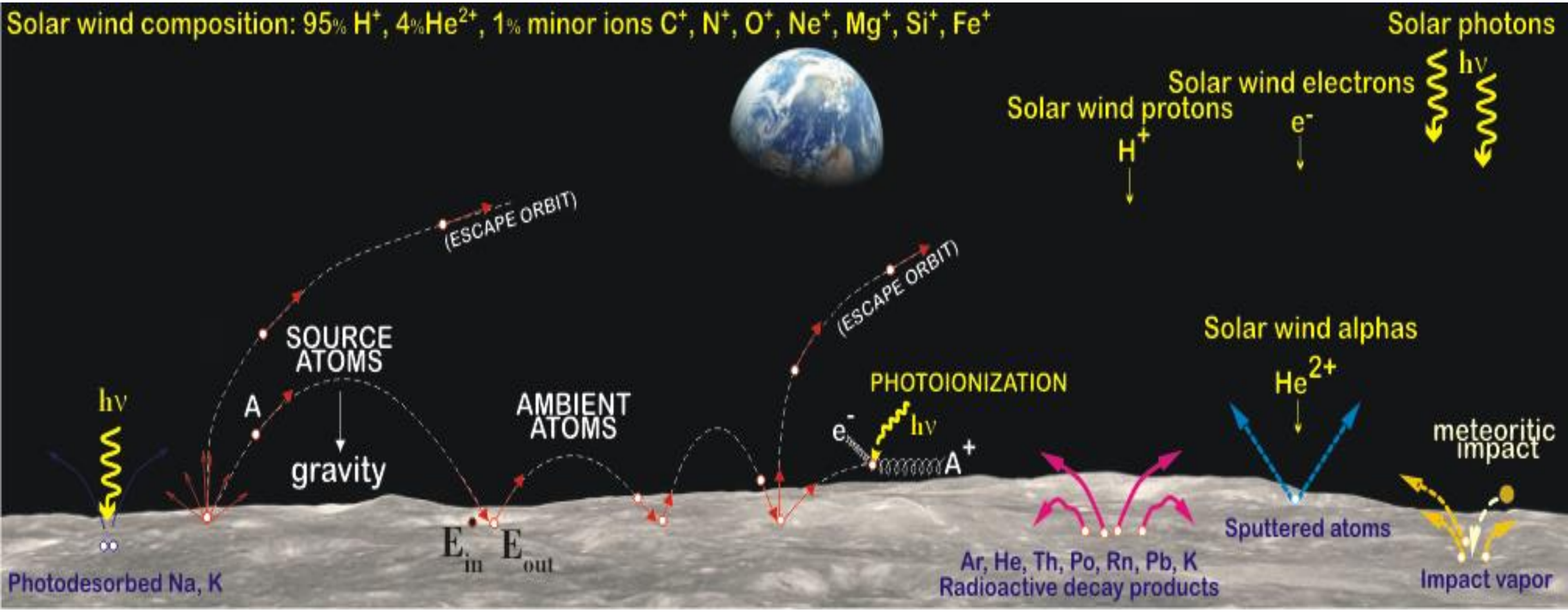


Development over past years allowed to increase the TRL level of all components to 5 with design implementations to support TRL 6.

Lunar Exospheric Composition

- Observation of time variability of multi-day lunar surface exospheric and radiation changes
- Identifying and quantifying exosphere species with abundances ≥ 10 molecules/cm^3
  - e.g. low abundance of CO and N2; not measured before e.g. Kr, Xe
- Primary mechanism for creation of lunar exosphere are:
  - Solar wind activities with next expected maximum in 2026+/-2 years
  - Radioactive decay
  - Meteorite impact

D. Nikolić and M. Darrach, *LADEEVIEW: Elemental Composition Analysis of Lunar Surface*, 3rd International Workshop on Instrumentation for Planetary Missions, October 24–27, 2016, Pasadena, CA; article 4014, 2pp (2016).



Requirements modeled/demonstrated in the Laboratory

Driving Measurement Requirement	Lunar Surface Observable	Instrument Performance Requirement		Projected Performance	Margin	
Determine which volatile species are present at the lunar surface at abundances ≥10 cm^{-3}	H, H_2, ^3He, ^4He, Ne, **N_2,** O_2, **Ar**, CH_4, **CO**, CO_2, **Kr**, **Xe**, OH, H_2O	Mass Range (Da)	1-140	0.75-230	65%	To reach Xe isotopes
		Mass Resolution (m/Δm FWHM)	200	1000	400%	
		Sensitivity (molecules/cm^3/sec)	0.001	0.0005	100%	
		Target species partial pressure (Torr), 2:1 SNR	$\leq 1\times10^{-14}$	$\leq 1.3\times10^{-15}$	700%	Low pressure

Sources used in compiling the required LUNAR targets are:

1) 2013-2022 Planetary Decadal Survey, Visions & Voyages, p. 118, critical science goal for the moon and other inner solar system bodies: "Understand the Composition and Distribution of Volatile Chemical Compounds…"
https://www.nap.edu/login.php?record_id=13117&page=https%3A%2F%2Fwww.nap.edu%2Fdownload%2F13117

2) 2007 NRC Report: Scientific Context for Exploration of the Moon
https://www.nap.edu/login.php?record_id=11954&page=https%3A%2F%2Fwww.nap.edu%2Fdownload%2F11954
8a. Determine the global density, composition, and time variability of the fragile lunar atmosphere before it is perturbed by further human activity.
8c. Use the time-variable release rate of atmospheric species such as 40Ar and radon to learn more about the inner workings of the lunar interior.
8d. How water vapor and other volatiles are released from the lunar surface and migrate to the poles where they are adsorbed in polar cold trap.

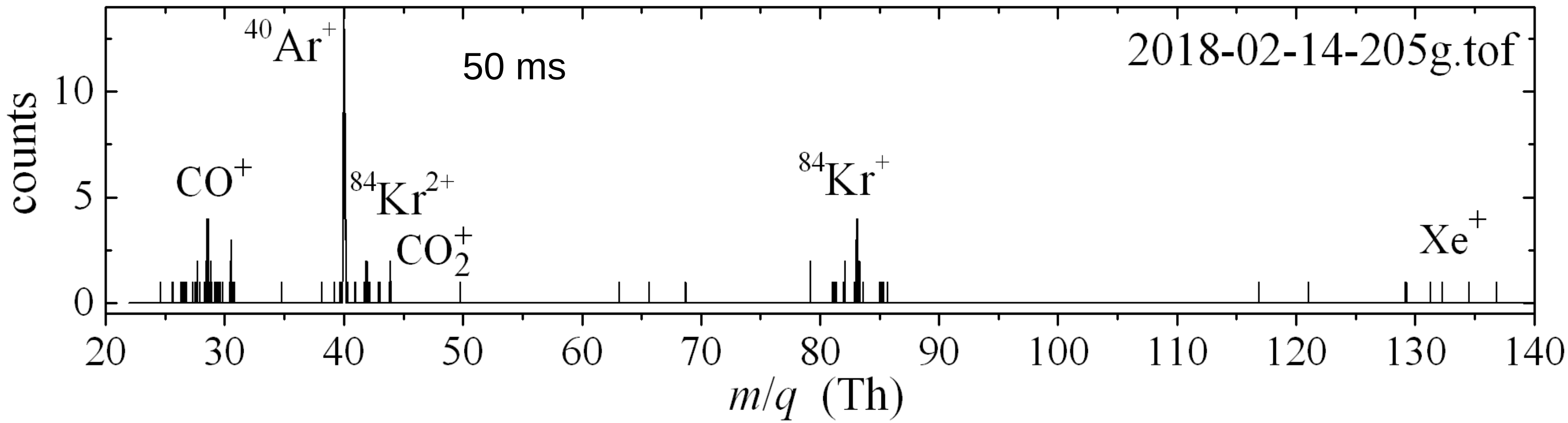
3) LEAG Specific Action Team Report, Goal 8a: "Systematically detect trace volatile species, like water, OH, and hydrocarbon in the exosphere."

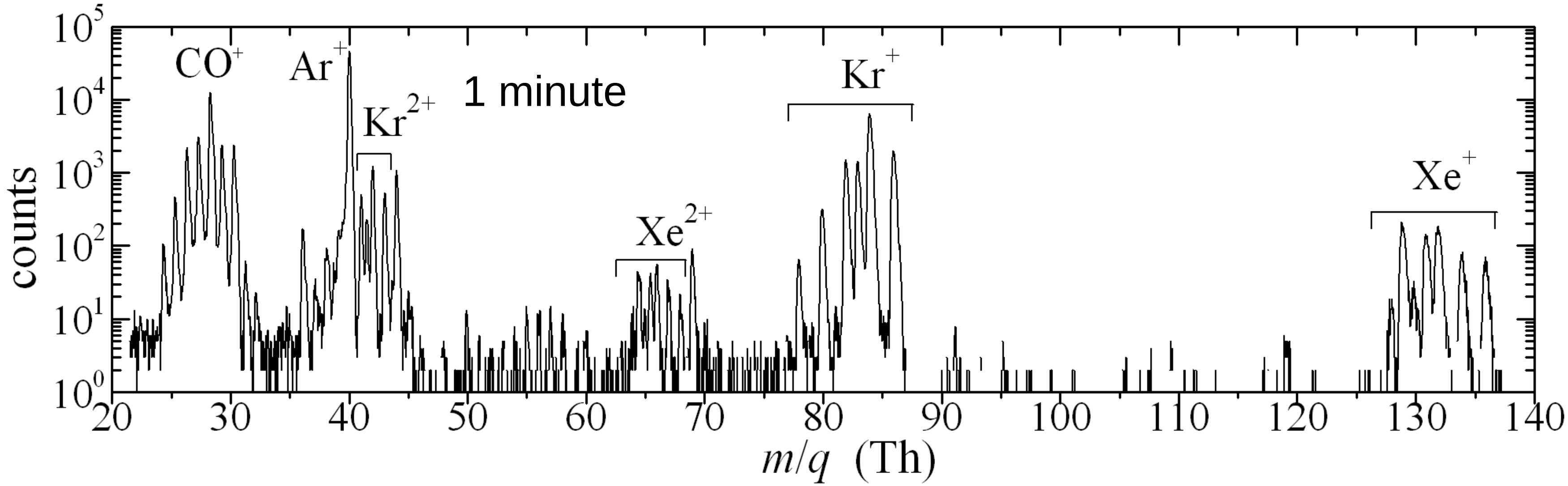
4) LEAG Specific Action Team Report, Goal 8b: "Detect volatile transport from mid- to high-latitudes as a function of driving space environmental (solar storm, meteor stream) conditions."
https://www.lpi.usra.edu/leag/reports/vsat_report_123114x.pdf

5) HEOMD / Lunar Human Exploration Strategic Knowledge Gap (SKG) Special Action Team Report, September 2016: I-C, Regolith Volatiles, in situ. "Quality/ quantity/ distribution/ form of H species and other volatiles in nonpolar mare/highlands regolith."
https://www.nasa.gov/sites/default/files/atoms/files/leag-gap-review-sat-2016.pdf

Noble Gas Mass Spectrum

Isotope spectra of an aliquot of calibrating gas (1.7E-10 Torr of Kr and 1.3E-11 Torr of Xe) measured continuously **for 7 hours yielded a 0.6 ‰ precision on the 86Kr/84Kr ratio**

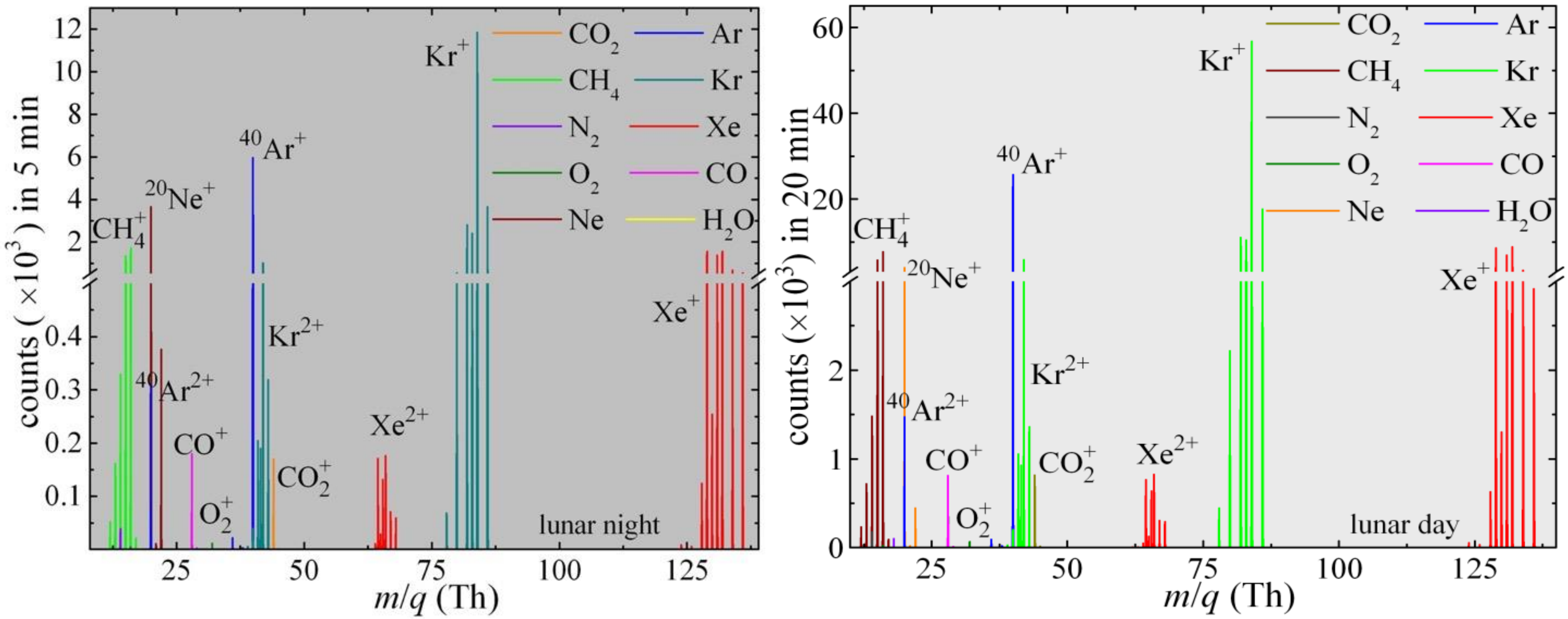




*G. Avice, A. Belousov, K. A. Farley, S. M. Madzunkov, J. Simcic, D. Nikolic, M. R. Darrach and C. Sotin, "High-precision measurements of krypton and xenon isotopes with a new static-mode quadrupole ion trap mass spectrometer," JAAS, Vol 34, January 2019

Predicted QIT-MS Response at Lunar Surface (diurnal)

Simulation results with JPL lunar model (based on previously published in peer reviewed journals)



D. Nikolić and M. Darrach, *LADEEVIEW: Elemental Composition Analysis of Lunar Surface*, 3rd International Workshop on Instrumentation for Planetary Missions, October 24–27, 2016, Pasadena, CA; article 4014, 2pp (2016).

Approx. 30% higher counts during sun exposure (lunar day)

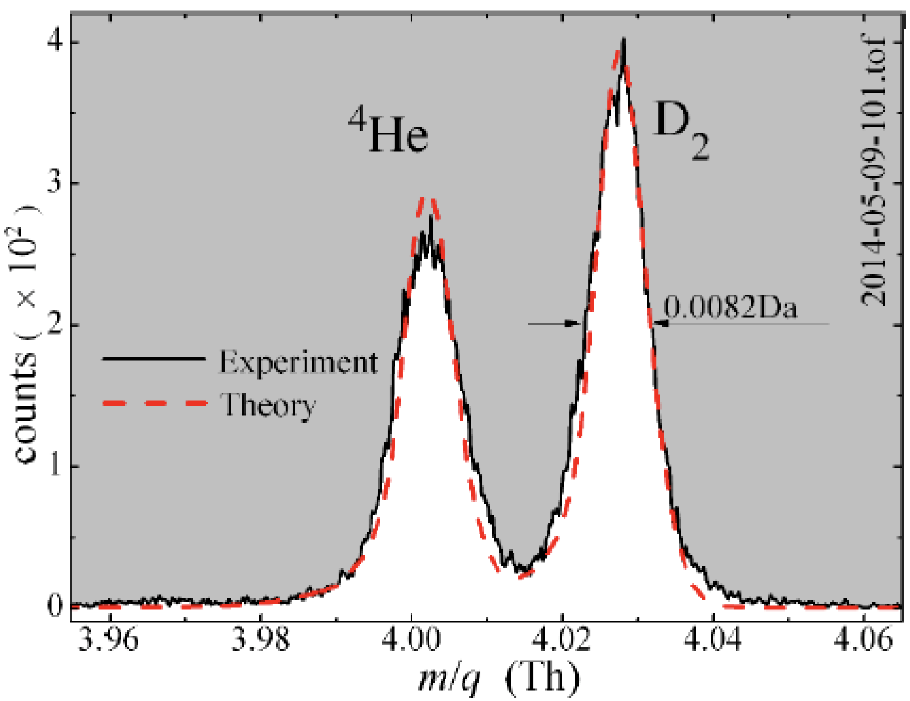
Lunar exosphere model based on past measurements with LADEE is detectable with QIT-MS.

Modelled and Measured High Resolution Mode

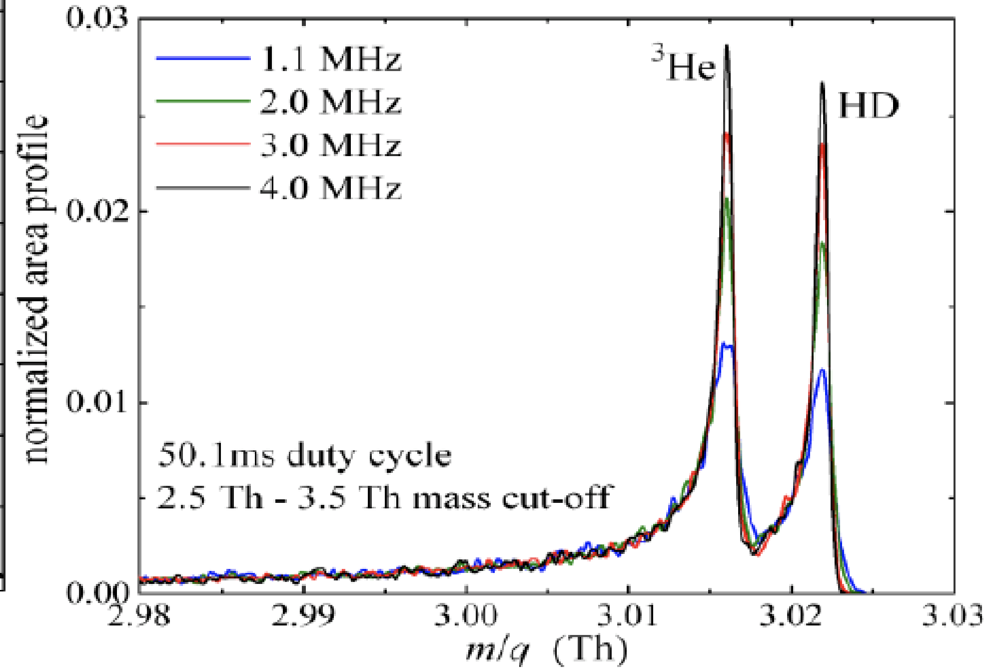
Measured and Modeled QITMS Mass Spectra

(Left) Measured QITMS spectra for 4He and D2 (dotted line) with a modeled 4He and D2 spectra.

(Right) Modeled spectra for 3He and HD, at identical abundances, for various RF frequencies. The equal 3He and HD abundances are based on the published isotopic ratios in the lunar regolith [Wiens (2003)] and the expected AtLAS H2 instrument off-gassing after < 1 day of lunar surface bakeout.



Amplitude optimization by tuning RF frequency



Nikolic, D., Madzunkov, S.M., Darrach, M.R., "Computer Modeling of an Ion Trap Mass Analyzer, Part I: Low Pressure Regime", J. Am. Soc. Mass Spec., 26, 2115-2124 (2015)

Well validated QIT-MS model.

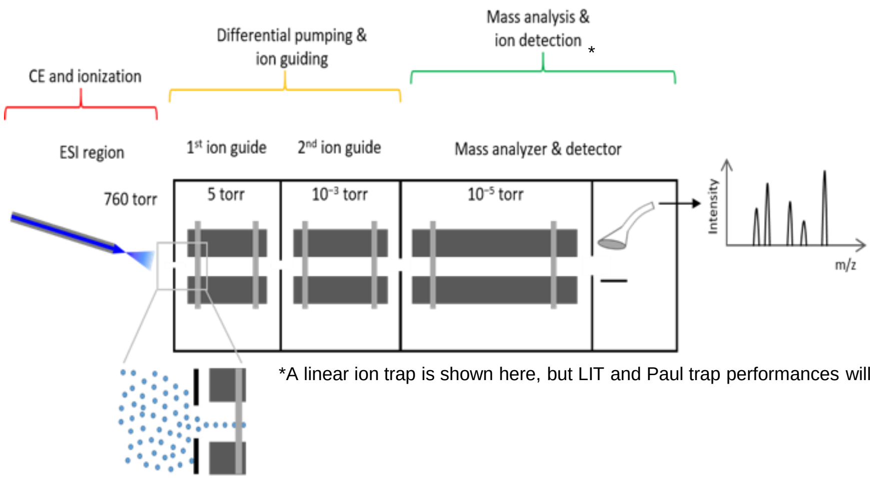
OCEAN World, QIT-Ms coupled with Electrospray liquid input system

Ocean Worlds Life Surveyor (OWLS)

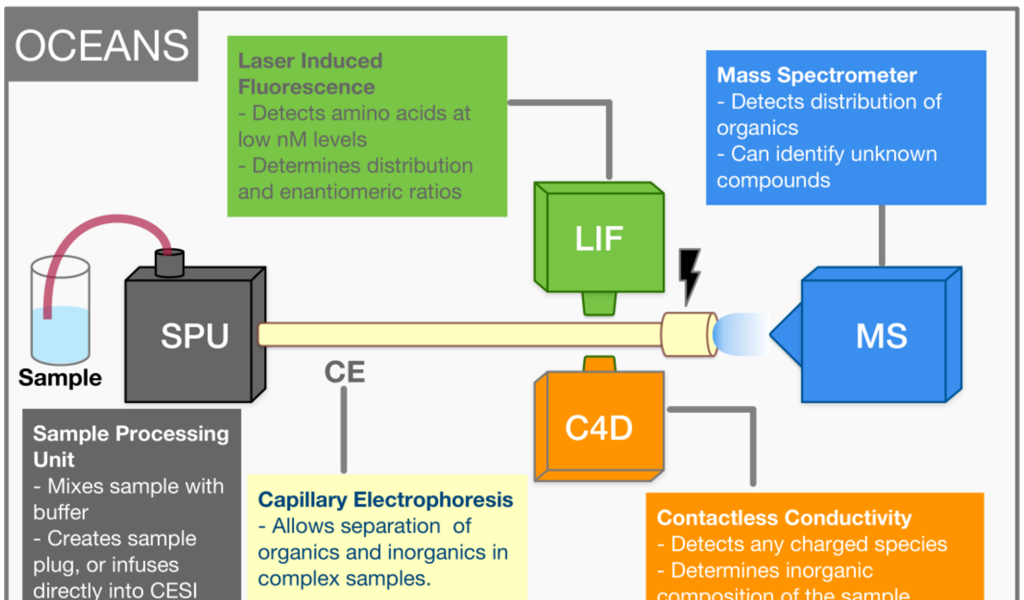
QIT-MS application in the quest of architecting the most capable organic chemical analyzer

- The Ocean Worlds Life Surveyor (OWLS) is funded under the JPL NEXT Program initiated in 2018.
  - Goal to build and field test (Borup Bjord Pass in the Canadian High Arctic) prototypes in preparation to select instruments for possible missions to Enceladus, or Europa
- Mass Spectrometer is part of Organic Capillary Electrophoresis Analysis System (OCEANS)
  - **E**lectro**s**pray **I**onization coupled to Mass Spectrometry (ESI-QIT-MS) for broad-based detection and characterization of collections of organic molecules.
- Life detection hinges upon identifying certain organic molecules
  - Amino acids are the building block of proteins and their distribution provide distinct biosignatures.
- Prototype of ESI system is ready for testing with laboratory setup and MS in near future
- https://microdevices.jpl.nasa.gov/capabilities/in-situ-instruments-chemical-analysis/owls-project/

Ocean Worlds Life Surveyor –OCEANS CE-ESI-MS



*A linear ion trap is shown here, but LIT and Paul trap performances will be compared



To be published by Peter Willis

The goal of OCEANS (Organic Capillary Electrophoresis Analysis System) is to design, build, and demonstrate an in situ chemical analyzer that can detect and characterize organic compounds.

The OCEAN Worlds Life Surveyor (OWLS) is funded under the JPL NEXT Program.

Goal to build and field test (Borup Bjord Pass in the Canadian High Arctic) prototypes in preparation to select instruments for possible missions to Enceladus, or Europa

Mass Spectrometer is part of Organic Capillary Electrophoresis Analysis System (OCEANS)

Electro**s**pray **I**onization coupled to Mass Spectrometry (ESI-QIT-MS) for broad-based detection and characterization of collections of organic molecules.

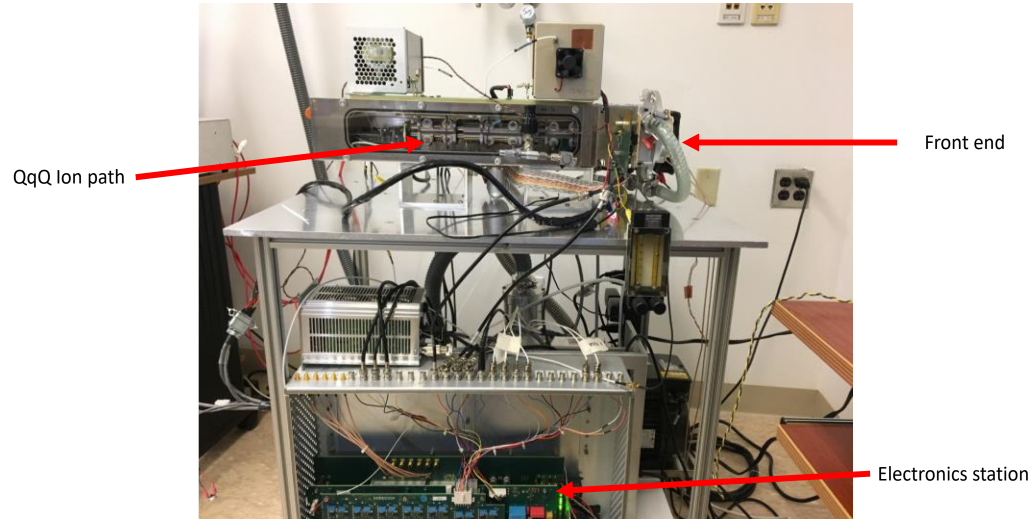
Capillary Electrophoresis (CE) will be coupled to ESI-QIT-MS. It allows to analyze organics at ppb levels, with 2% accuracy for relative amino acid abundances.

Life detection hinges upon identifying certain organic molecules

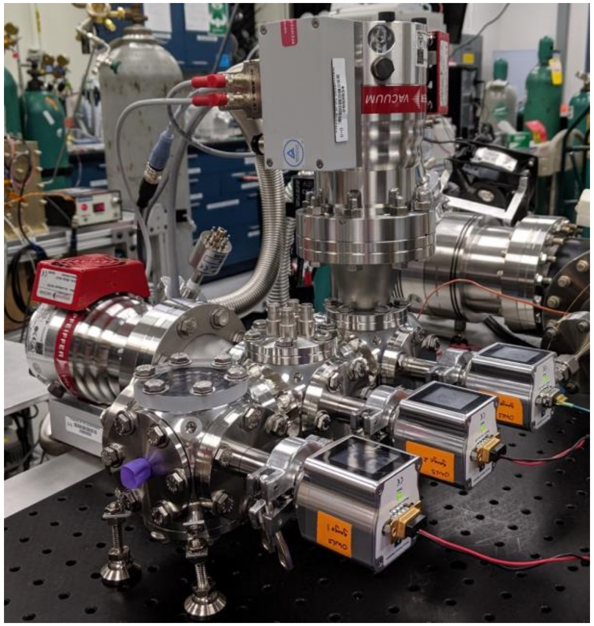
Amino acids are the building block of proteins and their distribution provide distinct biosignatures.

OWLS MS Laboratory Prototypes

- Performance comparison of ESI-QIT-MS and ESI-LIT-MS (QqQ config.)
  - Difficult to perform decomposition of organic molecules (ex. amino acids) with GC-MS at high temperatures
  - ESI transfers organic molecules into gas phase without decomposition/fragmentation
  - Transfer of gas from ambient pressure into vacuum requires ion optics and differential pumping (orifices) to interface (completed)
    - Developed by Sciex



Sciex QqQ setup



JPL Ion Optics setup efficiency measurements will be extended with QIT-MS

OWLS MS Requirements

- Requirements
  - Mass range: 70 – 500 Da
  - Resolution: 1 Da across range
  - Rep rate: 5 Hz
  - LOD: 500 nM for organic cations
  - Quantitation from: 500 nM –250 µM
- MS/MS capabilities a bonus

- Status
  - Demonstrated electrospray by ion detection
  - Completed SIMION simulations of ion optics and ion flow conductance models
  - Validation of test bed will start soon

Conclusions

- Preparation for Lunar application started with DALI program.
  - Further reduction in mass (< 7kg) and power (<30W)
- QIT-MS accuracy/precision matches with laboratory size magnetic sector MS at shorter integration times
- Proposing for near-future flight opportunities to raise the TRL level
  - Discovery and New Frontiers
  - Instrument developments
  - Internal funding
- Future work will focus on sample inlets designs to target different NASA missions
  - Development on Electro-Spray frontend for liquid sample
  - Investigations of an aerosol separator for high density atmospheres by utilizing the newly developed piezo controlled valve tested up to 69 bars for constant input flow during decent

S.A.M. is in the ISS but what is next?

Thank you for your attention!

National Aeronautics and Space Administration
Jet Propulsion Laboratory
California Institute of Technology

Questions?

Meet the Core 389Team

Dr. Frank Maiwald

Dr. Stojan Madzunkov
QIT-MS inventor;
technical lead

Dr. Jurij Simcic
MS component
Inventor

Dr. Dragan Nikolic
Theory, technologist

Dr. Richard Kidd
Chemistry and
Biology

Typical Education
- Physics
- Chemistry
- Electronics
- Geoscience

Dr. Anton Belousov
Technologist,
Implementor

Dr. Byunghoon Bae
MEMS component
Inventor

Marianne Gonzalez
Experimentalist

Dr. Max. Coleman
Scientist, inventor

Valeria Lopez
Student

Dr. Bohoon Kim
PostDoc

Experience
- Physics and Chemistry
- Theory and modelling
- Instrument development
- Publications and proposals
- Teamwork