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Titan Tholins: Simulating Titan Organic Chemistry in the Cassini-Huygens Era

Morgan L. Cable,[†] Sarah M. Hörst,[‡] Robert Hodyss,[†] Patricia M. Beauchamp,[†] Mark A. Smith,[§,∥] and Peter A. Willis[*,†]

[†]NASA Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109, United States
[‡]Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, Colorado 80309, United States
[§]Department of Chemistry, University of Arizona, Tucson, Arizona 85721, United States
[∥]College of Natural Sciences and Mathematics, University of Houston, Houston, Texas 77004, United States

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1. INTRODUCTION

Titan is the gem of the Saturnian system, an icy world laden with organics and shrouded in an auburn haze. Due in large part to the discoveries of the Cassini-Huygens mission to the Saturn system, our knowledge of Titan has deepened immensely, and this moon is now considered one of the best targets for the study of organic chemistry at a full planetary scale.[1,2]

Several NASA missions have flown by Titan and a lander built by the European Space Agency (ESA) successfully reached the surface. The data from these spacecraft, which include Pioneer 11 (1979), Voyager 1 (1980), Voyager 2 (1981), Cassini (2004—present day), and Huygens (2005), paint a picture of an alien, yet familiar world. Radar mapping, along with infrared (IR) imaging through the methane windows of the thick atmosphere, has revealed a rich mosaic of surface features, from mountain ranges and dunes to dendritic features believed to be channels with liquid methane-ethane flowing in a recent past, and the recently confirmed liquid lakes identified in the polar regions (see Figure 1). Titan is the only other world aside from the Earth in our solar system where the pressure and temperature conditions allow an active hydrological (also termed "hygrological" or "methanological") cycle as well as the permanent presence of liquid on the surface.[3] However, in this exotic world, methane

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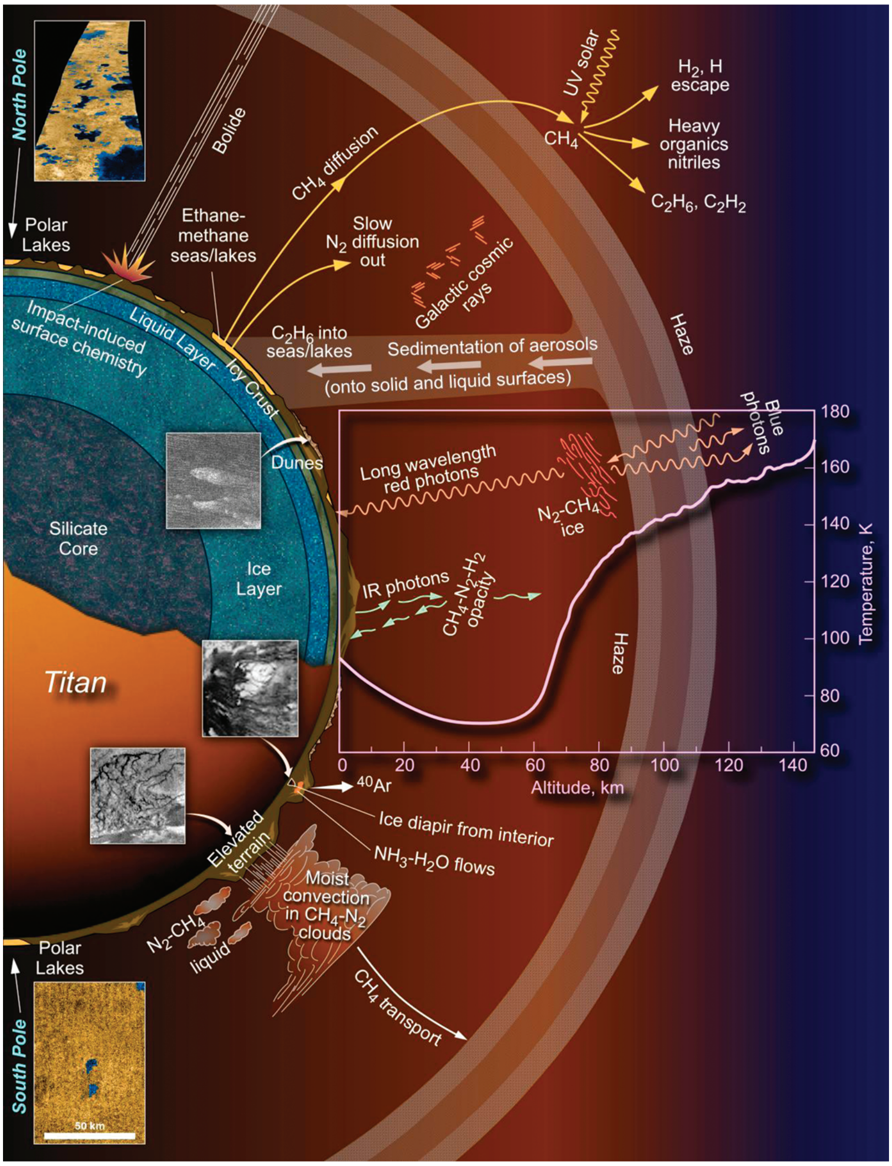


Figure 1. Diagram of the complex nature of the Titan environment. Processes in the atmosphere, lakes, surface and subsurface are all intrinsically linked. Image courtesy of the Jet Propulsion Laboratory, California Institute of Technology.

and ethane take the place of water, forming clouds and precipitating onto the surface to produce lakes, whereas water-ice plays the part of silicates, forming the crust and even possibly erupting as a slurry with ammonia in cryovolcanoes. Exogenous and endogenous energy sources initiate chemical reactions (photolysis, radiolysis) in the atmosphere that produce gaseous hydrocarbons and nitriles, which though various polymerization[4] processes yield solid aerosol particles that grow by a variety of mechanisms and fall to the surface. The end result is a veneer of organic material covering nearly the entire exterior of Titan.[5]

From a chemical perspective, the most interesting aspect of Titan is its inventory of complex organic compounds. The gas and aerosols in the atmosphere have been known for some time,[6,7] and with the recent discoveries of the dunes on the surface[8,9] and the liquid ethane and methane lakes,[10,11] we can also add solid and liquid phases to this inventory. The haze plays an important role in the transfer of radiation in Titan's atmosphere, producing an antigreenhouse effect that cools the surface.[12] The aerosols formed may act as a net sink for C and N atoms. Further, as the aerosols are the ultimate source of particle deposition onto the surface, the composition of the haze most likely dictates that of the dunes and other surface materials and also determines what kind of chemistry can occur there. The evolution of Titan's atmosphere is inexorably coupled to the evolution of its surface and underlying geophysical processes, so by studying the chemistry of the atmosphere and the surface, we may understand Titan as an organic chemical system.

Study of the organic chemistry on Titan involves three major efforts: (1) direct observations and in situ sampling of Titan's atmosphere and surface, (2) laboratory simulation and analysis of products formed in Titan reactors, and (3) generation of models of Titan's atmospheric and surface processes using the data from 1 and 2 (see Figure 2).[13] Many papers[14−16] and several books[5,17−19] have been published regarding Titan, and the reader is directed to these excellent resources for more details concerning Titan's chemistry, geology, and history.[20] Our current understanding of

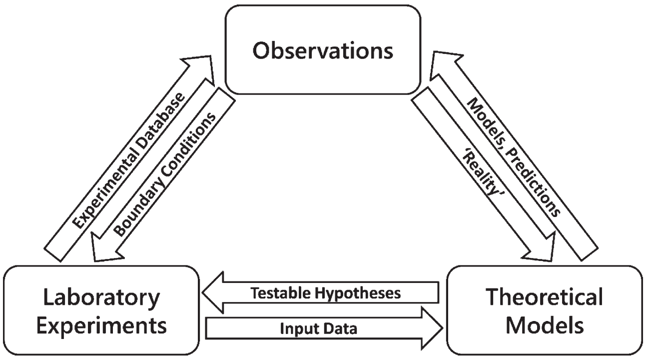


Figure 2. Methodology to study objects and phenomena in the solar system, with useful interactions indicated by arrows. Adapted with permission from ref 238. Copyright 1987 Elsevier.

Table 1. Composition of Titan Atmosphere

gas[a]	fraction (%)
N_2	94−98
CH_4	1.8−6.0
H_2	0.1−0.2
CO	0.005
^{40}Ar	0.005

[a] Trace components: C_2H_6, C_2H_2, C_3H_8, C_2H_4, ^{36}Ar, HCN, CH_3CN, CO_2, CH_3C_2H, C_4H_2, HC_3N, C_6H_6 and H_2O vapor.

Titan is constantly evolving, and the recent missions to this moon have greatly improved physical and chemical constraints on models of the atmosphere. However, laboratory experiments are still necessary to provide data and critical insight that feed into models of the processes occurring in Titan's atmosphere and on its surface. These insights are also instrumental in defining the next series of in situ experiments to perform on Titan, which could further elucidate the processes occurring in the atmosphere and on the surface.

According to recent data from the Cassini Composite Infrared Spectrometer (CIRS)[21] and other observations,[22−26] Titan's atmosphere is composed of nitrogen (95−98%), methane (1.8−5.0%), hydrogen (0.1−0.2%), and carbon monoxide (0.005%), with trace amounts of ethane, acetylene, propane, ethylene, hydrogen cyanide, cyanoacetylene, carbon dioxide, and water vapor (see Table 1). Titan's atmosphere is also denser than that of the Earth, reaching a pressure of 1.5 bar at the surface, and extends much further due to the lower gravity (see Figure 3). For example, to experience the same atmospheric pressure as one would at the summit of Mount Everest on Earth (8.85 km), one would have to be at an altitude of around 25 km on Titan—3 times higher! Briefly, the currently accepted atmospheric model of Titan starts with photochemistry in the high altitudes (thermosphere and ionosphere, 650 km and above). Short-wavelength UV radiation (<155 nm) is absorbed by methane and forms radicals, which lead to light hydrocarbons. Further, extreme ultraviolet (EUV) radiation (<80 nm) and the high-energy tail of the Saturnian magnetospheric energy flux produces ions through photoionization and dissociative photoionization, as well as radicals and atoms in ground and excited states either through direct photodissociation or electon−ion recombination.[27] The excited-state atomic nitrogen from dissociation of N_2 above 700 km reacts with the hydrocarbons to form nitriles.[28] At intermediate altitudes (∼520 km), long-wave UV radiation (>155 nm) causes photolysis of the light hydrocarbons, forming heavy hydrocarbons and more complex organics in a detached haze layer.[29] These spherical particles combine through various mechanisms to form fractal aggregates. At lower altitudes (400−500 km), particle surface chemistry dominates and the aerosols react directly with gas-phase radicals.[30] This complex photochemistry produces a main haze layer in the stratosphere 100−300 km above the surface, with several "detached" haze layers above this up to hundreds of kilometers.[31] The aerosols act as condensation nuclei for condensable species in the troposphere (42 km and below), including hydrogen cyanide and methane, as they fall to the surface.[32,33]

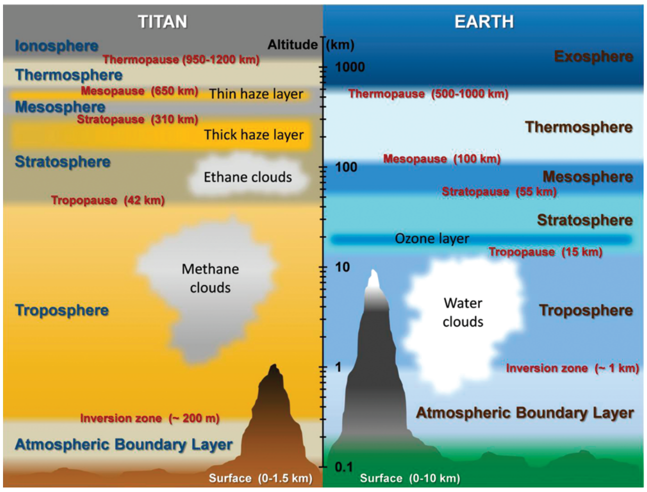


Figure 3. Vertical profile of the Titan and Earth atmospheres. Note the similarities in stratification (atmospheric boundary layer, troposphere, stratosphere, etc.) and the presence of clouds but the fact that the Titan atmosphere is extended due to less gravity on this moon than Earth. Figure adapted from ref 14. Copyright 2010 Nature Publishing Group.

At the surface of Titan, there are several putative energy sources. The heat from cometary and meteoritic impacts can produce oxygen-bearing molecules, if the water-ice regolith melts long enough to react with the deposited organic particulates from the atmosphere.[34,35] Similar organic chemistry might also occur in areas of cryovolcanism,[36,37] though the existence of conclusive evidence for cryovolcanoes is still under debate.[38,39] Lightning or corona discharges may also play a role in the complex chemistry of the atmosphere and surface at low altitudes;[40,41] however, no irrefutable evidence of lightning has yet been found, despite several experiments dedicated to this purpose.[42−45]

The complexities of Titan's organic chemistry have inspired many to simulate these conditions in the laboratory.[46−48] The resulting aerosols from such endeavors have been deemed "tholins" and are highly varied in their production methods and properties. No comprehensive, Cassini-Huygens era review of tholins exists; one thorough review by Coll et al. in 1998 summarized tholin production and properties,[49] another in 2002 by Raulin and Owen[13] gave a brief overview of the chemical composition of tholins, and a third recently published on radiolysis and photolysis of icy satellite surfaces included one short section on tholins.[50] This review summarizes the plethora of tholins reported in the literature since the arrival of Cassini-Huygens and devises a metric by which we can compare these materials in terms of their properties and relevance to our current understanding of the chemistry occurring on Titan.

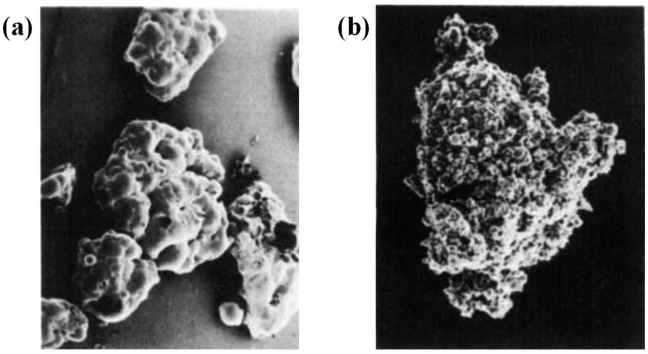


Figure 4. Scanning electron microscopy images of some of the first tholins, the sticky, brownish residue named for its "muddy" appearance. (a) SEM image of spark discharge tholins, 20× magnification. (b) SEM image of UV irradiation tholins, 207× magnification. Reproduced with permission from ref 46. Copyright 1979 Macmillan Publishers Ltd.

2. THOLINS: A HISTORY

Following the seminal Urey-Miller experiment in 1953,[51,52] experimental simulation of the chemical evolution of a planetary atmosphere has become a mainstay in atmospheric chemistry and related fields. Initial work focused on simulating conditions of the early Earth (for an excellent review of the first synthesis and discharge experiments performed in N_2/CH_4 mixtures, see Coll et al.[49]), but expansion to include the atmospheres of other planets and satellites soon followed.

The first experiment involving UV radiolysis of a N_2/CH_4 mixture was performed by Dodonova in 1966.[53] UV radiation (125−170 nm) was found to produce hydrocarbons and HCN, though this result is now considered controversial because the dissociation of N_2 requires wavelengths on the order of 80 nm[54,55] unless two-photon processes[56] or other mechanisms are invoked. Only after the application of an electric discharge, where charged particles influence the chemistry, were nitrogen compounds observed reproducibly.[57−59] Following this realization and its implications for Titan atmospheric chemistry, reactors started to include various energy sources, from hot and cold plasmas to γ-radiation and soft X-rays.

The term "tholin" was first used to describe the sticky brownish residue formed via irradiation (UV or electrical discharge) of cosmically relevant gas mixtures by Sagan and Khare in 1978 and published a year later (see Figure 4).[46] The word was derived from the Greek "tholos" (θολός), which translates directly as "dim" or "not clear" but was interpreted as "muddy", and the name stuck (though the authors also contemplated using the term "star-tar", which we enjoyed immensely). Since its introduction to the scientific literature, many discharge reactor products have been called tholins, including simulated material believed to be present on Jupiter, Neptune's moon Triton, and other comets, centaurs (minor planets), icy moons, and the early Earth.[60−64] However, as we are only interested in the tholins relevant to Titan, for the purposes of this review *we define tholin as a complex organic mixture formed specifically in Titan atmospheric simulation experiments, i.e., synonymous with "Titan tholin"*. We further constrain this definition to an aerosol or solid deposit composed of both large and small molecular constituents with a low C/N ratio and optical properties analogous to the Titan haze. Therefore, tholin composition may include large macromolecular species, such as those detected by the Cassini plasma spectrometer/electron spectrometer (CAPS/ELS)[65,66] and ion beam spectrometer (CAPS/IBS),[67] and also small species adsorbed or condensed onto the surface of these aerosol particles. This is significant when considering atmospheric modeling scenarios, which often will only perform calculations and simulations up to a few carbon atoms and then assume anything larger than this is a tholin.[27,31,68,69] This definition is also important in terms of understanding the chemistry of these materials, as gas-phase and liquid/solid-phase analyses are relevant to detect both the small adsorbed molecules and the large aggregate molecules, respectively. We should also stress the point that, according to the definition we use here, *there are no tholins on Titan*. The term tholin refers *only* to organic material produced in simulated Titan conditions here on Earth, and is therefore subject to our biases and limitations regarding effective reproduction of the Titan environment. Tholins are useful in teaching us *how* to think about the chemistry on Titan, but this information must not be taken out of context; what we actually discover on Titan may be much different. Ultimately, as our knowledge of the measured and observed properties of chemical species on Titan improves, we expect the properties of tholins to converge with those data, so that we may better model and understand Titan as a complete organic chemical system.

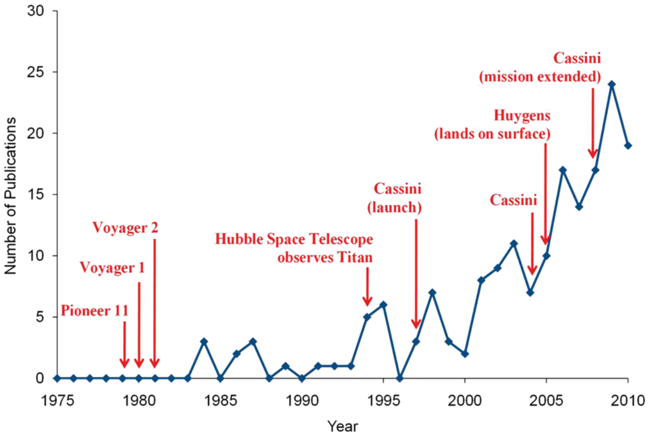


Figure 5. Number of publications with the terms "Titan" and "tholin" by year (records via Web of Science). Publication peaks correlate well with the dates of spacecraft launches and observations of Titan. Unless otherwise specified, mission labels indicate Titan flybys.

After Voyager data confirmed the presence of a thick atmosphere on Titan composed of nitrogen and methane (along with other trace constituents) in the early 1980s,[70,71] production and characterization of tholins began in earnest (see Figure 5).[46,48,72−75] It was soon recognized that study of solid products formed in the laboratory under simulated Titan conditions could yield important information regarding the role of aerosols in the behavior of Titan's atmosphere. These laboratory analogues could help provide data, such as optical properties and estimated mole fractions of constituents, to augment atmospheric models, aid in analysis of remote sensing data, and gain a better understanding of the complex processes at work. We are led to generating tholins in an attempt to interpret observations and data from Titan missions.

As improvements in atmospheric simulation reactors bring us closer to replicating the Titan environment, one might assume that tholins produced in these reactors would be more accurate representations of the actual material on Titan. However, many hurdles remain before this assertion can be made, and it is an iterative process. As we learn more from in situ experiments on

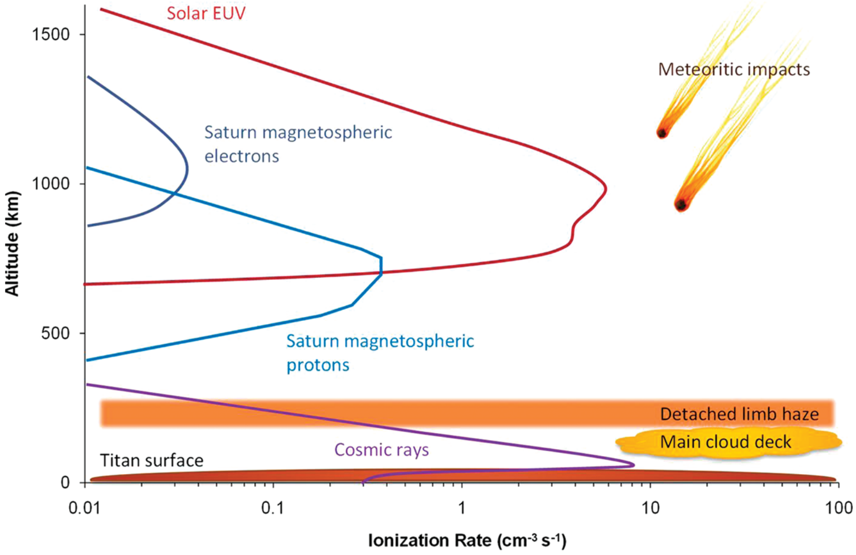


Figure 6. Exogenous energy sources capable of affecting the atmospheric chemistry on Titan. Photon fluxes at global mean conditions. Adapted with permission from ref 27. Copyright 2009 Elsevier.

Titan, we can work toward improving relevant simulants on Earth. We cite the properties of various tholins reported in the literature in an attempt to establish which remain consistent with the improving mission data and models, in order to better understand this enigmatic moon.

3. METHODS OF THOLIN PRODUCTION

In order to gain a better understanding of the chemistry of Titan, many attempts have been made to replicate the atmospheric (and potential surface) components of Titan in laboratories on Earth. All of these "Titan reactors" use some type of discharge or radiation source to mimic one or several of the energy sources capable of generating radicals and other activated species in Titan's atmosphere. For instance, a laser-induced plasma discharge replicates the heat released during a period of meteoritic impact, whereas UV irradiation simulates solar irradiation of the upper atmosphere (Figure 6). Here we will cover the following reported methods of tholin generation: cold plasma discharge, hot plasma discharge, UV irradiation, γ-radiation/soft X-rays, and proton and electron bombardment. We explore each technique, noting how organic material is produced and what processes on Titan are analogous. We then cover the common limitations present in most techniques,and finally describe recent and future advancements to overcome these limitations.

3.1. Tholin Production in the Laboratory

Historically, plasma discharge was the popular choice for production of organics in the laboratory due to the high yields associated with this method. In the context of Titan, however, where the composition of organic material produced is highly dependent on the type, intensity, and duration of ionization and dissociation processes, the energy source must be carefully considered. Solar UV radiation and EUV photons are the main drivers of photochemistry on Titan.[27] However, the energy inputs of charged particles (i.e., cosmic rays, magnetospheric protons, and electrons) in the upper atmosphere can exceed all other energy input processes, including solar UV (1.6×10^{-3} erg s cm^{-2}), during periods when Titan moves across the Saturnian magnetopause and is fully exposed to solar wind.[5,27,31,76] Further, estimates of aerosols produced by high-energy magnetospheric electrons alone indicate that this mechanism could result in enough organic solids to cover the entire surface of Titan in a layer 4−30 m thick over 4 Gyr.[77] Therefore, although photodissociation and photoionization are still the dominant drivers of atmospheric chemistry on Titan, organics produced by electron impact could also supply a significant fraction of Titan's haze and surface material.

3.1.1. Cold Plasma Discharge. Also known as direct current (dc) electrical discharge, corona discharge, glow discharge, inductive-coupled plasma (ICP) discharge, capacitively coupled plasma (CCP), or silent discharge (depending on the energy source), this method involves plasma electrically excited and sustained to yield reactive species in a gas. Power sources capable of forming a cold plasma discharge include a dc source with a conductive cathode, radio frequency (usually 13.56 MHz), and microwave radiation.[78] These discharges normally occur at low pressure (<10 mbar) and current (<100 mA), such that the electron density is low compared to the neutral gas density.[79,80] Contrary to the name, the electron temperature of "cold" plasmas can typically reach several thousand degrees Celsius. However, only a small fraction of the gas is ionized, usually constrained around the discharge electrode, so the neutral gas heating is low and therefore the *total* gas temperature is often only slightly higher than room temperature.[1,79,81,82] Cold plasmas are distinguished from hot plasmas in that they typically have insufficient field strength to cause electrical breakdown (arcing). Advantages of cold plasmas include the fact that chemical processes are driven by the discharge energy or electron temperature as opposed to the temperature of the neutral gas mixture, and that reactions occur at temperatures that are much lower than thermal reactions at thermodynamic equilibrium. Therefore, the chemistry occurring in cold plasmas is not bounded by thermal or equilibrium constraints, and hence reactive species can be efficiently generated in mild conditions.[83]

Cold plasma discharges can be classified as either positive or negative, determined by the electrode voltage polarity, though the plasmas themselves are neutral. Negative polarity cold plasma discharges involve propagation by electron impact; the electrons accelerated by the electric field collide with neutral molecules to generate ions, metastables, and free radicals, which form new stable compounds.[84,85] Positive polarity coronal discharges ionize gas both by electron impact and photoionization mechanisms, and they tend to produce electrons with higher energy (but with a lower electron density) than negative polarity discharges.[86] One of the first cold plasma discharge experiments to decompose methane applied both negative and positive polarity discharges.[87] It was discovered that both techniques produced "hydrogen, a polymer of composition $(CH_2)_n$, and ethane, ethylene, and acetylene". Typically, negative polarity discharges are used in atmospheric simulations, as the electron density is greater and the ionizing region extends further from the electrode. However, positive polarity discharges can transfer a larger total charge than negative discharges and therefore may provide useful information for trace analyses.[88] Alternating current (ac) discharges can also be used, where the nature of the plasma and electron distribution is basically the same as a negative discharge, but with the plasma formed symmetrically between the two electrodes.

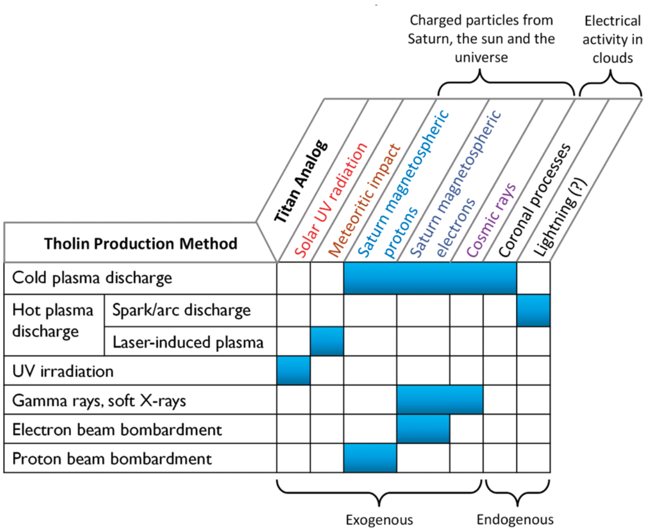
In terms of Titan, the use of cold plasma discharge is usually meant to simulate (1) electrical activity in the methane clouds of the troposphere,[89,90] specifically corona processes which can occur in conditions of low current densities, and (2) cosmic rays and charged particles from Saturn's magnetosphere (see Table 2).[91,92] Magnetospheric electrons enter the Titan atmosphere with energies in the range from 10 eV to 5 keV and produce secondary electrons via electron impact ionization with energies <20 eV.[5] As cold plasma discharges tend to produce electrons in the 5−15 eV range, these plasmas reasonably reproduce the processes occurring from magnetospheric electron precipitation and the resulting secondary electrons, but they do not directly replicate the initial "hot" magnetospheric electrons. In addition, as photolysis processes are actually the dominant mechanism for formation of stable end products in positive coronal discharges, this type of cold plasma discharge also simulates UV irradiation of the Titan atmosphere,[86] albeit in a less controlled manner than UV lamps. The wavelength range is dependent on the gases being ionized in the coronal discharge; for example, the most intense spectral bands of molecular nitrogen occur at 337 and 391 nm.[93]

3.1.2. Hot Plasma Discharge. Here we summarize two reported techniques for producing a hot plasma for atmospheric simulation: spark discharge and laser-induced plasma. Though spark discharges are easier to generate, laser-induced plasmas are more predictable in terms of energy output (spark discharge energies have an uncertainty of ±15%), and they eliminate contamination/catalysis from metals due to electrodes and tend to produce a higher yield of tholins.[94]

Spark Discharge. Spark or arc discharges form plasmas by electrical breakdown of the gas and rely on thermionic emission of electrons from the two electrodes supporting the arc. These discharges require much lower voltages than cold plasma techniques and produce much higher current densities. The very first atmospheric simulation, the Miller-Urey experiment, used a spark discharge as the energy source to form amino acids and formaldehyde from atmospheric conditions representing a hypothetical early Earth.[51] This method is capable of generating large quantities of organic product; experimental evidence suggests that spark discharge methods are approximately 10^4 times more efficient than UV radiation methods for organic synthesis.[95]

Spark discharges were originally meant to simulate lightning in the methane clouds of Titan's troposphere.[94] It was previously assumed that electrical activity in Titan's atmosphere was necessary to account for the abundance of compounds like ethene (C_2H_4) and the dissociation of N_2 in the troposphere.[96,97] However, current models, which take galactic cosmic rays into account, indicate that these compounds could also have been formed without any electrical activity in the troposphere,[28,29] so it is unclear whether lightning actually occurs on Titan; none has been observed to date.[45]

Table 2. Tholin Production Methods and Their Corresponding Titan Analogues[a]



Tholin Production Method		Titan Analog: Solar UV radiation	Meteoritic impact	Saturn magnetospheric protons	Saturn magnetospheric electrons	Cosmic rays	Coronal processes	Lightning (?)
				Charged particles from Saturn, the sun and the universe				Electrical activity in clouds
Cold plasma discharge				■	■	■	■	
Hot plasma discharge	Spark/arc discharge							■
	Laser-induced plasma		■					
UV irradiation		■						
Gamma rays, soft X-rays					■	■		
Electron beam bombardment					■			
Proton beam bombardment				■				
		Exogenous					Endogenous	

[a] More than one method will be necessary to reproduce all of the exogenous and endogenous energy sources of Titan's atmosphere.

Laser-Induced Plasma (LIP). In this technique, a laser (typically Nd:YAG) is used to ionize gas and form a plasma. As in the other plasma discharge methods, laser-induced plasmas are also driven by electron impact. Laser-induced plasmas are used to simulate the temperatures and shock waves of high-velocity meteors entering the atmosphere of Titan[94,98] and previously to replicate the putative lightning of the troposphere as well.[40,41] Though more infrequent than other exogenic energy sources, over time, ionization processes such as meteoritic impacts could be a significant source of atmospheric chemistry.

3.1.3. Ultraviolet (UV) Irradiation. UV radiation produces ions and radicals by photoionization and photodissociation (or photolysis), respectively, which further react to form stable end products. The extent and type of photochemistry is highly wavelength-dependent. For example, methane can be photolyzed effectively in the far-UV range (λ < 140 nm),[99] whereas photolysis of nitrogen requires much shorter wavelengths (λ < 80 nm)[54] (see Table 3). Typical UV light sources include lamps (xenon arc, mercury, deuterium, etc.) and lasers (Nd:YAG, KrF excimer, etc.). Extreme ultraviolet (EUV) and vacuum ultraviolet (VUV) radiation in the range of 10−200 nm can be produced by a synchrotron light source, the electromagnetic radiation produced by cyclic particle accelerators.[100]

Solar UV radiation is the primary source of chemistry in Titan's atmosphere, with a maximum atmospheric ionization rate on the order of 10 cm^{-3} s^{-1} (see Figure 6). Short-wavelength photons (λ < 155 nm) can thermodynamically dissociate methane, but sufficient absorption cross section does not arise until wavelengths of 140 nm or below. Such photons are absorbed by

Table 3. Photodissociation (d) and Photoionization (i) Energies for the Major Components of the Titan Atmosphere[a]

			threshold energy			
molecule	type	photochemical process	kJ/mol	eV	wavelength (λ) range (nm)	ref
nitrogen	d	$N_2 + h\nu \rightarrow N^+ + N + e^-$	2345	24.3	<51	100
	d	$N_2 + h\nu \rightarrow N_2^+ + e^-$	1505	15.6	<80	100
	i	$N_2 + h\nu \rightarrow 2N\bullet$	942	9.76	<80	55
methane	d	$CH_4 + h\nu \rightarrow CH_2^+ + H_2 + e^-$	1465	15.2	<82	100
	d	$CH_4 + h\nu \rightarrow CH_3^+ + H + e^-$	1380	14.3	<87	100
	d	$CH_4 + h\nu \rightarrow CH_4^+ + e^-$	1216	12.6	<99.1	241
	i	$CH_4 + h\nu \rightarrow CH_3\bullet + H\bullet$	439	4.55	<155	55, 99

[a] Note that in some cases the minimum wavelength required for photochemistry to be observed is different from the threshold energy. For example, the bond dissociation energy of N_2 is 942 kJ/mol, which corresponds to a wavelength of 127 nm, but photodissociation does not occur until $\lambda < 80$ nm.

methane in the upper atmosphere, while longer-wavelength photons ($\lambda > 155$ nm) penetrate down into the stratosphere and troposphere.[1] Multiphoton processes may also play a role in the photodissociation of methane in the lower atmosphere by these longer-wavelength photons.[46,99]

Previously, UV irradiation was not considered to be a practical energy source for tholin production because the available UV lamps either did not emit short enough wavelengths to photolyze nitrogen ($\lambda < 80$ nm) or were incompatible with closed or flow reactors.[5] Access to synchrotrons such as the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory in California and the synchroton light source at the Elettra radiation facility in Trieste, Italy, revolutionized the photochemical generation of Titan atmospheric gases, aerosols, and tholins.[100−102] There are many advantages to using UV irradiation as the driver for tholin generation. Most importantly, UV is the primary source of energy in Titan's atmosphere and probably plays the greatest role in affecting the atmospheric chemistry of Titan. In addition, the wavelength range and energy of the light used can be easily controlled, so techniques involving this energy source can be tailored to generate species formed in a particular energy regime (however, this also highlights a disadvantage as well, in that synchrotrons cannot produce a continuum of wavelengths to simulate the whole UV portion of the solar spectrum). Such data is important in understanding which photochemical pathways are dominant in particular regions of the Titan atmosphere, as different wavelengths penetrate to different altitudes. This, in turn, helps to better inform models of the Titan atmosphere.

3.1.4. γ-Radiation and Soft X-rays.

Gamma photons or "γ-rays" are very high frequency electromagnetic radiation photons produced by electron-positron annihilation, fusion, fission, and radioactive decay. These photons have energies above 100 eV and wavelengths in the picometer range. Interaction of γ-rays with molecules typically results in ionization, either by the photoelectric effect (ejecting an electron from an atom), Compton scattering (ejection of an electron and emission of another gamma photon), or pair production (conversion of the γ-photon into an electron−positron pair, followed by annihilation of the positron by a free electron). This ionization of methane and diatomic nitrogen via emitted γ-photons yields a variety of radicals and ions, which react to produce a wide range of compounds. The most common laboratory source of γ-radiation is the β-decay of cobalt-60 (^{60}Co), which is produced artificially by neutron activation of cobalt-59. Cobalt-60 emits two γ-rays (1.33 and 1.17 MeV) and an electron as it decays to the stable isotope nickel-60. As a tholin generation method, γ-radiation has the advantage of producing a high yield of organic material per unit of energy compared to other methods, such as cold plasma, spark discharge, and laser-induced plasma.[98]

X-rays are similar to γ-rays in their energies, though older literature tended to define them by wavelength (with γ-rays typically shorter than X-rays). Now X-rays and γ-rays are distinguished by their origin: X-rays are produced by electronic emission, while γ-rays are from nuclear emission.[103] "Soft" X-rays have energies in the range of 0.12−12 keV (10−0.1 nm), while "hard" X-rays are in the range of 12−120 keV (0.1−0.01 nm). Laboratory sources of X-rays include (1) X-ray tubes, which accelerate electrons toward a target (alloys with tungsten and other metals) with high voltages, causing emission of X-rays from the bombarded metal atoms, and (2) synchrotrons.

γ-Radiation and soft X-rays can simulate certain aspects of the high-energy Saturn magnetospheric electrons that penetrate Titan's upper atmosphere, in addition to the galactic cosmic rays and solar wind that reach the troposphere.[98] Cosmic rays are composed of mostly protons, with some α-particles and the nuclei of heavier elements, and have kinetic energies exceeding 1 GeV.[104,105] Due to the density of Titan's atmosphere, most of these high-energy particles are actually stopped before they hit the surface, resulting in ionization layers deep in the atmosphere.[5,28] In contrast, the solar wind—the stream of charged particles emitted from the upper atmosphere of the Sun (usually electrons and protons with energies in the range of 10^3−10^4 eV)—is typically absorbed at higher altitudes of the Titan atmosphere.[106]

3.1.5. Proton or Electron Beams.

Proton and electron beams are usually characterized by the energy used to generate the beam (i.e., 3×10^{-8} A, 1.5 MeV) or the radiation emitted by the beam (i.e., 20 krad/s).[48] Charged particle beams can be produced using particle accelerators, which mobilize protons or electrons via an electrostatic field of oscillating charge operated in sequence along the beam path. As with the cold plasma and γ-irradiation methods, proton and electron beams are meant to simulate the charged particle-induced processes resulting from exposure to the protons and electrons of Saturn's magnetosphere, respectively. A major advantage of using this type of radiation is that it can be highly tuned to study selective processes. For example, work is currently underway using tunable, low-energy, highly bright electron beams in the 5−500 eV range to selectively study Titan atmospheric ionization processes at high resolution.[107]

3.2. Challenges in Tholin Production Methods

Each technique described above is able to replicate a particular endogenous or exogenous energy source that influences Titan's

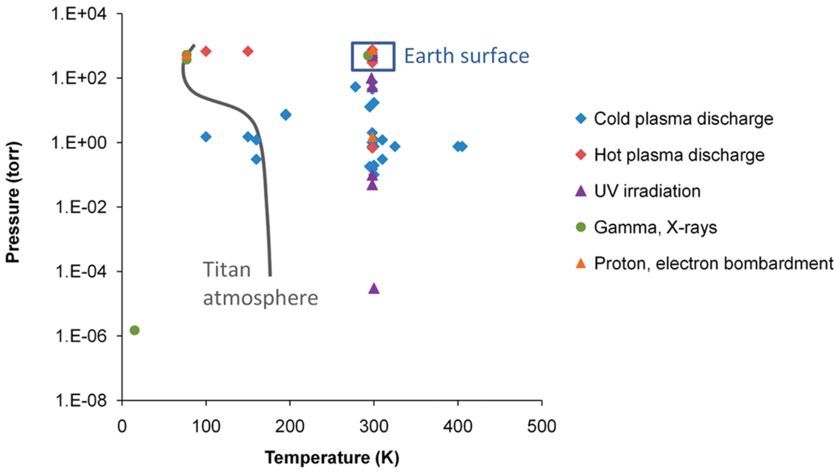


Figure 7. Plot of the temperature and pressure parameters for various tholin generation methods. Note that few methods fall along the profile of Titan's atmosphere.

atmospheric chemistry (see Table 2). However, replication of the energy source is only part of the challenge; the gaseous composition and conditions (temperature, pressure, stratification, etc.) of the Titan atmosphere must also be reproduced. No single method thus far has been able to accurately reproduce all observed conditions of the Titan atmosphere where aerosol formation occurs.[108] Further, issues such as contamination during tholin generation or prior to analysis can compromise results. Here we address the limitations of some of these techniques and how such limitations can detrimentally affect the properties of the tholins produced in terms of their relevance as Titan analogues.

3.2.1. Power Density. The production of significant amounts of organic material via atmospheric chemistry on Titan occurs on extended time scales (the rate of aerosol formation is approximately 3×10^{-13} kg m^{-2} s^{-1} [109,110]), and for obvious reasons these conditions cannot be duplicated in the laboratory. Most tholin-generation methods circumvent this problem by using power densities significantly greater than what is actually experienced in Titan's atmosphere.[111] For example, 24 h of exposure to cold plasma discharge (10^{20} eV/h) roughly corresponds to 1000 years of irradiation by Saturnian magnetospheric electrons (solar UV excluded) in the stratosphere of Titan.[61] In one extreme case, tholins generated by UV irradiation received a dose exceeding the interstellar near-UV density integrated over the lifetime of the entire galaxy![46] Though meant to yield a sufficient quantity of material for analysis, this most likely results in overpolymerization relative to the aerosol formation and transport processes in Titan's atmosphere.[112] Even limited exposure times using high power densities must be carefully considered, because secondary photolysis of initial photoproducts can occur if the reactant gas is irradiated for an extended period.[113−115] Exposure time should therefore be carefully monitored and the possibility of undesired byproduct formation evaluated for a given method of tholin production.

3.2.2. Oxygen and Water Contamination. The key to tholin production in the laboratory is to generate these organics in the absence of oxygen. No molecular oxygen is present on Titan and, with the exception of a small amount of CO (0.005%) and trace amounts of CO_2 and water vapor, no oxygen-containing molecules are present either. Therefore, the presence of greater than trace levels of water vapor (or even trace levels of O_2) in a Titan chamber can lead to unusual incorporation of oxygen in tholins, which changes the properties of the material significantly. It is difficult to replicate the oxygen-poor conditions of Titan when the experiments are performed on a world where oxygen and water are ubiquitous. Although protocols can be implemented to remove as much water vapor from the reaction chamber as possible (i.e., baking under vacuum and/or flushing with N_2), this contaminant may still be present and react with tholins either during or following production. Further, many of the techniques described here replicate the Titan atmosphere well during tholin formation, but often expose the product to ambient air during sample collection and/or analysis. Several groups have reported contamination due to oxidation and hydrolysis from oxygen and/or moisture.[111,116−121] An experiment by Tran et al. reported an increase in oxygen from 1.4% to 7.2% in tholin samples exposed to ambient air for 7 days.[113] Though it appears that oxygen incorporation from ambient air occurs on a slow time scale[112] and results in very little variation in terms of the IR spectra[122] and complex refractive indices[123] of tholins, the ideal setup would remove this variable completely. Nearly all tholin studies indicate the material produced has a high intrinsic chemical potential and, therefore, greater reactive potential (for more discussion on tholin reactivity, see section 5). Thus, the temporal stability of tholins must also be of concern, with self-reaction and polymerization observed in solution. Definition of the relevant temporal stage of a tholin must be explored when attempting to replicate naturally occurring material.

3.2.3. Incorporation of Trace Species. Higher mixing ratios of minor constituents are often necessary in order to obtain sufficient quantity of trace species in the tholin product for analysis. For instance, Tran et al. irradiated gas mixtures with mixing ratios of acetylene, ethylene, and cyanoacetylene that were 100-fold greater than what actually exists at the north pole of Titan,[116] while a mixture used by Jacovi et al. maintained mixing ratios of these species with 2000-fold greater concentrations than midatmospheric levels.[119] The impact of these changes in the types and relative abundances of products obtained is not fully understood and merits further study.

3.2.4. Temperature. Titan's atmosphere and surface are at cryogenic temperatures, which are often very challenging to maintain over the necessary time periods on Earth during a simulation. In many cases, temperature is not simulated and reactors are operated at room temperature, meaning that certain compounds that would normally condense at 180 K and below are volatile and behave differently than expected on Titan.[124,125] For example, dicyanoacetylene (C_4N_2) has been detected in Titan's atmosphere but not in any experimental simulations carried out at room temperature. Only after cooling the reactor to 100−150 K is this thermally unstable product observed.[126,127] In a similar manner, temperature also affects the physical adsorption of gases onto particle surfaces, and therefore, the implications of methane and ethane condensation onto aerosols cannot be effectively understood without appropriate temperature simulation. For more information on heterogeneous condensation and supersaturation, see section 4.2.1.

Temperature variations also affect reaction rate constants, which alter steady-state concentrations of many intermediates. It has been noted that temperature effects on ion-molecule reactivity in the Titan ionosphere, in particular with regard to branching effects, are largely unknown both in terms of experimental and theoretical studies.[128] In addition, vertical temperature and pressure gradients that exist in Titan's atmosphere are difficult to simulate (Figure 7).[129] These gradients are very likely to be important in the generation of organics, as gases transported downward from the altitude of maximum production can produce material at increasingly higher rates as pressure increases.[77] Therefore, accurate temperature reproduction is vital in order to effectively understand chemical and physical properties occurring on Titan.

3.2.5. Pressure.

High pressure can quench excited states and enhance three-body collisions that would not occur at a significant rate at lower pressures.[116,119] For instance, a study of tholins produced in a capacitively coupled cold plasma discharge found that the aerosol particles were formed faster at higher pressure over the range of 0.2−3 mbar.[80] For plasma generation methods in particular, pressure can affect the densities of the active species (electrons, ions, and radicals) in the plasma and, therefore, the collision frequencies and kinetic energies of these species.[130] Further, it has been demonstrated that nitrogen incorporation into tholins and the degree of aromaticity are quite pressure-dependent.[130,131] It must also be noted that recent analysis of the optical properties of the detached haze layer suggests that thermospheric, not stratospheric, chemistry is the main source of haze on Titan,[132] and therefore, tholin generation techniques should in theory be operating at much lower pressures than initially anticipated.

In practice, however, chamber size limits the realistic production of tholins at the correct pressures. A simple calculation of the mean free path—the average distance a molecule travels between collisions—of a gas mixture of 98.4% N_2 and 1.6% CH_4 at the temperature (175 K) and pressure (2×10^{-4} mbar) of the Titan thermosphere (700 km) yields a distance of 0.20 m. If this were replicated in a chamber at room temperature on Earth, the mean free path increases to 0.34 m. These values are on the same order as the dimensions of a typical tholin generation chamber, resulting in an extremely low collision frequency and exceedingly long periods of time to yield sufficient product for analysis. As a result, a balance must be achieved to simulate the appropriate degree of molecular interaction without biasing a given system toward high-pressure effects.

3.2.6. Wall Effects.

As explained in the previous section, one major limitation in reproducing the Titan atmosphere is the fact that the simulation must be performed in a chamber. Most tholins produced in reactors are deposited as thin films on the walls of the chamber[73,75,108,112,121,122,124,133−136] or on a designated solid substrate.[111,113,115,116,118,130,137,138] These complex organic films are dissimilar in morphology from the aerosols forming on Titan and the spherical particles produced by levitation in other chambers (see Figure 8), which has led many to dismiss these thin films as being adequate analogues due to the presence of a "wall effect".[82,114,139] However, it is not clear if such films are chemically different from either laboratory-generated particles or the aerosol particles on Titan. Catalysis and nucleation processes may differ in the first few monolayers of formation on a solid substrate compared to an aerosol particle; however, once the surface is blanketed with a coating of organic material, it is still unknown whether or not thin film chemistry is any different from that at the aerosol particle surface. In fact, the composition of seed particles on Titan and how they grow into aerosols is still a mystery, making any comparisons between formation mechanisms of tholins on Earth premature at this stage. Tholins produced as deposits on substrates can also be useful in studying how to analyze the complex organic species deposited on Titan's surface.

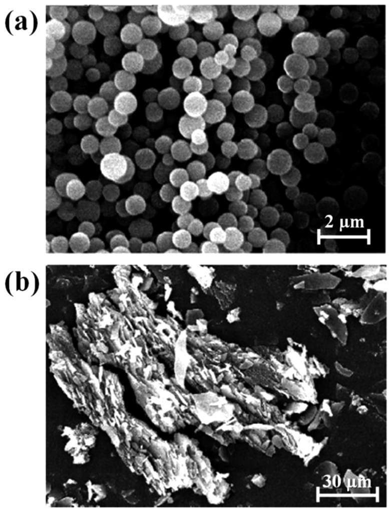


Figure 8. Example of the wall effect. SEM images of tholins produced in identical conditions (a) in levitation and (b) deposited on a surface. Further study is necessary to determine which material is a better analogue to the organics present on Titan. Reproduced with permission from ref 82. Copyright 2006 Elsevier.

3.3. Extending the State-of-the-Art in Tholin Production

Tholin generation methodologies are progressing in terms of (1) effectively replicating the environment of Titan and (2) minimizing exposure of tholin products to ambient conditions prior to or during analysis. A continuous flow reactor developed at Rensselaer Polytechnic Institute removes the problems of secondary photolysis and higher mixing ratios.[113,114,140,141] The flow reactor at the Laboratoire Atmosphères, Milieux, Observations Spatiales in France (nicknamed PAMPRE, a French acronym for aerosol production in microgravity by reactive plasma) takes advantage of electrostatics and flow dynamics to keep the forming aerosols in levitation.[82] However, this method may introduce a separate bias, in that only charged particles are levitated and therefore the aerosol particles are probably more strongly charged than their Titan counterparts.

Many of the techniques discussed here were able to maintain oxygen-free conditions during tholin generation and subsequent analysis via use of glove-boxes and in situ characterization.[108,115,118,124,126,135,139,142−145] Further improvements in cryogenic techniques are enhancing our abilities to maintain these experimental reactors at Titan temperatures. Reactors have been modified to operate at 100−195 K by submerging the gas reaction vessel in a cryogenic fluid such as liquid nitrogen (see Figure 9).[34,112,121,129,135,136,142−144,146,147] However, care should be taken to maintain the appropriate temperature in concert with the correct pressure of the desired altitude being simulated, to prevent undesired side reactions with certain species condensing on the walls of the chamber.[148] Further work is necessary to understand the effects of temperature and pressure on each tholin generation method.

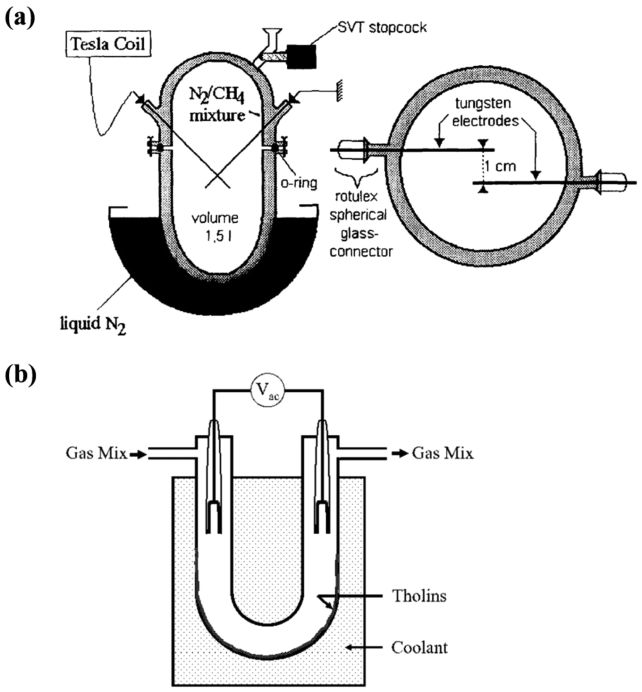


Figure 9. Schematics of tholin reaction vessels capable of operation at 100 K. (a) Spark discharge reactor developed by Coll et al. (Reproduced with permission from ref 135. Copyright 1995 Elsevier.) (b) Continuous flow cold plasma discharge reactor from Sarker et al. (Reproduced with permission from ref 142. Copyright 2003 Mary Ann Liebert, Inc.)

Each method reproduces some aspects of the atmospheric chemistry, but as of yet no single method can successfully replicate all phenomena observed in Titan's complex atmosphere. Techniques using EUV irradiation produce tholins both via photolytic processes and secondary electron (2−14 eV) processes due to the high energy of this radiation. As previously mentioned, positive corona cold plasma discharges also produce UV radiation, so electron impact and photolysis occur with this method as well. One group is developing a program called SETUP (a French acryonym for theoretical and experimental studies useful for planetology) based on a reactor that exposes gas mixtures to both UV radiation and a microwave cold plasma discharge. This method will generate both photon and electron energy sources simultaneously and in a controlled fashion,[149,150] though no results have been reported.

In summary, each method of tholin generation has its own strengths and weaknesses, and it is ultimately up to the researcher to determine which method is appropriate to model a particular phenomenon in Titan's atmosphere or on its surface. It must also be recognized that the results obtained from a given experiment are only valid for a unique set of conditions, and may not be (1) comparable to results from experiments performed in other conditions or (2) relevant to processes occurring on a global scale on Titan.

4. THOLIN COMPOSITION AND PROPERTIES

Sagan was the first to suggest that Titan aerosols are complex mixtures of many species of varying size and saturation;[19] the size variability was confirmed by the Cassini plasma spectrometer (CAPS) instrument, which detected positive ions with masses up to hundreds of daltons and negative ions approaching 10 000 Da.[65−67,151] A number of physical and chemical methods have been applied to determine the unique properties of tholins, and it has been discovered that these organics have widely varying compositions, optical properties, colors, and albedos. We will discuss some of the reported optical and physical properties of tholins, as well as the chemical composition and how these vary with production method.

Some simulation chambers utilize a simple N_2/CH_4 mixture to replicate initial conditions in the Titan atmosphere, while others include some or all of these minor constituents (though often at higher concentrations than actually exist on Titan). We will therefore discriminate between tholins produced from different initial gas mixtures as we investigate the various physical and chemical properties of these organic materials.

4.1. Optical Properties

4.1.1. Absorbance. Observations of the geometric albedo of Titan indicate that the haze material in the upper altitudes (∼520 km and above) is dark in the violet and ultraviolet and relatively bright in the visible and near-infrared.[152] The first tholins produced in the laboratory exhibited optical constants that were very similar to Titan haze, which is why they were proposed as a good analogue to this material.[1,12,60,73,153] Tholins typically exhibit substantial absorption in the blue, most likely due to their many π and nonbonding electronic transitions, giving them their characteristic orange-brown color (though the coloration in tholins reportedly varies from yellow to dark brown).[46,108,117,130,131] Strong absorption at specific frequencies in the infrared (IR) represents a fingerprint of the balance of functional groups within the tholin mixtures and typically shows definitive indication of unsaturated nitrogen (nitriles and imines) and carbon groups and possible aromaticity.[20,130,154,155] This is discussed further in section 4.3.

Many authors have noted differences in absorbance spectra among various tholins generated using different energy sources.[76,124] Even slight variation of experimental parameters within a single method (temperature, pressure, discharge intensity) can induce large changes in chemical composition and resulting spectral properties (see Figure 10).[108,131] For instance, the trend toward UV darkening with increased methane concentration for tholins produced by electric discharge is suggestive of changes in the elemental composition of the solid material as the C/N ratio becomes progressively larger.[124] Though it has been shown for cold plasma discharges that the IR absorbance spectra of tholins produced from capacitively coupled, inductively coupled or dc electric discharges are all similar,[73,108,117] significant variations in IR spectra as a function of deposition pressure have also been reported.[130] Clearly, a systematic study to give a range of measurements would be incredibly useful in generating a better link between tholin absorbance and chemical composition.

4.1.2. Refractive Index. The refractive index of Titan aerosol particles, a result of their chemical composition, is needed to interpret atmospheric measurements of the Titan haze and

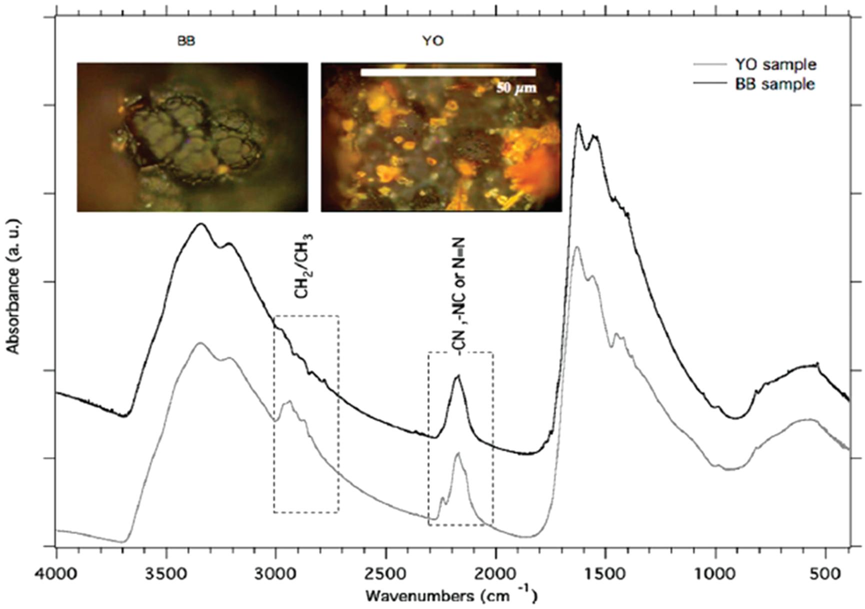


Figure 10. Mid-IR spectra of two tholins produced by dc plasma discharge in the same reactor, illustrating the large degree of variation in the properties of these materials. Images from an optical microscope are in the top left. Reproduced with permission from ref 108. Copyright 2006 Elsevier.

determine the particle size and single-scattering albedo with altitude.[156,157] Use of the refractive indices of laboratory tholins produces a remarkably good fit to the geometric albedo spectra of Titan (Table 4).[1,124]

Material produced in the initial cold plasma discharge experiments matches the optical constants of Titan in both the IR and UV regimes;[73] material produced in other methods (hot plasma, UV irradiation, etc.) has not been able to accomplish this. Tholins produced by UV photolysis are similar to plasma discharge in the real part of the refractive index,[123] but the complex (imaginary) part is an order of magnitude lower in the red and short-IR,[113,137] a property which may be related to the radiation dose.[1,158] The complex part of the refractive index can vary significantly with wavelength, and this variation must be known in order to calculate the aerosol heating rate and atmospheric temperature profile.[12,29,137] To address this problem, Ramirez et al. determined the complex refractive index of cold plasma discharge tholins from 200 to 900 nm and produced a range of measurements with error bars.[138]

Single-scattering albedos calculated from the refractive indices of laboratory tholins in the range of 100−10 000 monomer units yield results greater than the actual Titan value for those produced by electric discharge[73] and less than this value for those produced using UV irradiation.[156] This result suggests that perhaps the Titan haze is some combination of material produced by UV photochemistry and hot plasma discharge. However, McKay showed that these optical constants are highly dependent on the composition of the starting gas mixture.[124] In short, further investigations are necessary to better reconcile the differences in refractive index values of tholins and Titan aerosols.

4.1.3. Reflectance. Optical constants of laboratory tholins can aid in the modeling of Titan's atmosphere on the basis of data from the descent imager/spectral radiometer (DISR) and visual and infrared mapping spectrometer (VIMS) instruments of Cassini−Huygens. However, determining optical constants in the UV/visible range is very complicated and highly dependent on sample optical quality and thickness, and therefore reflectance spectra are a more useful measurement.

Tholins prepared by dc electric discharge are spectroscopically heterogeneous, as evidenced by variation in the visible and infrared reflectance of samples taken in different locations of the same reactor.[108] One sample, more yellow in color, exhibited greater transparency in the near-IR region than a sample that was brown/black in color and therefore revealed more intense absorption bands in this region. In contrast, samples formed using UV irradiation are uniform in color and have sharp IR reflectance bands characteristic of homogeneous material.[113,123,137] Due to the various differences in reflectance spectra, one group defined a set of criteria that can be used to ascertain whether or not they can be used as potential analogues.[108] The criteria are as follows:

(1) the reflectance level in the visible (200−800 nm),
(2) the slope and spectral shape of the reflectance curve in the visible and very near-IR,
(3) the lack/presence of overtone and combination bands in the NIR, and the position of these bands, and
(4) the presence or lack of the 3.4 μm feature of CH_2/CH_3 functional groups.

These criteria can be used to compare tholins produced in the laboratory to the spectra of Titan's remote atmospheric observations. For instance, alternative materials such as polyacetylene and poly-HCN are not considered to be adequate analogues, as their optical properties are inconsistent with Titan's reflection spectrum.[77]

4.1.4. Polarization. Polarization phase curves for tholins produced using capacitively coupled rf cold plasma discharge have a bell-shaped positive branch and a shallow negative branch, indicative of irregular particles. The maximum of polarization (P_{max}) is inversely proportional to particle grain size, such that the average grain diameter of particles in the Titan haze must be smaller than 100 nm.[159] However, it should be noted that this maximum value of 100 nm is highly altitude-dependent and is likely to be much greater in the lower atmosphere (stratosphere and troposphere).[30,32] The P_{max} value also increases with decreasing wavelength due to the increasing absorbance of these shorter wavelengths. These values are in agreement with Cassini−Huygens observations.[160,161]

Table 4. Measured Refractive Indices for Various Tholins[a]

tholin production method	real refractive index (n)	complex refractive index (k)	wavelength/range (μm)	ref
UV irradiation (115 nm < λ < 400 nm)	1.34–1.36	0.016–0.030	0.532	156
UV irradiation (λ > 155 nm)	nd[b]	0.008–0.20	0.375–1.55	137
	1.5–1.7	0.0101–0.2257	0.2–2.5	123
cold plasma discharge (dc)	1.53–1.68	0.0003–0.0287	0.200–0.900	138
	nd	0.0003–0.04	0.200–0.750	162
	1.6–1.7	0.004–0.08	0.025–1000	73

[a] Note that most of the real refractive indices are within the limits of 1.5 < n < 2.0 calculated for the Titan haze.[32,152] [b] No data.

4.1.5. Fluorescence. Tholins produced in a dc spark discharge at room temperature exhibited strong fluorescence under 514 nm laser excitation.[108] Tholins produced via electric discharge (60 Hz ac) at 195 K produced broad, featureless fluorescence around 471 nm under 410 nm excitation in acetonitrile.[143] Separation using thin-layer chromatography (TLC) indicates that these fluorescent species are polar. Further, the fluorescence spectra were unique for solid tholin, tholin in ice, and tholin that was heated in water, meaning that this can be used as an indicator of the exposure of these organics to water and/or heat.

4.2. Physical Properties

4.2.1. Solubility. Most solubility measurements of tholins are performed using a procedure developed by McKay, where a known mass of tholins is dissolved in a known volume of solvent, the cloudy mixture is filtered, and the solvent is evaporated from the filtrate to obtain the mass of tholins dissolved in the saturated solution.[124] Using this technique, it has been reported that most tholins exhibit an affinity to polar solvents.[61,124,129] Tholins produced using one cold plasma discharge method are soluble in nitriles on the order of a few milligrams per milliliter.[162] However, tholins produced in a photochemical flow reactor were found to be insoluble in all solvents tested.[123,140] This result supports the notion that tholins produced using different techniques are fundamentally different in terms of physical and chemical properties.

Another method for measuring solubility takes into account that, for nonhomogeneous solids, some molecules may be completely soluble in the solvent while others may be in saturation equilibrium. Therefore, Carrasco et al.[155] devised a protocol to quantify two parameters: (1) the solubility ratio of the insoluble to soluble molecules in a sample and (2) the average solubility of the soluble material alone. They first systematically added a supplementary amount of tholin to a supposedly saturated solution and then retrieved and massed both soluble and insoluble fractions. The average solubility of the soluble fraction was then obtained by partially dissolving the solid in a limited amount of solvent to obtain a saturated solution and then repeating the procedure of McKay. Using this technique, solubilities on the order of 19–35% in methanol and 3–5% in toluene were obtained, confirming the large percentage of polar species in tholins.[155] However, in most of these samples there existed a significant fraction, in some cases up to 81% by mass, of organic material that was insoluble in all solvents tested.[155] A similar finding was made for tholins produced in a photochemical flow reactor.[140] This suggests that the chemical structure might involve a limited fraction of polar molecules bound to a large, insoluble nucleus. The solubility of tholins both in polar and nonpolar solvents appears to increase after exposure to oxygen, suggesting the breakdown of this insoluble nucleus upon oxidation.[124]

The relative insolubility of tholins in nonpolar solvents has implications for various processes on Titan, namely, the lake/sediment composition and cloud processes. In terms of lake composition, this property strongly suggests that very little organic material will be dissolved in the liquid hydrocarbon lakes at the poles.[162] Most likely, the only detectable compounds in these lakes will be linear and cyclic alkanes (C_4–C_7) and alkenes and aromatics such as benzene and toluene.[163,164] The remaining tholin material will most likely exist as a sedimentary deposit of the lakebed, as virtually no organics float on liquid methane or ethane.[1] Further analyses are currently underway to explore the sedimentation of various organic species out of methane and ethane and will be reported in a subsequent publication.[165]

The solubility of tholin particles in methane and ethane is also significant in understanding cloud processes on Titan. If the organic material on Titan is not soluble in methane and ethane, then the particles in the Titan haze will not act as effective nucleation sites for these liquids in the atmosphere, reducing heterogeneous condensation and enabling supersaturation.[124,166] However, even submonolayer adsorption can explain the presence of clouds on Titan. Curtis et al. discovered that monolayers of methane adsorb onto the surface of tholin particles at saturations less than unity.[167] Therefore, methane cloud nucleation could still occur on the adsorbed methane, not the tholins themselves, forming methane cloud particles without reaching supersaturation. This is supported by recent measurements of the methane column abundance on Titan by Cassini, which suggests that methane is not supersaturated in the troposphere.[89]

A surprising finding was that some tholins produced using the same method—cold plasma discharge—exhibited poor solubility in polar solvents such as water and acetonitrile,[155] while others had 10-fold higher solubility[129,142] or were insoluble in liquid hydrocarbons but soluble in nitriles.[162] This underscores the fact that even tholins generated using similar techniques and with comparable C/N ratios can have very different properties.

4.2.2. Thermal Properties. Pyrolysis of tholins induces release of volatile components and yields various pyrolysates, with a maximum number of compounds released at around 300 °C and a gradual decrease after 700 °C.[74] The types of compounds produced will be addressed in section 5 (Tholin Reactivity). Heating tholins to temperatures of 450 °C and above appears to destroy short wavelength absorbance bands and increase continuum absorption.[46]

4.2.3. Particle Size Distribution and Morphology. The DISR spectral radiometer and aerosol collector and pyrolyser (ACP) carried by the Huygens probe provided the first in situ measurements of Titan's aerosols, and through scattering analysis the aggregate structure of these particles was verified.[30,161] The data indicate that the particles initially have spherical form above the stratosphere and then begin to aggregate into fractal-like (high surface area) structures at the detached haze layer.[132,168,169] Most Titan models assume a fractal dimension of 2, where aggregates grow under a ballistic cluster-cluster diffusion aggregation process (see Figure 11).[170]

Scanning electron microscopy (SEM) analysis of tholins produced in the PAMPRE reactor (capacitively coupled rf plasma discharge) indicate that the tholins produced in levitation are semispherical with rough surfaces, and the particle size (0.5−1.5 μm in diameter) is similar to estimates of Titan's aerosols[171,172] and tholins produced using UV irradiation (Table 5).[118,173] Conversely, tholin material deposited on a glass vessel inside the same chamber has the form of a multilayer film with no spherical particles present, emphasizing the morphological variation of the wall effect.

SEM analysis of tholins produced via UV irradiation of ∼2% acetylene in nitrogen revealed particles with a mean diameter of 0.6 μm that were amorphous, spherical, and "sticky".[173] The mean diameter was dependent on the mixing ratio of acetylene; 0.2% yielded 0.4 μm diameter particles, and 20% acetylene produced particles with diameters of 0.8 μm. This indicates that particles formed in different parts of the Titan atmosphere may have different size distributions.

High-resolution transmission electron microscopy (TEM) images of capacitively coupled cold plasma generated tholins (PAMPRE) reveal a very disordered nanostructure with some coherent domains on a nanometer scale.[117] For these tholins, average grain size increases when (1) methane concentration increases, (2) gas flow decreases, and (3) plasma duration increases up to a limit.[159]

SEM images of tholins produced at LISA (dc cold plasma discharge, 4 kV, 80 mA) at room temperature revealed aggregates of 100 nm spherical particles into quasihomogeneous distributions of larger 1 μm particles, visible to the naked eye as a yellow powder. However, tholins produced at low temperature (100−150 K) were much darker in color and semiliquid, and solubility experiments suggest condensation of nitriles on the surfaces of these ∼0.3 μm diameter spheres.[129] Therefore, further low-temperature studies of tholins may be necessary to better elucidate the morphology and growth of Titan aerosol particles.

4.3. Chemical Composition

4.3.1. Functional Groups. Early on, it was believed that long-chain alkanes and alkenes were important components of tholins.[46] Further work has shown that tholins are largely highly nitrogenous, unsaturated molecules consistent with highly unsymmetrical polycyclic aromatic nitrogenated hydrocarbons (PANHs), conjugated imines and nitriles with some degree of aromaticity. The various classes of compounds produced using each tholin generation method are summarized in Table 6, and discussed below.

Cold Plasma. Tholins produced in a capacitively coupled cold plasma discharge reactor at low pressure are composed of polar molecules, aliphatic chains, primary and secondary amines, conjugated nitriles and/or isocyanide, imines, and heteroatomic or heterocyclic groups. Most of the molecules identified by mass spectrometry in negative ion mode were terminated by methyl, amine, or nitrile groups.[155] This is fairly representative of the variety of compounds produced in this method of tholin generation, though it has been demonstrated that positive polarity cold plasma discharge leads to more saturated hydrocarbons (i.e., mostly single C−C bonds, or saturated in hydrogens), while negative polarity produces more unsaturated hydrocarbons (with many double and triple C−C bonds).[88] As mentioned previously, cold plasma discharge reactors are pressure-dependent. Work involving tholin formation at various deposition pressures indicates that tholins produced at low pressures (13−26 Pa) may be better representatives of Titan's haze than those formed at high pressures.[130]

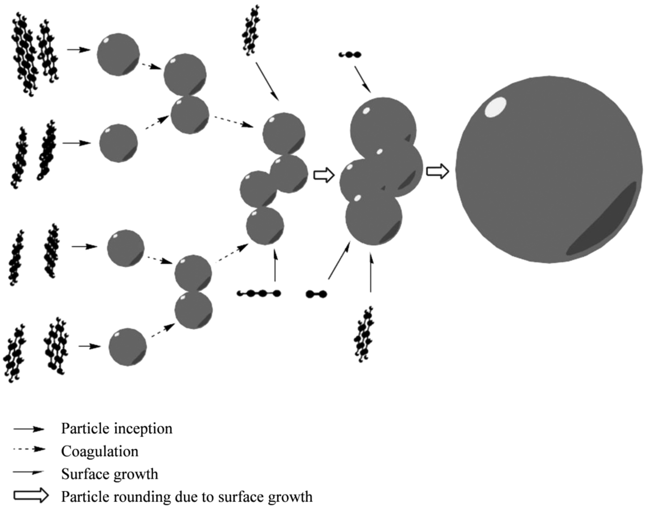


Figure 11. Method of aggregation of aerosols into larger particles, shown here for polycylic aromatic compounds. Eventually the surface chemistry yields a new, larger primary particle. Reproduced with permission from ref 30. Copyright 2011 Institute of Physics Publishing.

Sagan et al. found many polycyclic aromatic hydrocarbons (PAHs) in tholin material produced via cold plasma dc discharge in a continuous flow system, with an estimated 6% of all tholin carbon tied up in aromatic ring structures.[60] Fused-ring systems were observed in tholins produced using inductively coupled cold plasma discharge at low pressure;[130] this was confirmed by 3D fluorescence measurements of tholins produced in a similar reactor.[143] However, no PAHs were detected in tholins generated using capacitively coupled cold plasma discharge under similar conditions (300 K, 90/10 N_2/CH_4 mixture) but slightly higher pressure (0.75 Torr).[117] This may be due to reactor run time in the capacitively coupled cold plasma case or thermal degradation during laser desorption used for chemical interrogation. For the inductively coupled cold plasma discharge, it was discovered that aromatics form quickly (on the order of seconds), while nitriles and amines form later (hours).[122] At lower temperature (100−150 K), only benzene and no other aromatics are produced,[88] though it is possible that the reactor was run for an insufficient amount of time to see higher order PAHs due to decreased reaction rates at these temperatures. Exact mass Fourier transform mass spectrometery (FT-MS) of both cold plasma[112] and EUV generated tholins[115] show essentially no nitrogen-free material, with C/N ratios below 2 and unsaturation levels consistent with high degrees of both cyclization and aromaticity in midrange molecules (200−300 Da). This virtually rules out pure PAHs in favor of PANH-type structures.

Tholins produced in a cold plasma discharge of methane, nitrogen and 0.01% carbon monoxide at 100−150 K revealed a plethora of compounds (194 total) upon interrogation with IR and GC−MS, including hydrocarbons, nitriles, alcohols, diols, aldehydes, and ketones.[144] Of notable interest was the detection of oxirane (ethylene oxide, C_2H_4O), a heterocyclic species that

Table 5. Size and Morphology of Tholin Particles Generated from Various Methods

production method	analysis[a]	particle/grain size (nm)[b]	agglomerate size (μm)[b]	morphology	ref
capacitively coupled rf cold plasma (PAMPRE)	SEM	300−500	40−80	spherical, porous	155, 159
	TEM	200−1200	n/a	quasispherical, form clusters	117
	SEM	500−1500	larger than UV-generated aggregates	quasispherical, rough surface, solid, easily form aggregates	82
cold plasma at LISA (dc, 4 kV, 80 mA)	SEM	100	∼1	spherical, quasihomogeneous distribution	129
spark discharge (ac, 500 kHz)	SEM, TEM, SMPS	162−500	n/a	quasispherical, easily form aggregates	167, 239
UV irradiation (deuterium lamp, 115 < λ < 400 nm)	TEM	50	n/a	spherical	176
UV irradiation in a photochemical flow reactor (Hg lamp, λ = 185, 254 nm)	SEM	150−340	formed aggregates	spherical, amorphous, rough surface, easily form aggregates	114
UV irradiation (Hg lamp, λ = 185, 254 nm)	SEM	100−700	independent spheres and aggregates	spherical, amorphous, rough surface, easily form aggregates	118
	SEM	400−800 (dep. on amt. of C_2H_2)	up to 15 particles (no size given)	spherical, amorphous, easily form aggregates	173

[a] Abbreviations: Scanning electron microscopy, SEM; transmission electron microscopy, TEM; scanning particle mobility sizer, SMPS. [b] Huygens measurements suggest the spherical aerosol monomers are ∼100 nm in diameter, and aggregates will have diameters of ca. 0.1 μm[157].

was more than an order of magnitude more prevalent than any other oxygenated species. Previous atmospheric models[174] predict the formation of formaldehyde or methanol, neither of which were detected in this experiment. A reactive heterocyclic species such as oxirane could initiate interesting chemistry via ring-opening reactions such as nucleophilic addition, hydrolysis, or de-epoxidation.

Hot Plasma. It has been proposed that tholins produced by hot plasma discharge are more unsaturated due to the harsh conditions (high pressure and temperature) and potential for radical generation, while those in cold plasmas experience a milder environment driven mostly by electron-impact and therefore tend to contain linear and branched hydrocarbons and nitriles.[79,88] However, a thorough examination of the literature (Table 6) does not support this claim, as both cold and hot plasmas can yield tholins of varying degrees of saturation. We therefore note that, as with many complex organic compounds, such broad statements of tholin properties are often rendered inaccurate as soon as they appear in the literature. One observation that is consistent is that hot plasmas tend to produce more organic material than cold plasmas; in one case, laser-induced plasma generated 2 orders of magnitude more material than a dc cold plasma technique.[79]

The visible albedo of tholin samples from a dc spark discharge generator appears to be a function of the sp^2/sp^3 ratio and the nitrogen content.[108] Many studies show that unsaturations are most probably located on nitrogen as opposed to carbon, so few $C{=}C$ bonds are detected.[142] Raman spectra (λ_{ex} = 244 nm) of tholins produced using dc spark discharge indicate amorphous structure with small (5−6-fold), nitrogen-substituted aromatic rings and chemically bonded CN.[108]

Interestingly, for spark discharge-generated tholins, PAHs are a common component when the initial gas mixture has 10% methane. However, once the methane abundance drops below 1%, the amount of PAHs in the tholin sample falls off quickly.[175] At the average Titan atmospheric methane concentration, both the aromatic and aliphatic pathways persist.

UV Irradiation, Long Wavelength (λ > 100 nm). UV irradiation reactors unable to photodissociate nitrogen produce only saturated and unsaturated hydrocarbons,[116,141] unless cyanoacetylene is included in the initial gas mixture, upon which acetonitrile and various N-containing compounds are formed.[55,113]

UV irradiation reactors where 115 < λ < 400 nm generate tholins composed of aliphatic unsaturated hydrocarbons, benzene, and toluene.[119,176] For UV radiation at 121.6 nm, ethane was the primary product, while at 248 nm acetylene is the primary product.[99] This is most likely due to absorption of three photons rather than two, indicating that methane probably undergoes both photodissociation and photoionization at 248 nm.

UV Irradiation, Short Wavelength (λ < 100 nm). For UV irradiation, wavelengths capable of dissociating N_2 are critical in order to form tholins containing nitrogen. Experiments involving various mixtures of CH_4, N_2, H_2, and Ar suggest that tholin formation starts with photoionization of N_2 to form a primary N_2^+ ion, which reacts with CH_4 via the dissociative charge transfer reaction to produce CH_3^+.[100] Interestingly, this precursor seems to selectively enhance formation of unsaturated organics, specifically aromatics (benzene, toluene) in the presence of N_2, consistent with Cassini observations of the upper Titan atmosphere.[151,177]

Benzene can be formed using EUV irradiation (60 nm) of a nitrogen/methane gas mixture via N_2 catalytic photoionization;[100,102] highly nitrogenated, heavily unsaturated compounds are also formed due to processes involving the HCCN radical species generated by $N(^2D)$ formed at 60 nm.[115] Other products of this energetic radiation include ammonia, acetylene, ethylene, and various hydrocarbons (up to C_8), nitriles, and primary amines.[102]

γ- And X-rays. γ-Radiation produces tholins in high yield compared to laser-induced plasma, spark discharge, and cold plasma discharge.[98] Typical products include saturated hydrocarbons,

Table 6. Various Compounds Produced in Different Tholin Reactors Organized by Reference Number[a]

tholin production method		**saturated hydrocarbons (methane, ethane, etc.)**	**aromatic hydrocarbons (benzene, naphthalene, etc.)**	**unsaturated hydrocarbons (acetylene alkynes, etc.)**	amines (ammonia, primaryamines)	heterocyclic compounds (pyridine, tetrazine, etc.)	**nitriles (HCN, butenenitrile, etc.)**	O-containing compounds (aldehydes, ketones, etc.)	prebiotic molecules (amino acids, nucleobases)
cold plasma discharge		1, 61,74,[b] 79, 82,[b] 88, 92, 96, 98, 129, 130, 133,[b] 142, 144,[c] 155, 182,[b] 184,[c] 185, 231	60, 61, 74,[b] 79, 82,[b] 88, 92, 96, 108, 122, 126, 129, 130, 133,[b] 143,[d] 144,[c] 155, 180, 182,[b] 183,[b] 184,[c] 231[b,d]	1, 61, 74,[b]79, 82,[b] 88, 92, 96, 108, 117, 122, 126, 129, 130, 133,[b] 142, 143,[d] 144,[c] 145, 155, 180, 182,[b] 184,[c] 185, 206, 230	61, 74,[b] 112, 117, 122, 130, 142, 155, 182,[b] 183,[b] 206, 231	74,[b] 92, 108, 122, 130, 133,[b] 145, 155, 180, 182,[b] 183,[b] 185	1, 34, 61, 74,[b]79, 82,[b] 88, 92, 96, 98, 108, 112, 117, 122, 126, 129, 130, 133,[b] 142, 144,[c] 145, 155, 180, 182,[b] 183,[b] 184,[c] 185, 206, 230	34,[d] 112,[d] 146,[d] 179,[g] 182,[b f] 183,[b,d] 184,[c] 185[f]	61[g],74[g],75,[g] 121,[e] 147,[e] 179[g]
hot plasma discharge	spark/arc discharge	48, 94, 98, 127, 135	98, 135, 175	48, 94, 98, 124, 127, 135, 175			48, 94, 98, 124, 127, 135, 175	124[f]	199,[h,i] 200[h,i]
	laser-induced plasma	41, 79, 98	79, 98	41, 79, 94, 98			41, 79, 94, 98		
UV irradiation	short (λ < 80 nm)	100−102, 115	100−102, 115	100−102, 115	101, 115		101, 115	101[f]	
	long (λ > 100 nm)	48, 55,[l] 99, 102, 113,[l] 116,[k] 119,[j] 140,[m] 141[l]	55,[l] 118,[m] 119,[j] 176	48, 55,[l] 94, 99, 102, 116,[k] 119,[j] 140,[m] 141,[l] 176	118[m]		55,[l] 113,[l] 114,[m] 118,[m] 119,[j] 140[m]	113,[l] 116[f,k]	
γ-rays, soft X-rays		98, 111	98, 111	48, 98,		111	48, 98, 111	111[b,f]	111[b,f]
electron beam bombardment		48		48			48		
proton beam bombardment		47,[i] 178[i]		47,[i] 48, 178[i]	178[i]		47,[i] 48, 178[i]		

[a] Compounds in bold have been detected on Titan by the Cassini−Huygens mission; others have only been detected in the laboratory. Unless otherwise specified, initial gas mixtures are 1−10% CH_4 in N_2. Pressures, temperatures, and exposure times vary. Note that the detection of oxygen-containing compounds and prebiotic molecules in tholins are all the result of air/water exposure or the addition of CO to the initial gas mixture. [b] After pyrolysis. [c] Initial gas mixture included 0.01% CO. [d] After exposure to liquid water. [e] After exposure to NH_3/H_2O solution [f] Contamination (oxygen/water vapor) [g] After acid hydrolysis [h] Spark discharge over liquid water [i] Initial gas mixture of 1:1 N_2/CH_4 [j] Initial gas mixture of 73−88% N_2, 12−20% CH_4, 5−6% C_2H_2, 0.6% C_2H_4, and 0.6% HCN. [k] Initial gas mixture of 98% N_2, 1.8% CH_4, 0.035% C_2H_2, 0.03% C_2H_4, 0.0017% C_3HN, and 0.003% CO or 0.02% HCN [l] Initial gas mixture of 98% N_2, 1.8% CH_4, 0.035% C_2H_2, 0.03% C_2H_4, and 0.0017% C_3HN. [m] Initial gas mixture contained HC_3N.

HCN, and unsaturated and aromatic compounds. Soft X-rays produce nitriles and heteroatomic aromatic species.[111]

Proton and Electron Beams. Proton and electron beam bombardment of methane/nitrogen gas mixtures yields small saturated and unsaturated hydrocarbons such as ethane, ethylene, acetylene, and propene, in addition to HCN.[48] Another proton beam experiment with higher energy (2−4 MeV compared to 1.5 MeV) found similar compounds and acetonitrile, but no HCN.[47,178] This discrepancy could be due to secondary reactions emerging from the higher beam energy and/or pressure (750 compared to 350 Torr) of the latter method.

4.3.2. ^{13}C and ^{15}N Isotope Labeling. One study using ^{13}C-labeled methane did not detect any substantial enrichment or deficit of ^{13}C relative to ^{12}C. Interestingly, the authors also found that two cold plasma discharge methods of generating tholins produced different isotopic ratios of ^{12}C/^{13}C.[179] This difference could be due to the wall effect (see section 3.2), in that one method (PLASMA) generates tholin material as deposits on the walls of the chamber, while the other (PAMPRE) produces tholins as particles in levitation. The solid surface may catalyze or select for different polymerization mechanisms than can occur for aerosols formed in levitation, producing very different materials from otherwise similar reaction conditions. However, different reaction conditions at the center of the chamber compared to near the walls may also contribute to the difference, and further study is necessary to better understand the underlying mechanisms at work in both tholin generation techniques.

Tholins produced using electric discharges in 5% $^{13}CH_4$ and 95% $^{15}N_2$ were analyzed by 1D and 2D NMR methods.[180] These tholins were found to have little to no long, saturated hydrocarbon chains, with carbon-nitrogen bonding preferred over carbon-hydrogen bonds. Any aromatics in these structures were also likely to be highly substituted.

4.3.3. Elemental Analysis. Determination of the C/N and C/H ratios in tholins can provide insight into whether these organics act as sinks for carbon or nitrogen on Titan,[124,129] which is important in terms of effectively modeling processes in the atmosphere and on the surface. Varying the chamber pressure produces different C/N ratios for inductively coupled cold plasma discharge tholins, due to an increase in the formation of N-containing polycyclic aromatics at low pressure. At low pressure (13−26 Pa, 200−300 km altitude), the C/N ratio is on the order of ∼1.5−2, while at high pressure (160−2300 Pa, 80−180 km altitude) it is around 3.[130] Tholins generated by UV radiolysis at long wavelengths (λ > 155 nm), where N_2 does not undergo photodissociation, tend to have much higher C/N ratios, typically in the range of 10−24.[55,114,116,123] However, inclusion of shorter wavelengths (λ < 80 nm) capable of N_2 dissociation[115] or activated species such as cyanoacetylene in the initial gas mixture[118] brings the C/N ratio back down (Figure 12).

The degree of saturation/unsaturation in tholins is also significant, as this can determine the optical properties of the material and susceptibility to hydrolysis. For example, nitrogen is the dominant carrier of unsaturation in tholins produced by cold plasma,[142] meaning they are susceptible to hydrolysis and therefore incorporation of oxygen.

4.3.4. Prebiotic Molecules. Several tholin generation methods have produced molecules of prebiotic interest. This is not an uncommon occurrence; nitrogen-containing cyclic compounds such as purines and pyrimidines have been reported in syntheses from nonbiological matter in thermal heating and electric discharge experiments for the last 40 years.[181] Cold plasma discharge of a 90/10 initial mixture of N_2 and CH_4 at high pressure (600 Torr) yielded pyrimidine ($C_4H_4N_2$) and pyridine (C_5H_5N),[182] and at low pressure, pyridine, pyrrole, carbon dioxide and ammonia were formed (but it should be noted that this sample was exposed to ambient air).[183] Inductively coupled cold plasma discharge produced a variety of C- and N-containing molecules but no purines or pyrimidines.[61] When 0.01% CO was included in the initial gas mixture, cold plasma discharge at 100−150 K yielded 194 compounds with over 30 oxygen-containing species, including alcohols, diols, aldehydes, and ketones.[144,184] Tholin samples produced using capacitively coupled cold plasma discharge with 1.8% CO in the gas mixture yielded two biological amino acids (glycine and alanine) and all five nucleotide bases, representing the first detection of prebiotic molecules formed in conditions representative of the upper atmosphere of Titan.[120] However, the effects upon product composition of detected terrestrial oxygen contamination is still under investigation.[148]

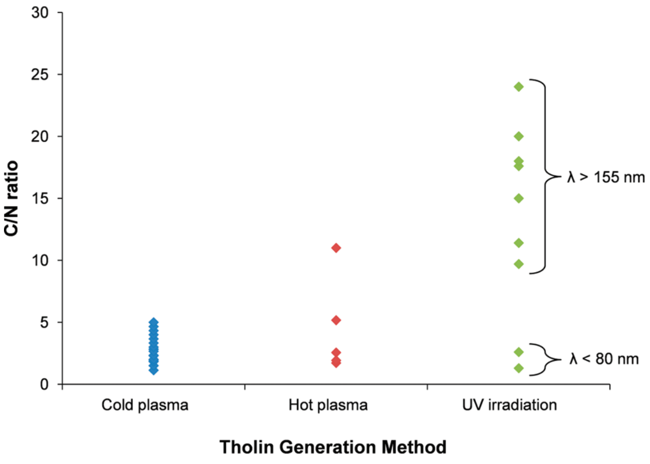


Figure 12. C/N ratios of tholins produced using various reactors. Cold plasma discharge produces material with the most consistent C/N ratios, while the carbon and nitrogen content in hot plasma discharge and UV irradiation reactors can vary significantly. Note that for shorter wavelengths of UV irradiation (λ < 80 nm), where N_2 dissociation can occur, the C/N ratio is much lower than for longer irradiation wavelengths, which do not efficiently incorporate nitrogen into the tholin material. C/N ratios were obtained from many references.[34,55,61,78,82,108,112,113,115−117,123,124,129,130,135,142,155,162,206,239,240]

In a gas mixture containing N_2, CH_4, and trace amounts of CO_2 and H_2O meant to simulate a period of cometary bombardment, irradiation with soft X-rays yielded the nucleobase adenine ($C_5H_5N_5$), as evidenced by GC−MS and ^{1}H NMR.[111] The abundance of CO_2 was about 10−20 times lower than water (roughly the same ratio as in comets). Though the existence of such conditions on Titan would be rare at best, the abiotic formation of a molecule significant in biochemistry is interesting and merits further study.

4.3.5. Monomers/Precursors. It has been suggested that tholins could be composed of HCN polymers or oligomers, HCN−C_2H_2 co-oligomers, HC_3N polymers, and/or HC_3N−HCN co-oligomers.[20,123] In tholins produced using capacitively coupled rf cold plasma discharge, it appears that both CH_2 and HCN play important roles in the structural composition of these complex organics. Linear and cyclic amino nitriles were proposed as the roots of some families of compounds, and HCN and C_2H_3N were identified as possible nitrogen growth units.[185]

Modeling by Lara et al. confirms the importance of HCN incorporation into tholins, either via polymerization or sticking, as a sink for nitrogen.[186] This is in contrast to a previous study[116] that suggests incorporation of HCN into Titan's haze is minimal. In another capacitively coupled rf cold plasma discharge, HC_2N_3 ($[N{\equiv}C{-}N{-}C{\equiv}N]^- H^+$) is found in all tholin samples studied.[155]

For UV irradiation at 60 and 82.5 nm, only a few pure hydrocarbons were observed in materials dominated by heavily unsaturated and heavily nitrogenated solids. HCN is the major seed at 82.5 nm, while the HCCN radical is the dominant precursor at 60 nm.[115] The fact that the HCCN radical is a carbene (containing a carbon atom with two unpaired electrons) permits this species to easily insert into single bonds or react with unsaturated or radical centers.[29,115] For UV irradiation at 185 and 254 nm, C_2H_2 and HC_3N have been identified as a possible structural basis for Titan tholins.[118] This work implies the importance of nitrile chemistry in aerosol formation on Titan, which is in agreement with the large nitrogen incorporation observed by the aerosol collector pyrolyser instrument of the Huygens probe.[187]

4.3.6. Macromolecular Structures. Most reports in the literature suggest that tholins are generally composed of macromolecules of relatively low molecular weight (a few kilodaltons) and largely irregular structure.[20] The peak distribution in mass spectra of tholins consists of ions organized in regular clusters separated by 13 or 14 mass/charge units, indicative of a polymeric but not necessarily linear structure.[112,142,155] Others have used methods previously developed for amorphous carbon and disordered graphites to analyze tholin films and found that structural models consisting of subparallel long polymeric chains are inaccurate to describe tholins.[117] Instead, it is suggested that sp^2-bonded planar clusters and highly branched polymeric or oligomeric compounds are more likely.

Tholins produced by UV irradiation, particularly those that are extremely insoluble (see Solubility section, above), most likely contain a high degree of cross-linking.[119,123] Analysis of material produced using capacitively coupled rf cold plasma discharge indicates that polymeric chains terminate in methyl, amine, and nitrile groups.[155] Tholins generated in spark discharges produced terpene-like aliphatics and polyacetylene.[175] Terpenes typically link together "head to tail" to form linear chains and rings, and their presence may be indicative of polymerization.

Polymeric $(HCN)_x$, also known as poly-HCN, is a complex disordered solid obtained from condensation of molecular HCN that has previously been used as an analogue for tholins, as they both belong to the same general class of "polymeric" hydrogenated carbon nitrides.[117,185] They also may both contain triazine (C_3N_3) rings.[117,188] Poly-HCN prepared under anhydrous conditions and tholins produced using cold plasma discharge have similar IR absorption spectra.[162] However, the chemical composition of tholins is most likely considerably more complex than poly-HCN due to the large number of polymerization reactions possible.[117] This was verified by a recent study comparing poly-HCN to three tholin samples produced using capacitively coupled cold plasma discharge, indicating differences in mass spectra and C/N ratio.[154] Any concurrence in IR absorption spectra was attributed to a similar distribution of functional groups rather than a detailed structural similarity. The most recent data therefore suggest that poly-HCN is not an effective analogue of Titan tholins, so any conclusions based on experiments performed with poly-HCN as the analyte cannot be extrapolated to tholins.

4.4. Degree of Tholin Variation

Exhaustive literature searches of Titan simulation experiments leads to the unsurprising conclusion that tholins produced using different methods are fundamentally different. Imanaka et al. noticed an increase with pressure of a particular nitrogen band (the second positive system or SPS band) in the UV range for a carefully controlled inductively coupled rf plasma discharge, whereas Szopa et al. noticed a peak at a particular pressure in a capacitively coupled rf plasma discharge followed by a decrease.[82,130] This could be due to the fact that the proportion of high-energy electrons is probably different in the inductively coupled versus capacitively coupled plasma discharge reactors. Tran et al. found optical and structural differences between tholins produced via spark discharge and those made in a photochemical flow reactor.[123] As the CH_4/N_2 ratio is decreased for cold plasma generated tholins, the proportion of double bonds increases, favoring sp^2 clustering and $\pi-\pi^*$ electronic transitions in the UV/visible range, controlling the color and optical constants across the spectral range.[117] However, this is in contrast to (1) UV-generated tholins, whose chemical composition does not appear to vary with changing methane concentration,[176] as well as (2) other cold plasma discharge tholins, where the C/N ratio was insensitive to the CH_4/N_2 ratio over the range 0.5−5%.[142] These are just a few examples of the many differences in properties and behavior of tholins produced in varying conditions. Broadly speaking, it appears that tholin composition is dependent on the following:

(i) methane/nitrogen ratio in the initial gas mixture;[131,175]
(ii) the choice of energy source, energy window, or range and its intensity;[102,123]
(iii) the pressure and temperature of the initial gas mixture;[130]
(iv) contamination (oxygen, carbon dioxide, and water vapor).[129]

It should also be noted that the parameters listed in the first three points (i−iii) all vary as a function of altitude in Titan's atmosphere.

5. THOLIN REACTIVITY

5.1. Pyrolysis Products

For capacitively coupled rf plasma discharge, pyrolysis of tholins produced mostly aliphatic unsaturated hydrocarbons, but also included HCN, propene, butene, C_2N_2, butadiene, toluene, ethylbenzene, dimethylbenzene, propenenitrile, and butanenitrile.[82,133] Pyrolysis products of tholins generated using dc cold plasma discharges include carbon dioxide, ammonia, water, pyridine, toluene, and benzonitrile[182] and, in a separate experiment, pyrroles, pyrazines, pyridines, pyrimidines, and the purine adenine.[75] Nucleobases (purines and pyrimidines) have been identified as pyrolysis products of Titan tholin produced by spark discharge,[74] as well as alkylbenzenes, indenes, indanes, pyrroles, and pyrazines.[72] This is consistent with pyrolytic studies of (1) cosmic materials, where thermal annealing increases the aromatic character of carbon-based samples,[189] and (2) the complex organic material kerogen (see section 6), where pyrolysates become increasingly aromatic with temperature.[190]

5.2. Acid Hydrolysis

Acid hydrolysis of tholins generates up to 16 racemic amino acids, with glycine, aspartate, and alanine the most abundant.[75,95,179] The currently accepted mechanism is the polyimino model proposed by Thompson and Sagan, where the polyimino chains, substituted with functional groups derived from abundant gas-phase radicals, form the side chains of the amino acids upon hydrolysis.[183,191] Urea has also been noted as a significant product in acid hydrolysis of tholins generated from a cold plasma discharge.[75] Acid hydrolysis of tholin particles produced using rf cold plasma discharge led to the attack of any terminating −CN functional groups, and IR measurements confirmed that this peak at 2200 cm^{-1} completely disappeared.[155]

5.3. Reactions in Liquid Water

Chemistry involving tholin material on Titan may involve the formation of melt pools via meteoritic and cometary impacts, as well as the possibility of cryvolcanoes.[192] The presence of ammonia on Titan has been proposed[193,194] but not proved; if present, it might act as a sort of "antifreeze" in a cryovolcanic fluid.[195,196] Models indicate that melt pools and cryovolcanoes could take on the order of 10^2-10^4 years to freeze,[36,197] implying the existence of long-standing liquid capable of chemical interaction with surface material.

Tholins produced by cold plasma discharge and placed in liquid water have been shown to produce oxygenated species, with activation energies on the order of 60 ± 10 kJ/mol and half-lives of 0.3−17 days at 273 K.[34] In addition, these tholins upon even short exposure to basic ammonia-water solutions or pure water release a significant fraction of amino acids.[75,198] Slow hydrolysis of cold plasma discharge tholins at 253 and 293 K (over 1 year) produced asparagine, aspartic acid, glutamine, and glutamic acid, as measured by high-resolution mass spectrometry.[147] It was also discovered that oxygen incorporation is more rapid in the presence of ammonia.[146] A similar experiment with cold plasma discharge tholins placed in 25 wt % ammonia aqueous solutions for 10 weeks produced amino acids as well as urea, though oxygen contamination might have been a factor.[121,136] When a spark discharge occurs over a solution of ammonium carbonate (pH 7.8) with an initial gas mixture of equimolar N_2 and CH_4, the organic compounds include all five nucleobases (adenine, guanine, cytosine, thymine, and uracil) and several nucleosides (cytidine, uridine, inosine, guanosine, xanthosine, 5-methyluridine, and adenosine).[199,200]

These results indicate that tholins are capable of generating biological precursors when exposed to liquid water, aside from the fact that these biologically relevant molecules may also be produced in the gas phase in Titan's atmosphere.[120] Therefore, we may entertain the idea that, in certain regions on Titan where liquid water might exist (such as cryovolcanic flows or impact-generated melt pools), chemistry important to life as we know it may be occurring on the surface. However, if life on Titan were to exist, it would most likely be very different from life on Earth (or very rare) due to the chemical and physical constraints of subsisting at such low temperatures (i.e., higher activation energies, lower reaction rates, and poor solubility of organics).[201−204]

5.4. Heterogeneous and Surface Chemistry

A number of recent aerosol modeling efforts include heterogeneous chemistry effects. Indeed, experimental work using UV irradiation has supported the possibility of heterogeneous chemistry on aerosols as a potential formation mechanism for HCN and NH_3 in the upper atmosphere of Titan.[30,101] It is theorized that the aerosols act as chemical "microreactors" by greatly increasing the gas-liquid interface.[64,205] Further, the adsorption of methane onto tholin particles occurs at a rate which implies that methane clouds should form.[167] Ethane nucleation occurs at a higher saturation ratio, meaning a smaller percentage of particles will nucleate an ethane cloud, and therefore, these clouds should resemble cirrus clouds on Earth. In addition, there is evidence that tholin polymers can effectively trap Ar, Kr, and Xe, which may explain the absence or trace levels of these noble gases on Titan.[109] However, the relatively high solubilities of these gases in liquid methane and ethane may suggest an alternative explanation—that the hydrocarbon lakes on the Titan surface act as sinks for Ar and Kr.[165]

Another heterogeneous mechanism relevant to Titan is the hydrogenation of aerosol particles from atomic hydrogen in the atmosphere. Tholins exposed to atomic hydrogen (or deuterium) have fewer unsaturated bonds ($C{=}C$, $C{=}N$, and $C{\equiv}N$) and experience hydrogenation of the surface.[206] At room temperature this hydrogenation reaches saturation, whereas at 160−180 K the surface is not saturated as rapidly, but this process still occurs much more quickly than expected. Hydrogenation saturates the surface down to the penetration depth of atomic hydrogen; further hydrogenation tracks with the much slower process of chemical erosion. On Titan, models taking this into account indicate that the aerosol surface would remain unsaturated with hydrogen in the mesosphere but might become saturated in the stratosphere. A subsequent study by the same authors using a one-dimensional model found that 60−75% of the atomic hydrogen in the stratosphere and mesosphere could be consumed by heterogeneous reactions on aerosol surfaces between 100 and 600 km.[207] Such heterogeneous chemistry might have overarching effects, such as thermal damping upon an exothermic episodic methane release from Titan's interior (methane photochemistry would produce more atomic hydrogen, which would in turn produce more haze and create an antigreenhouse effect).

5.5. Tholins as Putative Microbial Metabolites

Aerobic, anaerobic and facultatively anaerobic microorganisms are capable of using tholins as their sole carbon source and, in some cases, their sole nitrogen source. Organisms such as *Clostridium*, *Pseudomonas*, *Bacillus*, *Actinetobacter*, *Paracoccus*, *Alcaligenes*, *Aerobacter*, and *Flavobacterium* were able to survive on organics produced in a spark discharge reactor from an equimolar mixture of CH_4 and NH_3 with 2.5% water vapor.[208] It should be noted that some species of these genera, notably *Clostridium* and *Bacillus*, are bacterial spore-formers capable of surviving the extreme conditions of an interplanetary journey, such as UV radiation, temperature extremes, and the vacuum of space.[209−213] We may therefore consider tholins and related organics as potential growth substrates for microorganisms on other worlds, as well as the possibility that similar materials may have been an instrumental part of the food chain for heterotrophs on the early Earth.[151,214]

6. FUTURE DIRECTIONS IN THOLIN RESEARCH

Tholins are complex chemical tapestries, and it has become clear that current sample analysis techniques are not adequate to construct a complete picture of their composition and structure. As a result, creative methods and unique solutions must be implemented to address the analysis of these complex heterogeneous macromolecules. We must discover the most appropriate, unbiased analysis techniques using tholins on Earth in order to prepare the best instrument package for the next in situ mission to Titan. One group of researchers has attempted to build a general framework for understanding tholins as analogues by selecting two samples as "end-members" and determining the range of their properties.[108] Another group suggested the use of a chemometric approach to generate a "fingerprint" unique to each

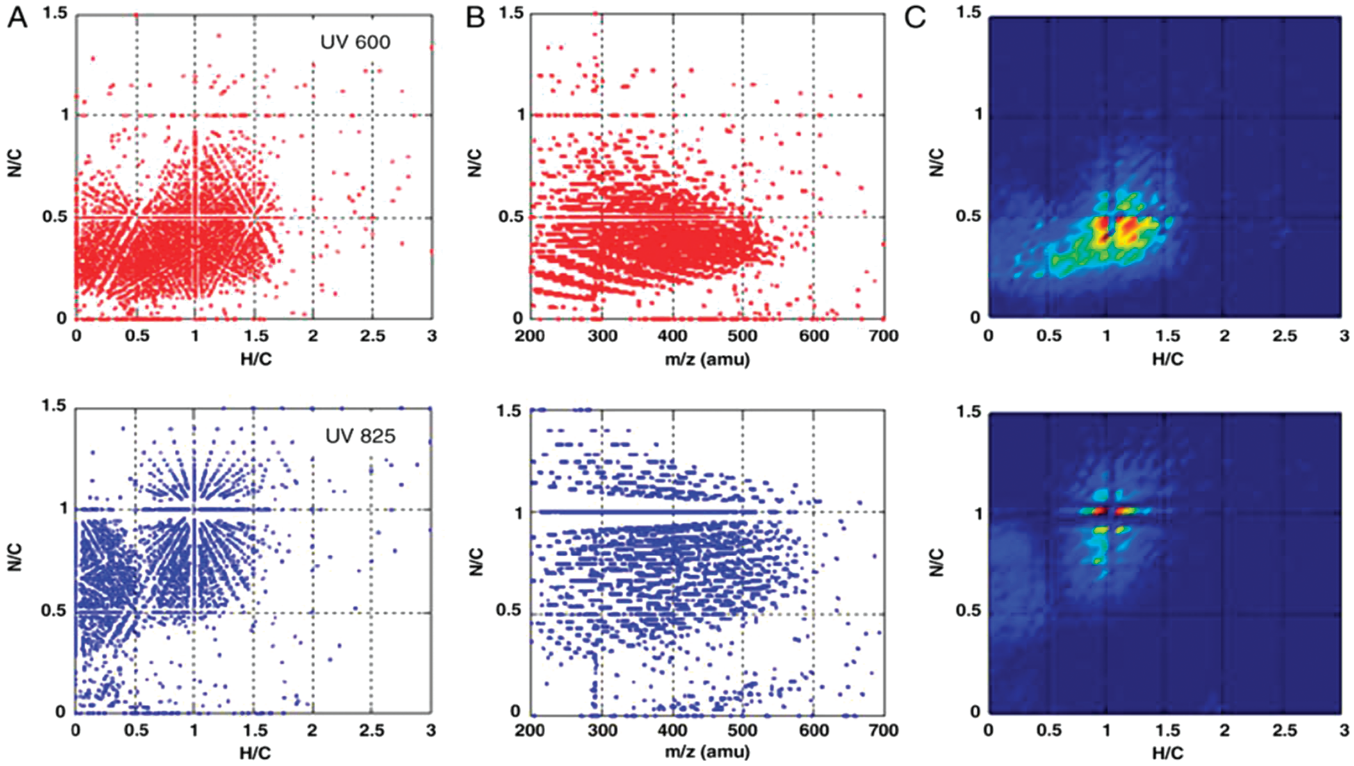


Figure 13. Modified Van Krevelen diagrams for tholins generated using UV irradiation at 60 nm (UV 600) and 82.5 nm (UV 825). Reproduced with permission from ref 115. Copyright 2010 National Academy of Sciences.

tholin sample.[182] These ideas are excellent starting points for viewing tholins from a broader perspective and providing certain constraints on tholin properties. An extension of such thinking may incorporate aspects of petroleomics into the future of tholin research.

Tholin chemistry can benefit from application of techniques already developed for the study of polymers and macromolecules on Earth. One natural, Earth-based analogue to tholins is kerogen. Kerogens are dark, complex organic materials produced on Earth from biologically derived organic material that has been incorporated into sediments and undergone geological processing.[215] Kerogen is distinguished from bitumen in that the former is insoluble in solvents, while the latter is the soluble fraction. Tholins are kerogen-like in structure[133,216] and have similar refractive indices.[217−219] Van Krevelen diagrams were invented in 1950 to help characterize kerogens using a graphical-statistical approach.[220] In these diagrams, the O/C ratio is plotted against the H/C ratio, because as a sedimentary rock becomes more mature over time, the kerogen becomes more depleted in oxygen and hydrogen relative to carbon. Van Krevelen diagrams are therefore used to identify the type of kerogen present (type I, II, or III) using bulk properties as opposed to obtaining specific stochastic chemical structures. As tholins have little if any oxygen and a significant amount of nitrogen, Imanaka et al. created van Krevelen diagrams that plot N/C against H/C ratios.[115] These plots (Figure 13) show clear differences between tholins produced using different UV irradiation wavelengths and imply that different chemical reaction pathways are responsible. Such information might not have been as easily discerned from analysis of functional groups and mass distributions alone. Though not the first time N/C and H/C ratios have been compared graphically for tholins,[117,130] this recent work explicitly states the connection between the methods used for analysis of petroleum and application to the study of tholins.

In a similar investigation seeking to develop a general-purpose framework for analysis of tholins, the authors extended use of the methods from petroleomics and proposed the term “tholinomics” to describe their reported work,[185] which included both van Krevelen plots and Kendrick plots. In this latter method first proposed in 1963,[221] no chemical formulas are needed, though a cursory knowledge of the predicted constituents is advantageous. A basic pattern is chosen, and the deviation or Kendrick mass defect (KMD) for each data point from that pattern is calculated. These KMD values are then plotted against the Kendrick mass of the given pattern, which is defined as

$$\text{Kendrick mass} = \text{IUPAC mass} \times (M_{\text{nominalmass}}/M_{\text{IUPACmass}})$$

This method classifies compounds in terms of a basis molecule, grouping homologous compounds together as horizontal lines. For example, a Kendrick plot with HCN chosen as the pattern (see Figure 14) will group a tholin sample using HCN as the basis of an integer mass (i.e., each data point is equivalent to x number of HCN units). Therefore, a Kendrick plot with a small dispersion and symmetric KMD distribution suggests that the chosen pattern is representative of the sample’s global composition.[222] Adding a z-axis to van Krevelen diagrams can provide additional information, such as trends in mass-to-charge ratio.[185] In addition, these methods can be applied to other complex macromolecular samples such as PANHs and carbon nitrides. As the demand for analysis of complex samples increases, we will continue to see more creative advancements to distill information from large data sets into a coherent picture of a given material. However, at this stage of development of such

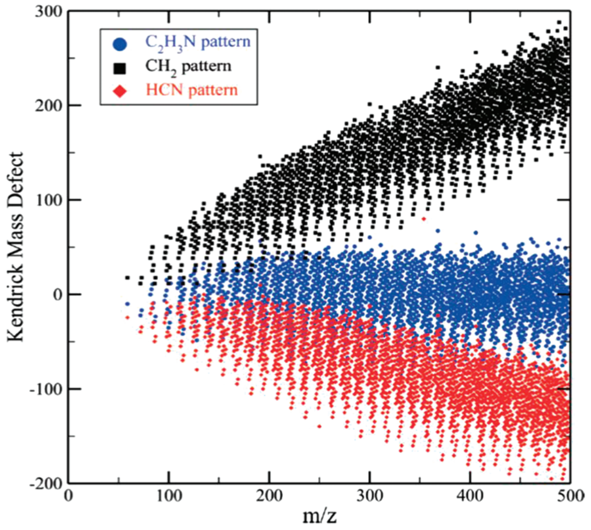


Figure 14. Kendrick plots for tholins produced using capacitively coupled cold plasma discharge. This plot discerns patterns for various repeating units in a macromolecular structure. Reproduced from ref 185. Copyright 2010, American Chemical Society.

methodologies, we posit that the application of a term such as tholinomics is premature, as this suggests that the field is very well-defined and tholins are well-understood, which is not the case.

Significant work has been reported on Titan tholins, but some future experiments could help address new questions about the chemistry of the Titan atmosphere and surface. For instance, submillimeter and millimeter wave spectroscopy on tholins has yet to be performed, and no radar measurements on tholins have been reported. This data could bolster current atmospheric models and give us a better idea of the structure of the organic layer covering Titan's surface. In addition, measurement of the indices of refraction, both real and complex, of tholins over the entire spectral range would greatly aid modeling endeavors (the values measured by Khare and Sagan in 1984 are still in use in models today,[223] over 25 years later!). The transition from large molecules and ions into tholins remains a mystery including the initial stages in which nitrogen is incorporated. Laboratory simulations that replicate the pressure regime of Titan's ionosphere (pressures less than 10^{-7} Torr) may elucidate chemical pathways which are not likely in higher pressure regimes, where termolecular reactions will dominate.[224] Further research into the heterogeneous chemistry of tholins could also help us understand how aerosol particles might trap gases and condense vapors onto their surfaces and may help explain the absence of certain noble gases (i.e., Kr and Xe) in Titan's atmosphere. As more data is obtained in the lab on these materials, our understanding of the complex processes occurring in Titan's atmosphere and on its surface improves, and we can better inform the next generation of in situ instruments.

Finally, the investigation of tholins and Titan in general may have greater implications in a cosmic context. M-dwarfs (i.e., red dwarfs) are 10 to hundreds of times more common in the universe than yellow G-dwarfs like our Sun, and are much cooler (~3700 K as opposed to ~6000 K).[225] Any planet orbiting at a safe distance (1 AU) around an M-dwarf will have a stable environment (any closer and coronal mass ejections and solar flares will destroy the planet's atmosphere); however, at this distance light from the M-dwarf is so faint that conditions similar to Titan will prevail — water will be frozen, and methane and ethane (if present) will be liquid. Therefore, it is much more likely that planets we discover in the universe will resemble Titan rather than Earth,[226] making Earth the exception and Titan the rule. Hence, the study of tholins may be a more broad-reaching endeavor than originally thought.

7. IN SITU CHEMICAL ANALYSIS ON TITAN

The ultimate goal of studying tholins produced in the laboratory is to inform models of the organics on the surface of Titan, to help us (1) understand chemical processes occurring on this moon and (2) develop more effective in situ analysis instruments and protocols for future Titan missions (see Table 7). However, the ambient conditions on Titan pose significant technological challenges, in that new cryogenic-capable sample handling and analysis systems with their corresponding infrastructure (i.e., low-temperature electronics, robust packaging materials, and long-life power systems) must be developed to operate effectively at ~90 K. Further, the amount of fuel required to reach Titan significantly constrains spacecraft payload mass, so instruments must be as small and light as possible.

A future in situ mission to Titan may involve a lake lander (such as the recently proposed Titan Mare Explorer or TiME mission[227]), a montgolfière balloon, a dune lander, or a combination of these.[228] All of the proposed designs involve sampling of aerosols and/or surface material (liquid and solid) for analysis, with most of the instrument suites including bulk chemical analysis (NMR, isotopic ratios, elemental analysis), aerosol measurements (electrical mobility analysis, optical scattering, etc.), and characterization of specific functional groups (i.e., IR absorbance, laser-induced fluorescence, and mass spectrometry).[229,230] Data from the mass spectrometers of both Cassini and Huygens[24,25,65,66,151] clearly demonstrate that a wider mass range with higher resolution is desired for analysis of the complex organics in the aerosols and on the surface of Titan. Further, MS−MS capability would enable better selectivity and characterization of parent ions, which could aid in the identification of aerosol growth units.[112,155] The most detailed analysis of Titan samples will probably involve wet chemistry (extraction, labeling reactions for specific functional groups, dilution, chromatographic separation) followed by high-resolution mass spectrometry.

There is considerable evidence that pyrolysis, though providing information on the elemental composition of tholins, increases the potential for unpredictable chemical processes that occur during heating.[117,231] Further, premature heating of a sample on Titan could result in the loss of important volatiles such as dicyanoacetylene (C_4N_2).[126,127] Liquid-based separations are less destructive and can provide a more comprehensive analysis of the sample with the appropriate choice of solvent. Though the possibility of chemical reaction with the solvent must be considered, liquid phase analyses of a Titan aerosol at temperatures well below the point where tholin decomposition products are observed (373 K) would provide a more complete picture of the original composition of these complex organic samples. In addition, the enhanced capability provided by introducing concentration gradients or performing multiple extractions makes liquid

Table 7. The Future of in Situ Chemical Analysis on Titan, Tempered by Cassini−Huygens Data and Tholin Analyses on Earth

analysis stage	previous Titan in situ technology (Huygens)	lessons from tholins in the laboratory	future state-of-the-art
sample processing	aerosol collector and pyrolyzer (ACP)	• Pyrolysis leads to unpredictable reactions in tholins • Tholins are partially soluble in some solvents and insoluble in others	extraction using multiple solvents (H_2O, methanol, toluene, etc.) to gently "tease apart" sample
separation	gas chromatograph (GC)	• Liquid chromatography (LC) preferred to GC • Separation technique must work for both polar and charged species	LC using capillary electrophoresis in microfluidic devices (lab-on-a-chip) with low power and mass
detection	mass spectrometer (MS) $m/z \leq 141$[24]	• MS needs very wide range • identification of functional groups is valuable, especially those containing oxygen • characterization of bulk properties and trends should also be performed	ultrasensitive detection of functional groups using laser-induced fluorescence (LIF) coupled to high-resolution MS

chromatography an attractive choice for analysis of complex organics such as tholins.

Microfluidic technologies, often termed "lab on a chip" (LOC), have enabled the development of liquid chromatography and similar fluidic assays for in situ applications. These devices conduct wet chemistry using small sample aliquots (nanoliters to microliters) with very low power and mass constraints, making them ideal for landed missions to other worlds. Separations are effected using capillary electrophoresis (CE) based on electroosmotic flow, which is capable of separating both charged and neutral species along a microchannel without using high pressure.[232] Ultrahighly sensitive (subparts-per-trillion) detection on-chip is performed using laser-induced fluorescence for intrinsically fluorescent species (i.e., PAHs) and nonfluorescent species labeled with a fluorescent dye (i.e., primary amines, aldehydes, ketones, and/or carboxylic acids).[233−235] Further, this detection method is nondestructive and can therefore be coupled to another detection technique, such as high-resolution mass spectrometry for concomitant analysis.[232,236,237] We are currently developing microfluidic technologies for separating and characterizing tholin samples using various labels to target specific functional groups. Most of the chemistry for these labeling reactions occurs in aqueous solution at or near room temperature, but nonaqueous capillary electrophoresis (NACE) has also been demonstrated on-chip and could be adapted for solvents with much lower freezing points.[232] Regardless of operation at ambient Earth (with water as the solvent) or ambient Titan (using another solvent) conditions, microfluidics is well-suited to meet the sample handling, separation, and characterization needs of a low power and mass chemical analysis platform on a future in situ mission.

In order to truly understand the global chemistry of Titan, highly robust, sensitive, and analytically powerful in situ instrumentation is required. This is readily achieved using microfabricated wet chemical processing with nondestructive CE techniques, which inherently boast low mass, volume, power, and reagent consumption requirements. Coupling a microfluidic device to a high-resolution mass spectrometer via nanospray ionization or a similar method would generate a formidable chemical interrogation platform for in situ analysis of organics on the surface of Titan.

8. CONCLUSIONS

Due to the large variations in tholin generation technology and the resulting properties of tholins produced in the laboratory, it has been noted that "the current state of the literature is rather confusing" in terms of understanding which tholins represent accurate analogues relevant to Titan's chemistry[108] and which tholin generation methods produce material best suited for analytical design and technique comparison. Tholin production methods vary widely in terms of temperature, pressure, exposure time, composition of initial gas mixture, and sample handling and analysis. Some tholins are soluble in certain solvents, while some are insoluble in all tested solvents. The degree of saturation in tholins varies, as do their optical properties and particle diameters. New data from the Cassini-Huygens mission has provided insights into some of the properties of the organic material on Titan; until a laboratory tholin can successfully reproduce *all* of these properties, such materials cannot be considered accurate analogues.

A thorough review of the tholins reported in the literature, in the context of the recent data from the Cassini−Huygens mission, leads us to construct a metric to determine which tholins are the most 'Titan-like', in order of importance:

(1) **Energy source:** Cold plasma discharge and UV irradiation (including $\lambda < 80$ nm) each replicate significant sources of energy in the Titan atmosphere and produce tholins with optical and chemical characteristics that are similar to the aerosols on Titan. Without definitive detection of lightning on Titan, hot plasma (spark discharge and LIP) should be considered a minor contributor to Titan chemistry. Other techniques such as proton and electron bombardment, γ-rays, and soft X-rays, are limited in their ability to best mimic the energy input mechanisms driving atmospheric chemistry on Titan.

(2) **Temperature:** The temperature of the Titan atmosphere and/or surface must be accurately replicated to produce

and retain volatiles (i.e., C_4N_2) in an analogous scenario as on Titan. Any work performed outside of the Titan temperature regime could be biased toward high molecular weight species and also might exclude important heterogeneous chemistry and aerosol surface interactions involving these volatiles.

(3) **Pressure:** Tholin properties are pressure-dependent, so this property should be carefully reproduced and monitored during aerosol formation. In cases where accurately simulating the pressure is physically impractical (i.e., the mean free paths exceed the dimensions of the chamber), care should be taken to replicate the proper collision regime (binary versus ternary, etc.). The researcher should also be cognizant while using a particular energy source to reproduce the pressure of the appropriate altitude on Titan where this energy source is most prevalent (i.e., simulating the stratosphere when using UV irradiation and the mesosphere when using cold plasma discharge).

(4) **Energy density:** Chambers should use the lowest energy density that is still practical in terms of experiment time. In particular, techniques using continuous flow systems are recommended to reduce secondary product formation. Further, exposure time must be accounted for and correlated to the environment that is being simulated (i.e., at certain altitudes and transport times, multiple exposures might best simulate the Titan environment).

Consideration of these tholin generation parameters can lead to at least a qualitative means of determining if a given tholin sample is a good analogue for the organic material of Titan. For example, a reactor using cold plasma and UV irradiation at cryogenic temperatures will most likely yield tholins that have properties similar to what we know of organics on Titan, whereas a method employing γ-radiation at room temperature will probably generate material with fewer 'Titan-like' properties.

The ideal reactor would operate at Titan ambient temperatures (90−175 K) and pressures (0.0001−1.5 bar), with the capability of accurately simulating the conditions of different parts of the atmosphere (stratosphere, troposphere, etc.) either separately or in sequence, to replicate Titan's vertical temperature and pressure gradients. A combination of cold plasma discharge and UV irradiation ($\lambda < 80$ nm) with the correct relative intensities as are present in the Titan atmosphere (approximately 200 to 1 in favor of UV irradiation) could be used to generate radicals and ions that initiate aerosol formation. A continuous flow system would reduce secondary product formation. Finally, in-chamber analysis techniques should be used for tholin interrogation to reduce contamination, postproduction reactions, and loss of volatile components.

By careful consideration of the many organic materials produced in the reaction chambers reported here, we conclude that the best tholin reactor is Titan itself. We must remind ourselves that even tholins produced with the best recognized methodology possible are still only simulants, and represent *our best guess* as to what is actually present on Titan. Any conclusions obtained from research of laboratory tholins must reflect this important fact. Production and analysis of tholins can tell us *how* to think about these complex organics, but cannot provide absolute information about their chemical and physical properties. This knowledge will only come from further in situ analysis by future missions to this enigmatic moon.

AUTHOR INFORMATION

Corresponding Author

*E-mail: Peter.A.Willis@jpl.nasa.gov. Phone: (818) 325-9356. Fax: (818) 393-4773.

BIOGRAPHIES

Dr. Morgan L. Cable is a postdoctoral fellow at the NASA Jet Propulsion Laboratory in Pasadena, CA. She grew up in Cape Canaveral, FL, and received her B.A. in Chemistry from the Honors College of Florida Atlantic University in 2005. She earned her Ph.D. in Chemistry from the California Institute of Technology in 2010, where she investigated various lanthanide-based receptor sites for the detection of bacterial spores in extreme environments under advisors Harry Gray and Adrian Ponce. Her current work as a NASA Postdoctoral Program (NPP) fellow involves the development of ultrasensitive micro-total analysis systems for the in situ detection of organics on Titan.

Dr. Sarah Hörst is currently a NSF Astronomy and Astrophysics Postdoctoral Fellow at the Cooperative Institute for Research in Environmental Sciences (CIRES) at the University of Colorado—Boulder. She received a B.S. in Planetary Science from the California Institute of Technology and a Ph.D in Planetary Sciences from the University of Arizona. Her current research interests include understanding the organic chemistry occurring in Titan's atmosphere and the formation and composition of aerosols in planetary atmospheres.

Dr. Robert Hodyss received his B.S. in Chemistry from the University of Florida in 1999. Afterwards he entered the graduate program at the California Institute of Technology, joining the research group of Prof. J. L Beauchamp. He was awarded a Ph.D. in physical chemistry at Caltech in 2006. A two-year postdoctoral position at the Jet Propulsion Laboratory led to a position as a research scientist at JPL. His research interests include the chemistry and physics of ices in the outer solar system and the chemistry of Titan's liquid ethane lakes.

Dr. Beauchamp joined the Jet Propulsion Laboratory in Pasadena, CA, in 1992 after a decade in surface science research at Aerojet Electrosystems Co. She is currently working on developing future outer planet missions and was responsible for coordinating the effort to define the scientific rationale for the next flagship mission to Titan, the instruments needed, and how the data could be obtained that would satisfy those requirements. She is also a convener and theme lead on the NASA Astrobiology Institute's "Titan as a Prebiotic Chemical System" session. Prior to that she managed the Planetary Instrument Development office and led the Center for In-Situ Exploration and Sample Return (CISSR) in the Engineering and Science Directorate. She was Project Manager for the Miniature Integrated Camera Spectrometer, which flew on the New Millennium DS1 mission in 1998, and has held several technical and management positions in the Observational Instruments Division. Dr. Beauchamp obtained her Ph.D in Chemistry from Caltech followed by postdoctoral research in Chemical Engineering at Caltech, where she conducted fundamental investigations of chemical reactions on single crystal surfaces. She received her B.S. in Chemistry and B.A. in Mathematics with honors from California State University, Fullerton, in 1976. She has received a number of student and professional awards, most recently JPL's highest Explorer award, and is the author or coauthor of over 40 scientific publications, a patent, and numerous government technical reports.

Dr. Mark Smith grew up in California and received degrees from the University of Oregon (B.S. in Chemistry), Massachusetts Institute of Technology (M.S. in Organic Chemistry), and University of Colorado and the Joint Institute for Laboratory Astrophysics (Ph.D. in Physical Chemistry). He did postdoctoral work with John Polanyi (Nobel Laureate in Chemistry, 1986) at the University of Toronto from 1983 to 1985, before assuming a faculty position in chemistry at the University of Arizona, in Tucson. His most recent positions were as Department Head, Department of Chemistry and Biochemistry (2002−2010) and Professor of Planetary Science. In January 2011, Dr. Smith moved to Houston to assume the role of Dean of the College of Natural Sciences and Mathematics at the University of Houston. His research focus is on instrument development for the study of space chemistry in support of astronomical observation, current mission data return, and future planetary mission design. Smith's lab has investigated how far organic chemistry can evolve in the absence of life and what forms that chemistry takes. In this way, his group can shape the development of future outer planetary mission instrumentation to maximize the information return in our search for complex chemistry and potential life beyond Earth's environment.

Dr. Peter A. Willis received his B.Sc. degree in Chemical Physics at Queen's University in Kingston, Ontario, Canada, in 1994, while performing undergraduate research as a member of the Atomic Energy of Canada Limited. He received his Ph.D. in Chemistry in 1999 at Cornell University in Ithaca, NY, as the first graduate student of Prof. H. Floyd Davis. He performed his postdoctoral research in nanoscience and sensing in the laboratories of Richard Smalley at Rice University and James Heath at the California Institute of Technology. His current research at NASA's Jet Propulsion Laboratory focuses on the development of miniaturized chemical instrumentation for in situ planetary exploration, with a particular focus on next-generation Titan missions.

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ACRONYMS AND ABBREVIATIONS

ac	alternating current
ACP	aerosol collector pyrolyzer (Huygens)
AU	astronomical unit
BCA	bicinchoninic protein assay
BDE	bond dissociation energy
CAPS	Cassini plasma spectrometer (Cassini)
CCP	capacitively coupled plasma
CE	capillary electrophoresis
CIRS	composite infrared spectrometer (Cassini)
Da	daltons (equivalent to atomic mass units, amu)
dc	direct current
DISR	descent imager spectral radiometer (Huygens)
ELS	electron spectrometer (Cassini)
ESA	European Space Agency
ESI	electrospray ionization
EUV	extreme ultraviolet
FT	Fourier transform
GC	gas chromatography
IBS	ion beam spectrometer (Cassini)
ICP	inductively coupled plasma
IR	infrared
IUPAC	International Union of Pure and Applied Chemistry
KISS	Keck Institute for Space Studies
KMD	Kendrick mass defect
LC	liquid chromatography
LIP	laser-induced plasma
LOC	lab on a chip
MS	mass spectrometry
NACE	nonaqueous capillary electrophoresis
NIR	near-infrared
PAH	polycyclic aromatic hydrocarbon
PANH	polycyclic aromatic nitrogenated hydrocarbons
PAMPRE	French acronym for aerosol production in microgravity by reactive plasma
rf	radio frequency
SEM	scanning electron microscopy
SETUP	French acronym for theoretical and experimental studies useful for planetology
SMPS	scanning particle mobility sizer
SPS	second positive system
TEM	transmission electron microscopy
TLC	thin-layer chromatography
UV	ultraviolet
VIMS	visual and infrared mapping spectrometer (Cassini)
VUV	vacuum ultraviolet
YAG	yttrium aluminum garnet

REFERENCES

(1) Sagan, C.; Thompson, W. R.; Khare, B. N. *Acc. Chem. Res.* **1992**, *25*, 286.

(2) Raulin, F. In *Planetary Systems and the Origins of Life*; Pudritz, R. E., Higgs, P. G., Stone, J. R., Eds.; Cambridge University Press: New York, 2007.

(3) Czechowski, L.; Kossacki, K. *Icarus* **2009**, *202*, 599.

(4) For the purposes of this review, we define "polymerization" as the formation of macromolecules (i.e., tholins) from many different monomers/precursors, akin to a random (statistical) copolymer.

(5) *Titan from Cassini—Huygens*; Brown, R. H., Lebreton, J.-P., Waite, J. H., Eds.; Springer: New York, 2009.

(6) Raulin, F.; Bruston, P.; Paillous, P.; Sternberg, R. *Adv. Space Res.* **1995**, *15*, 321.

(7) Raulin, F.; Coll, P.; Coscia, D.; Gazeau, M.-C.; Sternberg, R.; Bruston, P.; Israel, G.; Gautier, D. *Adv. Space Res.* **1998**, *22*, 353.

(8) Lorenz, R. D.; Wall, S.; Radebaugh, J.; Boubin, G.; Reffet, E.; Janssen, M.; Stofan, E.; Lopes, R.; Kirk, R.; Elachi, C.; Lunine, J. I.; Mitchell, K. A.; Paganelli, F.; Soderblom, L.; Wood, C. A.; Wye, L.; Zebker, H.; Ostro, S.; Allison, M. D.; Boehmer, R.; Callahan, P.; Encrenaz, P.; Ori, G. G.; Francescetti, G.; Gim, Y.; Hamilton, G.; Hensley, S.; Johnson, W.; Kelleher, K.; Muhleman, D.; Picardi, G.; Posa, F.; Roth, L.; Seu, R.; Shaffer, S.; Stiles, B.; Vetrella, S.; Flamini, E.; West, R. A. *Science* **2006**, *312*, 724.

(9) Radebaugh, J.; Lorenz, R. D.; Lunine, J. I.; Wall, S. D.; Boubin, G.; Reffet, E.; Kirk, R. L.; Lopes, R. M.; Stofan, E. R.; Soderblom, L.; Allison, M. D.; Janssen, M.; Paillou, P.; Callahan, P.; Spencer, J. R. *Icarus* **2008**, *194*, 690.

(10) Stofan, E. R.; Elachi, C.; Lunine, J. I.; Lorenz, R. D.; Stiles, B.; Mitchell, K. L.; Ostro, S.; Soderblom, L. A.; Wood, C. A.; Zebker, H.; Wall, S.; Janssen, M.; Kirk, R.; Lopes, R.; Paganelli, F.; Radebaugh, J.; Wye, L.; Anderson, Y.; Allison, M. D.; Boehmer, R.; Callahan, P.; Encrenaz, P.; Flamini, E.; Francescetti, G.; Gim, Y.; Hamilton, G.; Hensley, S.; Johnson, W. T. K.; Kelleher, K.; Muhleman, D.; Paillou, P.; Picardi, G.; Posa, F.; Roth, L.; Seu, R.; Shaffer, S.; Vetrella, S.; West, R. A. *Nature* **2007**, *445*, 61.

(11) Brown, R. H.; Soderblom, L. A.; Soderblom, J. M.; Clark, R. N.; Jaumann, R.; Barnes, J. W.; Sotin, C.; Buratti, B. J.; Baines, K. H.; Nicholson, P. D. *Nature* **2008**, *454*, 607.

(12) McKay, C. P.; Pollack, J. B.; Courtin, R. *Icarus* **1989**, *80*, 23.

(13) Raulin, F.; Owen, T. *Space Sci. Rev.* **2002**, *104*, 377.

(14) Lorenz, R. D.; Sotin, C. *Sci. Am.* **2010**, *302*, 36.

(15) Atreya, S. K. *Science* **2007**, *316*, 843.

(16) Lunine, J. I.; Atreya, S. K. *Nat. Geosci.* **2008**, *1*, 159.

(17) *Lifting Titan's Veil: Exploring the Giant Moon of Saturn*; Lorenz, R. D., Mitton, J., Eds.; Cambridge University Press: New York, 2002.

(18) *Titan Unveiled*; Lorenz, R. D., Mitton, J., Eds.; Princeton University Press: Princeton, NJ, 2008.

(19) Sagan, C. In *The Atmosphere of Titan*; Hunten, D. M., Ed.; NASA Special Publication 340; 1974; Vol. SP-340.

(20) Raulin, F. *Space Sci. Rev.* **2005**, *116*, 471.

(21) Flasar, F. M.; Acherberg, R. K.; Conrath, B. J.; Gierasch, P. J.; Kunde, V. G.; Nixon, C. A.; Bjoraker, G. L.; Jennings, D. E.; Romani, P. N.; Simon-Miller, A. A.; Bézard, B.; Coustenis, A.; Irwin, P. G. J.; Teanby, N. A.; Brasunas, J.; Pearl, J. C.; Segura, M. E.; Carlson, R. C.; Mamoutkine, A.; Schinder, P. J.; Barucci, A.; Courtin, R.; Fouchet, T.; Gautier, D.; Lellouch, E.; Marten, A.; Prangé, R.; Vinatier, S.; Strobel, D. F.; Calcutt, S. B.; Read, P. L.; Taylor, F. W.; Bowles, N. E.; Samuelson, R. E.; Orton, G. S.; Spilker, L. J.; Owen, T. C.; Spencer, J. R.; Showalter, M. R.; Ferrari, C.; Abbas, M. M.; Raulin, F.; Edgington, S.; Ade, P.; Wishnow, E. H. *Science* **2005**, *308*, 975.

(22) Samuelson, R. E.; Maguire, W. C.; Hanel, R. A.; Kunde, V. G.; Jennings, D. E.; Yung, Y. L.; Aikin, A. C. *J. Geophys. Res.* **1983**, *88*, 8709.

(23) Coustenis, A.; Salama, A.; Lellouch, E.; Encrenaz, T. H.; Bjoraker, G. L.; Samuelson, R. E.; de Graauw, T.; Feuchtgruber, H.; Kessler, M. F. *Astron. Astrophys.* **1998**, *336*, L85.

(24) Niemann, H. B.; Atreya, S. K.; Bauer, S. J.; Carignan, G. R.; Demick, J. E.; Frost, R. L.; Gautier, D.; Haberman, J. A.; Harpold, D. N.; Hunten, D. M.; Israël, G.; Lunine, J. I.; Kazprzak, W. T.; Owen, T. C.; Paulkovich, M.; Raulin, F.; Raaen, E.; Way, S. H. *Nature* **2005**, *438*, 779.

(25) Niemann, H.; Atreya, S. K.; Demick, J. E.; Gautier, D.; Haberman, J. A.; Harpold, D. N.; Kasprzak, W. T.; Lunine, J. I.; Owen, T. C.; Raulin, F. *J. Geophys. Res.* **2010**, *115*, E12006.

(26) Strobel, D. F. *Icarus* **2010**, *208*, 878.

(27) Krasnopolsky, V. A. *Icarus* **2009**, *201*, 226.

(28) Lavvas, P. P.; Coustenis, A.; Vardavas, I. M. *Planet. Space Sci.* **2008**, *56*, 27.

(29) Lavvas, P. P. *Planet. Space Sci.* **2008**, *56*, 67.

(30) Lavvas, P.; Sander, M.; Kraft, M.; Imanaka, H. *Astrophys. J.* **2011**, *728*, 1.

(31) Krasnopolsky, V. A. *Planet. Space Sci.* **2010**, *58*, 1507.

(32) Lavvas, P.; Yelle, R. V.; Griffith, C. A. *Icarus* **2010**, *210*, 832.

(33) Lavvas, P.; Griffith, C. A.; Yelle, R. V. *Icarus* **2011**in press.

(34) Neish, C. D.; Somogyi, A.; Imanaka, H.; Lunine, J. I.; Smith, M. A. *Astrobiology* **2008**, *8*, 273.

(35) Artemieva, N.; Lunine, J. I. *Icarus* **2003**, *164*, 471.

(36) Neish, C. D.; Lorenz, R. D.; O'Brien, D. P. *Int. J. Astrobiol.* **2006**, *5*, 57.

(37) Lopes, R.; Mitchell, K. L.; Stofan, E. R.; Lunine, J. I.; Lorenz, R. D.; Paganelli, F.; Kirk, R. L.; Wood, C. A.; Wall, S. D.; Robshaw, L. E.; Fortes, A. D.; Neish, C. D.; Radebaugh, J.; Reffet, E.; Ostro, S. J.; Elachi, C.; Allison, M. D.; Anderson, Y.; Boehmer, R.; Boubin, G.; Callahan, P.; Encrenaz, P.; Flamini, E.; Francescetti, G.; Gim, Y.; Hamilton, G.; Hensley, S.; Janssen, M. A.; Johnson, W. T. K.; Kelleher, K.; Muhleman, D. O.; Ori, G.; Orosei, R.; Picardi, G.; Posa, F.; Roth, L. E.; Seu, R.; Shaffer, S.; Soderblom, L. A.; Stiles, B.; Vetrella, S.; West, R. D.; Wye, L.; Zebker, H. *Icarus* **2007**, *186*, 395.

(38) Moore, J. M.; Pappalardo, R. T. *Icarus* **2011**, *212*, 790.

(39) Kirk, R. L.; Howington-Kraus, E.; Barnes, J. W.; Hayes, A. G.; Lopes, R. M.; Lorenz, R. D.; Lunine, J. I.; Mitchell, K. L.; Stofan, E. R.; Wall, S. D. In *American Geophysical Union 2010 Fall Meeting, San Francisco, CA*; AGU: Washington, DC, 2010.

(40) Borucki, W. J.; McKay, C. P. *Nature* **1987**, *328*, 509.

(41) Borucki, W. J.; Giver, L. P.; McKay, C. P.; Scattergood, T.; Parris, J. E. *Icarus* **1988**, *76*, 125.

(42) Fischer, G.; Gurnett, D. A.; Kurth, W. S.; Farrell, W. M.; Kaiser, M. L.; Zarka, P. *Geophys. Res. Lett.* **2007**, *34*, L22104.

(43) Fulchignoni, M.; Ferri, F.; Angrilli, F.; Bar-Nun, A.; Barucci, A.; Bianchini, G.; Borucki, W.; Coradini, A.; Coustenis, A.; Falkner, P.; Flamini, E.; Grard, R.; Hamelin, M.; Harri, A. M.; Leppelmeier, G. W.; Lopez-Moreno, J. J.; McDonnell, J. A. M.; McKay, C. P.; Neubauer, F. M.; Pedersen, A.; Picardi, G.; Pirronello, V.; Rodrigo, R.; Schwingenschuh, K.; Seiff, A.; Svedhem, H.; Vanzani, V.; Zarnecki, J. C. *Space Sci. Rev.* **2002**, *104*, 395.

(44) Gurnett, D. A.; Kurth, W. S.; Kirchner, D. L.; Hospodarsky, G. B.; Averkamp, T. F.; Zarka, P.; Lecacheux, A.; Manning, R.; Roux, A.; Canu, P.; Cornilleau-Wehrlin, N.; Galopeau, P.; Meyer, A.; Bostrom, R.; Gustafsson, G.; Wahlund, J.-E.; Ahlen, L.; Rucker, H. O.; Ladreiter, H. P.; Macher, W.; Woolliscroft, L. J. C.; Alleyne, H.; Kaiser, M. L.; Desch, M. D.; Farrell, W. M.; Harvey, C. C.; Louarn, P.; Kellogg, P. J.; Goetz, K.; Pedersen, A. *Space Sci. Rev.* **2004**, *114*, 395.

(45) Fischer, G.; Gurnett, D. A. *Geophys. Res. Lett.* **2011**, *38*, L08206.

(46) Sagan, C.; Khare, B. N. *Nature* **1979**, *277*, 102.

(47) Scattergood, T.; Lesser, P.; Owen, T. *Icarus* **1975**, *24*, 465.

(48) Gupta, S.; Ochiai, E.; Ponnamperuma, C. *Nature* **1981**, *293*, 725.

(49) Coll, P.; Coscia, D.; Smith, N.; Gazeau, M.-C.; Guez, L.; Raulin, F. *Origins Life Evol. Biosphere* **1998**, *28*, 195.

(50) Cassidy, T.; Coll, P.; Raulin, F.; Carlson, R. W.; Johnson, R. E.; Loeffler, M. J.; Hand, K. P.; Baragiola, R. A. *Space Sci. Rev.* **2010**, *153*, 299.

(51) Miller, S. L. *Science* **1953**, *117*, 528.

(52) Miller, S. L.; Urey, H. C. *Science* **1959**, *130*, 245.

(53) Dodonova, N. Y. *Russ. J. Phys. Chem. A* **1966**, *40*, 523.

(54) Richards, P. G.; Torr, D. G.; Torr, M. R. *J. Geophys. Res.* **1981**, *86*, 1495.

(55) Ferris, J. P.; Tran, B.; Joseph, J.; Vuitton, V.; Briggs, R.; Force, M. *Adv. Space Res.* **2005**, *36*, 251.

(56) Hodyss, R.; Howard, H. R.; Johnson, P. V.; Goguen, J. D.; Kanik, I. *Icarus* **2011**, *214*, 748.

(57) Miller, S. L. *J. Am. Chem. Soc.* **1955**, *77*, 2351.

(58) Miller, S. L. *Biochim. Biophys. Acta* **1957**, *23*, 480.

(59) Sanchez, R. A.; Ferris, J. P.; Orgel, L. E. *Science* **1966**, *154*, 784.

(60) Sagan, C.; Khare, B. N.; Thompson, W. R.; McDonald, G. D.; Wing, M. R.; Bada, J. L.; VoDinh, T.; Arakawa, E. T. *Astrophys. J.* **1993**, *414*, 399.

(61) McDonald, G. D.; Thompson, W. R.; Heinrich, M.; Khare, B. N.; Sagan, C. *Icarus* **1994**, *108*, 137.

(62) Ruiz-Bermejo, M.; Menor-Salvan, C.; Fuente, J. L. d. l.; Mateo-Marti, E.; Osuna-Esteban, S.; Martin-Gago, J. A.; Veintemillas-Verdaguer, S. *Icarus* **2009**, *204*, 672.

(63) Ruiz-Bermejo, M.; Menor-Salvan, C.; Mateo-Marti, E.; Osuna-Esteban, S.; Martin-Gago, J. A.; Veintemillas-Verdaguer, S. *Icarus* **2008**, *198*, 232.

(64) Ruiz-Bermejo, M.; Menor-Salvan, C.; Osuna-Esteban, S.; Veintemillas-Verdaguer, S. *Origins Life Evol. Biosphere* **2007**, *37*, 123.

(65) Coates, A. J.; Crary, F.; Lewis, G.; Young, D. T.; J. H. Waite, J.; Sittler, E. C. *J. Geophys. Res. Lett.* **2007**, *34*, L22103.

(66) Coates, A. J.; Wellbrock, A.; Lewis, G. R.; Jones, G. H.; Young, D. T.; Crary, F. J.; J. H. Waite, J. *Planet. Space Sci.* **2009**, *57*, 1866.

(67) Crary, F. J.; Magee, B. A.; Mandt, K. E.; Waite, J. H.; Westlake, J.; Young, D. T. *Planet. Space Sci.* **2009**, *57*, 1847.

(68) Lara, L. M.; Lorenz, R. D.; Rodrigo, R. *Planet. Space Sci.* **1994**, *42*, 5.

(69) Zhang, X.; Ajello, J. M.; Yung, Y. L. *Astrophys. J. Lett.* **2010**, *708*, L18.

(70) Lindal, G. F.; Wood, G. E.; Hotz, H. B.; Sweetnam, D. N.; Eschleman, V. R.; Tyler, G. L. *Icarus* **1983**, *53*, 348.

(71) Hanel, R.; Conrath, B.; Flasar, F. M.; Kunde, V. G.; Maguire, W.; Pearl, J. C.; Pirraglia, J.; Samuelson, R. E.; Herath, L.; Allison, M. D.; Cruikshank, D.; Gautier, D.; Gierasch, P. J.; Horn, L.; Koppany, R. *Science* **1981**, *114*, 144.

(72) Khare, B. N.; Sagan, C.; Zumberge, J.; Sklarew, D.; Nagy, B. *Icarus* **1981**, *48*, 290.

(73) Khare, B. N.; Sagan, C.; Arakawa, E. T.; Suits, F.; Calllcott, T. A.; Williams, M. W. *Icarus* **1984**, *60*, 127.

(74) Khare, B. N.; Sagan, C.; Thompson, W. R.; Arakawa, E. T.; Suits, F.; Callcott, T. A.; Williams, M. W.; Schrader, S.; Ogino, H.; Willingham, T. O.; Nagy, B. *Adv. Space Res.* **1984**, *4*, 59.

(75) Khare, B. N.; Sagan, C.; Ogino, H.; Nagy, C.; Er, C.; Schram, K. H.; Arakawa, E. T. *Icarus* **1986**, *68*, 176.

(76) Sagan, C.; Thompson, W. R. *Icarus* **1984**, *59*, 133.

(77) Thompson, W. R.; McDonald, G. D.; Sagan, C. *Icarus* **1994**, *112*, 376.

(78) Coll, P.; Coscia, D.; Gazeau, M. C.; Raulin, F. *Adv. Space Res.* **1997**, *19*, 1113.

(79) Navarro-Gonzalez, R.; Ramirez, S. I.; Rosa, J. G. d. l.; Coll, P.; Raulin, F. *Adv. Space Res.* **2001**, *27*, 271.

(80) Alcouffe, G.; Cavarroc, M.; Cernogora, G.; Ouni, F.; Jolly, A.; Boufendi, L.; Szopa, C. *Plasma Sources Sci. Technol.* **2010**, *19*, 015008.

(81) Jaworek, A.; Krupa, A. *Czech. J. Phys.* **1995**, *45*, 1035.

(82) Szopa, C.; Cernogora, G.; Boufendi, L.; Correia, J.-J.; Coll, P. *Planet. Space Sci.* **2006**, *54*, 394.

(83) Chang, J.-S.; Maezono, I. *J. Phys. D: Appl. Phys.* **1988**, *21*, 1023.

(84) Pintassilgo, C. D.; Loureiro, L.; Cernogora, G.; Touzeau, M. *Plasma Sources Sci. Technol.* **1999**, *8*, 463.

(85) Pintassilgo, C. D.; Cernogora, G.; Loureiro, L. *Plasma Sources Sci. Technol.* **2001**, *10*, 147.

(86) Chang, J.-S.; Lawless, P. A.; Yamamoto, T. *IEEE Trans. Plasma Sci.* **1991**, *19*, 1152.

(87) Yeddanapalli, L. M. *J. Chem. Phys.* **1942**, *10*, 249.

(88) Ramirez, S. I.; Navarro-Gonzalez, R.; Coll, P.; Raulin, F. *Adv. Space Res.* **2005**, *36*, 274.

(89) Tokano, T.; McKay, C. P.; Neubauer, F. M.; Atreya, S. K.; Francesca, F.; Fulchignoni, M.; Niemann, H. B. *Nature* **2006**, *442*, 432.

(90) Lammer, H.; Tokano, T.; Fischer, G.; Stumptner, W.; Molina-Cuberos, G. J.; Schwingenschuh, K.; Rucker, H. O. *Planet. Space Sci.* **2001**, *49*, 561.

(91) Cabane, M.; Chassefière, E. *Planet. Space Sci.* **1995**, *43*, 47.

(92) Thompson, W. R.; Henry, T. J.; Schwartz, J. M.; Khare, B. N.; Sagan, C. *Icarus* **1991**, *90*, 57.

(93) Paris, P.; Aints, M.; Valk, F.; Plank, T.; Haljaste, A.; Kozlov, K. V.; Wagner, H.-E. *J. Phys. D: Appl. Phys.* **2005**, *38*, 3894.

(94) Scattergood, T. W.; McKay, C. P.; Borucki, W. J.; Giver, L. P.; Ghyseghem, H. v.; Parris, J. E.; Miller, S. L. *Icarus* **1989**, *81*, 413.

(95) Sagan, C.; Khare, B. N. *Science* **1971**, *173*, 417.

(96) Navarro-Gonzalez, R.; Ramirez, S. I. *Adv. Space Res.* **1997**, *19*, 1121.

(97) Kovacs, T.; Turanyi, T. *Icarus* **2010**, *207*, 938.

(98) Ramirez, S. I.; Navarro-Gonzalez, R.; Coll, P.; Raulin, F. *Adv. Space Res.* **2001**, *27*, 261.

(99) Romanzin, C.; Arzoumanian, E.; Es-sebbar, E.; Jolly, A.; Perrier, S.; Gazeau, M.-C.; Benilan, Y. *Planet. Space Sci.* **2010**, *58*, 1748.

(100) Imanaka, H.; Smith, M. A. *J. Phys. Chem. A* **2009**, *113*, 11187.

(101) Thissen, R.; Vuitton, V.; Lavvas, P.; Lemaire, J.; Dehon, C.; Dutuit, O.; Smith, M. A.; Turchini, S.; Catone, D.; Yelle, R. V.; Pernot, P. N.; Somogyi, A.; Coreno, M. *J. Phys. Chem. A* **2009**, *113*, 11211.

(102) Imanaka, H.; Smith, M. A. *Geophys. Res. Lett.* **2007**, *34*, L02204.

(103) Dendy, P. P.; Heaton, B. In *Physics for Diagnostic Radiology*, 2nd ed.; Dendy, P. P., Heaton, B., Eds.; Institute of Physics Publishing: London, 1999.

(104) Molina-Cuberos, G. J.; Lopez-Moreno, J. J.; Rodrigo, R.; Lara, L. M.; O'Brien, K. *Planet. Space Sci.* **1999**, *47*, 1347.

(105) Capone, L. A.; Dubach, J.; Prasad, S. S.; Whitten, R. C. *Icarus* **1983**, *55*, 73.

(106) Penz, T.; Lammer, H.; Kulikov, Y. N.; Biernat, H. K. *Adv. Space Res.* **2005**, *36*, 241.

(107) Imanaka, H.; Smith, M. A. Manuscript in preparation.

(108) Bernard, J.-M.; Quirico, E.; Brissaud, O.; Montagnac, G.; Reynard, B.; McMillan, P. F.; Coll, P.; Nguyen, M.-J.; Raulin, F.; Schmitt, B. *Icarus* **2006**, *185*, 301.

(109) Jacovi, R.; Bar-Nun, A. *Icarus* **2008**, *196*, 302.

(110) McKay, C. P.; Coustenis, A.; Samuelson, R. E.; Lemmon, M. T.; Lorenz, R. D.; Cabane, M.; Rannou, P.; Drossart, P. *Planet. Space Sci.* **2001**, *49*, 79.

(111) Pilling, S.; Andrade, D. P. P.; Neto, A. C.; Rittner, R.; Brito, A. N. d. *J. Phys. Chem. A* **2009**, *113*, 11161.

(112) Somogyi, A.; Oh, C.; Smith, M. A.; Lunine, J. I. *J. Am. Soc. Mass Spectrom.* **2005**, *16*, 850.

(113) Tran, B. N.; Ferris, J. P.; Chera, J. J. *Icarus* **2003**, *162*, 114.

(114) Clarke, D. W.; Joseph, J. C.; Ferris, J. P. *Icarus* **2000**, *147*, 282.

(115) Imanaka, H.; Smith, M. A. *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107*, 12423.

(116) Tran, B.; Force, M.; Briggs, R.; Ferris, J. P.; Persans, P.; Chera, J. *Icarus* **2008**, *193*, 224.

(117) Quirico, E.; Montagnac, G.; Lees, V.; McMillan, P. F.; Szopa, C.; Cernogora, G.; Rouzaud, J.-N.; Simon, P.; Bernard, J.-M.; Coll, P.; Fray, N.; Minard, R. D.; Raulin, F.; Reynard, B.; Schmitt, B. *Icarus* **2008**, *198*, 218.

(118) Clarke, D. W.; Ferris, J. P. *Icarus* **1997**, *127*, 158.

(119) Jacovi, R.; Laufer, D.; Dimitrov, V.; Bar-Nun, A. *J. Geophys. Res.—Planet* **2010**, *115*, E07006.

(120) Hörst, S. M.; Yelle, R. V.; Buch, A.; Carrasco, N.; Cernogora, G.; Dutuit, O.; Quirico, E.; Sciamma-O'Brien, E.; Smith, M. A.; Somogyi, A.; Szopa, C.; Thissen, R.; Vuitton, V. *Astrobiology* **2011**in press.

(121) Poch, O.; Coll, P.; Buch, A.; Ramirez, S. I.; Raulin, F. *Planet. Space Sci.* **2011**in press.

(122) Khare, B. N.; Bakes, E. L. O.; Imanaka, H.; McKay, C. P.; Cruikshank, D. P.; Arakawa, E. T. *Icarus* **2002**, *160*, 172.

(123) Tran, B. N.; Joseph, J. C.; Ferris, J. P.; Persans, P. D.; Chera, J. J. *Icarus* **2003**, *165*, 379.

(124) McKay, C. P. *Planet. Space Sci.* **1996**, *44*, 741.

(125) Raulin, F.; Dubouloz, N.; Frere, C. *Adv. Space Res.* **1989**, *9*, 35.

(126) Coll, P.; Coscia, D.; Smith, N.; Gazeau, M.-C.; Ramirez, S. I.; Cernogora, G.; Israel, G.; Raulin, F. *Planet. Space Sci.* **1999**, *47*, 1433.

(127) Vanssay, E. d.; Gazeau, M. C.; Guillemin, J. C.; Raulin, F. *Planet. Space Sci.* **1995**, *43*, 25.

(128) Carrasco, N.; Alcaraz, C.; Dutuit, O.; Plessis, S.; Thissen, R.; Vuitton, V.; Yelle, R. V.; Pernot, P. *Planet. Space Sci.* **2008**, *56*, 1644.

(129) Coll, P.; Coscia, D.; Smith, N.; Gazeau, M.-C.; Ramirez, S. I.; Cernogora, G.; Israel, G.; Raulin, F. *Planet. Space Sci.* **1999**, *47*, 1331.

(130) Imanaka, H.; Khare, B. N.; E., E. J.; Bakes, E. L. O.; McKay, C. P.; Cruikshank, D. P.; Sugita, S.; Matsui, T.; Zare, R. N. *Icarus* **2004**, *168*, 344.

(131) Cruikshank, D. P.; Imanaka, H.; Dalle, O. C. *Adv. Space Res.* **2005**, *36*, 178.

(132) Lavvas, P.; Yelle, R. V.; Vuitton, V. *Icarus* **2009**, *201*, 626.

(133) McGuigan, M.; Waite, J. H.; Imanaka, H.; Sacks, R. D. *J. Chromatogr., A* **2006**, *1132*, 280.

(134) Roush, T. L.; Dalton, J. B. *Icarus* **2004**, *168*, 158.

(135) Coll, P.; Coscia, D.; Gazeau, M. C.; Vanssay, E. d.; Guillemin, J. C.; Raulin, F. *Adv. Space Res.* **1995**, *16*, 93.

(136) Ramirez, S. I.; Coll, P.; Buch, A.; Brassé, C.; Poch, O.; Raulin, F. *Faraday Discuss.* **2010**, *147*, 419.

(137) Vuitton, V.; Tran, B. N.; Persans, P. D.; Ferris, J. P. *Icarus* **2009**, *203*, 663.

(138) Ramirez, S. I.; Coll, P.; Silva, A. d.; Navarro-Gonzalez, R.; Lafait, J.; Raulin, F. *Icarus* **2002**, *156*, 515.

(139) Nguyen, M.-J.; Raulin, F.; Coll, P.; Derenne, S.; Szopa, C.; Cernogora, G.; Israel, G.; Bernard, J.-M. *Planet. Space Sci.* **2007**, *55*, 2010.

(140) Joseph, J. C., Ph.D. Thesis, Rensselaer Polytechnic Institute, 1999.

(141) Tran, B.; Joseph, J.; Force, M.; Briggs, R.; Vuitton, V.; Ferris, J. P. *Icarus* **2005**, *177*, 106.

(142) Sarker, N.; Somogyi, A.; Lunine, J. I.; Smith, M. A. *Astrobiology* **2003**, *3*, 719.

(143) Hodyss, R.; McDonald, G. D.; Sarker, N.; Smith, M. A.; Beauchamp, P. M.; Beauchamp, J. L. *Icarus* **2004**, *171*, 525.

(144) Coll, P.; Bernard, J.-M.; Navarro-Gonzalez, R.; Raulin, F. *Astrophys. J.* **2003**, *598*, 700.

(145) Majumdar, A.; Behnke, J. F.; Hippler, H.; Matyash, K.; Schneider, R. *J. Phys. Chem. A* **2005**, *109*, 9371.

(146) Neish, C. D.; Somogyi, A.; Lunine, J. I.; Smith, M. A. *Icarus* **2009**, *201*, 412.

(147) Neish, C. D.; Somogyi, A.; Smith, M. A. *Astrobiology* **2010**, *10*, 337.

(148) Hörst, S. M., personal communication.

(149) Romanzin, C.; Benilan, Y.; Jolly, A.; Gazeau, M.-C. *Adv. Space Res.* **2008**, *42*, 2036.

(150) Gazeau, M.-C.; Es-Sebbar, E.; Arzoumanian, E.; Romanzin, C.; Jolly, A.; Perrier, S.; Benilan, Y. In *European Planetary Science Congress*, 2009; Vol. 4.

(151) Waite, J. H.; Young, D. T.; Cravens, T. E.; Coates, A. J.; Crary, F. J.; Magee, B.; Westlake, J. *Science* **2007**, *316*, 870.

(152) Rages, K.; Pollack, J. B. *Icarus* **1980**, *41*, 119.

(153) Samuelson, E.; Mayo, L. A. *Icarus* **1991**, *91*, 207.

(154) Vuitton, V.; Bonnet, J.-Y.; Frisari, M.; Thissen, R.; Quirico, E.; Dutuit, O.; Schmitt, B.; Le Roy, L.; Fray, N.; Cottin, H.; Sciamma-O'Brien, E.; Carrasco, N.; Szopa, C. *Faraday Discuss.* **2010**, *147*, 495.

(155) Carrasco, N.; Schmitz-Afonso, I.; Bonnet, J.-Y.; Quirico, E.; Thissen, R.; Dutuit, O.; Bagag, A.; Laprevote, O.; Buch, A.; Guilani, A.; Adande, G.; Ouni, F.; Hadamcik, E.; Szopa, C.; Cernogora, G. *J. Phys. Chem. A* **2009**, *113*, 11195.

(156) Hasenkopf, C. A.; Beaver, M. R.; Trainer, M. G.; Dewitt, H. L.; Freedman, M. A.; Toon, O. B.; McKay, C. P.; Tolbert, M. A. *Icarus* **2010**, *207*, 903.

(157) Tomasko, M. G.; Archinal, B.; Becker, T.; Bézard, B.; Bushroe, M.; Combes, M.; Cook, D.; Coustenis, A.; de Bergh, C.; Dafoe, L. E.; Doose, L.; Douté, S.; Eibl, A.; Engel, S.; Gliem, F.; Grieger, B.; Holso, K.; Howington-Kraus, E.; Karkoschka, E.; Keller, H. U.; Kirk, R.; Kramm, R.; Küppers, M.; Lanagan, P.; Lellouch, E.; Lemmon, M. T.; Lunine, J. I.; McFarlane, E.; Moores, J.; Prout, G. M.; Rizk, B.; Rosiek, M.; Rueffer, P.; Schröder, S. E.; Schmitt, B.; See, C.; Smith, P. H.; Soderblom, L. A.; Thomas, N.; West, R. A. *Nature* **2005**, *438*, 765.

(158) Khare, B. N.; Sagan, C.; Thompson, W. R.; Arakawa, E. T.; Tuminello, P. S. *Bull. Am. Astron. Soc.* **1993**, *25*, 1100.

(159) Hadamcik, E.; Renard, J.-B.; Alcouffe, G.; Cernogora, G.; Levasseur-Regourd, A.-C.; Szopa, C. *Planet. Space Sci.* **2009**, *57*, 1631.

(160) Elachi, C.; Wall, S.; Allison, M. D.; Anderson, Y.; Boehmer, R.; Callahan, P.; Encrenaz, P.; Flamini, E.; Francescetti, G.; Gim, Y.; Hamilton, G.; Hensley, S.; Janssen, M.; Johnson, W.; Kelleher, K.; Kirk, R.; Lopes, R.; Lorenz, R. D.; Lunine, J. I.; Muhleman, D.; Ostro, S.; Paganelli, F.; Picardi, G.; Posa, F.; Roth, L.; Seu, R.; Shaffer, S.; Soderblom, L.; Stiles, B.; Stofan, E.; Vetrella, S.; West, R. A.; Wood, C. A.; Wye, L.; Zebker, H. *Science* **2005**, *308*, 970.

(161) Tomasko, M. G.; Doose, L.; Engel, S.; Dafoe, L. E.; West, R.; Lemmon, M.; Karkoschka, E.; See, C. *Planet. Space Sci.* **2008**, *56*, 669.

(162) Coll, P.; Ramirez, S. I.; Navarro-Gonzalez, R.; Raulin, F. *Adv. Space Res.* **2001**, *27*, 289.

(163) Hodyss, R.; Johnson, P. V.; Kanik, I. In *Astrobiology Science Conference*, 2010.

(164) Raulin, F. *Adv. Space Res.* **1987**, *7*, 71.

(165) Hodyss, R., personal communication.

(166) Courtin, R.; Gautier, D.; McKay, C. P. *Icarus* **1995**, *114*, 144.

(167) Curtis, D. B.; Hatch, C. D.; Hasenkopf, C. A.; Toon, O. B.; Tolbert, M. A.; McKay, C. P.; Khare, B. N. *Icarus* **2008**, *195*, 792.

(168) Rannou, P.; Cours, T.; Mouelic, S. L.; Rodriguez, S.; Sotin, C.; Drossart, P.; Brown, R. *Icarus* **2010**, *208*, 850.

(169) Rannou, P.; McKay, C. P.; Lorenz, R. D. *Planet. Space Sci.* **2003**, *51*, 963.

(170) Rannou, P.; McKay, C. P.; Botet, R.; Cabane, M. *Planet. Space Sci.* **1999**, *47*, 385.

(171) Rages, K.; Pollack, J. B.; Smith, P. H. *J. Geophys. Res.—Planet* **1983**, *88*, 8721.

(172) West, R. A.; Smith, P. H. *Icarus* **1991**, *90*, 330.

(173) Scattergood, T. W.; Lau, E. Y.; Stone, B. M. *Icarus* **1992**, *99*, 98.

(174) Toublanc, D.; Parisot, J. P.; Brillet, J.; Gautier, D.; Raulin, F.; McKay, C. P. *Icarus* **1995**, *113*, 2.

(175) Trainer, M. G.; Pavlov, A. A.; Jimenez, J. L.; McKay, C. P.; Worsnop, D. R.; Toon, O. B.; Tolbert, M. A. *Geophys. Res. Lett.* **2004**, *31*, L17S0.

(176) Trainer, M. G.; Pavlov, A. A.; DeWitt, H. L.; Jimenez, J. L.; McKay, C. P.; Toon, O. B.; Tolbert, M. A. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 18035.

(177) Waite, J. H.; Niemann, H.; Yelle, R. V.; Kasprsak, W. T.; Cravens, T. E.; Luhmann, J. G.; McNutt, R. L.; Ip, W.-H.; Gell, D.; De la Haye, V.; Müller-Wordag, I.; Magee, B.; Borggren, N.; Ledvina, S.; Fletcher, G.; Walter, E.; Miller, R.; Scherer, S.; Thorpe, R.; Xu, J.; Block, B.; Arnett, K. *Science* **2005**, *308*, 982.

(178) Scattergood, T.; Owen, T. *Icarus* **1977**, *30*, 780.

(179) Nguyen, M.-J.; Raulin, F.; Coll, P.; Derenne, S.; Szopa, C.; Cernogora, G.; Israel, G.; Bernard, J.-M. *Adv. Space Res.* **2008**, *42*, 48.

(180) Upton, K. T.; Liu, G.; Munsch, T. E.; Imanaka, H.; Smith, M. A. *Bull. Am. Astron. Soc.* **2010**, *42*, 1069.

(181) Basile, B.; Lazcano, A.; Oro, J. *Adv. Space Res.* **1984**, *4*, 125.

(182) Pietrogrande, M. C.; Coll, P.; Sternberg, R.; Szopa, C.; Navarro-Gonzalez, R.; Vidal-Madjar, C.; Dondi, F. *J. Chromatogr., A* **2001**, *939*, 69.

(183) Ehrenfreund, P.; Boon, J. J.; Commandeur, J.; Sagan, C.; Thompson, W. R.; Khare, B. N. *Adv. Space Res.* **1995**, *15*, 335.

(184) Bernard, J.-M.; Coll, P.; Coustenis, A.; Raulin, F. *Planet. Space Sci.* **2003**, *51*, 1003.

(185) Pernot, P. N.; Carrasco, N.; Thissen, R.; Schmitz-Afonso, I. *Anal. Chem.* **2010**, *82*, 1371.

(186) Lara, L. M.; Lellouch, E.; Shematovich, V. *Astron. Astrophys.* **1999**, *341*, 312.

(187) Israël, G.; Szopa, C.; Raulin, F.; Cabane, M.; Niemann, H. B.; Atreya, S. K.; Bauer, S. J.; Brun, J.-F.; Chassefière, E.; P. Coll, E. C.; Coscia, D.; Hauchecorne, A.; Millian, P.; Nguyen, M.-J.; Owen, T.; Riedler, W.; Samuelson, R. E.; Siguier, J.-M.; Steller, M.; Sternberg, R.; Vidal-Madjar, C. *Nature* **2005**, *438*, 796.

(188) Minard, R. D.; Hatcher, P. G.; Gourley, R. C.; Matthews, C. N. *Origins Life Evol. Biosphere* **1998**, *28*, 461.

(189) Colangeli, L.; Brucato, J. R.; Ferrini, L.; Mennella, V.; Bussoletti, E.; Palumbo, P.; Rotundi, A. *Adv. Space Res.* **1999**, *23*, 1243.

(190) Eglinton, T. I.; Douglas, A. G.; Rowland, S. J. *Org. Geochem.* **1988**, *13*, 655.

(191) Thompson, W. R.; Sagan, C. *Origins Life Evol. Biosphere* **1989**, *19*, 503.

(192) Tobie, G.; Grasset, O.; Lunine, J. I.; Mocquet, A.; Sotin, C. *Icarus* **2005**, *175*, 496.

(193) Lunine, J. I.; Stevenson, D. J. *Icarus* **1987**, *70*, 61.

(194) Grasset, O.; Pargamin, J. *Planet. Space Sci.* **2005**, *53*, 371.

(195) Mitri, G.; Showman, A. P.; Lunine, J. I.; Lopes, R. M. C. *Icarus* **2008**, *196*, 216.

(196) Coll, P.; Ramirez, S. I.; Buch, A.; Brassé, C.; Raulin, F. In *Division of Planetary Sciences Meeting*; American Astronomical Society, 2009.

(197) O'Brien, D. P.; Lorenz, R. D.; Lunine, J. I. *Icarus* **2005**, *173*, 243.

(198) McDonald, G. N.; Khare, B. N.; Thompson, W. R.; Sagan, C. *Icarus* **1991**, *94*, 354.

(199) Kobayashi, K.; Hua, L.-L.; Gehrke, C. W.; Gerhardt, K. O.; Ponnamperuma, C. *Origins Life Evol. Biosphere* **1986**, *16*, 299.

(200) Kobayashi, K.; Hua, L.-L.; Hare, P. E.; Hobish, M. K.; Ponnamperuma, C. *Origins Life Evol. Biosphere* **1986**, *16*, 277.

(201) McKay, C. P.; Smith, H. D. *Icarus* **2005**, *178*, 274.

(202) Fortes, A. D. *Icarus* **2000**, *146*, 444.

(203) Raulin, F. *Space Sci. Rev.* **2008**, *135*, 37.

(204) Raulin, F.; Nguyen, M.-J.; Coll, P. In *Instruments, Methods and Missions for Astrobiology X*; Hoover, R. B., Levin, G. V., Rozanov, A. Y., Davies, P. C. W., Eds.; Proceedings of SPIE, San Diego, CA, 2007; Vol. 6694.

(205) Lerman, L. *Origins Life Evol. Biosphere* **1996**, *26*, 369.

(206) Sekine, Y.; Imanaka, H.; Matsui, T.; Khare, B. N.; Bakes, E. L. O.; McKay, C. P.; Sugita, S. *Icarus* **2008**, *194*, 186.

(207) Sekine, Y.; Lebonnois, S.; Imanaka, H.; Matsui, T.; Khare, B. N.; Bakes, E. L. O.; McKay, C. P.; Khare, B. N.; Sugita, S. *Icarus* **2008**, *194*, 201.

(208) Stoker, C. R.; Boston, P. J.; Mancinelli, R. L.; Segal, W.; Khare, B. N.; Sagan, C. *Icarus* **1990**, *85*, 241.

(209) Roberts, T. A.; Hitchins, A. D. In *The Bacterial Spore*; Gould, G. W., Hurst, A., Eds.; Academic Press: New York, 1969; Vol. 1.

(210) Nicholson, W. L. *Origins Life Evol. Biosphere* **2003**, *33*, 621.

(211) Nicholson, W. L.; Munakata, N.; Horneck, G.; Melosh, H. J.; Setlow, P. *Microbiol. Mol. Biol. Rev.* **2000**, *64*, 548.

(212) Horneck, G.; Bucker, H.; Reitz, G. *Adv. Space Res.* **1994**, *14*, 41.

(213) Shafaat, H. S.; Ponce, A. *Appl. Environ. Microbiol.* **2006**, *72*, 6808.

(214) Pavlov, A. A.; Hurtgen, M. T.; Kasting, J. F.; Arthur, M. A. *Geology* **2003**, *31*, 87.

(215) Durand, B. In *Kerogen: Insoluble Organic Matter from Sedimentary Rocks*; Durand, B., Ed.; Editions Technip: Paris, 1980.

(216) Budil, D. E.; Roebber, J. L.; Liebman, S. A.; Matthews, C. N. *Astrobiology* **2003**, *3*, 323.

(217) Khare, B. N.; Sagan, C.; Thompson, W. R.; Arakawa, E. T.; Meisse, C.; Tuminello, P. S. *Can. J. Chem.* **1994**, *72*, 678.

(218) Khare, B. N.; Thompson, W. R.; Cheng, L.; Chyba, C.; Sagan, C.; Arakawa, E. T.; Meisse, C.; Tuminello, P. S. *Icarus* **1993**, *103*, 290.

(219) Khare, B. N.; Thompson, W. R.; Sagan, C.; Arakawa, E. T.; Meisse, C.; Gilmour, I. *Proceedings of the International Conference of Laboratory Research: Planetary Atmospheres*; 1991; p 340.

(220) Krevelen, W. V. *Fuel* **1950**, *29*, 269.

(221) Kendrick, E. *Anal. Chem.* **1963**, *35*, 2146.

(222) Hughey, C.; Hendrickson, C.; Rodgers, R.; Marshall, A.; Qian, K. *Anal. Chem.* **2001**, *73*, 4676.

(223) Anderson, C. M.; Samuelson, R. E. *Icarus* **2011**, *212*, 762.

(224) Westlake, J., personal communication.

(225) *Allen's Astrophysical Quantities*; Cox, A. N., Ed.; AIP Press: New York, 2000.

(226) Lunine, J. I. *Proc. Am. Philos. Soc.* **2009**, *153*, 403.

(227) Stofan, E. R.; Lunine, J. I.; Lorenz, R. D.; Aharonson, O.; Bierhaus, E.; Clark, B.; Griffith, C. A.; Harri, A.-M.; Karkoschka, E.; Kirk, R.; Kantsiper, B.; Mahaffy, P.; Newman, C.; Ravine, M.; Trainer, M. G.; Waite, J. H.; Zarnecki, J. C. *Proc. Lunar Planet. Sci.* **2010**, *41*, #1236.

(228) A recent study involving a collaborative effort at the Keck Institute for Space Studies (KISS) addressed the unique challenges posed by the Titan environment for sample handling and chemical analysis. It was concluded that a sample analysis platform based on ultrasensitive detection in small sample volumes would address the critical issues of low mass and power while maximizing science return. The KISS study team also recognized the importance of understanding sample properties at Titan pressure and temperature prior to extracting more information through chemical/physical alteration (i.e., melting, extraction, labeling reactions). A potential instrument architecture designed with these goals in mind would include a solution-state NMR (for analysis of lake samples at 94 K), followed by sample interrogation using wet chemistry and laser-induced fluorescence on a microfluidic device (which also serves as the sample distribution hub via a grid of microvalves) and finally analysis using a high-resolution mass spectrometer. A copy of the report is available for download: http://kiss.caltech.edu/workshops/titan2010/index.html.

(229) Reh, K.; Magner, T.; Lunine, J. I.; Lebreton, J.-P.; Matson, D. L.; Coustenis, A.; Jones, C.; Sommerer, J. *Titan Saturn System Mission Study 2008: Final Report*; NASA Jet Propulsion Laboratory, 2008.

(230) Clark, K. B.; Stankov, A.; Pappalardo, R. T.; Blanc, M.; Greeley, R.; Lebreton, J.-P. *Europa Jupiter System Mission Joint Summary Report*; NASA/ESA Study Team, 2009.

(231) Hodyss, R. Ph.D. Thesis, California Institute of Technology, 2006.

(232) *Handbook of Capillary and Microchip Electrophoresis and Associated Microtechniques*; 3rd ed.; Landers, J. P., Ed.; CRC Press, Taylor & Francis Group: New York, 2008.

(233) Chiesl, T. N.; Chu, W. K.; Stockton, A. M.; Amashukeli, X.; Grunthaner, F. J.; Mathies, R. A. *Anal. Chem.* **2009**, *81*, 2537.

(234) Stockton, A. M.; Chiesl, T. N.; Scherer, J. R.; Mathies, R. A. *Anal. Chem.* **2009**, *81*, 790.

(235) Stockton, A. M.; Tjin, C. C.; Huang, G. L.; Benhabib, M.; Chiesl, T. N.; Mathies, R. A. *Electrophoresis* **2010**, *31*, 3642.

(236) Wilm, M.; Mann, M. *Anal. Chem.* **1996**, *68*, 1.

(237) Wakayama, M.; Aoki, N.; Sasaki, H.; Ohsugi, R. *Anal. Chem.* **2010**, *82*, 9967.

(238) Scattergood, T. W. *Adv. Space Res.* **1987**, *7*, 99.

(239) Curtis, D. B.; Glandorf, D. L.; Toon, O. B.; Tolbert, M. A.; McKay, C. P.; Khare, B. N. *J. Phys. Chem. A* **2005**, *109*, 1382.

(240) Sagan, C.; Khare, B. N.; Lewis, J. S. In *Saturn*; University of Arizona Press: Tucson, AZ, 1984.

(241) Samson, J. A. R.; Haddad, G. N.; Masuoka, T.; Pareek, P. N.; Kilcoyne, D. A. L. *J. Chem. Phys.* **1989**, *90*, 6925.