

OASIS: Organics Analyzer for Sampling Icy Surfaces. S. A. Getty,¹ J. P. Dworkin,¹ D. P. Glavin,¹ M. Martin,² Y. Zheng,¹ M. Balvin,¹ A. E. Southard,³ J. Ferrance,⁴ and C. Malespin,¹ ¹NASA Goddard Space Flight Center (Mailstop 699.0, Greenbelt, MD 20771; Stephanie.A.Getty@nasa.gov), ²Catholic University of America, Washington, DC 20064, ³Universities Space Research Association, Greenbelt, MD 20771, ⁴J2F Engineering, Charlottesville, VA 22911.

Introduction: Liquid chromatography mass spectrometry (LC-MS) is a well established laboratory technique for detecting and analyzing organic molecules. This approach has been especially fruitful in the analysis of nucleobases, amino acids, and establishing chiral ratios [1-3]. We are developing OASIS, Organics Analyzer for Sampling Icy Surfaces, for future *in situ* landed missions to astrochemically important icy bodies, such as asteroids, comets, and icy moons.

The OASIS design employs a microfabricated, on-chip analytical column to chromatographically separate liquid analytes using known LC stationary phase chemistries. The elution products are then interfaced through electrospray ionization (ESI) and analyzed by a time-of-flight mass spectrometer (TOF-MS). A particular advantage of this design is its suitability for microgravity environments, such as for a primitive small body.

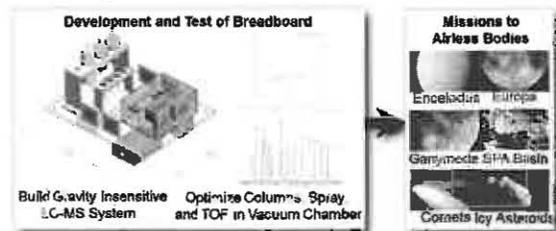


Figure 1. OASIS is an *in situ* capability for detection and analysis of small biologically relevant molecules on a future landed mission to a primitive or icy body.

Instrument Design Overview: The OASIS instrument is estimated to be a 5 kg-class instrument. The breadboard instrument design is shown in Figure 1. To start an analysis, ice melt is ingested into the instrument plumbing. Liquid flow of the analyte and the LC mobile phases is passively controlled by a pressurized gas cylinder and a series of valves. The LC front-end consists of multiplexed chip-based analytical columns that span a broad stationary phase chemistry to investigate a variety of organic species that are likely to be present in an ice melt sample on a primitive or astrobiologically important planetary surface. An electrospray nozzle is interfaced to the inlet of a time-of-flight mass spectrometer through a differential pumping manifold, and a reflectron time-of-flight mass spectrometer enables the mass assignments within each

elution peak for confidence in molecular species assignment.

On-Chip Liquid Chromatography: Our approach to on-chip LC analytical column fabrication focuses on overcoming two challenges: (1) sustaining the high delivery pressures (> 5000 psi) needed for LC analysis and (2) maintaining organic cleanliness for high sensitivity and low background contamination. The chip itself is formed out of etched wafer die of silicon and glass that mate together to form a round cross-section channel. The stationary phase microbeads are then introduced into the channel by a pressurized slurry packing method. Once dried, the beads are held together and to the channel walls via van der Waals forces forming a packed stationary phase that is robust to backpressure. One such column is shown in Figure 2. Commercial nanoferrule connectors are used to interface between fluidic components.

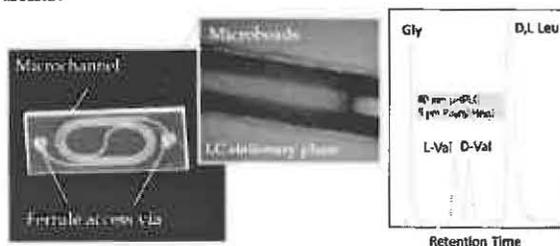


Figure 2. A microfabricated channel was packed with phenyl-hexyl 5 μm microbeads. Analysis of a mixture of amino acid standards produced a resolved chromatogram, demonstrating chiral separation in the case of valine.

Demonstration of chiral separation. A mixture of amino acid standards were analyzed in an on-chip analytical column (80 mm long x 75 μm diameter, phenyl-hexyl column chemistry) using GSFC Astrobiology Analytical Laboratory (AAL) infrastructure to provide the backpressure, gradient elution, and laser induced fluorescence detection of retention time. A chromatogram is shown in Figure 3 for a mixture of glycine, leucine, and D,L valine. For this proof-of-concept demonstration, OPA/NAC derivatization was performed, according to standard protocols of the AAL [1]. The elution peaks are well resolved for these three model amino acids, and chiral separation is shown for the enantiomers of valine.

Electrospray Ionization: Our electrospray ionization nozzle is microfabricated to produce a spray from the edge of a bonded chip [4]. The component-level demonstration is shown in Figure 3, where a Taylor cone is clearly visible. We are currently addressing the challenge of interfacing this ambient-pressure device to the vacuum inlet of a time-of-flight mass spectrometer (described below). Our design employs a combination of differential pumping and a curtain gas to enable this ion interface.

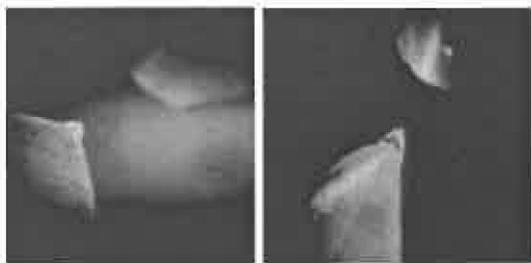


Figure 3. Electrospray has been demonstrated with an edge-terminated nozzle design. Prototype nozzles are shown here, positioned at the inlet of a commercial mass spectrometer.

Time-of-Flight Mass Spectrometer: The mass analyzer employed on OASIS is derived from the TOF-MS developed for the VAPoR (Volatile Analysis by Pyrolysis of Regolith) instrument, shown in Figure 4. The performance of this TOF-MS is currently in optimization with an electron impact ionization source for analysis of pyrolysis products from regolith or crushed rock samples. Thorough SIMION modeling is used to simulate the ion trajectories in the instrument and has been used extensively by our group [5] to guide the design and operational configuration of the TOF-MS towards high sensitivity with sufficient mass resolution to address important science goals for the Moon and other airless bodies [6].



Figure 4. The VAPoR time-of-flight mass spectrometer will allow definitive mass assignments of the LC eluents. It is currently being optimized for gas-phase analysis of pyrolysis products, but integrating an ESI interface is a goal of the OASIS development effort.

A recent pyrolysis demonstration with JSC Mars-1A regolith simulant has confirmed good agreement with a co-located commercial residual gas analyzer (SRS RGA300).

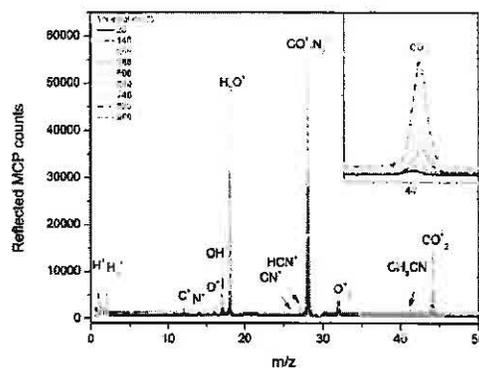


Figure 4. Temperature dependence of time-of-flight mass spectra is shown for VAPoR pyrolysis oven temperatures ranging from room temperature to 980°C. The temperature dependence of each mass peak can be used to infer, for example, mineralogy, the presence of organics, and the degree of hydration.

The mass spectra that contributed to this sample analysis are shown in Figure 5 as a function of oven temperature. These data show better than unit mass resolution at the CO₂ peak and a calculated mass resolution exceeding $m/\Delta m = 200$. These electron ionization spectra were obtained with the use of a large-area (2 mm x 60 mm emitting area) carbon nanotube field emission electron gun [7]. The integration of the ESI nozzle with the TOF-MS is a near-term goal, and we are currently using SIMION to ensure an optimized ion interface between the components.

References: [1] Glavin D.P. *et al.* (2006) *Meteorit. Planet. Sci.* 41, 889. [2] Elsila J. E. *et al.* (2009) *Meteorit. Planet. Sci.* 44, 1323-1330. [3] Callahan M. P. *et al.*, (2011) *PNAS* 108, 13995-13998. [4] Marchiarullo D. J. *et al.* (2008) *J. Chrom. A* 1200, 198-203. [5] King *et al.* (2008) *Proc. SPIE* 6959, 6959E., [6] Getty *et al.* (2010) *Int. J. Mass Spec.* 295, 124-132. [7] Getty *et al.* (2009) *Proc. SPIE* 7318, 731816.

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