

**ANALYSIS OF TITAN THOLINS BY LASER DESORPTION MASS SPECTROMETRY.** A. L. Ganesan<sup>1</sup>, W. B. Brinckerhoff<sup>1</sup>, P. Coll<sup>2</sup>, M.-J. Nguyen<sup>2</sup>, F. Raulin<sup>2</sup>, T.J. Cornish<sup>1</sup>, S.A. Ecelberger<sup>1</sup> <sup>1</sup>JHU/ Applied Physics Lab, 11100 Johns Hopkins Road, Laurel MD 20723 ([Anita.Ganesan@jhuapl.edu](mailto:Anita.Ganesan@jhuapl.edu)), <sup>2</sup>Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), Université Paris 7 and Paris 12, 61 ave du Général de Gaulle, 94010 Créteil Cedex, France

**Introduction:** A thick haze exists in the atmosphere of Titan, where it is believed that energetic processing of  $N_2$  and  $CH_4$  leads to the vast production of organics [1]. Data from the Ion and Neutral Mass Spectrometer (INMS) of the Cassini-Huygens mission to Saturn confirm the presence of hydrocarbon and nitrile species up to  $C_7$  [2].

The term tholin was given by Carl Sagan to laboratory analogs of complex heteropolymers in Titan's aerosols [3]. Various analytical techniques have been used to elucidate the structure and composition of tholin samples [4].

We present an analysis of tholins by laser-desorption time-of-flight mass spectrometry (LDMS), including a comparison of a commercial instrument with a miniature LDMS instrument built at APL. Pulsed laser desorption can form gas phase ions directly from solid sample surfaces. The time-of-flight (TOF) technique works for both positive and negative ion detection and is sensitive to high mass. Furthermore, no sample preparation is required. This technique is in development for flight opportunities [5].

**Samples:** The tholins used in this study were prepared at LISA. A mixture of  $N_2:CH_4$  (98:2) at 4 mbar was subjected to electrical discharge. This was performed at room temperature and at Titan atmospheric temperature ( $\sim 100$ -150 K) [6]. For convenience, these samples are referred to as "hot" and "cold" samples. Samples were synthesized without exposure to air or

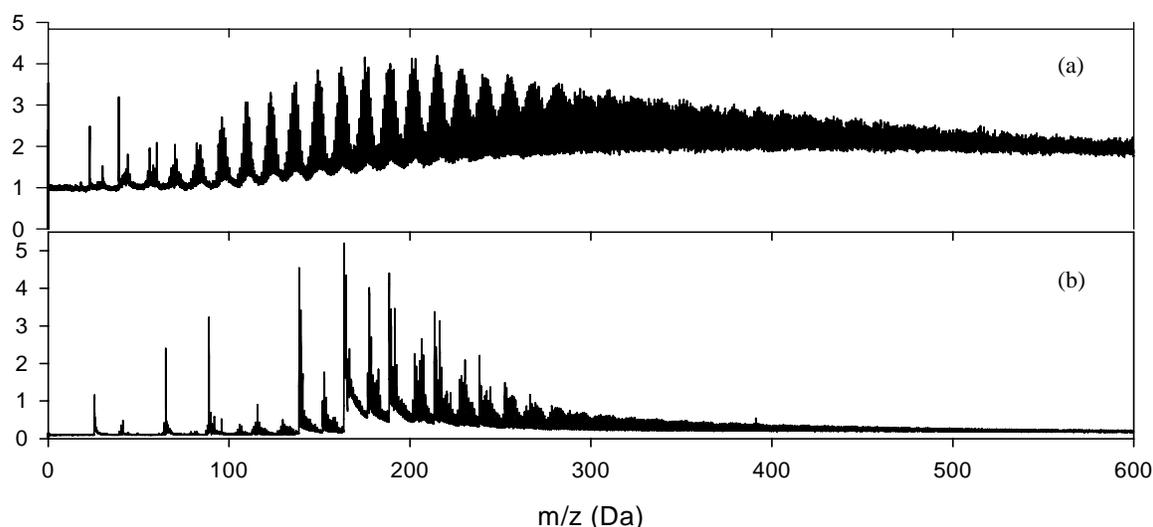
moisture and stored in Eppendorf vials; no oxygen is expected in their composition.

**Experimental:** Samples were analyzed by LDMS, using a Bruker Autoflex TOF/TOF. Desorption and ionization occurred by means of a 337 nm  $N_2$  laser with laser energy of up to 100  $\mu J$  and spot diameter of  $\sim 100$   $\mu m$ . Samples were affixed to double-sided tape and mounted on aluminum sample holders. Double-sided tape added no significant background signal. Further analyses were performed by tandem mass spectrometry, to allow for the deliberate fragmentation of selected mass/charge ( $m/z$ ) values.

A similar analysis was performed on a miniature LDMS instrument developed at APL. This instrument operated in a mode analogous to the Autoflex, however the laser used was a 355 nm Nd:YAG and the mass analyzer used a lower extraction voltage to compensate for a much shorter flight tube.

#### Results:

*Bruker Autoflex:* The spectra reveal a polymeric structure to the tholins and this is evident in both positive and negative ions (Fig. 1). Peaks occur in repetitive cluster units. There is no significant difference between the hot and cold sample spectra, in respective polarities. The peak clusters of hot and cold sample spectra occur at essentially the same  $m/z$  values over a wide range, with a slight difference only in amplitude. The overall oligomer size distribution is consistent for both samples.



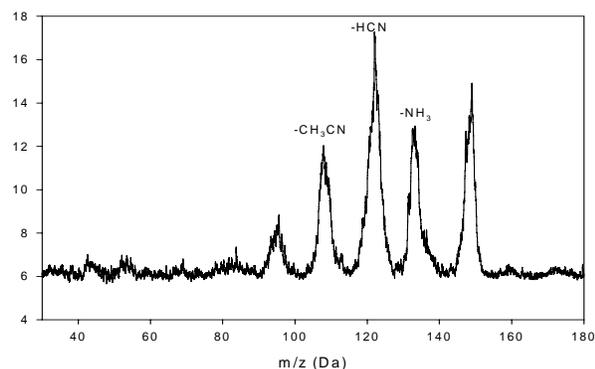
**Fig. 1:** Autoflex spectra of hot tholins. (a) Positive ion detection, (b) Negative ion detection

The individual and cluster peak profiles in positive and negative ion spectra differ: negative ion peaks have a sharp onset followed by a high-time tail, in contrast to positive ion peaks which exhibit a more symmetric shape. This difference may result from negative ions having a broader distribution of formation times, potentially due to the additional  $[M-H]^-$  route available for prompt negative ionization in laser desorption.

From a coarse viewpoint, the positive ion clusters appear to be spaced at 13 Da intervals. However, the intervals are also consistent with alternating 14 Da and 12 Da units. These data are highly suggestive of a conjugated polymeric structure, such as polyacetylene. The formation of stable polyacetylene-based oligomers may occur via an alternating  $-CH_2$  and  $-C$  addition scheme. It is also possible that there are multiple polymeric structures that result in what appears to be a single structure spaced by 13 Da. Some studies of other tholin samples indicate the presence of a regular 14 Da cluster spacing corresponding to the addition of a methylene unit [4].

Negative ion clusters exhibit a bimodal spacing, alternating between 13 Da and 12 Da. This pattern is also consistent with negative ions forming as either  $M^-$  or  $[M-H]^-$ . As such, the positive and negative spectra are very likely two views of a common parent molecular structure.

The results of tandem mass spectrometry, or MS/MS, performed on the positive parent ion at  $m/z$  149, reveal losses of small molecules, including  $NH_3$ , HCN, and  $CH_3CN$  (Fig. 2). This indicates the presence of nitrogen-containing functional groups, such as nitriles and amines, likely as oligomer terminating units.



**Fig. 2:** Autoflex MS/MS of the positive parent ion at  $m/z$  149.

**Miniature LDMS:** A polymeric structure similar to that obtained with the Autoflex is evident in the positive ion spectra of the miniature instrument (Fig. 3).

Clusters can be clearly discerned, however, the distribution peaks at a lower mass than in the analogous Autoflex spectrum. Such a difference could be explained by differing mass dependence of ion transmission in the two instruments.

**Discussion:** In accordance with the Autoflex data, including the results from MS/MS, it is possible that these tholin samples contain polyacetylene with terminal nitrile and amine groups. It has been hypothesized that polyacetylene is a component of the Titan haze and these results are consistent with that claim. Polyacetylene would preferentially form in the upper atmosphere of Titan (>500 km) [7].

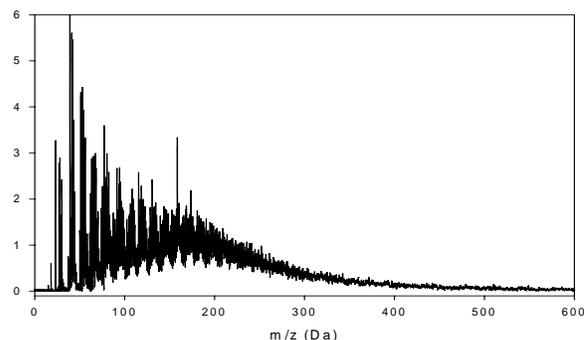
It is not apparent that tholins synthesized at different temperatures exhibit a difference in LDMS-detected composition. This may be consistent with previous work by Hodyss et al. [5]. However, other studies indicate that initial gas concentration and pressure do play a significant role [6]. LDMS is very sensitive to nonvolatile polymeric compounds and future analyses may assist with the resolution of these issues.

LDMS instrumentation can evidently be miniaturized without major losses in performance with polymeric samples. As such, this technique may be a key enabling element of a future *in situ* mission to Titan.

Continuing LDMS analyses of Titan tholins include examining a wider variety of synthetic conditions, using different laser wavelengths, and more detailed studies of negative ionization and MS/MS spectra.

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**References:** [1] Yung Y.L et al. (1984) *Astrophys. J. Suppl. Ser.*, 55, 465-506. [2] Waite J. H. et al. (2005) *Science*, 308, 982-985. [3] Sagan C. and Khare B.N. (1979) *Nature*, 277, 102-107. [4] Hodyss R. (2006) *Ph.D. Diss. California Institute of Technology* [5] Brinckerhoff W.B. et al. (2004) *Appl. Phys. A*, 79, 953-956. [6] Coll P. et al. (1999) *Planet. & Spa. Sci.*, 47, 1331-1340 [7] Wilson E.H and Atreya S.K *Planet. & Spa. Sci.*, 51, 1017-1033



**Fig. 3:** Positive ion spectrum obtained on a miniature LDMS instrument.