National Aeronautics and Space Administration

Investigating alternative molecular surveying techniques with OASIS (Organic Analysis System utilizing Ion Sprays)

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Objective: Develop a soft-ionization technique that will allow for the generation of large (100–1000+ amu), intact biomolecular ions under vacuum conditions for in-situ mass spectrometry in future planetary missions.

Background: Planetary missions of the past two decades have established the ubiquity of organic compounds across the solar system. Although these detections are tantalizing with regard to prebiotic chemistry, thorough chemical analysis has been limited by the inability of flight instruments to process intact large and complex organic molecules. On Earth, the *de facto* technique for analyzing large biomolecules is electrospray ionization mass spectrometry (ESI-MS; **Figure 1**). ESI-MS softly ionizes target molecules, keeping them intact for processing so that the full mass spectrum can be identified. The possibility for analogously large biomolecules existing in martian ice or regolith and in or on icy bodies like Enceladus makes ESI-MS an attractive approach for future astrobiological investigations.

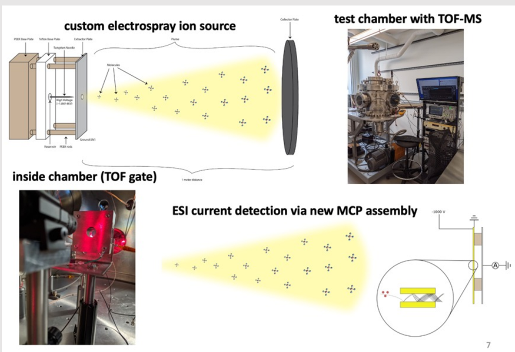

Figure 2. Cartoons illustrating general design of custom ESI source and current detection via an in-house-built multi-channel plate (MCP) assembly housed at the end of the flight tube for time-of-flight mass spectrometry (TOF-MS). Photos show exterior of vacuum test chamber with flight tube and control electronics as well as chamber interior where a laser is used to align the electrospray needle with the electronic gates into the flight tube for signal optimization. All components were designed and fabricated by graduate students in Co-PI Petro's ASTRA Lab at Cornell University.

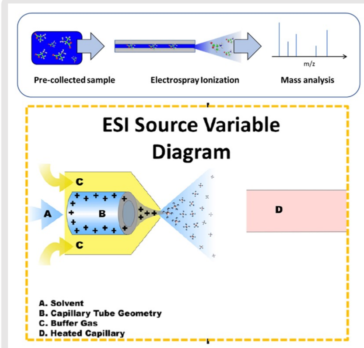

Figure 1. Basic operations of ESI-MS and fundamental components. **Top:** Workflow for analysis of organic molecules collected from, e.g., the Enceladus plume. **Bottom:** The four components of ESI systems (A-D) to be modified for performance in vacuum.

Approach: Standard ESI techniques have four components (**Figure 1**) which have been tuned for earth-bound operation but through this work will be adjusted to enable end-to-end operation in vacuum. These components include the liquid solvent, spray capillary, buffer gas, and heater capillary, which together enable a series of events that transfers a 'biological' sample dissolved in a liquid matrix to gas-phase ions ready to be analyzed by a mass spectrometer. Planned modifications to each of the components and the significance **(→ bold)** of each to operation are outlined below. Letters correspond to those given in **Figure 1**. Photos of and generalized designs for some of the in-house experimental setup built during Year 1 are shown in **Figure 2**.

A) Solvent: exploration of low-volatility solvents including ionic liquids → **impacts operating pressure**
B) Spray capillary: the degree of solvation is influenced by the emitter capillary geometry → **impacts quality of spray**
C) Buffer: elimination will be explored through thermally enhanced desorption and emitter geometry → **impacts consumables required on orbit**
D) Heater capillary: temperature will be varied to enhance solvation from low volatility solvents → **controls final ion state prior to entering MS**

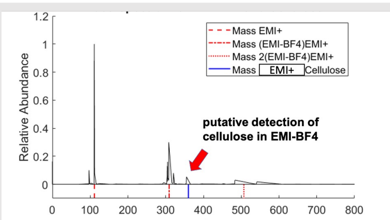

Figure 3. Mass spectrum with peaks from EMI cations, EMI-BF4 complexes, and the putative detection of a cellulose fragment complexed to the EMI cation.

Results: Year 1 tasks focused on (1) developing techniques for spraying organic ions under vacuum (vESI) and (2) constructing a prototype vESI source. Year 1 accomplishments include:

- Development of a laboratory electrospray source compatible with pure vacuum operation, some of which is shown in **Figure 2**.
- Initial, proof-of-concept 'firing' experiments performed with large biopolymers and amino acids dissolved in two ionic liquids, EMI-BF4 and EMI-Ac. Example mass spectrum shown in **Figure 3**.

Significance/Benefits to JPL and NASA

OASIS involves the development of a novel mass spectrometry front-end specifically designed for in-situ analysis of large biomolecules. Our device will provide a unique complement to the existing toolset available to future planetary missions in the search for life and could be coupled to flight instruments being developed at JPL, such as the CESI-MS subsystem of OWLS, and elsewhere as funded by NASA (e.g., MASPEX at SwRI).

Of equal, if not greater, importance, our Cornell team includes four undergraduates recruited through the Cornell Women of Aeronautics and Astronautics chapter who have been **key contributors** to this project since Spring 2021. Highlights from their year are shown in the photos to the right.

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Publications:

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