

Heading:

In Situ Instrument to Detect Prebiotic Compounds in Planetary Ices

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Summary:

The development of an *in situ* LC-MS instrument for future planetary science missions to icy surfaces that are of high astrobiology and astrochemistry potential will advance our understanding of organics in the solar system.

Article:

Understanding the distribution of organic molecules in Solar System materials is a high priority goal of NASA's Astrobiology Program. To this end, our team at NASA Goddard Space Flight Center is now developing a compact instrument prototype, the Organics Analyzer for Sampling Icy Surfaces (OASIS), that will be compatible with a flight mission to the surface of an icy planetary body. The technique of liquid chromatography-mass spectrometry (LC-MS) has revealed important new understanding in Earth-based investigations of the inventory of prebiotic organics in extraterrestrial materials, and we are demonstrating that LC-MS is compatible with instrument miniaturization (Figure 1) through the use of microfluidic components and a compact time-of-flight mass spectrometer (TOF-MS) [Getty 2011, Glavin 2012].

LC-MS is a liquid-phase technique that is well suited to the analysis of small, non-volatile organic molecules. It works by entraining a sample in a liquid mobile phase and flowing the mixture through an analytical column, which separates the analytes according to their structure and chemistry. The separated compound packets are then analyzed by the time-of-flight technique to acquire a mass spectrum. In this way, both dimensions of the measurement – chromatographic and mass spectral – can increase confidence in the identification of sample compounds.

The key to reversed-phase high performance liquid chromatography (HPLC) is the physicochemical interaction between a high surface area resin (the stationary phase) and the targeted molecular species. The analytes are dissolved in a liquid (the mobile phase), and the solution is passed through an analytical column, a linear channel filled with the stationary phase. Because different chemical structures interact at varying strengths with the stationary phase, a spatial and temporal separation of a series of

compounds is achieved as the analyte solution is passed through the column. The time that it takes for a given compound to traverse the column is known as the retention time.

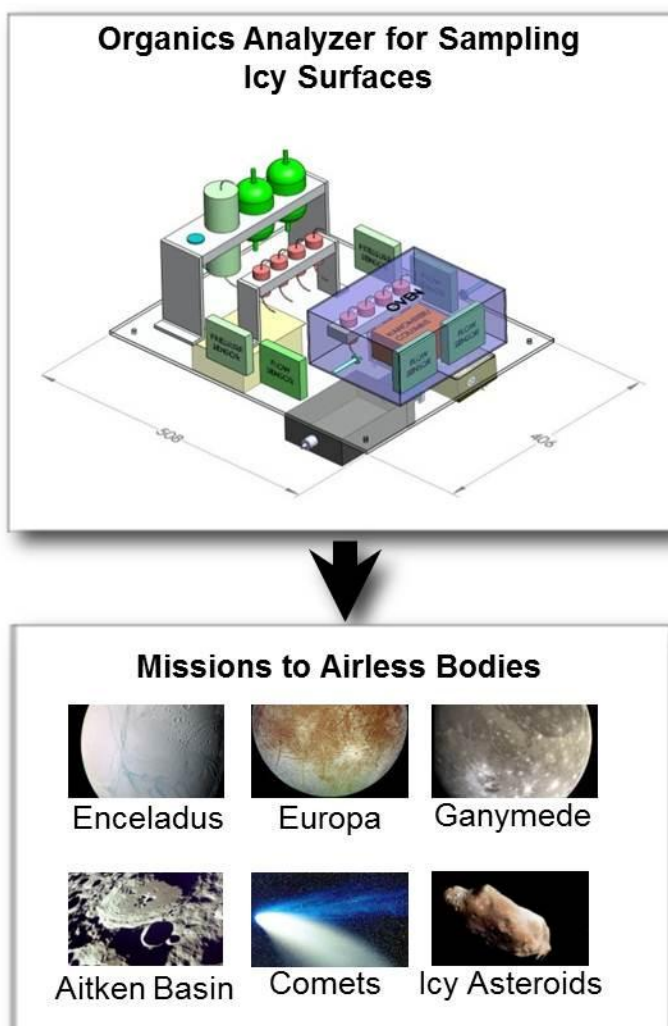


Figure 1. The Organics Analyzer for Sampling Icy Surfaces pairs liquid chromatography and time-of-flight mass spectrometry for an *in situ* instrument capable of investigating prebiotic chemistry in planetary ices.

The elution products can then be interfaced to a mass analyzer through an ion spray technique that releases the separated analytes into the gas phase. Ion spray techniques are also considered “soft” ionization methods, in that fragmentation effects that can obscure intrinsic molecular structures are minimized. The mass analyzer employs a time-of-flight technique, which offers the dual advantage of high performance with a large mass range to be compatible with complex compounds and low power requirements to be compatible with the resource constraints of future mission payloads.

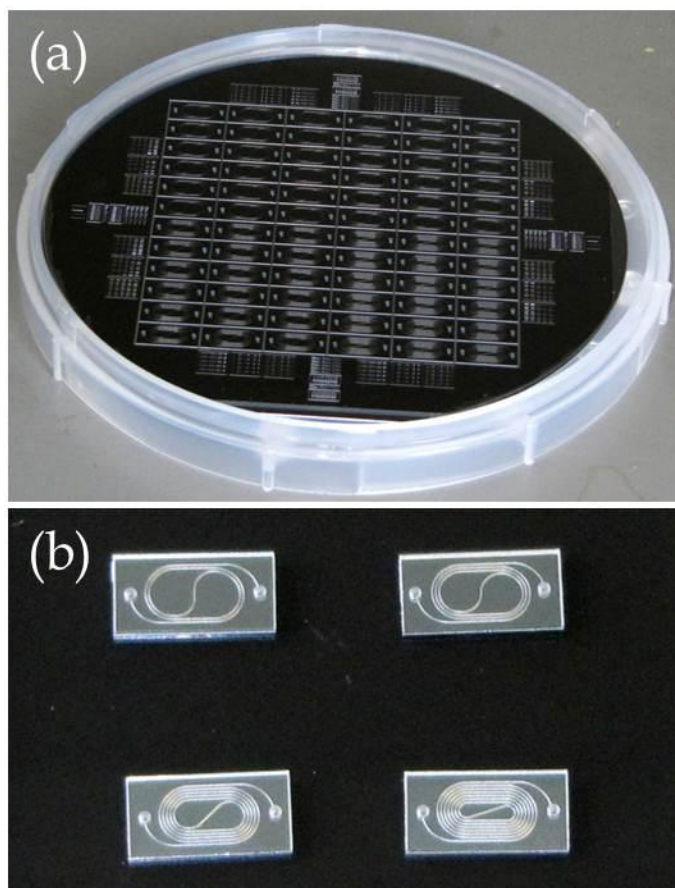


Figure 2. The microscale HPLC component is fabricated using silicon and glass micromachining techniques.

Our liquid chromatograph is constructed of inert materials using micromachining and microfabrication techniques (Figure 2). We have taken measures to limit retention time peak broadening through the effects of turbulence by forming a smooth, circular channel of 75 micron diameter in a pyrex-silicon chip stack. The analyte solution is introduced into the microscale channel using a commercial nanoferrule connector (Upchurch), and this chip configuration has been shown to sustain backpressures up to 5000 psi to be compatible with HPLC operational conditions. The analytical column is formed by filling this channel with a slurry of stationary phase resin, for example, beads with tailored surface chemistry to target separations of amino acids, including determining enantiomeric ratios.

The ion spray nozzle is compatible with an edge outlet configuration, as was previously reported in [ref]. Pulsed orthogonal extraction is used to extract the ions into the TOF-MS analyzer (Figure 3), which has a rectangular symmetry with a wide acceptance aperture for transmission of ions into the flight region. The ion source consists of a series of elongated acceleration, focusing, and steering electrodes, and the flight region is constructed from resistive glass (Photonis) that is patterned with conductive traces to define the desired electric field profile in the dual-stage reflectron. A rectangular microchannel plate detector (Photonis) is used to detect the arrival of ion packets by recording the time of flight for each mass packet as a function of time using an analog-to-digital time-of-flight board (FASTComTec).

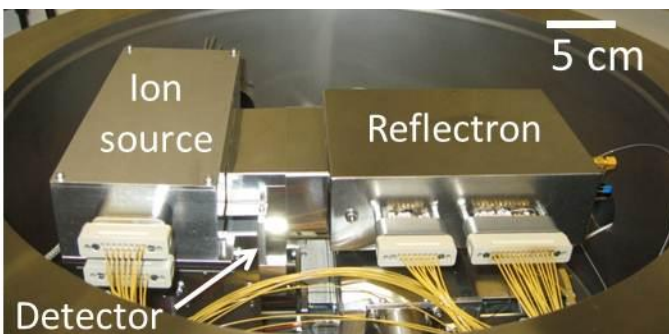


Figure 3. The time-of-flight mass spectrometer operates at low power and enables high mass range detection of prebiotic organics.

Our OASIS efforts aim to develop an *in situ* capability for liquid chromatographic and mass spectrometric analyses of planetary surface of high priority to NASA's astrobiology and astrochemistry goals. LC-MS is a highly capable and sensitive analytical tool in terrestrial laboratories, and the implementation of the technique as a part of a future NASA planetary mission would advance our understanding of the distribution, abundances, and enantiomeric ratios of key prebiotic compounds on icy surfaces. The use of microfabrication methods and a compact mass spectrometer prototype will address future mission science needs while minimizing mass and power requirements of the instrument system.

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References

- [1] S. A. Getty *et al.* "Development of an evolved gas-time-of-flight mass spectrometer for the Volatile Analysis by Pyrolysis of Regolith (VAPoR) instrument," *International Journal of Mass Spectrometry* **295**, pp. 124-132, 2010.
- [2] D. P. Glavin *et al.* "Volatile Analysis by Pyrolysis of Regolith for Planetary Resource Exploration," *IEEE Aerospace Conference Proceedings*, 2012, DOI: 10.1109/AERO.2012.6187065.
- [3] S. A. Getty *et al.* "Organics Analyzer for Sampling Icy Surfaces: a Liquid Chromatograph-Mass Spectrometer for Future *in situ* Small Body Missions," *IEEE Aerospace Conference Proceedings*, 2013, accepted.