GC/MS/MS Analysis of Astrobiologically Significant Aerosols: The Hunt for Prebiotic Molecules

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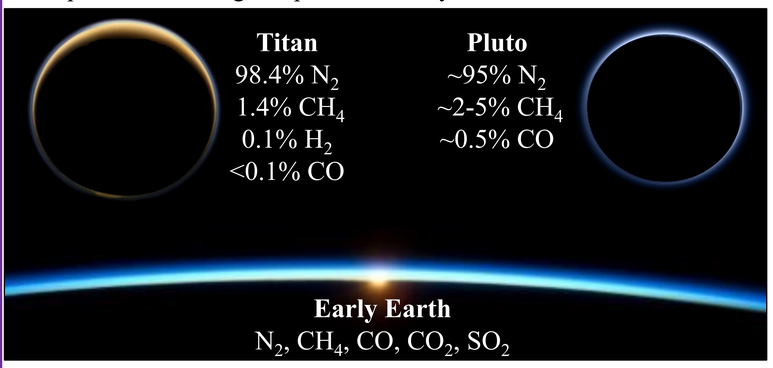
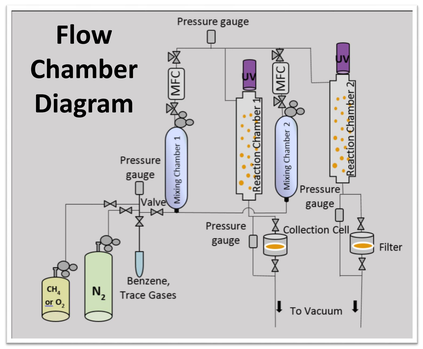
Background

In our solar system, only one planet is known to have life. One of the hypotheses for the start of life on Earth is that the primordial hazes that shrouded the planet, were sources of photochemically created prebiotic molecules. In the present day, the reducing atmosphere of the early Earth has been transformed into the oxygen rich one we have today, but Titan, the largest moon of Saturn, and Pluto, both have nitrogen based reducing atmospheres rich in organic photochemistry.



By understanding the Titan and Pluto of today, and the astrobiological processes taking place, we can gain insights regarding the origin of life.

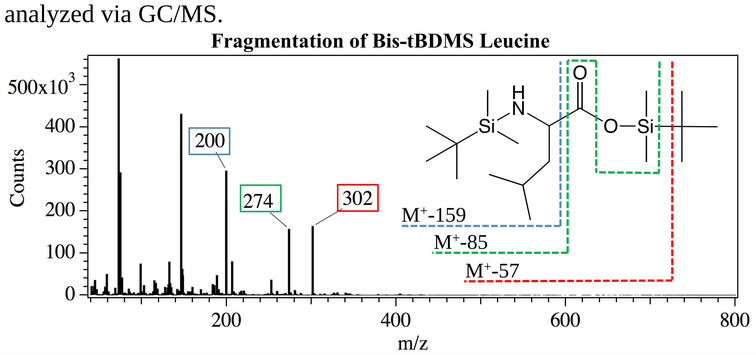
Aerosol Generation



Organic aerosol analogs were produced via VUV photolysis of nitrogen (N_2) based gas mixtures with trace (50 ppm) levels of benzene (C_6H_6). The lack of acidic hydrogens in the final aerosols made this a good matrix for GC/MS/MS method testing.

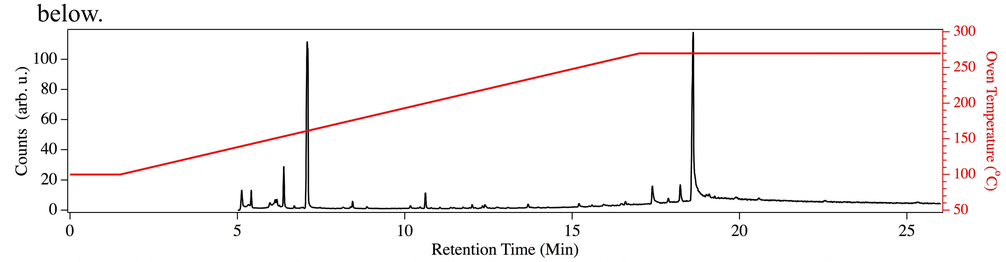
Derivatization

Standards of amino acids, nucleobases, and other compounds were added to aerosols and derivatized with N-tert-butyldimethylsilyl- N-methyltrifluoroacetamide (MTBSTFA). The tert-butyl dimethylsilyl (TBDMS) derivatives could then be extracted from the bulk aerosol and analyzed via GC/MS.



GC/MS Method

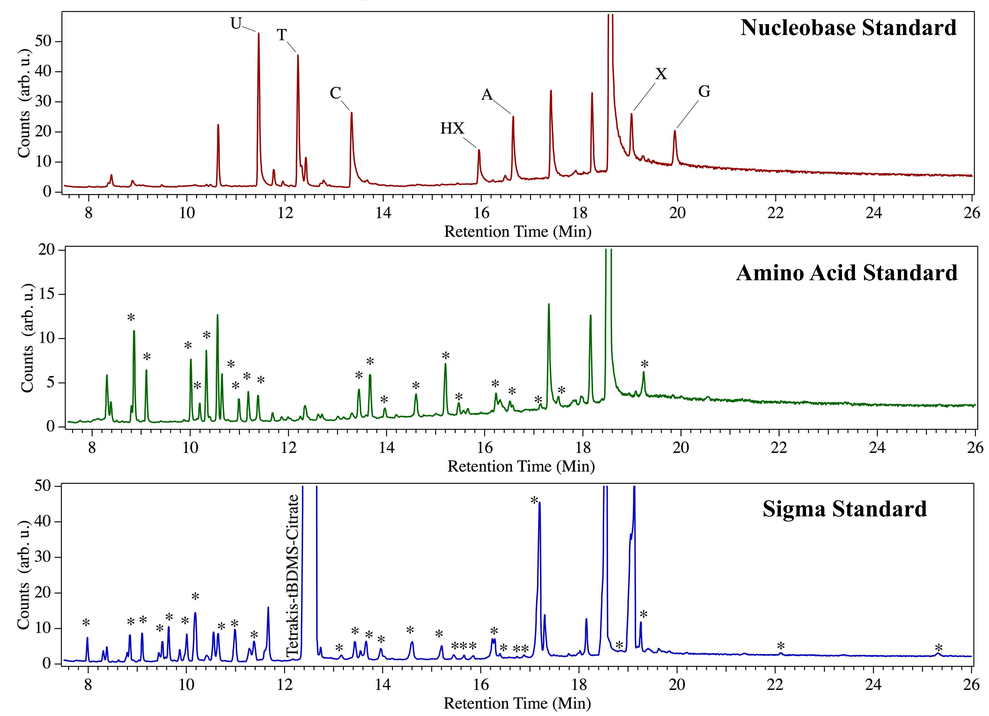
- Standards and aerosols were dried in GC vials with 200 μL inserts.
- Derivatization was carried out with 30 μL of MTBSTFA and 30 μL of DMF at 95°C.
- 1 μL of sample was injected into a GC/MS at 100°C with the thermal ramp (red) shown below.



- A blank (black) was run for each derivatization to check for cross contamination.
- The peaks observed above are expected side products of the reaction.

Detection of Biomolecules

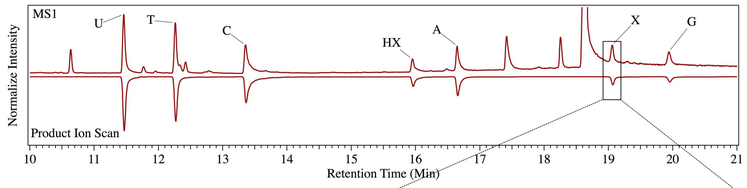
Three standards of biological compounds were used to validate the selectivity of the GC method. The full list of 30+ detectable compounds is listed below.



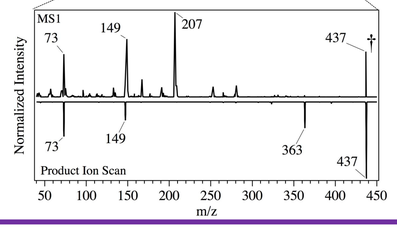
Nucleobase Standard	Uracil, Thymine, Cytosine, Hypoxanthine, Adenine, Xanthine, Guanine
Amino Acid Standard	Alanine, Glycine, β-alanine, Valine, Norvaline, Leucine, Isoleucine, Norleucine, Proline, Methionine, Serine, Threonine, Phenylalanine, Aspartic acid, 4-hydroxy-proline, Cysteine, Glutamic Acid, Asparagine, Lysine, Glutamine, Tyrosine
Sigma Standard	Ethanolamine, Alanine, Glycine, Sarcosine, Aminobutyric acid, β-alanine, Urea, Valine, Leucine, Isoleucine, Proline, Taurine, Methionine, Serine, Threonine, Phenylalanine, Aspartic Acid, 4-hydroxy-proline, Glutamic Acid, Ornithine, Homocystine, Methyl-histidine, Lysine, Histidine, Tyrosine, Tryptophan, Cystathionine

MS/MS Methodology

In order to increase sensitivity, an MS/MS method was developed using a triple-quad GC/MS. A parent mass (†) was selected from the MS scan for each species and fragmented using CID removing extra species from the GC chromatogram that did not have those masses.

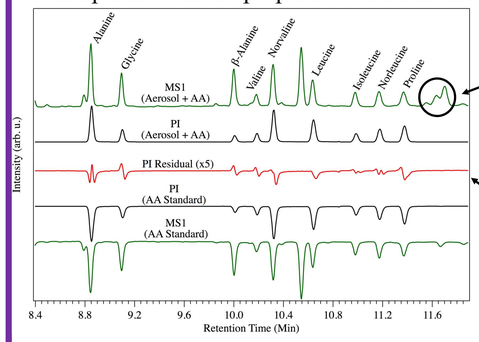


This had the dual effect of increasing signal to noise in both the GC data and providing an additional MS pattern for unique product identification.



The Aerosol Matrix

To check for bulk effects of the aerosol matrix on derivatization, a sample of aerosol made from photolysis of 50ppm benzene in nitrogen was spiked with the prepared standards and derivatized.



MS1 scans showed presence of species unique to the aerosol.

The residual of the PI scans showed negligible effect of the aerosol on bulk derivatization.

Conclusions/Future Plans

We have developed a method that can differentiate over 30 compounds important for life on Earth using GC/MS/MS techniques. It has also been shown that the organic matrix of the aerosol does not effect the efficiency of the technique. Moving forward we will begin analyzing aerosols that will contain higher abundances of acidic hydrogens and possible biomolecules.

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References

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