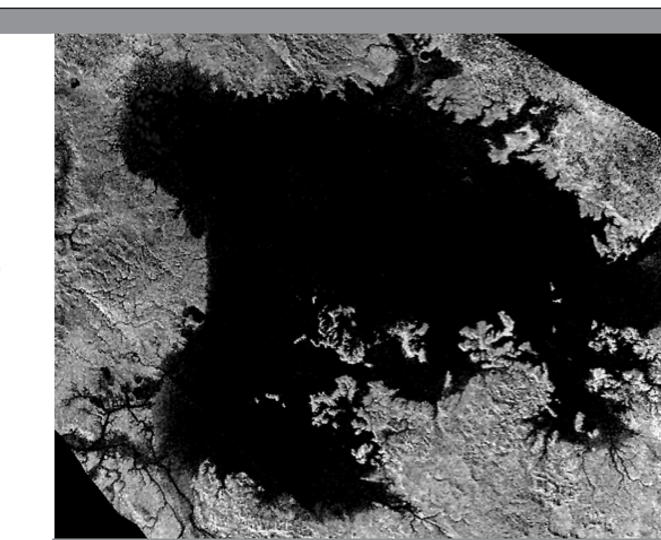
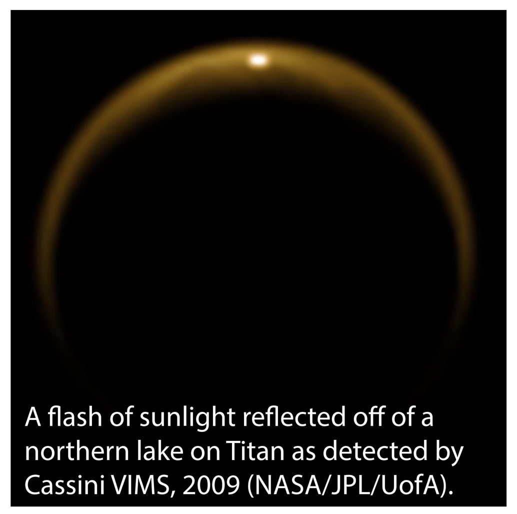
Measuring the Composition of a Cryogenic Sea

Melissa G. Trainer[1], Paul R. Mahaffy[1], Ellen R. Stofan[2], Jonathan I. Lunine[3], and Ralph D. Lorenz[4]

[1]Code 699, NASA Goddard Space Flight Center, Greenbelt, MD 20771, **melissa.trainer@nasa.gov**;
[2]Proxemy Research; [3]Cornell University; [4]Applied Physics Lab, Johns Hopkins University



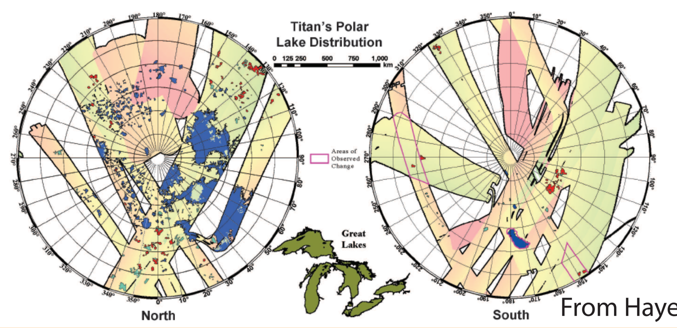
Cryogenic Seas: Where and Why?



A flash of sunlight reflected off of a northern lake on Titan as detected by Cassini VIMS, 2009 (NASA/JPL/UofA).

The hydrocarbon lakes and seas of Titan

- Only known extraterrestrial seas!
- Polar lakes/seas at ~ **90 K**
- Composed primarily of ethane and methane



From Hayes et al., *GRL*, 2008.

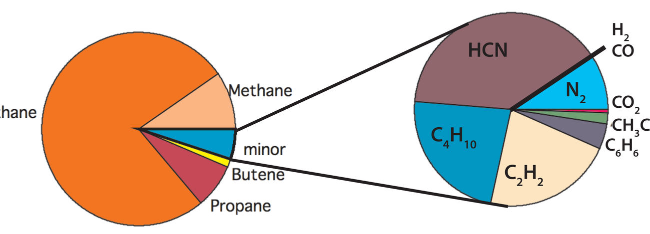
Composition

Seas on Titan are part of a methane cycle that drives weather, climate, chemical, and geologic change on the moon.

$CH_4/C_2H_6/C_3H_8$ → **Evaporation and heat transfer**, **CH_4 outgassing**, **Chemical transformation processes**

minor CxHyNz → **Extent of chemical processing**

Estimates on polar lake composition from Cordier et al., *ApJL*, 2009



Titan Origins

Noble gases, not detected in the atmosphere, may be stored in the sea liquid. Stable isotopes of CH_4 provide clues to its origin and evolution.

Ar/Kr/Xe → Formation temperature, Origin of N_2

$^{13/12}C$ → CH_4 outgassing

Prebiotic Chemistry

Organic chemistry in the atmosphere is known to produce high molecular weight species, which deposit on the surface in aerosol particles.

- Trace CxHyNz molecules within the sea provide evidence of the extent of the atmosheric chemistry
- Unexpected high molecular weight species, especially O-containing, give insight into the extent of prebiotic chemistry taking place in the sea liquid.

NASA/JPL/Space Science Institute

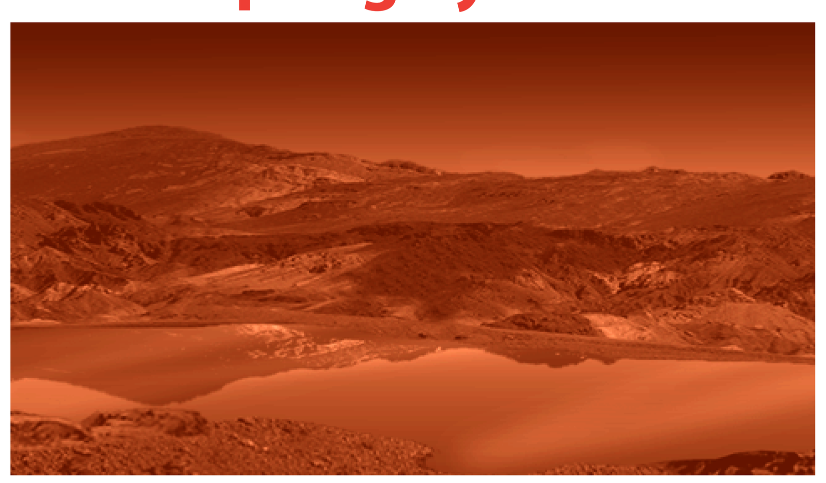
Measurement Challenges

Although rich with scientific opportunities, proper sampling of sea fluid and measurement of the composition is fraught with challenges:

- Cold sea temperatures, ~ 90 K
- Hot temperatures required to vaporize sample *(for MS)*
- Uncertain composition, components with varying b.p.'s
- Unknown particulate sizes/concentrations
- Unknown viscosity, related to composition & particulates

We have designed a robust sampling and measurement technique to address these challenges, as part of Titan Mare Explorer (TiME) Phase A study

Robust Sampling System is Critical

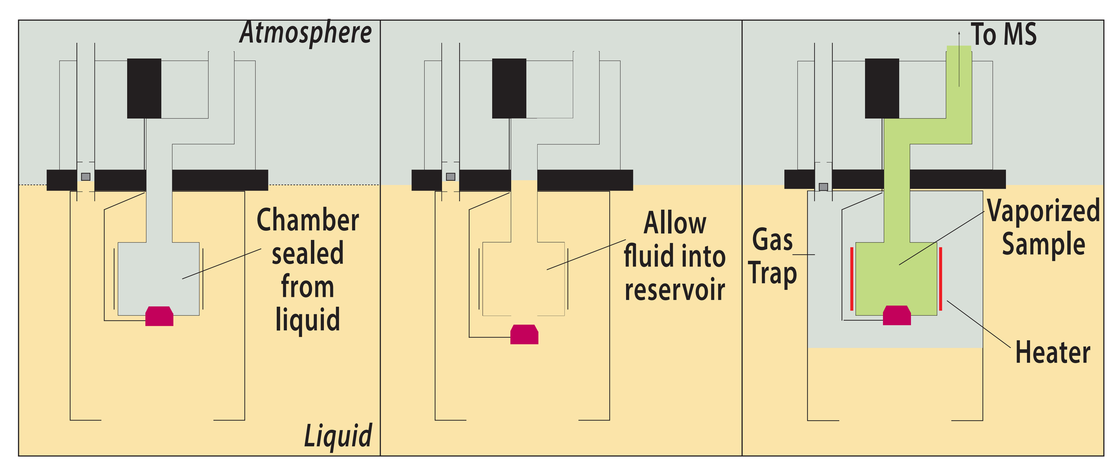


NASA/JPL

For compositional measurement, the highest-fidelity sample must be obtained from the sea:

Sampling Requirement	System Requirement
Avoid fractionation (*ie* preferential boiling) of sea components	Sample capture must occur at sea temperature
Retain sample during phase transitions	Sufficient sealing across broad temperature range
Repeated sampling with consistent performance and sample quality	Maintain full functionality after several exposures to sea (temperature, particulates, etc.)

Sampling System Concept



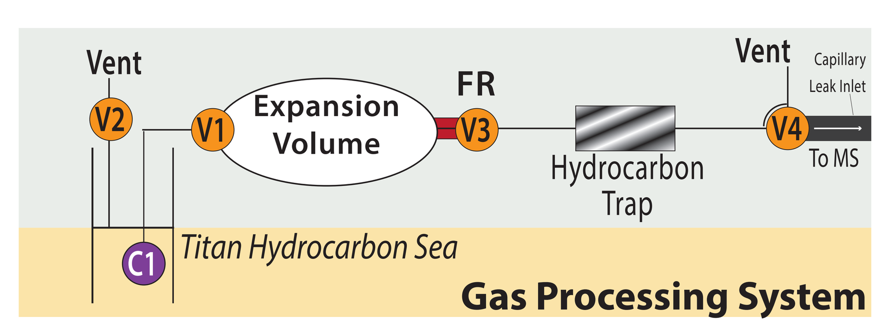
Sample chamber is immersed in sea liquid to equilibrate to sea temperature; vent allows for gravity fill of sample

Cryogenic valve design and materials accommodate temperature ramping from sea (90 K) to heating endpoint (~450 K), vaporizing major and minor components

'Gas trap' generated around sample chamber keeps power requirements down, reduces contact of valve to sea during heating

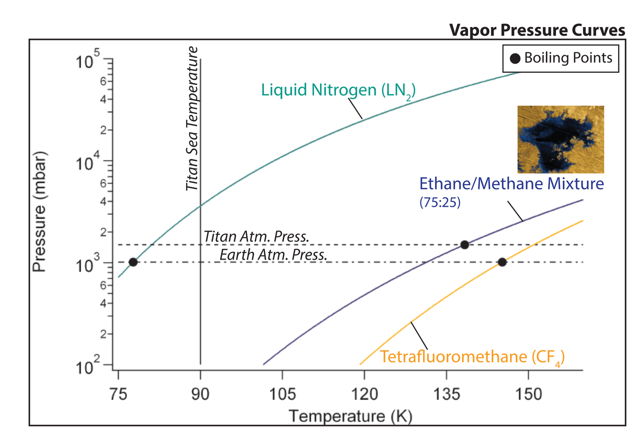
Sample is transferred (volume expansion) to gas processing system (GPS) for mass spectrometer measurement (*below*)

Sampling system brought to **TRL 6** through testing program (*right*), including vibration



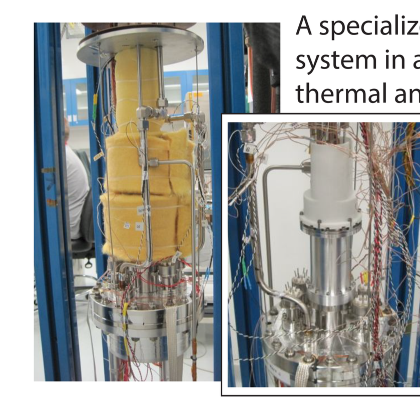
A general concept for the gas processing system (GPS) linking the sampling inlet to the neutral mass spectrometer

Thermal End-to-End Testing



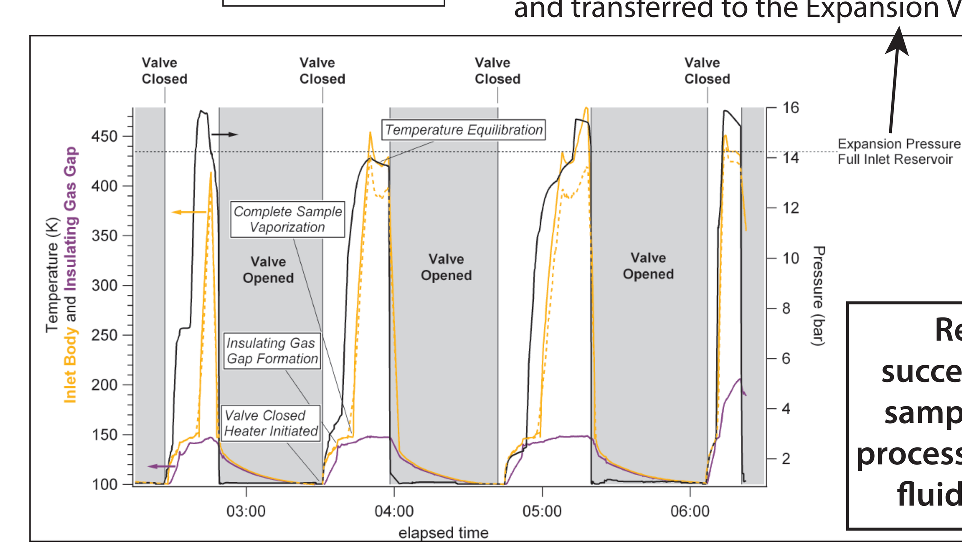
Cryogenic fluids were carefully chosen to provide most realistic test environment for inlet function:

- LN_2 tests valve operation at low-temperature limit
- CF_4 tests ingestion and heating of fluid with similar thermal properties to sea
- CF_4 requires **enclosed dewar** for condensation of simulated sea



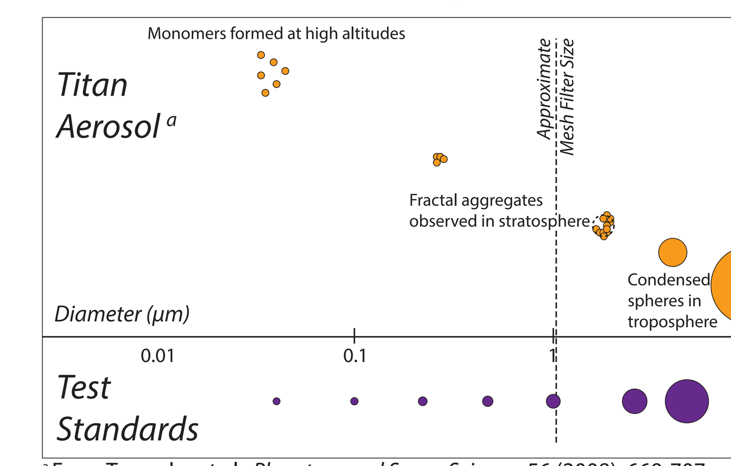
A specialized dewar was constructed to test the sampling system in a realistic fluid environment with appropriate thermal and mechanical interfaces

Expansion pressures indicate that the sample chamber was completely filled (~2.5 cm³ liquid) and that sample was captured, completely vaporized, and transferred to the Expansion Volume.



Results show successful, repeated sample capture and processing in cryogenic fluid environment

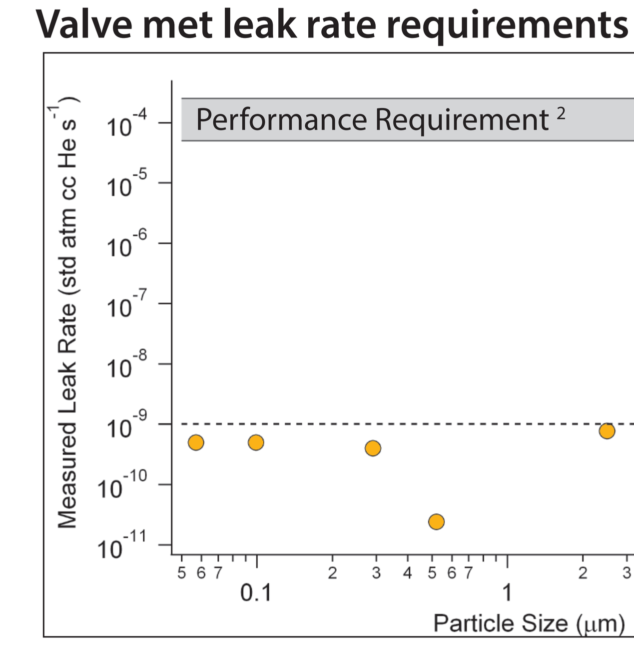
Particulate Testing



[a] From Tomasko et al., *Planetary and Space Science*, 56 (2008), 669-707.

A mesh filter at the entrance to the sampling inlet could be used to protect valve from large particulates. Small particulates may also be present in the sea.
The sampling inlet was tested against polystyrene particle standards across range of relevant sizes (left).

Valve met leak rate requirements even at largest particle size

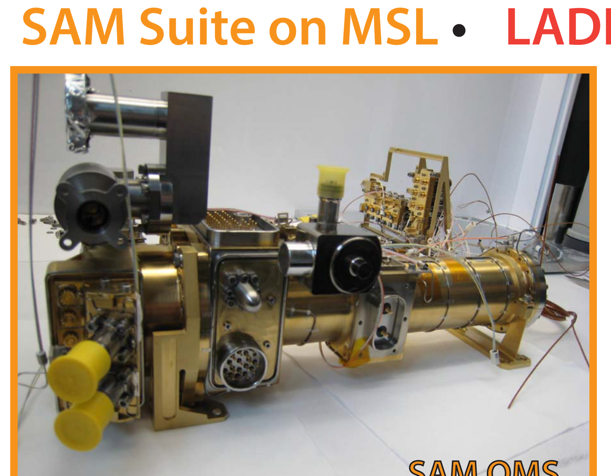


[1] A test was run using JSC-1a Mars Simulant dust, sieved to particle sizes ≤ 20 μm. This is a more extreme worst-case than will be encountered on Titan.
[2] The range of acceptable leak rates was calculated to ensure good accuracy on NMS compositional measurements. This calculation accounted for possible sample fractionation and sample heating times.

Neutral Mass Spectrometry for Versatile Compositional Analysis

Appropriate sensitivity and versatility can be provided by a quadrupole mass spectrometer (QMS) similar to those on current missions:

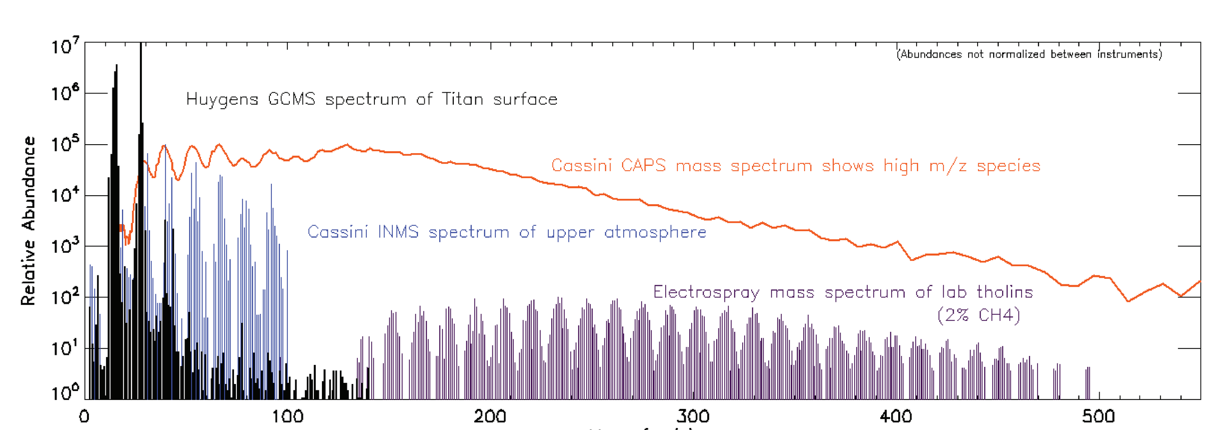
SAM Suite on MSL • LADEE • MAVEN



SAM QMS

CONTOUR NGIMS - model for LADEE/MAVEN MS

Composition of Major and Minor Organic Species



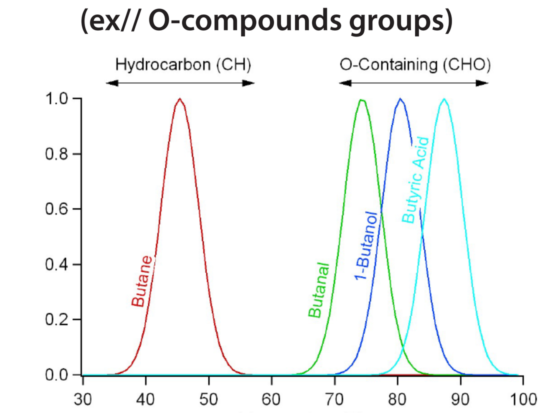
Wide mass range (to 550 Da) with unit resolution would allow for measurement of high molecular weight species present in sea, such as those predicted by atmospheric measurements and laboratory studies

The use of the hydrocarbon trap (GPS figure, above) enables simple separations to achieve important compositional measurements:

$CH_4/C_2H_6/C_3H_8$

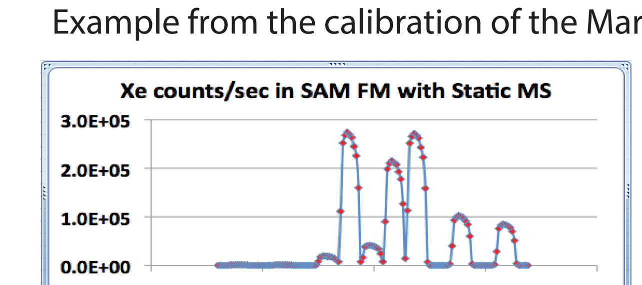
High MW CxHyNz

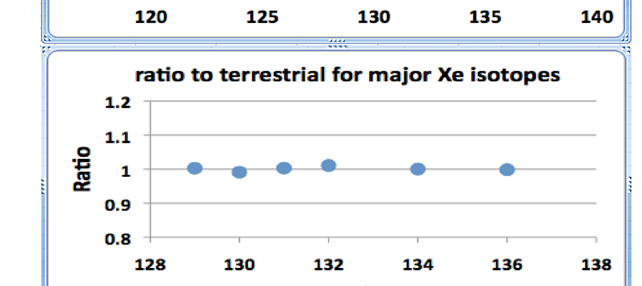
Molecules with different functionalities (ex// O-compounds groups)



Noble Gases and Isotopes

Trace noble gases and their isotope ratios are measured with **static mass spectrometry**
Example from the calibration of the Mars Science Laboratory SAM mass spectrometer:





A getter in the pumping system removes all active gases from the manifold except **CH_4** and the **noble gases**.
Allows for quantification of noble gas ratios and isotopic measurements of more abundant (Argon/CH_4) species.

(Mahaffy et al., *SSR*, 2012)

Data for ratio plot (left) secured in ~ 30 sec during SAM QMS calibration for terrestrial Xe.
Isotope ratios match terrestrial accuracy ~0.3%