National Aeronautics and Space Administration

FY24 Strategic University Research Partnership (SURP)

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 is limited by the inability of flight instruments to process intact large organic molecules. On Earth, the *de facto* technique for analyzing large biomolecules is electrospray ionization mass spectrometry (ESI-MS) because molecules remain intact following ionization, and the full mass spectrum can thus be visualized. The possibility for 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.

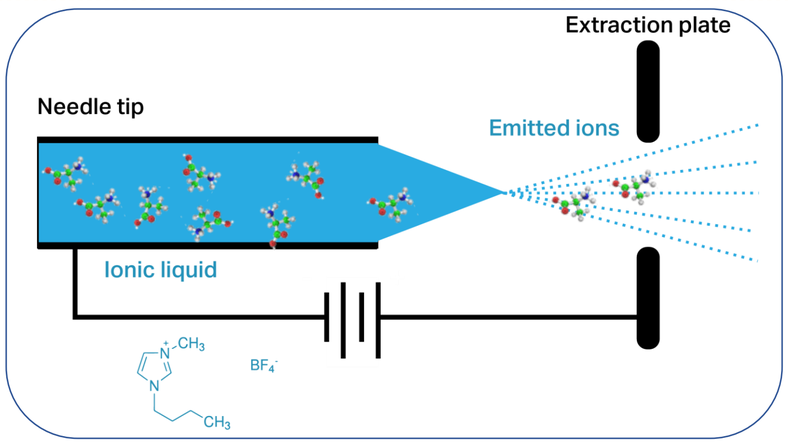
Hypothesis: Vacuum compatible electrospray ionization can enable detection of high molecular weight organics for future icy world missions.

Approach: Standard ESI techniques have four components which have been tuned for earth-bound operation but through this work will be adjusted to enable end-to-end operation in vacuum via the adaptation of electrospray propulsion technologies to mass spectrometry.

Direct Ionization Mode (vESI)

GOAL: Vacuum spray of high molecular weight organics

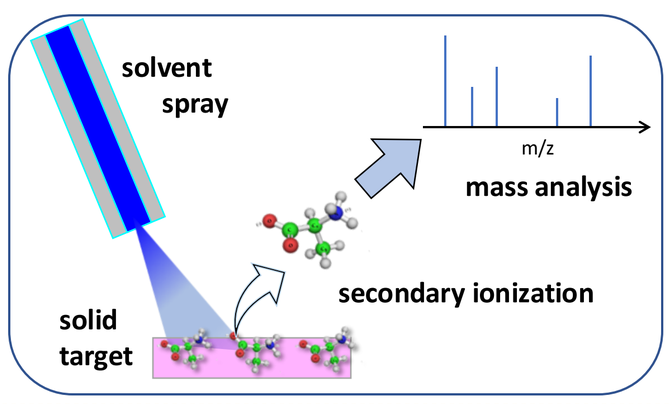
- Standard ESI-MS sources require (1) atmospheric pressure and (2) buffer gas.
- ESI sources for space propulsion produce pure ion sprays under vacuum.
- Ionic liquids may be used as vacuum stable solvent.



Secondary Ionization Mode (DESI)

GOAL: Generation of high molecular weight organics from solid target with surface layer sample

- Great for molecules that do not dissolve in traditional solvents.
- Commonly used to study lipids and other high-mass biomolecules.
- Can intentionally vary impact energy to fragment molecules for more chemical information.



Year 3 Results: A key finding from this work is that while histidine and other amino acids are sometimes detectable in ionic liquid solution (Figs. 1 & 2), they are much more easily identifiable in glycerol (Fig. 1), which is a vacuum-stable solvent frequently used in capillary electrophoresis (CE). Glycerol's use in CE—a component of JPL's OWLS instrument suite—makes it a compelling solvent for future vESI work. We also validated our DESI source design using an ionic liquid primary ion beam on gold and silver targets (Fig. 3).

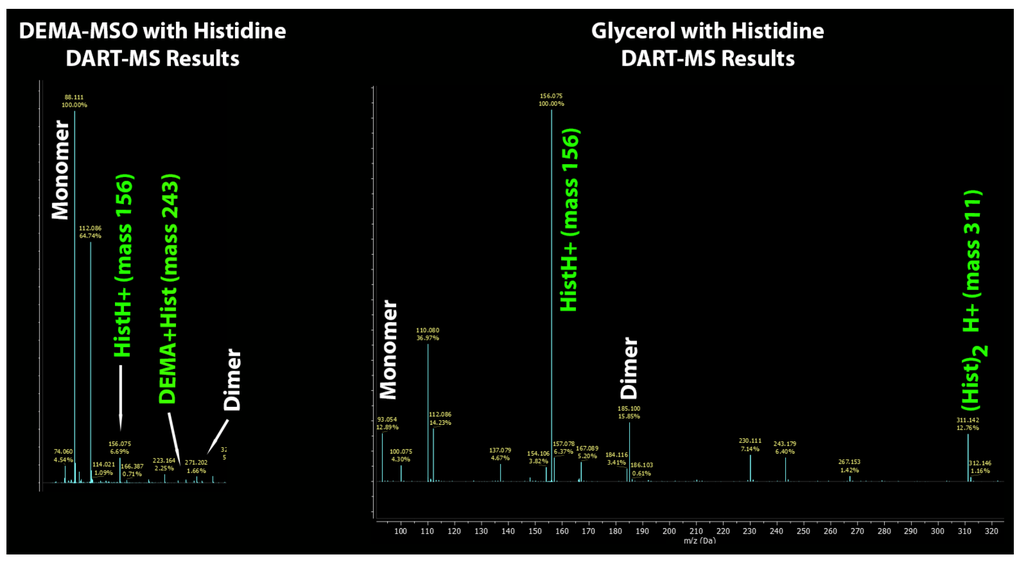


Figure 1. Commercial DART-MS spectra in positive ion mode comparing the relative intensities of protonated histidine ($HistH^+$) when dissolved in the ionic liquid DEMA-MsO (left panel) versus in glycerol (right panel). The commercial instrument was used to ground-truth our prototype results.

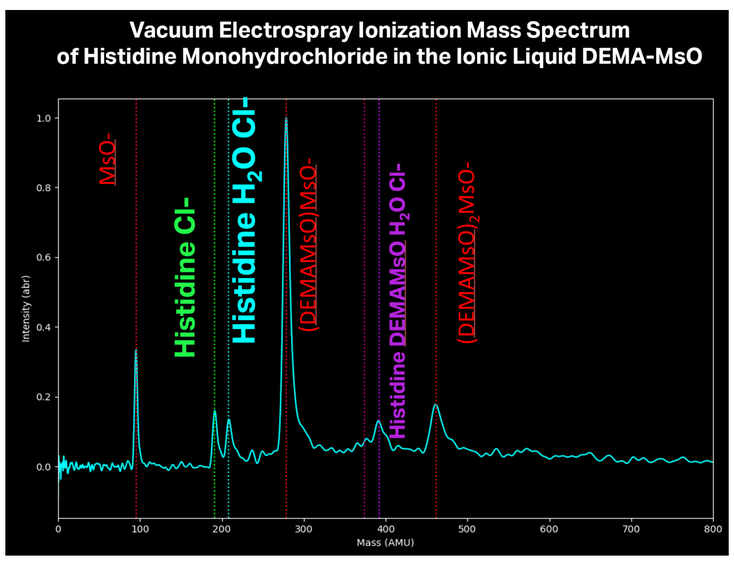


Figure 2. Data collected in negative ion mode with the Cornell prototype vESI-TOF-MS demonstrating the detection of histidine dissolved in DEMA-MsO.

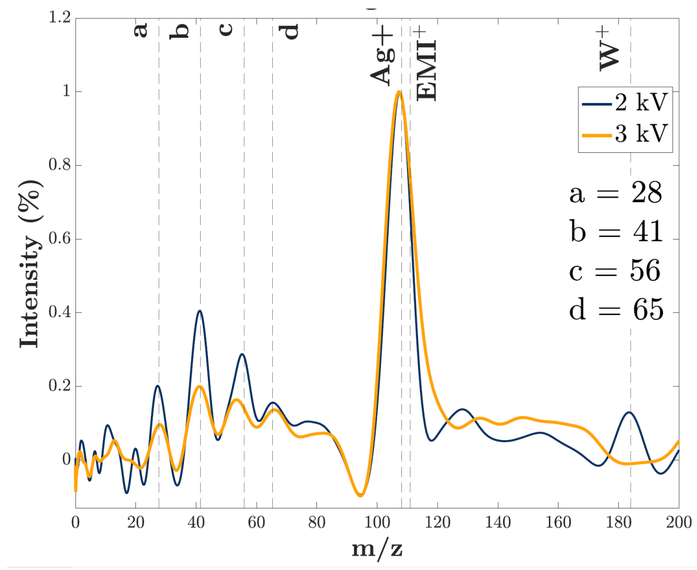


Figure 3. Mass spectrum generated in positive ion mode following the soft sputtering of a silver (Ag) target with a primary beam of EMI-BF_4 via the Cornell prototype DESI-MS system.

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Conference Papers and Presentations:

Ulibarri et al., "**Initial Studies with a Vacuum Electrospray Ionization Mass Spectrometer**", Abstract #404-02, *Astrobiology Science Conference*, Providence, RI, 2024.

Chavez et al., "**Determining ideal ionic liquids for direct electrospray ionization mass spectrometry under vacuum**", Abstract #419-08, *Astrobiology Science Conference,* Providence, RI, 2024.

Ulibarri et al., "**Vacuum concentration of organic biomolecules with ionic liquids for in-situ astrobiology instruments**", Abstract #35859, *45th COSPAR Scientific Assembly*, Busan, South Korea, 2024.

Hofheins et al., "**Electrospray Secondary Ion Mass Spectrometry Diagnostic–Design and Preliminary Results**", *International Electric Propulsion Conference*, Toulouse, France, 2024.

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