Titan’s Atmosphere of Yesterday, Today, and Tomorrow: Chemical and Optical Properties of Titan Haze Aerosol Analogs

by

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Titan, the moon of Saturn, has an atmosphere composed of methane (CH$_4$), nitrogen (N$_2$), and a thick, orange haze that obscures its surface. Titan haze aerosol analogs were generated by electric spark in a laboratory setting and the chemical and optical properties of the analogs were studied through infrared spectroscopy and UV-Vis spectroscopy. Haze aerosol analogs were generated from initial gas mixture concentrations of 10% CH$_4$ in N$_2$, 2% CH$_4$ in N$_2$, and 0.4% CH$_4$ in N$_2$ for studying the chemical properties, while haze aerosol analogs were generated from initial gas mixture concentrations of 10% CH$_4$ in N$_2$ and 2% CH$_4$ in N$_2$ for studying the optical properties.

The infrared spectroscopy data showed that overall chemical mass, specifically aliphatic hydrocarbon mass, increased with increasing initial CH$_4$ gas concentrations, as did the polycyclic aromatic hydrocarbon concentration. These results directly support previous chemical composition data of aerosol analogs (Trainer et al., 2004).

The UV-Vis data were used to calculate a relative imaginary refractive index $k$ value, which revealed that haze aerosol analogs generated at lower initial CH$_4$ concentrations absorbed more in the shorter wavelengths of the visible range, while haze aerosol analogs generated at higher initial CH$_4$ concentrations absorbed more evenly over all visible wavelengths. This data did not closely support previous laboratory data regarding $k$ values (Khare et al., 1984), which might be due to variations in pressure parameters of the experimental set-up.
These results can be used to formulate a historical hypothesis of the chemical and optical properties of Titan’s haze aerosols and predict how the haze will behave chemically and optically in the future as atmospheric CH₄ concentration decreases over time.
for my friends and family who have encouraged
me throughout my entire undergraduate education
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Table of Contents

Chapter I: Introduction

1.1 Titan........................................................................................................................................1
1.2 Producing Titan Haze Aerosols...............................................................................................3
1.3 Titan Haze Aerosol Analogs .....................................................................................................3
1.4 Thesis Outline ..........................................................................................................................5

Chapter II: Chemical Properties of Titan Haze Aerosol Analogs through Infrared Spectroscopy

2.1 Introduction ..............................................................................................................................6
2.2 Experimental Methods ............................................................................................................7
2.3 Infrared Spectroscopy Results ...............................................................................................12
2.4 Implications of Chemical Properties for Titan .......................................................................12

Chapter III: Optical Properties of Titan Haze Aerosol Analogs through UV-Vis Spectroscopy

3.1 Introduction .............................................................................................................................14
3.2 Experimental Methods ..........................................................................................................18
3.3 Instrumentation Validation .....................................................................................................20
3.4 Imaginary Refractive Index $k$ Values ....................................................................................25
3.5 Implications for Titan .............................................................................................................29

Chapter IV: Summary, Conclusions, and Further Research

4.1 Summary and Conclusions ......................................................................................................33
4.2 Further Research ....................................................................................................................34

References ........................................................................................................................................36
List of Figures:

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Titan</td>
<td></td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>6</td>
</tr>
<tr>
<td>2.4 Implications of Chemical Properties for Titan</td>
<td>12</td>
</tr>
<tr>
<td>Optical Properties of Titan Haze Aerosol Analogs through UV-Vis Spectroscopy</td>
<td>14</td>
</tr>
<tr>
<td>3.1 Introduction</td>
<td>14</td>
</tr>
<tr>
<td>3.4 Imaginary Refractive Index $k$ Values</td>
<td>25</td>
</tr>
<tr>
<td>3.5 Implications of Optical Properties for Titan</td>
<td>29</td>
</tr>
<tr>
<td>Summary, Conclusions, and Further Research</td>
<td>33</td>
</tr>
<tr>
<td>4.1 Summary and Conclusions</td>
<td>33</td>
</tr>
<tr>
<td>4.2 Further Research</td>
<td>34</td>
</tr>
<tr>
<td>References</td>
<td>37</td>
</tr>
</tbody>
</table>
Chapter I

Introduction

1.1 Titan

Titan, the sixth and largest moon of Saturn, can best be seen from Earth using a telescope (figure 1.1d). Titan was discovered in 1665 by the Dutch mathematician, physicist, horologist and astronomer, Christiaan Huygens. It was this man after whom the Huygens probe was named. Titan has a mass of $1.35 \times 10^{24}$ kg, which is approximately 2.3% of Earth’s mass. It has a mean radius of 2,576 km, which is about 40% of Earth’s radius. Titan has a very dense atmosphere that appears orange (figure 1.1c) due to the presence of suspended haze aerosols, called “tholins”. Although it is known that tholins are rich in carbon, nitrogen and hydrogen with no presence of oxygen (Quirico et al., 2008), current technology could not determine the structure of these particles. The atmosphere is also rich in molecular nitrogen ($N_2$) and methane ($CH_4$).

1.1.1 Interest in Titan

Titan is of interest to the scientific community because it has an atmosphere comparable to that of Earth and a terrain similar to that of Earth. The atmosphere of Titan has several layers (figure 1.1c) just like that of Earth, and the Huygens probe has revealed that Titan has a rocky terrain (figure 1.1f) with lakebeds and riverbeds (figure 1.1a,b). Another similarity to Earth is that Titan is also the only other planet with a substance that occurs naturally in all three phases. Just as the average temperature of Earth’s surface is near the triple point of water, the average surface temperature, 94 K, (Imanaka 2004), of Titan’s surface is near the triple point of $CH_4$, 90.685 K (Kleinrahm and Wagner, 1986).
Figure 1.1  Compilation of images of Titan. (a) An artist’s rendition of the Huygens probe landing on Titan. Saturn and its rings can be seen in the background obscured by Titan’s haze. Image courtesy of Astrobiology Magazine. (b) Radar images of CH₄ lakes on Titan. (c) An image of Titan taken by Voyager I in 1980. (d) an image of Titan from Earth using a telescope. Photo credit: Peter Muks Photography. (e) An image of the haze layers of Titan taken by Cassini. (f) An image of the surface of Titan taken by the Huygens probe. Images (b), (c), (e) and (f) courtesy of NASA.
1.2 Producing Titan Haze Aerosols

Haze aerosols on Titan are believed to be generated by an energy source that dissociates molecular N\textsubscript{2} and gaseous CH\textsubscript{4} in the outer layers of the atmosphere, subsequently allowing complex chemical reactions to occur that form hydrocarbon monomers about 50 nm in diameter that conglomerate into large particles with \~250 monomers per particle (Tomasko et al., 2005). These particles are the haze aerosols that give Titan its orange color. Energy sources on Titan that are believed to cause initiation of this reaction include energetic electrons from Saturn as well as ultraviolet (UV) radiation from the sun. In the laboratory, electric spark is used to mimic the energetic electrons, while UV lamps are used to mimic the UV radiation. The current gas mixture concentration in Titan’s stratosphere is roughly 2% CH\textsubscript{4} in N\textsubscript{2}. Therefore, this is a common gas percent to study in a laboratory setting.

Since there are no known sources of CH\textsubscript{4} to replenish the CH\textsubscript{4} concentration on Titan (Owen, 2005), it is expected that as time progresses, the CH\textsubscript{4} concentration in the atmosphere will decrease as it is consumed by the formation of haze aerosols. This also indicates that CH\textsubscript{4} concentrations might have been higher in the past.

1.3 Titan Haze Aerosol Analogs

Extensive research has been performed on haze aerosol analogs generated in the lab using gas mixtures of CH\textsubscript{4} in N\textsubscript{2}. These studies have focused on both chemical and optical properties, and have varied parameters such as initial gas mixture concentrations, pressure and energy source for reaction initiation. These haze aerosols have also been compared to Early Earth as Titan is often considered the model for a colder, Archean Earth.

In this study we study how the composition of haze aerosol analogs changes as CH\textsubscript{4} concentrations change. Previous research has revealed that the chemical and optical properties of haze aerosol analogs created in the laboratory vary with respect to gas percent (figure 1.2a). When generated with higher gas percents of CH\textsubscript{4}, aromatics were the more
Figure 1.2  Previous data from Trainer et al. (2004) (a) AMS plot showing total mass of Titan haze aerosol analogs as a function of initial gas percent. At higher CH$_4$ concentrations, aromatics dominate while at lower CH$_4$ concentrations aliphatics are the dominant structure. (b) AMS data showing relative mass concentrations of different initial gas percents. At higher CH$_4$ concentrations, the haze aerosol analogs contain more overall mass in addition to higher concentrations of PAH’s.
abundant structure while aliphatic structures dominated at lower gas percents of CH₄ (Trainer et al., 2004). Data from Trainer et al. (2004) (figure 1.2b) also indicate that at higher CH₄ concentrations more aerosol mass is generated, most prominently hydrocarbon mass, while at lower CH₄ concentrations the haze aerosol analogs show less overall mass with the predominant presence of aliphatics.

As a result of this data, one might wonder: if the chemical properties of Titan are shown to change with CH₄ concentration and therefore over time, wouldn’t it be expected that the optical properties of Titan would also change?

1.4 Thesis Outline

This thesis studies the chemical and optical properties of Titan haze aerosol analogs with respect to initial gas percents of CH₄ in N₂. The results from this thesis will attempt to suggest a history for Titan’s atmosphere as the CH₄ concentration decreases over time. Chapter II presents the investigation of chemical properties of the analogs through infrared spectroscopy. Chapter III details the optical properties of the analogs through UV-Visible (UV-Vis) spectroscopy, which will be used to calculate relative imaginary refractive index values. This data will suggest implications for a change in the optical properties of the tholins on Titan. Chapter IV offers an overall summary and conclusion of the work in this thesis as well as possible future research.
Chapter II

Chemical Properties of Titan Haze Aerosol Analogs through Infrared Spectroscopy

2.1 Introduction

Infrared (IR) spectroscopy can be used to determine chemical composition by detecting vibrational and rotational transitions within molecules. The small energies absorbed by vibrations within the bonds of a molecule correspond to the energies of infrared wavelengths. For a molecule to be able to absorb IR radiation, it must undergo a net change in dipole. That is, the electron density cannot be evenly distributed across the bond between two atoms. In a vibration, the electron density exhibits a constant oscillation between the two atoms if there is a net dipole moment. In a rotation, the two atoms spin around their center of mass, which similarly results in a dipole oscillation. If the frequency of the oscillation is exactly equal to the frequency of the incident infrared radiation, that IR radiation can be absorbed into the bond.

In IR spectroscopy, a light source is passed through a beamsplitter to select one wavelength that will be passed through the sample. As the incident light passes through the sample, vibrations and rotations within the molecule will absorb the energy of the light if the frequency of the light is exactly equal to the frequency of the dipole oscillation created by the vibration or rotation. Any radiation that isn’t absorbed by the molecule passes through a detector that measures the intensity of the radiation at that wavelength in relation to the intensity of the incident radiation. A decrease in intensity indicates that the molecule absorbs radiation at that wavelength.

The Fourier transform IR (FTIR) spectrometer is the preferred type of instrument in IR spectroscopy. In an FTIR instrument, two light sources, the infrared light source and a laser, are used to obtain absorption spectra of the sample. The infrared light source is used to
scan all infrared wavelengths for absorption by the sample while the radiation from the laser is monitored as the intensity of the incident beam. Figure 2.1 shows a schematic of an FTIR spectrometer similar to the one used in this study. The resulting graph will be a plot of absorbance or transmittance against wavenumbers. Wavenumbers is most frequently used due to its direct correlation to energy: higher wavenumbers means higher energy.

IR spectroscopy will be used in this study to investigate the chemical composition of haze aerosol analogs as a function of initial CH$_4$ concentration to determine how the chemical composition of tholins on Titan might change over time.

2.2 Experimental Methods

2.2.1 Aerosol Generation and Collection

A stainless steel gas chamber was filled with CH$_4$ (ultra-high purity grade from Airgas, Inc) and N$_2$ (ultra-high purity grade from Airgas, Inc) in various ratios and was allowed to sit overnight to mix diffusively. Samples were prepared with initial gas mixtures of 10% CH$_4$ in N$_2$, 2% CH$_4$ in N$_2$, and 0.4% CH$_4$ in N$_2$.

The gas mixture was flowed into the system at 60 sccm (standard cubic centimeters per minute) as controlled by a mass flow controller (TN 2900 from Celerity). A vacuum was applied at the end of the system to keep the system pressure at atmospheric pressure, 630 torr, which was monitored with a baratron capacitance manometer (Type 626 by MKS Instruments). The gas mixture entered a glass reaction chamber, made by Dennis Steffey of the CRES glass shop, with tungsten electrodes that delivered constant electric spark generated by a tesla coil (Electro-technic Products, Inc.). The aerosols were collected on plates enclosed within the collection chamber (polycarbonate 47 mm in-line filter holder by Pall Corporation). For IR analysis, aerosols were collected on a circular NaCl plate from International Crystal Laboratories with a diameter of 25 mm and a thickness of 4 mm. Figure 2.2 shows a pictorial representation of the collection set-up.
Figure 2.1  Schematic of a simple, single-beam FTIR spectrometer. (Courtesy of Thermo Electron Corp., Madison, WI.)
Figure 2.2  Schematic of apparatus set-up. NaCl discs were used as the substrate for sample collection in the IR spectroscopy studies.
2.2.2 Infrared Spectroscopy Instrumentation

IR data were taken with a Thermo Nicolet FTIR spectrometer with 8 cm\(^{-1}\) resolution. Spectra obtained were averages of 16 scans. NaCl plates were used for sample collection because NaCl absorbs very weakly in the infrared wavelengths and is therefore virtually invisible in the IR spectra. A new plate was used for each collection because NaCl plates cannot easily be cleaned with polar solvents due to dissolution of the NaCl, and the extent of solvent reactions with the sample are not known. Spectra taken are the absorbances of the sample plus the salt plate, then the absorbance of just the salt plate was used to take a ratio of sample to salt plate. An absorption spectrum was taken of a clean salt plate and was saved for use as a background. The same background was used for all sample spectra. Care was taken to ensure the salt plates were placed in the sample holder at 90° to the incident beam to ensure that light passed through the sample was not bent away from the detector. Because carbon dioxide (CO\(_2\)) and gaseous (H\(_2\)O) are highly visible in IR wavelengths, a purge with N\(_2\) was necessary to remove traces of atmospheric CO\(_2\) and H\(_2\)O.

The effectiveness of the purge with respect to time was investigated to determine the optimal purge duration. A 10% CH\(_4\) sample was placed in the FTIR instrument and a spectrum was taken immediately, then again at increments of 20 minutes for a total purge duration of 100 minutes. Figure 2.3 shows the overlaid spectra. The greatest decrease in CO\(_2\) and H\(_2\)O signal occurred within 20 minutes; all spectra taken after 20 minutes showed no change in CO\(_2\) and H\(_2\)O signal intensity. Therefore, a purge duration of 20 minutes was used for all samples before obtaining the FTIR spectra. Although this purge method greatly decreased the atmospheric CO\(_2\) and H\(_2\)O signals, the signals could not be eliminated completely. Therefore, the wavelengths where signal interference is the greatest were not included in the analysis of this data. Only data from 2050 cm\(^{-1}\) to 3500 cm\(^{-1}\) were used for analysis.
Figure 2.3  Infrared absorption of sample over time showing decrease of CO$_2$ and H$_2$O with respect to purge duration. Intensities have been offset for visibility.
2.3 Infrared Spectroscopy Results

Haze aerosols analogs generated from three different initial gas percents (10% CH₄ in N₂, 2% CH₄ in N₂, and 0.4 % CH₄ in N₂) were analyzed through IR spectroscopy to determine changes in the chemical composition as a function of initial gas percent. Figure 2.4 shows the IR spectra of the three samples from this study against previous IR data (Quirico et al., 2008). The peak near 2200 cm⁻¹ which corresponds to a –CN stretch can be seen in the data from this study growing in as CH₄ concentration increases. The same peak can be seen in the data from Quirico et al. (2008). The data from this study and the data from Quirico et al. (2008) similarly show a stretch at 2800-3000 cm⁻¹ corresponding to aliphatics, which appears as CH₄ concentration increases. A broad stretch in the 3300 cm⁻¹ region corresponding to secondary amines in the form of aromatics can be seen in the spectra from this study as well as the Quirico et al. (2008) data. This stretch also begins to emerge as initial CH₄ concentration increases.

2.4 Implications of Chemical Properties for Titan

The IR data agrees with the data from Trainer et al. (2004) as described in §1.3. The –CN peak near 2200 cm⁻¹ which grows in as CH₄ concentration increases indicates that the aerosols contain more overall chemical mass as the initial CH₄ concentration increases. The appearance of a –CH stretch near 2800-3000 cm⁻¹ indicates the presence of alkanes in all gas mixtures as well as the increase of hydrocarbon mass as initial CH₄ concentration increases. The R₂N-H stretch at 3300 cm⁻¹ indicates an increase in polycyclic aromatic hydrocarbons (PAH’s) as the initial CH₄ concentration increases. Therefore, the overall chemical and hydrocarbon mass as well as the PAH concentration is expected to decrease as the CH₄ concentration in Titan’s atmosphere decreases over time.
Figure 2.4  IR absorbance of Titan haze aerosol analogs from this work compared with infrared absorbance of other analogs (Quirico et al., 2008). Intensities have been offset for visibility.
3.1 Introduction

3.1.1 UV-Vis Spectroscopy

UV-Vis spectroscopy can be used to determine the wavelength of absorbance of a sample within the UV and visible wavelengths, therefore indicating what wavelengths might be reflected back to the human eye for color determination. In UV-Vis spectroscopy, incident radiation passes through a sample and some of that radiation can be absorbed by the molecules within the sample to cause excitation of electrons within the bonds. When excited, an electron absorbs radiation as energy which allows the electron to move from the ground state, the lowest possible energy level, to an excited electronic state, or from an excited electronic state to another excited electronic state of higher energy. The energy separations between various electronic states are discrete values and the energy of the incident radiation must be equal to or greater than the energy separation for an electron to be able to excite into a higher energy level. Figure 3.1 shows a schematic of the electronic transitions possible for an electron excited by radiation of ultraviolet and visible wavelengths.

UV-Vis Spectrometers can be used to measure absorption across the full ultraviolet-visible spectrum. Radiation from a light source, most often a continuum source, is passed through a filter or monochromator so that only one wavelength of radiation reaches the sample at a time. As that wavelength of radiation passes through the sample, a photodetector on the opposite side of the sample is used to determine how much radiation was transmitted, or allowed to pass through the sample, and therefore how much radiation at that wavelength
Figure 3.1  Schematic of electronic states possible for excitation. Energy separations between electronic states are discrete values and energy equal to or greater than this energy separation are required for an electron to excite into a higher electronic state.
was absorbed by the sample. An amplifier is often placed after the photodetector to increase the signal so that it can be detected and digitized for a read-out. Absorption determined by the photodetector is the absorption of the sample plus the absorption of the substrate on which the sample is deposited. Therefore, an absorption spectrum of the substrate, the reference spectrum, must be obtained to ratio the absorbances due to the substrate from the absorption determined by the photodetector. This way, the read-out will only display absorptions as a result of the sample at a specific wavelength. All wavelengths within the ultraviolet and visible wavelengths are scanned to obtain an absorbance value at each wavelength. The resulting graph will be absorbance against wavelength, often given in nanometers.

UV-Vis Spectrometers come in two general types, a single-beam and a double-beam instrument. With a single-beam instrument, the reference spectrum is taken either before or after the sample-plus-substrate spectrum is taken and stored for use in calculating the sample-only spectrum. In a double-beam instrument, the incident radiation beam is split so that identical light paths pass through the substrate and sample-plus-substrate simultaneously. These two light beams then reach two separate photodetectors and a difference amplifier is used to calculate the absorption of the sample-only spectrum.

Figure 3.2 shows the schematic of a single-beam instrument similar to the one used in this study.

3.1.2 Imaginary Refractive Index k values

The UV-Vis absorption data obtained from this experiment will be used to calculate the imaginary refractive index \( k \) according to the following equation:

\[
k = \ln \left( \frac{I_0}{I} \right) \frac{\lambda}{4\pi d}
\]

where \( d \) is the thickness of the sample layer, which was assumed to be 1 nm and held constant in all calculations since the thickness of the film cannot be easily measured. Due to possible
**Figure 3.2** Schematic of single-beam UV-Vis spectrometer.
differences in this layer, all data reported will be scaled values. \( I_o \) is the intensity of the incident radiation and \( I \) is the intensity of the transmitted radiation. Wavelength, \( \lambda \), is the wavelength of measurement and \( I_o/I \) is calculated from the absorbance measured at that wavelength according to Equation 2:

\[
10^A = \frac{I_o}{I}
\]

The imaginary refractive index \( k \) is a measure of how much radiation a given molecule can absorb at each wavelength, which can be useful in determining what wavelengths an object will reflect. Although we are only measuring relative \( k \) values, we can still determine what general color the aerosol analogs have based on the shape of their relative \( k \) – spectra. If these reflected wavelengths are within the visible range, then these wavelengths are what the human eye perceives as color. An object that absorbs in the blue wavelengths will reflect back orange, the color exactly opposite the color wheel (Figure 3.3). An object that absorbs red will reflect green, etc.

The relative imaginary refractive index will be calculated in this study to investigate the optical properties of haze aerosol analogs as a function of initial CH\(_4\) concentration to determine how the optical properties of tholins on Titan might change over time. This can give insight into the unique, orange color of Titan’s haze and how this might change as CH\(_4\) in the atmosphere is depleted.

### 3.2 Experimental Methods

#### 3.2.1 Aerosol Generation and Collection

As in §2.2.1, samples were prepared by filling a stainless steel gas chamber with various gas percents and allowed to mix diffusively overnight. Samples were prepared with initial gas mixtures of 10% CH\(_4\) in N\(_2\) and 0.4% CH\(_4\) in N\(_2\). The apparatus set-up was the same as that described §2.2.1. For UV-Vis analysis, aerosols were collected on square quartz
Figure 3.3  The color wheel. Objects reflect visible light in the wavelengths exactly opposite the absorbed wavelengths on the color wheel. The reflected light is the color that the human eye perceives.
plates with a side length of 25mm and a thickness of 3 mm. Figure 3.4 shows a pictorial representation of the collection set-up.

3.2.2 Sample Oxidation

Transferring the sample from the system to the instrument exposed the sample to atmospheric air for several minutes, so the effects of oxidation by exposure to atmospheric air were investigated to ensure that this assumption could be made. After a 10% CH₄ in N₂ sample was collected, an initial UV-Vis spectrum was obtained; then the sample was exposed to atmospheric air and UV-Vis spectra were obtained after 18.5 hours and 93 hours of exposure. Figure 3.5 shows the absorption spectra of the sample at each time. There were no noticeable changes in the spectra; therefore any oxidation of the sample caused by exposure to laboratory air did not affect our results.

3.3 Instrumentation Validation

UV-Vis spectroscopy is more commonly used for aqueous samples rather than particulate or thin-film samples because scattering of the incident light beam can lead to falsely high absorption intensities as incident light is scattered in all directions rather than transmitted through the sample to the detector. Scattering can occur if the sample is too opaque for the incident radiation to be transmitted through the sample. Scattering can also occur if the diameter of the particles within the sample are similar to or larger than the wavelength of the incident radiation. In this case, the sample needs to be concentrated enough to cover the quartz plate as a constant, thin film. To ensure the UV-Vis spectra of the aerosols were not results of scattering, two scenarios were created to mimic the aerosols deposited on the quartz plates: a thin film model and an aerosol size distribution model were investigated. Nigrosin dye was atomized onto quartz plates to mimic the aerosol model. Nigrosin dye was
Figure 3.4  Schematic of apparatus set-up. Quartz plates were used as the substrate for sample collection.
Figure 3.5  Normalized absorbance of 10% CH₄ in N₂ 3 hour collection after 0 hours, 18.5 hours and 93 hours after exposure to atmospheric air.
also dissolved in HPLC grade water then dried onto quartz plates to mimic the thin film model.

Polystyrene latex spheres (PSLs) were also dried onto quartz plates to mimic the thin film model with an aerosol size distribution.

3.3.1 Nigrosin

Aqueous nigrosin dye (Aldrich, CAS 8005-03-6) was prepared at a concentration of 0.05 wt % and a few drops of the solution were dried onto a quartz slide. Another portion of the nigrosin solution was atomized onto the quartz plate as particles with diameters of 200 nm to 305 nm, according to Hasenkopf et al. (2010). UV-Vis spectra were taken of the dried and atomized nigrosin samples. The two spectra were compared against a spectrum of the aqueous nigrosin dye in a cuvette since aqueous UV-Vis is the most common method. In an aqueous solution, scattering does not occur unless particles large enough to be seen by the human eye are suspended in the solution or the solution is at a concentration high enough that the solution is no longer transparent to the human eye (Skoog et al. 2007). Both of these can be easily verified to ensure scattering has not occurred. The spectra of the dried and atomized nigrosin samples were compared (figure 3.6) against the spectrum of the aqueous nigrosin. Absorption peaks were seen near 300 nm and 560 nm in all three spectra, indicating that the dried and atomized nigrosin samples were not scattering, but were instead acting similarly to the aqueous nigrosin solution.

3.3.2 Polystyrene Latex Spheres

PSLs with diameters of 80.0 ± 2.7 nm, 125.0 ± 5.4 nm and 350.0 ± 4.7 nm (Duke Scientific Corporation) were chosen to mimic the tholin size distribution, which is expected to range from 60 nm to 280 nm within a laboratory setting (West and Smith, 1991). The PSLs come as solutions of PSLs suspended in water. Initially, one drop of each PSL size was
Figure 3.6  UV-Vis absorption spectra of nigrosin dye as an atomized sample, a dried sample, and an aqueous sample.
placed on the substrate, giving three drops total PSLs and all three PSL sizes were mixed by swirling the droplets around the plate. The solution was then placed in an oven (Quincy Lab) at 75°C to evaporate the water, resulting in a layer of PSLs for UV-Vis analysis. Then, one more drop of each of the PSL sizes was added to the substrate, giving a total of six drops of PSLs, the water was evaporated and a spectrum was taken. This was repeated two more times to give a PSL layer from a total of 12 drops of PSLs with three different diameters. Figure 3.7 shows the absorption spectra of the PSLs. Significant scattering can be seen in the spectrum of 1 drop each of the PSLs. The high absorbance in the smaller wavelengths compared to the small absorbance in the longer wavelengths indicates that the PSLs were not a consistent, thin film on the substrate and therefore acted as particulates rather than a thin film. The consistent absorbances seen in the spectra taken of 2 drops, 3 drops and 4 drops each of the three PSL diameters indicate that scattering did not occur and therefore these PSLs acted as a thin film.

UV-Vis data taken below 350 nm was not used in the calculation of the imaginary refractive index $k$ value in the case that the haze aerosol analog deposited on the substrate was not concentrated enough to conform to the thin film scenario. This way, effects from scattering of the incident radiation were minimized.

### 3.4 Imaginary Refractive Index $k$ Values

From the absorption data obtained by UV-Vis spectroscopy, the relative imaginary refractive index $k$ values were be calculated according equations (1) and (2) as described in §3.1.2. A plot of $k$ values against wavelength from this study compared to previous data from Khare et al. (1984) is shown in figure 3.8. Both plots from this study show an approximately linear relationship between $k$ and wavelength. The relative $k$ values for the 10% CH$_4$ in N$_2$ sample from this study show a more horizontal slope than the $k$ values for the 2% CH$_4$ in N$_2$ which shows a more negative slope. A linear regression was used to calculate the slopes of
Figure 3.7  Normalized absorption spectra of PSLs with three different diameters: 80.0±2.7 nm, 125.0±5.4 nm and 350.0±4.7 nm (Duke Scientific Corporation).
Figure 3.8  Normalized $k$ values from this work compared with $k$ values of previous work (Khare et al. 1984).
### Table 3.1
Calculated slopes for $k$ value plots (figure 3.8) for data from this study and for values from Khare et al. (1984). The slopes from this study were determined by using a linear regression, the slope for the Khare et al. (1984) data was determined by using a quadratic regression.

<table>
<thead>
<tr>
<th>Initial Gas Mixture</th>
<th>Slope of $k$ values (AU/nm)</th>
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<tbody>
<tr>
<td>10% CH$_4$ in N$_2$</td>
<td>$-4.55 \times 10^7 \pm 1.0 \times 10^{-8}$</td>
</tr>
<tr>
<td>2% CH$_4$ in N$_2$</td>
<td>$-1.962 \times 10^6 \pm 1.2 \times 10^{-8}$</td>
</tr>
<tr>
<td>10% CH$_4$ in N$_2$, Khare et al. (1984)</td>
<td>$(0.44 \pm 0.02)x + (-3.3 \times 10^{-4} \pm 4 \times 10^{-5})$</td>
</tr>
</tbody>
</table>
the plots for $k$ values determined for the haze aerosol analogs in this study (table 3.1). The slopes of the $k$ values from this study differ greatly from that of the 10% CH$_4$ in N$_2$ $k$ values from Khare et al. (1984) of which a quadratic regression was used to fit the data.

The main difference between this study and the Khare study is that the tholins in this study were generated at 840 mbars, whereas the tholins in Khare’s study were generated at 0.2 mbars. Figure 3.9 shows previous studies in which infrared absorption spectra were taken of analogs generated at varying pressures (Imanaka et al. 2004). Changes can be seen in the spectra as the pressure changes. As a general trend, the four major peaks (near 1600 cm$^{-1}$, 2200 cm$^{-1}$, and and 2900 cm$^{-1}$ 3300 cm$^{-1}$) become less intense as pressure increases. Changes in the absorption spectra indicate that the chemical composition of the tholins can vary with pressure; if the chemical composition of the tholins change with pressure, the optical properties and therefore the $k$ value must also change with pressure. This would give different $k$ values between this study and Khare’s study.

3.5 Implications of Optical Properties for Titan

The relative $k$ values calculated indicate that at lower initial concentrations of CH$_4$, the haze aerosol analogs absorbed more in the shorter wavelengths than at longer wavelengths while the haze aerosol analogs generated with higher initial concentrations of CH$_4$ absorb slightly more evenly over all wavelengths. Since the 2% CH$_4$ analog absorbed more in the blue wavelengths, this might explain why the tholins on Titan today appear orange. The current CH$_4$ concentration in Titan’s atmosphere is around 2%; therefore the tholins might absorb in similar wavelengths as our haze aerosol analogs, reflecting longer wavelengths in the red and orange color regions back to the human eye. In Titan’s past when the tholins might have formed at higher CH$_4$ concentration such as a 10% CH$_4$ gas mixture, the tholins might have absorbed evenly over all wavelengths similarly to the haze aerosol analogs generated at 10% CH$_4$ concentrations in the lab, resulting in haze aerosols with an
overall grey-ish color (figure 3.10). As the concentration of CH\textsubscript{4} in Titan’s atmosphere decreases over time, this trend might indicate that in the future, Titan will appear a brighter red color as shorter wavelengths are absorbed more intensely.
Figure 3.9  Infrared transmission data from Imanaka et al. (2004) showing changes in chemical composition with respect to pressure. For reference points, tholins from this study were generated at 84,000 Pa while tholins from Khare et al. (1984) were generated at 20 pascals. Changes in chemical composition with respect to pressure can result in varying $k$ values with respect to pressure. Intensities have been offset.
Figure 3.10  Projected images of Titan’s atmosphere in the past, present, and future. (a) A projected image of Titan’s atmosphere in the past when CH₄ concentrations might have been higher than the current concentration. The atmosphere might have appeared as a grey-ish color. (b) A current-day image of Titan shows an atmosphere of an orange-ish yellow color. Image courtesy of NASA/JPL/Space Science Institute. (c) A projected image of Titan’s atmosphere in the future when CH₄ concentrations might have been lower than the current concentration. The atmosphere might have appeared a red- ish orange color.
Chapter IV

Summary, Conclusions, and Further Research

4.1 Summary and Conclusions

In this work, the chemical and optical properties of Titan haze aerosol analogs were investigated as the initial gas mixtures of CH$_4$ in N$_2$ were varied. Infrared spectroscopy was used to investigate the chemical properties and UV-Vis spectroscopy was used to investigate the optical properties of the haze aerosol analogs. The goal of this work was to formulate a historical hypothesis of the chemical and optical properties of Titan’s haze aerosols as the CH$_4$ concentration in Titan’s atmosphere changes over time.

The work in Chapter II described the investigation of the chemical properties of the haze aerosol analogs through infrared spectroscopy. Haze aerosol analogs were generated from initial gas concentrations of 10% CH$_4$ in N$_2$, and 2% CH$_4$ in N$_2$ and 0.4% CH$_4$ in N$_2$ in the lab and IR absorption spectra were taken. The data indicates that as CH$_4$ concentration increases, the overall chemical and hydrocarbon mass increases, as does the concentration of PAH’s. This data is consistent with previous research on the effects of initial gas percents (Trainer et al. 2004).

Chapter III detailed the examination of the optical properties of the haze aerosol analogs through UV-Vis spectroscopy. The imaginary refractive index $k$ values calculated from the data indicate that as initial CH$_4$ concentration decreases, the haze aerosol analogs absorb more intensely in the shorter wavelengths. The $k$ values calculated here do not closely correspond with the $k$ values from previous data (Khare et al. 1984). This might be due to differences in experimental parameters for generating the haze aerosol analogs such as large differences in pressures.
With this data, predictions could be made regarding the chemical and optical properties of Titan’s past and future haze aerosols compared to those of today.

4.2 Further Research

While this study provides preliminary data on the chemical and optical properties of Titan haze aerosol analogs as initial gas percents are varied, there are several parameters of this experiment that are still to be investigated. It is suspected that pressure dependence is the cause of differences between our data and previous data, which might be representative of tholins generated at various altitudes in Titan’s atmosphere; therefore, varying initial gas percents at several different pressures might give insight to the effects of aerosol generation on Titan near the surface at pressures of ~1.5 bar or in the haze formation layer at pressures of 0.1 mbar (Imanaka et al. 2004).

Temperature studies might also be conducted to supplement this study. While the analogs in this study were generated at room temperature, the actual temperature of the haze layer on Titan is ~170K (McKay et al. 1999). This brings about the argument between kinetic and thermodynamic products of haze aerosol analogs. Analogs generated at higher temperatures might favor a thermodynamic product while analogs generated at lower temperatures might favor a kinetically favorable product; these two products might be optically different as well as chemically different.

Additionally, absolute imaginary refractive index values might be studied to determine the dominating factor in the overall optical characteristics of the tholins on Titan. The $k$ values presented in this data are scaled values; therefore assumptions about absolute absorbances cannot be made. It might be the case that the absolute $k$ values for 10% CH$_4$ in N$_4$ are much higher than those for the 2% CH$_4$ mixture and therefore the optical properties of
the 2% CH₄ data become insignificant in the shadow of the 10% CH₄ optical properties, or vice versa.
References


