

Future Missions to Titan: Scientific and Engineering Challenges

Technical Development Progress Report #3

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It is useful to begin this progress report with a brief background from the Final Summary of our initial Study to provide a foundation and the motivation for this technical development work.

BACKGROUND.

Saturn's largest moon, Titan, has been an enigma at every stage of its exploration. For three decades after the hazy atmosphere was discovered from the ground in the 1940s, debate ensued over whether it was a thin layer of methane or a dense shield of methane and nitrogen. Voyager 1 settled the matter in favor of the latter in 1980, but the details of the thick atmosphere discovered raised even more intriguing questions about the nature of the hidden surface, and the sources of resupply of methane to the atmosphere. The simplest possibility, that an ocean of methane and its major photochemical product ethane might cover the globe, was cast in doubt by Earth-based radar studies and then eliminated by Hubble Space Telescope and adaptive optics imaging in the near-infrared from large ground-based telescopes in the 1990s. These data, however, did not reveal the complexity of the surface that Cassini-Huygens would uncover beginning in 2004. A hydrological cycle appears to exist in which methane (in concert with ethane in some processes) plays the role on Titan that water plays on Earth.

Channels likely carved by liquid methane and/or ethane, lakes and seas of these materials—some rivaling or exceeding North America's Great Lakes in size—vast equatorial dune fields of complex organics made high in the atmosphere and shaped by wind, and intriguing hints of geologic activity suggest a world with a balance of geologic and atmospheric processes that is the solar system's best analogue to Earth. Deep underneath Titan's dense atmosphere and active, diverse surface is an interior



ocean discovered by Cassini and thought to be largely composed of liquid water. Cassini-Huygens has provided spectacular data and has enabled us to glimpse the mysterious surface of Titan. However the mission will leave us with many questions that require future missions to answer. These include determining the composition of the surface and the geographic distribution of various organic constituents. Key questions remain about the ages of surface features, specifically whether crvovolcanism and tectonism are actively ongoing or are relics of a

more active past. Ammonia, circumstantially suggested to be present by a variety of different kinds of Cassini-Huygens data, has yet to be seen. Is methane out-gassing from the interior or ice crust today? Are the lakes fed primarily by rain or underground methane-ethane aquifers (more properly, "alkanofers") and how often have heavy methane rains come to the equatorial region? We should investigate whether Titan's surface supported vaster seas of methane in the past, and whether complex self-organizing chemical systems have come and gone in the water volcanism, or even exist in exotic form today in the high latitude lakes. The presence of a magnetic field has yet to be established. A large

altitude range in the atmosphere, from 400–900 km in altitude, will remain poorly explored after Cassini. Much remains to be understood about seasonal changes of the atmosphere at all levels, and the long-term escape of constituents to space.

Other than Earth, Titan is the only world in our solar system known to have standing liquids and an active "hydrologic cycle" with clouds, rains, lakes and streams. The dense atmosphere and liquid lakes on Titan's surface can be explored with airborne platforms and landed probes, but the key aspect ensuring the success of future investigations is the conceptualization and design of instruments that are small enough to fit on the landed probes and airborne platforms, yet sophisticated enough to conduct the kinds of detailed chemical (including isotopic), physical, and structural analyses needed to investigate the history and cycling of the organic materials. In addition, they must be capable of operating at cryogenic temperatures while maintaining the integrity of the sample throughout the analytic process. Illuminating accurate chemistries also requires that the instruments and tools are not simultaneously biasing the measurements due to localized temperature increases. While the requirements for these techniques are well understood, their implementation in an extremely low temperature environment with limited mass, power and volume is acutely challenging. No such instrument systems exist today, and developing a comprehensive technical approach and instrument to conduct in-situ chemical analysis on Titan represents the key scientific and engineering challenge of this proposal.

TECHNICAL CHALLENGE: To develop a low mass, low power instrument concept and advance sub-system technologies to produce a high resolution, high sensitivity instrument that has the dynamic range and sensitivity to both provide the required information on the major species and simultaneously find the interesting complex species within the light hydrocarbon soup found in Titan lakes.

OBJECTIVES:

- Perform system level trades and developing the instrument concept
- Identify specific sub-system technological challenges
- Develop specific breakthrough technologies to overcome specific technical challenges and enable the measurements to be successfully made in the Titan lake environment.
- Increase the instrument concept TRL level from 2 to 3.

EXPECTED PERFORMANCE

- Cryogenically-operated NMR will be able to detect and quantify the abundance of ethane, methane, propane butane and butene
- Mass Spectrometer: 1000 Daltons range and 100,000 mass resolution for major and minor species
- Reduce mass, power and volume of current flight instruments by ~75% (MS, sample acquisition and handling only. No NMR has flown and no instruments operating at ambient Titan temperature have ever flown)

TEAM's HIGH-LEVEL OVERALL ACHIEVEMENTS:

- All Caltech PI's have been actively pursuing their proposed tasks, with each sub-team having a strong collaboration with JPL and among each other. Specifically, PI Greer's team, which consists of post-doc Seok-Woo Lee and a Ph.D. student Lucas Meza, collaborates closely with Austin Minnich (Caltech) on developing ultra-lightweight, low-thermal conductivity structural materials that are capable of operating at cryogenic temperatures.
- PI Greer has also been engaged in fruitful discussions with Rob Hodyss (JPL) on measuring the mechanical properties (hardness and Young's modulus) of organic materials found on Titan's surface. Hodyss and Greer submitted a proposal on this topic to the President's/Director's Fund (PDF) solicitation.
- PI Greer has been interacting with multiple external potential collaborators on measuring mechanical properties of highly volatile organic materials (Cal Poly in San Luis Obispo and UCSB)
- Co-PI Beauchamp's team has been in close collaboration with Rick Flagan (Caltech), as well as with

P. Beauchamp, Evan Neidholt, and Mark Anderson (JPL). Several external collaborations have also been setup, which are discussed in detail in each section.

- JPL and Caltech Co-PI's, along with external collaborators, have held monthly meetings to define the instrument concepts and perform system level trades, with minutes published and distributed after each meeting. A final report has been generated and JPL team held a successful review in March.
- Monthly JPL-Caltech meeting among the principals have been taking place since October of 2011 followed by the strong team interactions during the trade study. These meetings/telecons will continue to take place each month to ensure information sharing and alignment of all participants in addition to offline discussions by relevant individual sub-groups.
- External collaborator J. Lunine, JPL's C. Sotin and Caltech's R. Flagan have also been in close communication providing crucial information about the Titan's atmosphere constituents, for example the atmospheric gas/aerosol constituencies.

SPECIFIC DETAILS OF TEAMS' PROGRESS:

1. Development of Miniaturized NMR

Lead: S. Kim (JPL) and G. Cody (Carnegie Institution)

Cody's efforts have been focused on performing numerical simulations of actual spectrometer performance taking into account all aspects of the measurements at the level of the multi-spin density (matrix) operator, an exact treatment of the physics of NMR. These simulations will enable full prediction regarding sample analysis time that will feed into actual instrumentation design. The team at JPL will focus on testing critical components. This will occur in the Electronic Component Testing Facilities (389D) with testing in the range 77K – room temperature. JPL will build a breadboard for continuous testing over the temperature range and conduct in-situ functionality testing of digital components: Xilinx and Actel FPGA to -180° C. This work complements the work occurring at Caltech on the low temperature materials development in Greer's lab.

Molecular dynamics simulations were run on 1) pure methane, 2) pure ethane, 3) Titan rain composition (Cordier et al. 2009) and 4) Titan Mare composition (Cordier et al. 2009). Our estimates are slightly and systematically lower than other estimates, but not by much. Using either our values or published values enables us to estimate the spin-lattice relaxation time, T_1 (a value that is critical for quantitative signal acquisition) for both ¹H and ¹³C. From a knowledge of T_1 we can determine the actual acquisition times that will determine the number of measurements that may be made during a mission. From the molecular mechanics simulations the viscosity of Titan Mare (Cordier 2009) is 0.4 centipoise indicating a ${}^{1}HT_{1}$ of 3.3 seconds, the corresponding T_1 for ¹³C is estimated to be 53 seconds. Assuming a 90 ° tip angle excitation RF pulse this would necessitate a recycle delay of 5 x T_1 , i.e. 16.5 s (¹H) and 4.4 min (¹³C) thus assuming the # of acquisitions to be 100 the total acquisition time would be 27.5 minutes for ¹H and 7.3 hours for ¹³C. Note: for Lorenz et al. 2010, max. acq. Time for ¹H NMR would be 9 mins and 100 acq's may be unnecessary. The viscosities of Titan Mare from Lorenz et al. (2010) and from the present molecular dynamics simulations are similar and either are highly favorable for multiple NMR measurements during a Titan Lake Lander mission. In either case the T₁ relaxation falls within the regime where $T_1 = T_2$ (where T_2 is the spin-spin relaxation time that dictates the ultimate line width hence spectral resolution) and where T2 is long, hence spectral resolution will be excellent.

The next stage of this project is to perform exact simulations of the NMR measurements utilizing density matrix calculations to include chemical shift and indirect coupling, signal enhancement due to more favorable Boltzmann distribution at low T, and relaxation (T_1 and T_2) behavior on optimum recycle delay and ideal line width estimates. Integration of these data with engineering specifications of excitation volume and filling factor will allow for a realistic estimate of actual operational specifications

2. Modeling Atmospheric Chemistry

Lead: J. Lunine (Cornell)

Lunine worked on concepts for Titan surface science sampling. In particular, in a study at JPL last summer he led an examination of the desired organic products to be sampled in Titan lander missions on solid, liquid and damp surfaces. This work provides input into the studies of specific sampling systems to be designed for eventual Titan missions.

Lunine also worked on others projects related to understanding the nature of Titan's surface. In particular, he collaborated with a group at JPL that measured the dielectric constants of ethane and methane, which when applied to recent Cassini RADAR measurements, established the bulk composition (ethane-methane ratio) of one of the large seas of Titan. (Although this work used Cassini data it was not funded by the Cassini project). Lunine assisted the work through modeling of the thermodynamics of the hydrocarbon mixtures and in particular on the solubility of the main atmospheric gas, nitrogen. The implications of this work for the KISS study is to deemphasize measurement of bulk liquid compositions versus trace species in the lakes and seas.

3. Development of Sampling and Analysis Methodology for Complex Organics Found in Titan's Atmosphere, Lakes, and Surface

Lead: co-PI J. Beauchamp, Kate Upton, Jinshan Gao, and Daniel Thomas (Caltech) in Collaboration with P. Beauchamp, E. Niedholt, and M. Anderson (JPL)

<u>Titan Organics Analyzer.</u> A key component of our joint Caltech-JPL-European research and development effort is the implementation of instrumentation for sampling and analyzing the complex organics found in Titan's atmosphere, lakes, and surface. We have continued this development program in collaboration with our colleagues in France and at Thermo Scientific in Germany as described in our previous reports. Construction of a test facility that moves closer to a functional instrument is underway in France. Starting next fall we will be testing the combined rectilinear ion trap/Orbitrap system with Titan simulant samples. Discussions are underway considering a test of the system on a stratospheric balloon flight to sample organic aerosols.

DART Ion Source. The analysis of low volatility high molecular weight organics present as aerosols and on the surface presents a major challenge which we are addressing in our technology development efforts. We are exploring a technique for ambient mass spectrometry known as Direct Analysis in Real Time (DART) that involves the formation of electronically excited atomic or molecular species that assist desorption of organics from solid samples and generate a cold plasma of gas phase reagent ions that provide a chemical ionization environment for target molecules. A key element in the source design is that the electron density and energy distribution remains relatively low, able to ionize atmospheric species but not destroy the target molecules. The miniature DART source developed at Caltech (Figure 1) uses a glow discharge in helium or nitrogen to generate the reactant species. This source has been tested with a wide range of samples, including Titan tholins (simulants produced by using different discharge techniques in mixtures of nitrogen and methane), and aerosols collected on Teflon filters in Caltech's smog chamber simulator. Recently we have been working with the AMES laboratory research group of Farid Saleem, using their COSMIC pulsed discharge/supersonic expansion source to produce Titan simulants (Tholins) from a nitrogen/methane mixture. In this system organics formed in a pulsed discharge are rapidly cooled in a supersonic expansion and collected on a clean aluminum foil that is subsequently analyzed with the DART source and linear ion trap quadrupole mass spectrometer (Thermo Scientific LTQ-XL) at Caltech. The resulting mass spectrum is shown in Figure 2 is typical of the results obtained with this procedure. Many abundant low mass products are observed with the DART

source that are not observed with electrospray ionization. The latter ionization technique heavily favors detection of high molecular weight species with high proton affinity along with high surface activity in the solvent selected to dissolve the sample. With the DART methodology there is no need for a complex solvent extraction or other pretreatment of the sample.

Rectilinear Ion Trap. A key component of the Titan Organics Analyzer is the rectilinear ion trap (Figure 3) being developed as part of our technology development program. The electronics for this system are still in the design and construction stage, and will provide for data dependent analysis. When a mass spectrum is recorded, the software picks out several of the most abundant peaks, isolates them in turn, and effects collision induced dissociation to provide structural information. An example of this procedure is shown in Figure 4, where the peak at m/z 74 in Figure 2 is isolated and subjected to collision induced dissociation. The results indicate that this nominal mass comprises two species, a complex of propanenitrile with H_2O , and a complex of aminoacetonitrile with NH_3 . The aminoacetonitrile species is of particular interest since it is produced in virtually all of the experimental methodologies employed to generate Titan atmospheric organics (Tholins) using a wide variety of excitation methods. This species has recently been shown in our laboratory (Daniel Thomas and J.L. Beauchamp, unpublished results) to produce the simplest amino acid, glycine, in tribochemical reactions occurring in Titan's vast organic dunes. We have fabricated three of these sources and made them available to other laboratories on campus where they are being used for a variety of problems where ambient ionization is an effective means of chemical analysis.



Figure 1. Miniature DART (Direct Analysis in Real Time) Source for in situ sampling of complex organics present in Titan's atmosphere, lakes and surface. A glow discharge is used to generate excited state atomic and molecular species that act to desorb molecules from solid and liquid samples while creating a cold plasma that ionizes desorbed neutrals for analysis by mass spectrometry (the inlet to the mass spectrometer is on the left). The source is 10 mm in diameter and 70 mm in length. With appropriate microfabrication methods it can be made even smaller.



Figure 2. Mass spectrum showing ionic species observed from a Tholin sample from the AMES COSMIC simulator (collected on aluminum foil), placed between the angled DART source and the mass spectrometer atmospheric pressure inlet.



Figure 3. Rectilinear Ion Trap. This instrument represents a novel design of a mass spectrometer analyzer based on the linear quadrupole ion trap. Although small it has capability for better than unit mass resolution up to m/z 500 and will be able to fragment mass selected ions to provide structural information. This analyze

r serves as the front end for an Orbitrap mass spectrometer being built by collaborators in France and Germany. It will have capabilities for isolating ions of a selected m/z, fragmenting them by collision induced dissociation, with subsequent analysis of the product ions to provide structural information. Ejection of ions from the rectilinear ion trap into the Orbitrap provides for exact mass measurement to determine elemental compositions. An example of this procedure (performed using the Thermo Scientific LTQ-XL linear ion trap quadrupole mass spectrometer, which has similar capabilities) is

shown in Figure 4.



Figure 4. MS/MS spectrum of the peak appearing at the nominal mass of 74 m/z in figure 3. The MS/MS spectrum indicates that this nominal m/z (red arrow in upper MS spectrum) mainly comprises two species. One is aminoacetonitrile complexed with ammonia and the other is propanenitrile complexed with water. This illustrates the importance of MS/MS capabilities to identify species detected using ambient ionization methodology with complex samples at atmospheric pressures. While high resolution analysis of nominal mass 74 m/z would reveal two distinct atomic compositions, it would not indicate that they were adducts of two molecular species with water and ammonia.

Reports/Publications: Manuscript in preparation describing new methods to target specific functional groups in complex Titan Organics (Kate Upton, Taylor Townes, Daniel Thomas, and J. L. Beauchamp). **Students working on project:** Graduate student Kate Upton (supported by NASA doctoral fellowship), graduate student Daniel Thomas (supported by GRA funded by NASA Astrobiology Institute: Titan as Prebiotic System) and Jinshan Gao (postdoctoral student, supported by KISS funds).

3. Development of Lightweight Thermally Insulating Nanolattices for Cryogenic Operation Lead: J.R. Greer

Greer's group has been conducting mechanical experiments in the Cryogenic Module that we constructed inside of our in-Situ Nano-Mechanical Instrument, SEMentor, for mechanical testing of small-scale metallic samples. Greer group members (specifically, Ph.D. student Lucas Meza and post-doc Seok-Woo Lee, both partially supported by this KISS grant) have been fabricating 3-dimensional nano-lattices out of thermally insulating materials like alumina (ceramic) and metallic glasses (metallic alloys) and performing nanomechanical experiments at temperatures down to ~110K. Efforts are underway to improve thermal insulation to attain Titan-relevant temperatures

of ~95K.

- Seok-Woo Lee, Greer's post-doc partially supported by this KISS grant and Lucas Meza (Ph. D. student) conducted a series of experiments on metals and metallic glasses, with several publications either already accepted for publication or in submission for example, S.-W. Lee, Y. Cheng, I. Ryu, J. R. Greer "Deformation mechanisms in nano-sized body-centered-cubic metals at low temperatures through *in-situ* cryogenic experiments" *China Science Letters* (accepted, 2013) and L. R. Meza¹, S. Das¹[†], J. R. Greer^{1,2*} Ultralight, Strong, and Energy-Absorbing Ceramic Nanolattices" (in submission, 2014).
 - Ceramics have some of the highest strengths- and stiffness-per-unit weight of any material, but are sub-optimal for use as structural materials due to their brittle and flaw sensitive nature. We present structural meta-materials comprised of nanoscale ceramics that are simultaneously strong, stiff, energy absorbing and recoverable. Nanolattice structures are fabricated using two-photon lithography followed by atomic layer deposition of alumina and oxygen plasma etching. The resulting hollow tube ceramic structures have wall thicknesses from 5-60 nm and densities spanning 6.3-258 mg/cm³. Compression experiments revealed that tuning the wall thickness-to-radius ratio of the tubes can suppress brittle catastrophic failure and cause a ductile-like deformation, with nearly complete recovery after compressions in excess of 50% strain. By combining high strength nanoscale ceramics with stretching-dominated architectures, the nanolattices in this study area able to reach a previously unattained high strength and ultralight weight material property space.



4. Development of Extremely Lightweight Structures with Low Thermal Conductivity Lead: Co-PI A. Minnich (Caltech) in collaboration with PI Greer

We have been making progress in studying thermal transport in nanolattices using both experiment and computation. Computationally, we are implementing a Monte Carlo simulation that allows us to determine the reduction in thermal conductivity due to boundary scattering of phonons in the thin trusses

of the structure. When combined with a mechanical model from the Greer group, this model will allow us to predict the novel combinations of mechanical and thermal properties that can be achieved in nanolattices. Experimentally, we are using technique an optical to carefully characterize the thermal conductivities of the materials used for the nanotrusses such as ALD coated alumina. We anticipate obtaining the first measurement of nanolattice thermal conductivity in the next 2 months.



5. Titan RTD System Architecture and Technology Trades Study (JPL Team's Progress) Lead: P. Beauchamp (JPL)

Trade Study Lead: W. Zimmerman (JPL); Science: Wayne F. Zimmerman (PI), Science Instruments (380) Pat Beauchamp, Solar System Exploration (416) Robert Hodyss, Planetary Science (322) Sam Soon Kim, Propulsion and Materials (353) Evan Neidholdt, Planetary Surface Instruments (382) Stewart Sherrit, Space Mechanical Engineering (352)

APPROACH AND RESULTS

1. The technical approach for this second year research effort was four fold: 1) Strengthen our overall system design relative to our triage approach of three primary instruments and how we integrate the sample acquisition/distribution subsystem with those instruments (**see Figure 1**); 2) Continue the build/test of the prototype instruments, namely the Orbi-trap mass spec, NMR along with the control electronics, and use the SPME fibers to extract the minor lake species, 3) Complete our design of the sample acquisition system and demonstrate a prototype sample distribution system, and 4) Continue to partner with our CalTech KISS research peers and our French (CNRS Orleans) Orbi-trap researchers.

2. *RIT/Orbitrap Mass Spectrometer System (see Fig. 2a,2b,2c):* The CNRS in Orleans are developing a flight qualified Orbitrap mass analyzer and JPL has developed a teaming arrangement with that team. Additionally, we have a NDA with Alexander Makarov, the Orbitrap inventor. With that as a given, JPL concentrated on developing breadboards of the injector trap and control electronics. The injector trap has to packetize the ions for delivery to the Orbitrap mass analyzer. We determined early on (Q1) that a rectilinear ion trap (RIT) and Orbi-trap can operate at the same pressure. This joint architecture also allows us to monitor low mass species (1-50 Da) in addition to the Orbi-trap's capability of analyzing masses up to 800 Da with a mid-range resolution of 50,000. Overall, the

instrument will have analysis capabilities from mass 12-1000, with the highest resolution (50,000) capabilities from mass 50-200. Given that our CalTech partners had developed an RIT, we were able to focus on the design/build/test of the control electronics to enable selective ion injection. The milestones for year 2 were:

- Resolve the pumping high pressure differential issue by seeing if the RIT can replace the C-trap (Q1)

- Build and test the ion trap control system that allows for ion accumulation and manipulation (including MS/MS analysis) prior to ion injection into Orbitrap mass analyzer and take it over to France to test with the Orbitrap breadboard in Orleans. (Q1-4)

a. Results:

a1. The RIT is responsible for a number of critical functions in the instrument, including recording low resolution mass spectra, isolation and excitation of major constituent ions, and packetization and ejection of ions into the Orbi-trap. We chose a digital ion trap (DIT) drive for the RIT because in a single electronics architecture we will be able to generate all the arbitrary waveforms necessary for the functions required to isolate masses and read mass spectra as well 'feed' the orbitrap, which requires being able to shut the waveform off 'dead' and pulse the ions out of the RIT. DIT drive is a switched high voltage square wave, nominally of 50% duty cycle. To read mass spectra and isolate masses, the frequency and duty cycle are changed with the digital waveform control.

a 2. Digital RF switching of a 2 kV pk-pk (peak-to-peak) waveform at 1 MHz was demonstrated and is shown in Figure 2a. The circuit for switching this voltage was developed using a PIC microcontroller for waveform timing which allowed us to switch an output between a positive and negative high voltage supply. This demonstrated the switching architecture capable of sufficient voltage and frequency for driving the RIT when trapping ions. Typical trapping frequencies are between 200 and 500 kHz, and 200 – 500 V pk-pk. After we developed the switching circuit, we began constructing an integrated electronics/power supply which could be interfaced with the Caltech built RIT. Detailed analysis and testing resulted in a unit capable of 200 kHz waveform switching at 400 V pk-pk using small EMCO power supplies, which is shown as part of our experimental field test setup in Figure 2b. A field test with our collaborators at LPC2E in Orleans, France resulted in demonstration of this supply and that it could indeed drive the 'load' that the RIT presented.

a 3. The demonstration in France showed we could generate waveform and subsequently stop this waveform in nanoseconds and hold the output of the supply 'high' for a predetermined period of time, then go back to generating the trapping waveform. An additional state, holding the output at +1200 V, was necessary. This is the 'eject' portion of the experiment where the ions that were trapped are ejected from the RIT and into the Orbi-trap. After the trip to France, we concluded the year by testing and developing a method to overcome leakage in the FET body diodes and generate this additional switching 'state'. Figure 2c shows the output held 'high' at 1200 V before returning to waveform generation.

3. Cryogenic NMR(see Fig. 3a,3b,3c): The nuclear magnetic resonance (NMR) spectrometer offers distinct advantages over state of the art mass specs like GCMS because

it operates at lower power and mass, has superior performance at ambient Titan temperatures (enhanced polarization), generates very small data sets (512 Kb), and, most importantly, can isolate the chemical structure of complex liquid hydro-carbons and detect functional groups of major constituents down to $\sim 1\%$. For Year 2 the task milestones were:

Breadboard and test the NMR Electronics/Design, Magnet and Coil, which consisted of: -Engineering design of pulsed NMR circuit with low temperature qualified components. (Q1) -Fabrication of NMR Test-bed circuit (surface mount version) per engineering design.

- Functional test at RT.(Q2)

- Fabrication of NMR circuit for low temperature functional testing. (Q2)

-Testing at Low temperature (-60, -130, -196°C) (Q3)

- Integration Testing of NMR Electronics with purchased Miniature NMR magnet. (Q4) **a. Results:**

a1. A new pulsed NMR control circuit has been designed and fabricated with low temperature

compatible components (Figure 3a). Since the bipolar transistors failed below -150°C due to carrier freeze phenomenon of silicon, they were replaced with CMOS type, e.g., voltage regulator (MCP1825). The new NMR electronic circuit were evaluated starting from room temperature to 77K (RT, -60, -130, -196°C) by blowing cold N₂ gas. The new circuit performed properly down to 77K, and qualified as Titan temperature compatible.

a2. The NMR sample coil holder (made of Teflon) was designed, fabricated. integrated, and tested with a laboratory magnet (1T). As a proof of functionality, Fourier transform (FT) NMR spectrum from a water sample was obtained at room temperature (Figure 3b).

a3. A low Temperature Compatible NMR Magnet was developed. As shown in, a permanent magnet assembly (SmCo magnet, 950 g, 1 T field) with iron pole pieces has been custom designed and purchased from a commercial vendor (One Resonance, San Diego, CA). The iron pole pieces are ground to optical grade to achieve high magnetic field homogeneity for a sample volume of 1.5 mm dia. x 1.5 mm long cylinder. Measurements showed that the magnetic field homogeneity at the sample volume is 0.5 ppm level. Inhomogeneity of the magnetic field can be expressed as a superposition of spherical harmonics and could be further improved by installation of single channel correction coils (2 flexible printed circuit boards, each @ 1 mm thick) on the pole pieces to make within 0.1 ppm level. Also, in order to compensate for the anticipated temperature fluctuation (< \pm 1K) at the Titan lake surface, a set of temperature compensation coils (B₀ coils, \pm 3 Gauss, 19 grams, 24.7 Gauss/Amp, power @ <10 mW) are required for a field-frequency-lock circuit. Both coils are fabricated by the commercial vendor and installed into the NMR magnet.

a4. The final NMR Spectrometer was integrated. The NMR electronics board, sample coil holder and the permanent magnet has been assembled as a cryogenic NMR spectrometer as shown in Figure 3c. The permanent magnet has a magnetic field of 10,514 Gauss and the NMR frequency was adjusted until a signal could be seen at a frequency of 44.518MHz.

4. SPME(see Fig. 4a,4b): Solid phase micro-extraction (SPME) fibers for preconcentration of analytes from cryogenic liquid ethane offer the ability to trap suspended lake particles and perform bulk organic analysis of the lake particles. SPME fibers are used to extract and concentrate analytes from liquids by adsorption into a polymer matrix bound to a silica fiber [Ref 1]. By controlling the polarity of the coating material, various analytes can be precipitated out. After adsorbtion, the fiber is heated to release the analyte, which can then be analyzed by standard techniques, such as gas chromatography or mass spectrometry. They can be tuned to select for the analytes of interest. The milestone for year 2 of this RTD was:

Refine the use of solid phase micro-extraction (SPME) probes for sampling complex organic species from Titan lakes. Test different SPME fibers against relevant Titan analytes representing a variety of functional groups and polarities, select a "best choice" fiber and determine the limits of detection. (Q1-Q4)

a. Results:

SPME fibers were immersed for 1-60 minutes in solutions of various organics in liquid ethane held at 94 K in a custom built cryostat. The fiber was withdrawn from the solution and allowed to warm to room temperature before analysis by mass spectrometry. Mass spectrometric analysis was performed using an SRS200 quadrupole mass spectrometer with electron impact ionization. The fiber was introduced through a rubber septum into a heated (~200 °C) steel tube with a glass liner connected to the mass spectrometer vacuum chamber. Mass spectra were continually recorded as a function of time as the organics desorbed from the fiber. A diagram of the experimental apparatus is shown in Figure 4a. Figure 4b shows some initial results from a solution of benzene in liquid ethane. An 85 µm Carboxen/PDMS fiber was exposed to the solution for 10 minutes. Immediately after insertion of the fiber into the mass spectrometer system, a prominent signal appears at 78 m/z, corresponding to benzene. We have evaluated several different fibers types and a range of analytes. Fiber types include Carboxen/polydi- methylsiloxane(PDMS), PDMS/divinvlbenzene(DVB), and DVB/Carboxen/PDMS. No significant differences were found in adsorbtion capability between the different fibers for the analytes studied. Mainly nonpolar analytes were tested, as these are expected to be most soluble in Titan's. Benzene, naphthalene, and a range of alkanes and alkenes from C5-C11, as well as npropylamine (an example of a polar analyte) were all shown to adsorb onto the fiber from solution and desorb on heating. Results indicate that solid phase micro-extraction fibers work well at concentrating trace species from cryogenic hydrocarbon liquids such as Useful immersion times for the fibers are within practical in situ liquid ethane. experimental timescales (minutes to hours). We can estimate a limit of detection of 2 mg/L for benzene in ethane.

5. Sampling system (see Fig. 5a,5b,5c,5d,5e): The overall sample acquisition and distribution functional approach is shown in the previous Figure 1. Although funding was cut from this work element relative to the original proposal, significant progress was still made in the development/demonstration of a sample distribution system for the triage of instruments. The year 2 "adjusted" milestones for this task were:

1. Investigate a variety of elastomer materials (Torlon, Viton, Teflons) seating and sealing of valves at cryogenic temperatures (Q1)

2. Do a literature survey to determine what miniature cryogenic actuation mechanisms are available (Q2)

3. Procure/test a cryogenic actuator (e.g., based on the recently discovered PMN-PT piezoelectric material (Q4).

4. Build/test a prototype liquid delivery system based on COTS components and complete the

design of a flex-tensional cryogenic piezoelectric actuated/valve system (Q3-Q4) 5. Complete the design of an actuated needle penetrator for acquiring both liquid and solid Titan temperature organics to the NMR and Orbitrap (Q3-4)

a. Results:

a1. In order to develop a sample distribution system into a flight capability we investigated both seals and low mass/volume/power cryogenic actuators and valves for space. We found that teflon derivatives appear to be reasonable sealing materials but we had insufficient funding to procure/test these materials. However, a variety of materials and implementations were considered for actuation including low temperature shape memory alloys, cryogenic solenoid valves, and single crystal materials that have been developed for cryogenic applications. The single crystal piezo materials exhibited the best properties for actuation of valves. These piezoelectric materials convert applied electrical signals into a displacement which can be used and amplified to produce strokes up to 1 mm. For a piezoelectric material the stroke per volt is represented by the piezoelectric charge coefficient d_{33} . Currently, the majority of piezoelectric materials for such transducers are ferroelectric materials due to their high electromechanical properties, which arise from the two types of contributions- 1) the intrinsic (lattice effects) and, 2) extrinsic contributions (the motion of ferroelectric-ferroelastic domain walls) in ferroelectric materials (Refs 2 and 3). Since the origin of such high electromechanical properties of relaxor-PT single crystals is due to the polarization rotation effect, (i.e., intrinsic contributions), the property degradation at cryogenic temperatures is much lower than in PZT ceramics, making them promising candidates for cryogenic actuators from the perspective of stroke and power loss in the actuator when activated. In this task, the relaxor-PT single crystal transducers, specifically <110> oriented binary PMN-PT or ternary PIN-PMN-PT, will be incorporated into flextensional frame and used to as the valve actuator. An example of a flextensional single crystal actuator is shown in Figure 5a. A cross sectional diagram of the valve including the actuators chosen for the cryogenic valve are shown in Figure 5b along with a blow up of the valve assembly. We completed the impedance testing but to date have not completed displacement tests.

a 2. The bench-top sampling system designed and tested at JPL under the RTD program that has the required functionality is shown in Figure 5c along with a schematic diagram of the valving and the activation sequence chart for each sampling state. The system was built to demonstrate the required functionality of a Titan Sampling system for sample distribution to three separate instruments. The system has four different sampling states for the solid and liquid samples depending on which valves are actuated. The system can:

- Draw unfiltered fluid to an optional instrument.
- Draw filtered fluid to the NMR.
- Draw filtered fluid to the Rectilinear Ion Trap (RIT)/Orbitrap inlet.
- Draw the filtrate solution and the filtrate to the SPME and RIT/Orbitrap inlet.

The system shown in Figure 5c adequately demonstrated all the various fluid transfer functions. **a 3.** The prototype system discussed above was successful in demonstrating the needed sample distribution control but is not close to a flight configuration. The flight configuration is shown in Figure 5d and only has a volume (0.004 m^3) , mass (<1 kg) and power (<5 W) which is well below previously proposed mission specifications for a sampler. The larger tube in the inlet is the solid sampler, A close up of this is shown in Figure 5e. A high pressure N2 chamber is connected pneumatically to a bellows which is mechanically connected to a needle (1mm ID) penetrator. A valve is opened and N2 gas at about 6 atmospheres expands the bellows and drives the penetrator into the ice. As the base of the bellows passes an exhaust port the nitrogen is vented and a mechanical spring pulls the penetrator tip into an elastomer seal and heater. The sample is heated and melted and sampling proceeds in the same manner as for a direct liquid sample. Previous penetrator studies suggested that the energy per volume required to sample cryogenic ice was less than 50 J/gram. The ice on the shoreline of a Titan lake is thought to be comparable to a crusty slush rather than consolidated cryogenic ice. Studies done on needle penetrators in frozen ice (-13 °C) samples demonstrated the collection of >7 mg of ice in under 1 J impact energy which is easily achievable with the pneumatic system described in Figure 5e and provides more than the required sample size for the RIT/Orbitrap and double the volume required for the NMR.

E. SIGNIFICANCE OF RESULTS

1. RIT/Orbi-trap: Instruments like the MSL SAM mass spec are not capable of making complex organic measurements and the gas chromatograph column is subject to clogging. The Orbitrap MS (with the rectilinear ion trap front end) is capable of analyzing both organic aerosols and solids with the ability to measure light and high mass hydrocarbons as well as structure. The results of this second year effort demonstrate clearly that we now have, in combination with the CalTech RIT and French Orbi-trap, the building blocks in place for an integrated RIT/Orbi-trap mass spectrometer instrument with a much higher mass range.

2. Cryogenic NMR: The NMR provides a means by which to analyze complex liquid organics and their structure at Titan cryogenic temps. This instrument is the first entirely cryogenic analytical instrument which is now in a flight-like miniature configuration.

3. SPME: This instrument provides a means of capturing filtered lake solids for bulk analysis as well as providing a medium for holding the organic residue for eventual heating and release into the MS/MS. The results of this second year of research clearly show that SPME can not only provide high resolution spectra of organics, but can do so at very low concentrations, i.e., 2mg/L.

4. Sample acquisition/distribution: We now have a uniform design for delivering both liquids and solids to the triage of instruments and have not only demonstrated the capability through our prototype, but also were able to complete a more flight-like design and identify a viable miniature piezo cryogenic actuator for that design.

FIGURES



Figure 1. Titan Organic Analyzer Functional Block Diagram



Figure 2. 2a) Demonstration of switching architecture, 50 % duty cycle square wave at 1 MHz and 2 kV pk-pk using PIC processor control and FET switching, 2b) Experiment setup in France, demonstrating interface of RIT to our switcher box (center) and generation of trapping waveform with the supply fully loaded, 2c) Development and demonstration of the necessary 'third' switching state, where the waveform is held at a high voltage relative to the ground referenced trapping waveform.



Figure 3a. A miniature low temperature (90K) compatible NMR electronics controller board fabricated at JPL, 80g, .5W



Figure 3b. NMR water spectra obtained from the assembled NMR spectrometer. The upper trace shows free induction decay (marked as "difference," time domain) and the lower trace shows FT NMR spectrum (frequency domain).



Figure 3c. *Left*- the assembled NMR spectrometer w. advanced magnetic coil design. *Right*-the NMR spectrometer with a lap-top PC for data collection, signal processing and display- coke can is shown for a size comparison.



Figure 4a. Diagram of SPME-MS system.





Figure 5a. Recently procured cryo-actuator (25mm dia., thickness 10mm)



Figure 5b. Cross section of the CAD model of the cryogenic actuator and valve along with an assembly blow up



Figure 5c. Bench top sampling system and schematic diagram of the valving with an activation sequence chart.



Figure 5d. Miniature sample and sample handling system in flight like configuration using miniature cryo-actuators



Figure 5e. CAD view of the miniature solid sampler that shows a needle penetrator driven by high pressure N2 gas