Chapter 1. Introduction

The term “tholin” was coined by Carl Sagan in 1979 (Sagan and Khare, 1979), to describe the products obtained by the energetic processing of mixtures of gases abundant in the cosmos, such as CH_4, N_2, and H_2O. Tholin comes from the Greek, meaning “muddy”, an apt description for the brownish, sticky residues formed by such experiments. These experiments, using either electrical discharges or ultraviolet irradiation, are the natural extensions of the well-known Miller-Urey experiment (Miller and Urey, 1959). While the Miller-Urey experiment focused on an atmosphere meant to be like that of the early Earth, Sagan and others attempted to simulate the atmospheres of other planets and moons in the Solar System, such as Titan, Triton (McDonald, et al., 1994), and Jupiter (Khare and Sagan, 1975).

As one would expect, tholins are a very complex mixture of organics, and are a great challenge for most analytical methods. A laser desorption ionization mass spectrum of a tholin created by electrical discharge of an N_2/CH_4 mixture is shown in Figure 1.1. There are literally thousands of distinct compounds represented here, and an even larger number of isomers will exist that cannot be separated by mass spectrometry. But there is still order apparent in the mixture. The spectrum shows groups of peaks differing by 14 m/z, the mass of a methylene unit. This kind of pattern gives us hope that a more detailed understanding of the structure of the tholins is possible.

Since our interest is in Titan, the focus of this thesis is on the Titan tholins, those made from mixtures of N_2 and CH_4, the predominant components of Titan’s atmosphere.

Titan is of great interest as an astrobiological target because it is a unique place in the Solar System. Titan has a dense atmosphere, and so is thought to have a great abundance of organics on its surface, the result of photochemical reactions in the upper atmosphere.

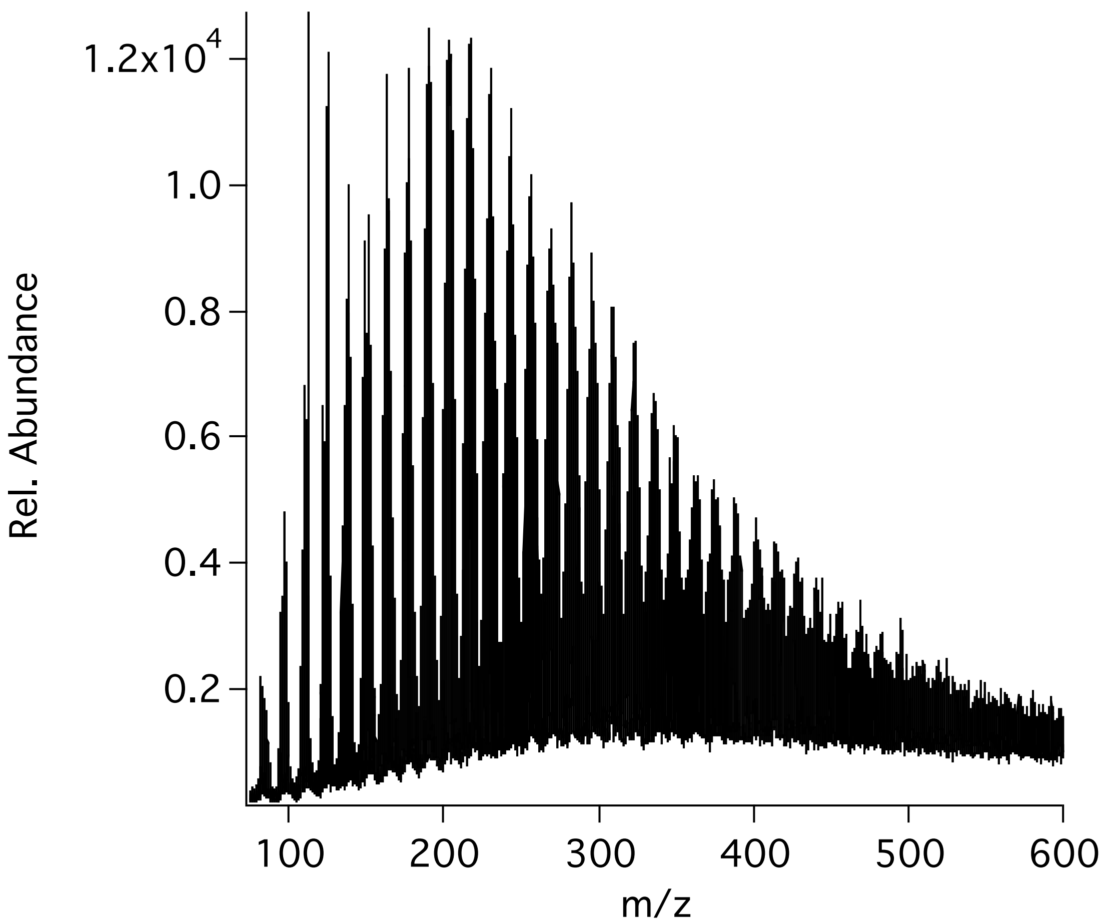

Figure 1.1 Laser desorption ionization mass spectrum of $CH_4 + N_2$ tholins.

Titan also has a surface expected to be composed primarily of water ice, with a surface temperature of ~90 K. Impactors or cryovolcanism would result in a mixture of organics and liquid water, which would eventually freeze (Artemieva and Lunine, 2003; Artemieva and Lunine, 2005). Each impact site or volcanic event represents an individual experiment in prebiotic chemistry, preserved by the cold for later study. Chapter two discusses the promise of Titan as a laboratory for prebiotic chemistry in greater detail.

This thesis explores two broad themes. The first is the characterization of Titan tholins. While many researchers characterize their tholin materials as a matter of course, using infrared spectroscopy and mass spectrometry, we have instead concentrated on techniques that have been more infrequently used for tholin analysis, and we hope this approach has led to a greater understanding of the nature of the tholins.

Chapter three is a detailed study of the near infrared reflectance spectrum of tholins at temperatures close to those of Titan's surface. Few studies of the spectrum exist between 1 and 5 microns, and these spectra help fill that gap. Near-infrared spectra of tholins are useful in models of the albedo of asteroids and other small interplanetary bodies, and may prove of value in the future exploration of Titan.

Chapter four discusses the chemical changes that occur when tholins are heated. A variety of techniques have been used here; thermal gravimetric analysis, differential scanning calorimetry, headspace GC-MS, LDI-MS, and ultraviolet evolved gas analysis. The results of these techniques are synthesized into the beginning of an understanding of the processes that occur when the tholins are heated. While it is impossible to ever have a complete understanding of the processes that occur in a material as complex as the tholins, we have discovered that they are very unstable when heated, releasing large amounts of ammonia at only 100 °C, and as heating continues, cyclizing and aromatizing. These results have implications for the further study of tholins, especially by pyrolytic techniques, and for the surface of Titan as well.

Chapter five uses mass spectrometry to separate a particular portion of the tholins for analysis. Electrospray ionization mass spectrometry is used to introduce the tholins into the gas phase in association with 18-crown-6, a molecule that forms a strong non-covalent complex with protonated primary amines. Two related homologous series of ions are seen complexed with the crown ether. This is the first identification of these molecules in the tholin mixtures.

Chapter six separates another subset of the tholins for study: the fluorescent components. Three-dimensional fluorescence spectra and thin layer chromatography are used to classify the fluorescent components. Tholins are highly fluorescent, and several distinct fluorophores can be identified.

Chapter six also begins the exploration of our second theme, the development of instrumentation for the future exploration of the chemistry of Titan. Spaceflight instrumentation must meet stringent limitations on power, weight and size, and so the design of equipment for chemical analysis can be challenging. In Chapter six, we use our knowledge of the fluorescent properties of the tholins to construct a small fiber optic spectrometer that can examine the fluorescent properties of ices. Tholin in a water ice matrix is shown to have a fluorescence distinct from the aqueous or solid phases. Such an instrument incorporated into a Titan probe would be able to locate areas where tholins had been exposed to liquid water, and then frozen. These areas would be of great astrobiological interest.

Chapter seven discusses the use of an unusual instrument, a gas chromatograph with a gas phase far-ultraviolet absorption detection system. The use of far-ultraviolet spectroscopy as a detection method for gas chromatography (GC) allows for the identification of functional groups by their characteristic absorptions. We demonstrate the use of the system on the pyrolysis products of the tholins. GC-UV has the advantage over GC-MS systems in weight and power requirements, since a vacuum system is not required.

Chapter eight discusses our efforts to build enantiomerically selective detectors. The detection of enatioenrichment on Titan would be a step towards understanding the role enantioenrichment played in the origin of life. We have chosen quartz crystal microbalances as the transduction device, and use derivatized self-assembled monolayers as the sensing medium.

Finally, the appendices present some instruments that were developed along the way, although they have no direct application to Titan chemistry. Appendix A shows the utility of GC-UV (with minor modifications) for the detection of explosives. Appendix B is a detailed study of the characteristics of a simple, highly sensitive amine and ammonia detector developed in our labs.

1.1. References

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