

Chapter 1

INTRODUCTION

1.1 The Astrochemical Environment of Titan

While there are many chemically interesting environments within the solar system, Saturn's moon of Titan is of continuous intrigue. One of the largest moons in the solar system, Titan is unique as the only solid body in the outer solar system with a dense atmosphere.¹ This icy moon has multiple types of geological features: large lakes around its poles, dry river valleys, and dunes around the equator.²⁻⁴ Gravitational studies have shown that a water and ammonia ocean or slurry likely exists under its crust.⁵ While this may sound like a second Earth, Titan deviates greatly. The atmosphere and surface are extremely cold, with minimums of approximately 95K, and the lakes are liquid methane and ethane.^{5,6} As such any water present on the surface would be unreactive and closer to granite than water on Earth.⁷ Any chemistry involving water is proposed to involve the subsurface ocean. The geological diversity possible with lakes of methane and ethane does increase the variety of chemical environments, the implications of which have been investigated in other studies.⁸⁻
¹⁰ These different features present Titan as a frozen early Earth, the study of which provides insights into the chemical evolution of our own planet.¹¹⁻¹³

Nowhere is this more evident than in the study of Titan's dense atmosphere. This atmosphere is visibly brown-orange in color and optically opaque, requiring techniques such as radar to study the features of the surface.^{14, 15} The atmosphere is composed mostly of nitrogen (90-98%), with methane (2-10%) being the second most abundant constituent.¹¹ Trace amounts of other gases, such as carbon monoxide and helium, along with small

hydrocarbons and hydrogen cyanide round out the other components.¹⁶ The interest in the study of Titan's atmosphere stems from how this composition mirrors that of early Earth.¹² Models of Earth's Archean atmosphere, supported by geochemical data, predict that two stable states existed: with and without a haze layer. These states were driven by the atmospheric methane content, with more methane contributing to increased haze formation.¹⁷ Titan thus presents a frozen version of the stable haze state, allowing for the study of atmospheric processes during this regime of Earth's atmosphere.

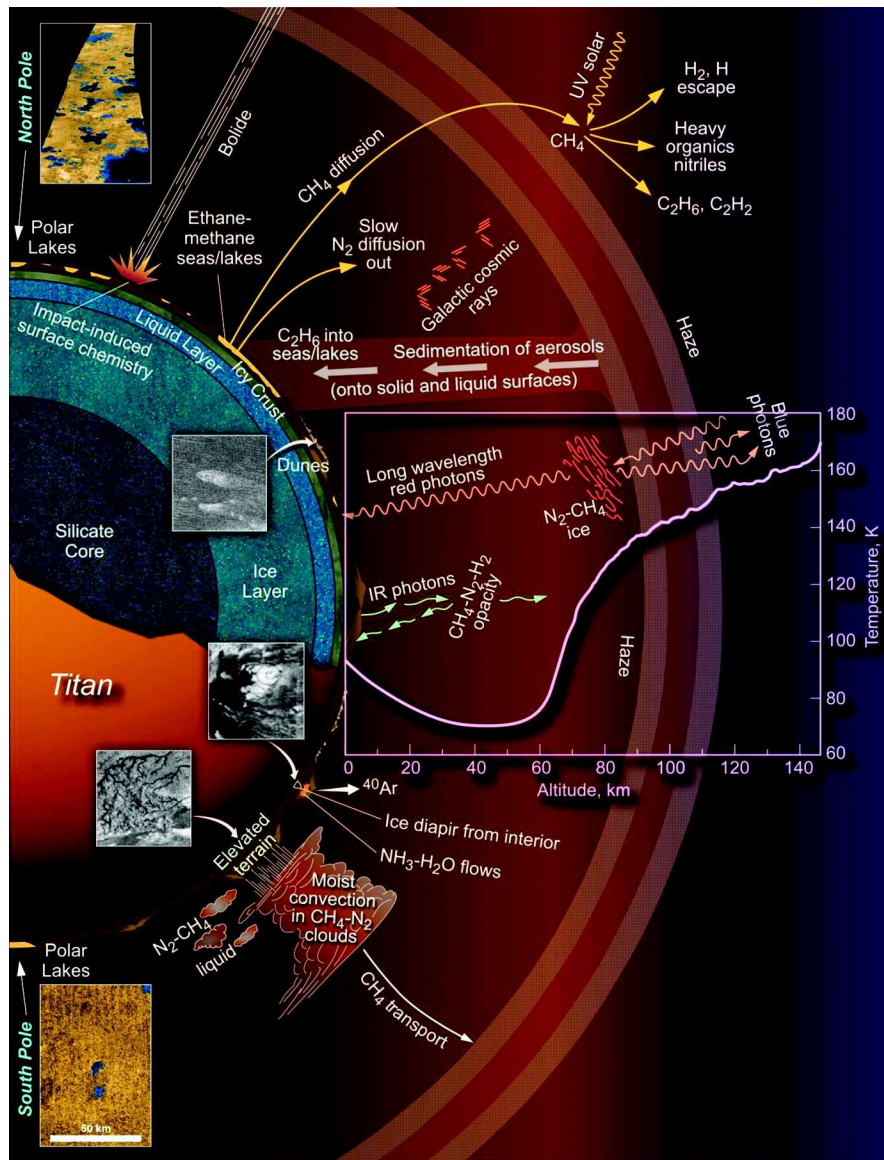


Figure 1.1. A cross section of Titan showing the complex processes at work in the atmosphere along with the various geographical features. Reproduced with permission from Cable et al. 2012¹⁸

The haze formation on Titan is driven mostly by photochemical processes in the atmosphere. Here nitrogen and methane are photoionized or photodissociated by solar radiation.^{12, 19-21} The products of these reactions along with the wavelengths required to induce the chemistry are shown in Table 1 below. These reactions produce ions and radicals that can undergo subsequent chemistry to produce hydrogen cyanide and small hydrocarbons

such as acetylene.²²⁻²⁴ These molecules undergo further photochemistry to produce heavier nitriles and hydrocarbons.²⁵⁻²⁷ Photochemical processes dominate in the upper atmosphere at altitudes of 1000 km, but other processes such as meteor impacts, particles from Saturn's magnetosphere, and cosmic rays can drive additional chemistry throughout different atmospheric layers.²⁸

Photochemical reaction	Wavelength maximum (nm)
$N_2 + h\nu \rightarrow N^+ + N + e^-$	51 ²⁹
$N_2 + h\nu \rightarrow 2N^\bullet$	80 ²¹
$CH_4 + h\nu \rightarrow CH_3^+ + H + e^-$	87 ²⁹
$CH_4 + h\nu \rightarrow CH_3^\bullet + H^\bullet$	155 ^{20, 21}

Table 1.1. Example photoionization and photodissociation reactions for methane and nitrogen with required wavelengths. All wavelengths reported are maximums for their respective reaction. Table adapted from Cable et al. 2012¹⁸

Gas phase molecules produced from the abundant photochemistry in the upper atmosphere condense into aerosols through a variety of mechanisms.¹⁸ These aerosols provide sources for further condensation of other molecules through direct particle surface chemistry, subsequently producing larger aerosols.³⁰ Since the condensation occurs at different temperatures and pressures stratification of the haze occurs, with a thin haze in the thermosphere and a thicker haze layer in the mesosphere.³¹ These aerosols act as condensation sources for other species, increasing their size as they approach the surface.³² This aerosol rain coats every surface on Titan, sinking to the bottom of methane lakes and composing the dunes, providing rich chemical diversity to the surface.^{7, 33} With the possibility of transport to the subsurface ocean, there is the significant probability for the

synthesis of prebiotic molecules. This, combined with the chemical variety of the atmosphere, makes Titan a continual target for astrochemical study.

1.2 Simulating Titan's Atmosphere in the Laboratory

Due to the diversity of chemistry possible in Titan's atmosphere, many laboratories have developed methods to simulate the atmosphere of Titan and enable aerosol production.¹⁸ These simulation processes have roots in the original Miller-Urey experiment. In that work a vial with a simulated early Earth ocean and atmosphere was exposed to an electrical discharge to simulate lightning.³⁴ The products from this discharge chemistry were found to include many prebiotic molecules such as amino acids.³⁵ Considering the similar chemical possibilities with Titan's atmosphere, replicating the aerosols with a similar apparatus presents an experimental starting point.

When replicating the conditions on Titan to produce aerosols there are many more difficulties compared to the Miller-Urey experiment. These Titan atmospheric simulation experiments take into account the gas mixture on Titan, low temperature, pressure, and possible sources of energy for the chemistry.¹⁸ Since Titan's atmosphere has been well characterized most experiments utilize a 90-95% nitrogen and 5-10% methane gas mixture as a base.^{18, 36} Depending on the type of chemistry of interest for a particular experiment other gases may be added that are known to exist in Titan's atmosphere, such as carbon monoxide, hydrogen, or acetylene to name a few.³⁷⁻⁴⁰ The temperature of Titan's atmosphere displays a large variation throughout the different layers, as discussed above, leading to multiple different temperatures being used for the atmospheric simulation experiments. The top of the temperature range, 195K, and the bottom of 95K, are two of the more commonly

used temperature points for study, but multiple different cooling methods make temperature control a simpler parameter to account for and adjust.¹⁸ As such the majority of studies take some temperature control into consideration and few simulation experiments are performed outside of Titan's atmospheric temperature range.

Pressure is one area where many of the adjustments made during simulation experiments fall outside of representative Titan conditions.¹⁸ At lower pressures for the photochemically active upper atmosphere, the small number of molecules inhibit aerosol production unless prohibitively long timescales are used.^{41, 42} This is due to the mean free path of a representative gas mixture being 0.20 m at Titan conditions and 0.34 m at Earth ambient conditions, as calculated by Cable et al.¹⁸ The majority of apparatuses used for the production of these simulated aerosols are of similar dimensions, making reactions under Titan pressure unfeasible in experimental timescales. When increasing the pressure to overcome this limitation other concerns are introduced. The amount of nitrogen incorporation and aromaticity generation increase with higher pressure, impacted in part by the increasing density of reactive species at these pressures with some apparatuses.⁴²⁻⁴⁶ These deviations from Titan's atmospheric chemistry are balanced against increased aerosol generation depending on experimental goals.

Energy sources to simulate the photochemistry vary considerably between experiments and are often cited as the largest source of chemical variation between simulations. The sources used focus both on the types of energy possible on Titan, and those that enable the dissociation reactions shown above.¹⁸ UV irradiation methods are considered the most representative considering it is the major source of photochemistry on Titan, but photolyzing nitrogen can be difficult with most apparatuses and aerosol yields can be low.^{26,}

^{29, 42, 44, 47} Plasma based sources can be used to overcome these low yields. Hot plasma sources typically mimic lightning, similar to the original Miller-Urey experiment. The high aerosol production of these methods have the drawback of decreased relation to actual conditions since lightning has not been recorded on Titan and the high energy can lead to high levels of polymerization.^{18, 39, 40, 48, 49} Cold plasma is more representative of chemistry induced by charged particles originating from Saturn and allows for most photochemical reactions discussed above.^{37, 38, 50} Although aerosol yields can still be low, cold plasma conditions are a bridge between hot plasma discharges and UV irradiation. Other possible energy sources include gamma-rays,⁵¹ soft x-rays,⁵² and proton or electron beams,¹⁸ all of which have their own advantages or disadvantages. Regardless of the energy source used to cause the chemistry, the end result is a brown to orange colored solid, or tholin, which is collected and subjected to further analysis.

In the analyzes presented in this thesis two different tholins are used, both of which have been the subject to prior study. The work discussed in chapters 4 and 5 utilized a hot plasma tholin while chapter 3 concentrates on a cold plasma tholin. While the reasoning behind the selection of these tholins was multifaceted, the selection of the cold plasma tholin in chapter 3 was due to the technique chosen for characterization being well suited to the lower aerosol yield. Additionally this tholin had minimal prior characterization, presenting an ideal initial target.^{37, 38} The hot plasma discharge tholin used in the other chapters enabled a large amount of analytical method development due to larger aerosol yields. Prior work utilizing the hot plasma discharge tholins also enables comparison.^{45, 49, 53, 54} Overall the selection of each tholin in each chapter was influenced by the overarching analytical goals of this thesis, discussed below.

1.3 Motivation: Analytical Goals

With any study of tholins the primary goal is characterization of the solid. By developing a thorough understanding of the different types of molecules present in the material, one hopes to better understand the atmospheric chemistry of Titan. Prior studies have identified an extraordinary amount of chemical complexity in tholins. For tholins produced from AC discharge, analyses have found a statistical mixture of carbon, hydrogen, and nitrogen.^{45,55} Within each of these possibilities are multiple functional groups, including aromatics, alkynes, amines, and nitriles to name a few. Each chemical functionality is best identified with different analytical methods, and few methods work well for bulk analysis. Spectroscopy is ideal for identifying different functional groups, but cannot characterize a compound's size when used alone. Chromatography is well suited to structural information, but usually depends on choosing a target functionality prior to analysis. Most tholin samples are analyzed by a battery of different methods to overcome this, with a single method used for each analytical goal. Typically a single type of functionality of interest is identified in initial studies of tholins, driving the choices for analytical methods used in subsequent studies. The high complexity consequently mandates a high number of tests and minimalizes the amount of characterization that can reasonably be obtained by any single analysis.

While characterization is a process of applying an increasing number of specific tests to the tholins, the complexity of the material itself leads to a new goal: the identification of mission applicable analytical methods. A major goal during *in-situ* analysis is to identify and characterize as much of the material as possible with minimal sample processing and simple instrumental requirements. The multitude of different analytical methods required to analyze tholins presents complications for missions, since payloads need to be well defined

and emphasize the highest amount of data from the fewest possible instruments.⁵⁶ Additionally many of the instruments that can provide a high amount of detailed information, such as nuclear magnetic resonance, have requirements making them incompatible with spaceflight. As such, developing techniques well suited to broad tholin characterization is imperative, with mission applicable instrumentation a secondary goal underpinning tholin research.

The work presented in this thesis strives towards both the development of mission applicable analytical methods and the characterization of particular compounds and functionalities within the tholins. To further the mission applicability goal, mass spectrometry is used in all presented methods. Analysis with mass spectrometry is accomplished by desorption of analytes into the gas phase followed by ionization and subsequent detection as a mass to charge ratio. Various mass spectrometers have been included on a multitude of missions, including the original Huygens lander,^{16, 57, 58} making it a well suited type of instrumentation for the development of mission applicable analytical methods. Since mass spectrometers detect a mass to charge ratio, it already enables the determination of molecule size and even chemical formula with high enough resolution. Additional structural information can be obtained by either interfacing with a chromatography system, or utilizing a mass spectrometer that allows for tandem mass spectrometry. By obtaining characteristic fragments from a target ion, tandem mass spectrometry allows for the elucidation of important structural information, even if more specific techniques cannot be used.

1.4 Contents of Thesis

While the research discussed in this thesis utilizes mass spectrometry, the research does not always accomplish both tholin characterization and development of a mission applicable method. Chapters two and three focus on the development of an ambient mass spectrometry method and its use in tholin characterization respectively. The chromatography method presented in chapter 4 accomplishes both goals, while the supramolecular chemistry method discussed in chapter 5 allows only for characterization without mission applicability. The research in each of these chapter is discussed in more detail below.

Chapter 2 presents the development of a miniature plasma ionization source based on the technique known as direct analysis in real time (DART). This technique utilizes heated helium metastables to desorb and ionize samples. This ambient mass spectrometry source is shown to be reliable for multiple different types of samples, from pharmaceuticals to vicious liquid asphalt. The source is presented with low power and gas consumption, which combined with the use of helium enable its consideration for Titan mission applications. Being able to analyze multiple different sample types in addition to complex organic mixtures makes this miniaturized source a low technology readiness level presentation of how an ambient plasma source may be utilized.

This mini-DART source is applied to the analysis of cold plasma tholins in chapter 3, further presenting its mission applications while performing an analysis of solid tholin samples unstudied by mass spectrometry. Using the mini-DART for this analysis shows that the source described in chapter 2 can be successfully applied to tholin samples. The use of benzene and acetylene dopants within these tholins enabled a comparative study to characterize the impact these higher molecular weight species have on the different synthetic products observed. The results from this study show that dopants have unexpected effects

and bias the products towards certain molecules. While multiple different compounds are identified, some prebiotic molecules are seen. Since the tholins analyzed are proposed to be more representative of the early stage aerosols, the identified molecules present implications for reaction products in different layers of Titan's atmosphere. The mini-DART shows itself to be effective at the analysis of low molecular weight and polar species within the tholin, without analyzing heavier species or hydrocarbons. As such this method allows for the characterization of an important fraction of tholins, enabling necessary insights for other analyzes.

In chapter 4 a solid phase microextraction gas chromatography (SPME-GC) method and its application to a hot plasma tholin is discussed. GC has been applied to tholins extensively and was included as part of the instrumental payload on the Huygens Titan lander of the Cassini mission to the Saturn system.^{16, 58} Additionally GC is well suited to the characterization of hydrocarbons and heavier, less polar molecules. These are known constituents of tholins, but difficult to analyze with other methods, making them a well suited target for GC analysis. The application of SPME is where this method differs from prior studies. SPME utilizes an adsorbent fiber to preconcentrate gas phase analytes prior to analysis by GC, targeting specific analytes depending on the fiber media. Multiple different compounds are found, with the identification of multiple nitriles fitting with compounds identified in earlier work. The application of solid phase extraction to mission applications has been discussed and this SPME method demonstrates it is well suited to the characterization of tholins, accomplishing both analytical goals of this thesis.

A hot plasma tholin is also examined in chapter 5, concentrating on the analysis of large primary amines using 18-crown-6 ether complexation. Primary amines are difficult to

detect with gas chromatography and larger molecules are difficult to detect with DART, allowing this technique to fill that analytical gap. The 18-crown-6 ether selectively forms a supramolecular complex to the primary amines, which can subsequently be readily identified by electrospray ionization mass spectrometry. Using electrospray excludes this technique from mission applications, but enables specific identification upon which other analytical methods can be developed. There are two different primary amine series identified, and the inclusion of nitrile functionality in one of the series relates to possible prebiotic molecules. The technique thus provides a reliable way of characterizing the primary amines present in tholins that remain unidentified with other methods.

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