

# Organics Analyzer for Sampling Icy Surfaces: a Liquid Chromatograph-Mass Spectrometer for Future *in situ* Small Body Missions

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**Abstract**—Liquid chromatography mass spectrometry (LC-MS) is an important laboratory technique for the detection and analysis of organic molecules with high sensitivity and selectivity. This approach has been especially fruitful in the analysis of nucleobases, amino acids, and measuring amino acid enantiomeric ratios in extraterrestrial materials. We are developing OASIS, Organics Analyzer for Sampling Icy Surfaces, for *in situ* analysis on future 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 spray ionization and analyzed by a time-of-flight mass spectrometer (TOF-MS). A particular advantage of our design is its suitability for microgravity environments, such as for a primitive small body.

**Index Terms**—Liquid chromatography, mass spectrometry, *in situ*, microfluidic

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## 1. INTRODUCTION

LIQUID chromatography mass spectrometry (LC-MS) is a well established laboratory technique for detecting and analyzing organic molecules such as nucleobases and amino acids, and for quantifying chiral ratios. We report on the development of OASIS (Organics Analyzer for Sampling Icy Surfaces) for future *in situ* landed missions to astrochemically important icy bodies, such as asteroids, comets, and Outer Planet icy moons, with a particular focus on its suitability for microgravity environments. OASIS (Figure 1) will interface a microfabricated liquid chromatography (LC)-electrospray ionization component to a time-of-flight mass spectrometer (TOF-MS) that has been previously demonstrated as part of the Volatile Analysis by Pyrolysis of Regolith (VAPoR) instrument development effort [1,2].

The VAPoR development effort has focused on coupling high temperature (> 1300°C) vacuum pyrolysis to electron-ionization TOF-MS. Previous and currently operating analytical instruments on Mars, such as Curiosity's Sample Analysis at Mars (SAM) instrument suite, have employed pyrolysis for the study of evolved gases from solid samples to produce data supporting mineralogical and organic content of acquired geologic samples. While pyrolysis is an informative technique that can access the composition of surface materials by volatilizing key constituents and analyzing the gas-phase products by mass spectrometry, it is not optimized for the detection and identification of key organic molecules that are prone to thermal alteration or fragmentation, such as amino acids and nucleobases.

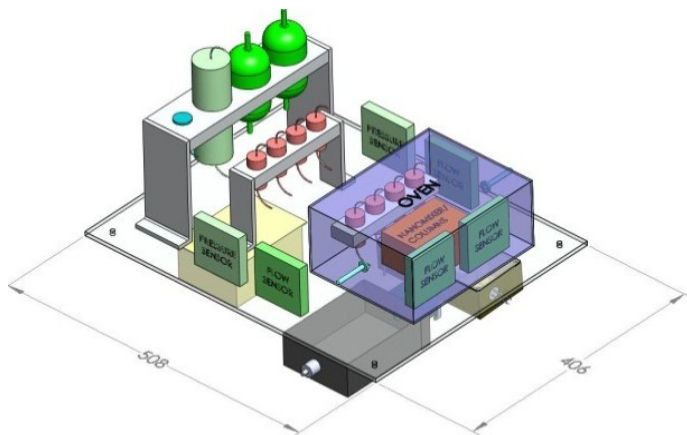


Fig. 1. OASIS is a liquid chromatograph-mass spectrometer that is under development at the breadboard level for demonstration in high vacuum conditions.

Liquid chromatography mass spectrometry offers an advanced liquid analysis capability that is well suited to targeted analyses of biologically relevant organics, such as nucleobases and amino acids and their chiral ratios. The OASIS design employs a microfabricated, on-chip analytical column to chromatographically separate liquid analytes using proven LC stationary phase chemistries. We will discuss the design and development of the TOF-MS that will measure LC retention times and allow direct mass assignment of the elution products. Here we discuss design and component-level development efforts of a clean microfluidic architecture for on-chip HPLC that will be interfaced through a microfabricated on-chip electrospray ionization nozzle to the front end of the TOF-MS. We also discuss the use of SIMION to guide the design and test configuration of the TOF-MS, and we present results of VAPoR TOF-MS testing on gas-phase analytes that form the baseline for performance of the OASIS breadboard.

## 2. MOTIVATION

### A. *In Situ Analysis of Prebiotic Organics*

Amino acids are the fundamental building blocks for proteins and enzymes common to all life on Earth. Chiral analyses of any amino acids detected will be important for establishing an abiotic or biotic origin of these compounds as part of an *in situ* astrobiology mission to planetary bodies, including the Outer Planet icy moons. Traditionally, electron ionization has been used in spaceflight mass spectrometers, but this technique leads to excessive fragmentation of organic molecules and can destroy critical structural information needed to identify key organic compounds, including amino acids. Front-end pyrolysis coupled with one-pot chemical derivatization for GC separation of amino acids is a technique that will be used by the Sample Analysis on Mars (SAM) instrument on Mars Science Laboratory, but this technique has not been optimized for sensitive amino acid and nucleobase

detection and analysis of amino acid chirality. Although current state-of-the-art flight mass spectrometer packages, such as SAM, have recognized the need for an *in situ* wet chemical extraction capability, SAM is not optimized for the detection and identification of trace (part-per-billion, ppb) amounts of amino acids and nucleobases, that are expected to be present in complex organic mixtures on icy bodies.

Members of our group have demonstrated that even the most sensitive laboratory GCMS techniques are over 100 times less sensitive for amino acids and nucleobases than using LCMS [3-7]. Careful investigations of various meteorites that have been delivered to the Earth's surface and returned cometary samples from the Stardust mission have detected measurable abundances of a diversity of organic molecules, including the amino acid glycine. In some cases, carbonaceous meteorites have been found to contain large (up to 60%) L-amino acid enantiomeric excesses, suggesting that abiotic chemical processes could have provided the initial bias that led to homochirality in life on Earth [5, 8-10]. Many planetary surfaces are likely to harbor similar organic inventories.

Most amino acids found in carbonaceous meteorites are structurally chiral, meaning they possess two nonsuperimposable mirror image structures or enantiomers (by convention: left = L and right = D). With a few very rare exceptions, predominantly L-amino acids are found in biology, whereas amino acids formed by abiotic processes are generally racemic (equal or near-equal mixtures of L- and D-enantiomers). Therefore, molecular structure of these compounds can be a useful tool to help discriminate between biotic and abiotic origins of amino acids. Perhaps one of the most important meteoritic discoveries was the finding of nonracemic  $\alpha$ -dialkyl amino acids in the CM and CI carbonaceous chondrites, e.g. Murchison, with significant L-isovaline excesses as high as 18-20% [5,8,9]. For amino acids that are common in proteins on Earth, e.g. alanine and valine, terrestrial L-amino acid contamination of meteorites after their fall to Earth makes it very difficult to assess whether slight L-enantiomeric biases observed for these amino acids in meteorites are in fact extraterrestrial in origin.

Although LCMS has not yet been proposed for spaceflight, it will be a critical technique in future astrobiology missions where the goal is to detect trace amounts ( $< 10^{-15}$  moles) of amino acids and other prebiotic organic molecules in complex mixtures, distinguish between molecules of abiotic and biotic origins, and measure small amino acid enantiomeric biases that may be present. Scaling down the well-established tool of LC-TOF-MS is a promising route to *in situ* detection of diverse classes of organic molecules important to life.

### B. *Current Status of the Field*

Capillary electrophoresis with laser induced UV fluorescence (CE-LIF) detection is one technique that has been optimized for the separation of chemically labeled primary amines, including amino acids and their enantiomers in water extracts of a variety

of terrestrial materials [11-14]. Recent efforts have demonstrated a sophisticated degree of automation of a CE-LIF analyzer, allowing on-chip derivatization, CE analysis, and LIF detection of up to eight liquid-phase samples, and the technique has been demonstrated in both a laboratory and field setting. UV fluorescence detection of amino acids by CE-LIF is a highly sensitive technique, and CE-LIF has further been shown to be broadly effective in the detection of several classes of organic molecules in addition to amino acids, such as carboxylic acids, amines, aldehydes, and ketones [15]. However, in some cases, definitive mass identification of sample constituents can be important to resolving interferences. For example, enantiomeric measurements of amino acids can be complicated due to the presence of other interfering UV fluorescent compounds that are common and abundant in carbonaceous meteorite extracts.

The work reported here describes an alternative technique, emphasizing detection and identification of prebiotic organics in solar system ices. The use of mass spectrometry as the detection method for liquid separation analysis is an important next step in the development of highly capable instrumentation for unambiguous organics analysis on planetary surfaces.

### 3. INSTRUMENT DESIGN

OASIS is a liquid chromatograph-mass spectrometer designed to chromatographically separate liquid-phase sample constituents based on their physicochemical properties. The liquid eluents will then be spray-ionized and a correlated mass spectrum will be obtained. The LCMS technique is of particular use in the analysis of complex mixtures of volatile prebiotic and organic molecules, as it will provide the *in situ* capability to resolve common sources of ambiguity, such as coelution of compounds in the liquid chromatograph and isomolecular interferences in the mass spectra.

OASIS will be capable of delivering liquid from two mobile phase reservoirs, each pressurized passively by compressed helium through a bellows membrane interface to prevent gas/liquid mixing. This will enable sample handling in either a gravitational environment, such as an icy moon, or in microgravity, such as a comet or asteroid. Liquid flow control will be achieved with flow and pressure monitoring and a minimum number of microvalves.

Prior to each analysis, the system can be flushed using Mobile Phase 1 and vented through direct spray into the vacuum of the TOF-MS. The sample will be acquired at an inlet and drawn via vacuum capillary forces into a length of tubing. Mobile Phase 1 will be used to trap the sample onto one of an array of microfluidic analytical LC columns. These columns will be designed to generate complementary composition and chirality data, while maintaining a measure of redundancy for risk mitigation. Mobile Phase 2 will then be used to elute the analyte, producing retention time separation based on chemical and steric interactions with the LC stationary phase. A

gradient elution can be achieved by mixing Phases 1 and 2 and actuating each Mobile Phase valve accordingly. The separated eluent will then be ionized using an ion spray nozzle and delivered to our TOF-MS for mass analysis correlated to LC retention time.

The three major components of OASIS are described below: the on-chip  $\mu$ HPLC analytical column, the liquid-gas ion interface to the mass spectrometer, and the time-of-flight mass analyzer that derives instrument maturity from the VAPoR development effort. A particular emphasis in the design of the instrument is on cleanliness of materials, fabrication, and assembly processes. Silicon, glass, metal, and machinable ceramic forms the majority of the instrument assembly, and we have minimized use of polymers, using inert, chemically resistant polymers such as poly ether ether ketone (PEEK) where necessary.

### 4. ON-CHIP LIQUID CHROMATOGRAPHY

Liquid chromatography is the separation of compounds in liquid phase through interactions with a solid stationary phase, which is often characterized by chemical moieties that are attached to a high surface-area resin, such as microbeads or a gel. Based on their chemical structure and functional groups, compounds traveling within the column have different degrees of affinity to the stationary phase. Those with stronger affinity are retained in the column for a longer time, whereas the compounds with weak affinity to the stationary phase will pass more quickly through the column. Another factor influencing retention time is the liquid mobile phase flowing through the column. The mobile phase is typically a mixture composed of two fluids, of different polarities (e.g., water and methanol). The mixing ratio of these two liquids is varied throughout the analytical separation to sequentially promote the on-column trapping and mobilization of the dissolved analytes of interest in a controlled way. When the stationary phase is non-polar, or hydrophobic, then this process is called reverse-phase liquid chromatography, and a typical mobile phase gradient transitions from polar to non-polar mobile phase to enable chromatographic separation of a diversity of compounds.

One type of liquid chromatography is High Performance Liquid Chromatography (HPLC), which refers to the separation of compounds through reversible interactions with a high surface area stationary phase, typically in the form of micron-scale functionalized silica or polymer beads or porous gel. The higher relative surface area of HPLC requires the use of correspondingly higher pressure.

In the preliminary proof-of-concept work described here, our  $\mu$ HPLC on-chip column employs a reverse-phase chemistry with gradient elution. The  $\mu$ HPLC column is packed by our team and is therefore quite flexible to column chemistry and elution conditions. In the development of the OASIS breadboard, we will explore a variety of column stationary phase chemistries and mobile phase elution conditions to

maintain compatibility of the instrument protocols with an automated *in situ* mission application.

Our  $\mu$ HPLC is fabricated using 100 mm-diameter, 500  $\mu$ m-thick silicon and Pyrex wafers that are micromachined with half channels and fused together by anodic bonding. Each individual analytical chip measures 10 mm x 5 mm x 1 mm, and each fabrication run produces 72  $\mu$ HPLC chips, as shown in Figure 2. Photolithographic patterning was used to define a compact modified spiral pattern for the  $\mu$ HPLC microchannel. This pattern was optimized to produce channels as long as 100 mm in a 10 mm x 5 mm footprint, while maintaining a large radius of curvature throughout the chromatographic length. Mirror image patterns were defined in the silicon and Pyrex wafers that are later mated to enclose the channel.

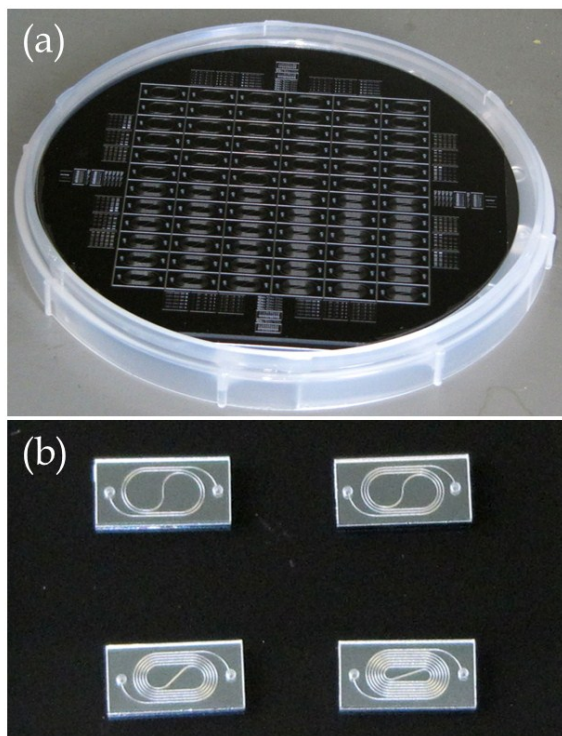


Fig. 2. (a) Microchannel fabrication at the wafer level. (b) While optimizing channel filling methods, we used a series of channel lengths: 40 mm, 60 mm, 80 mm, and 100 mm.

To produce a circular cross-section of the microchannel, the silicon side of the column is etched into a semicircular shape using deep reactive ion etching (DRIE), followed by isotropic reactive ion etching in xenon difluoride. The Pyrex side of the column is separately etched isotropically in 49% hydrofluoric acid (in water) to match the desired column cross-section.

The liquid interface to capillary tubing was formed using a commercial NanoFerrule fitting (Upchurch Scientific), which requires a tapered via for adhesive-free, high pressure-compatible sealing between the NanoFerrule PEEK surface and the microchannel inlet. The vias in our devices were formed in the Pyrex at the inlet and outlet of the microchannel using microabrasive jet machining.

The silicon and Pyrex wafers were cleaned using Piranha solution (3 H<sub>2</sub>SO<sub>4</sub> : 1 H<sub>2</sub>O<sub>2</sub>) prior to bonding. The microchannel patterns were then aligned between the wafers, and anodic bonding was used to enclose the channel.

### C. Leak Testing

The anodic bond was found to sustain backpressures exceeding 4000 psi, comparable to backpressures traditionally used in HPLC. To conduct these leak tests, we attached the inlet of the on-chip microchannel, prior to filling with a stationary phase, to the diagnostic capability of a Waters NanoAcquity system. The outlet of the channel was sealed with a fused capillary tube to preclude flow under nominal operation. The backpressure was then progressively increased, and the flow rate was monitored. Non-leaking conditions were characterized by flow rates at the performance floor of this instrument, < 10 nL/min. At the point of failure, the flow rate was observed to increase dramatically into the  $\mu$ L/min regime. Post-failure inspection showed that the leak developed within the Pyrex layer, not at the anodic bonding interface.

### D. Stationary Phase Packing

For proof-of-concept testing of our on-chip  $\mu$ HPLC column, we selected a commercially available non-polar phenyl hexyl bead chemistry. The bead diameter is 5  $\mu$ m. The beads were suspended in ethanol, and the resulting slurry was pumped into the channel using a syringe pump. The filling fraction was monitored by visual inspection using an optical stereomicroscope. A filled channel is shown in Figure 3.

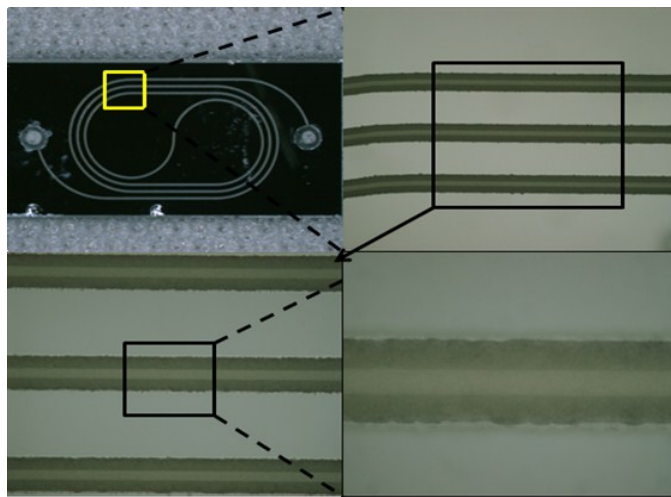


Fig. 3. A filled  $\mu$ HPLC column with length of 60 mm and channel cross-section diameter of 75  $\mu$ m.

This on-chip microfluidic  $\mu$ HPLC column is constructed of clean materials to minimize sample contamination and spurious contributions to the chromatographic and mass spectrometric measurements. The Pyrex-silicon microfabrication methods are compatible with the integration of other instrument components, such as on-chip heaters, thermal conductance-type flow meters, and in the future, potential on-chip pumping



and valving. Of particular interest to this miniature instrument effort is the compatibility of the Pyrex and silicon architecture to an ion spray capability that will provide a soft-ionizing interface to the time-of-flight mass spectrometer.

### E. $\mu$ HPLC Separation

We have successfully demonstrated amino acid separation using an 80 mm-long on-chip, custom-packed phenyl-hexyl column, as shown in Fig. 4. We used a series of three amino acid standards, glycine, D,L leucine, and D,L valine. For this proof-of-concept chiral separation, we used OPA/NAC derivatization according to routine AAL protocols. It is worth noting that the enantiomers of leucine were not separated, in part, because the OPA/NAC-phenyl hexyl column chemistry is not optimized for this compound.

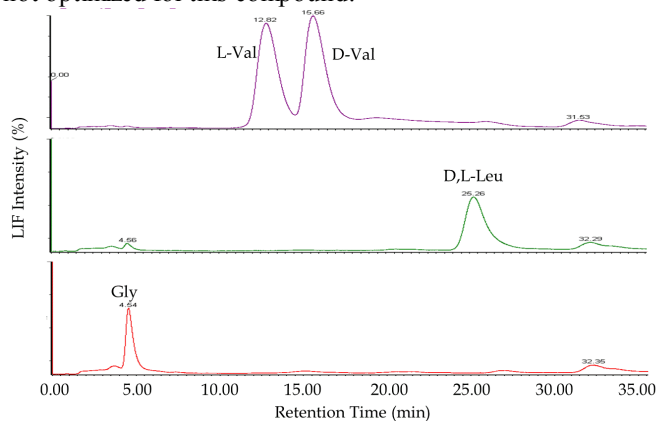


Fig. 4. Amino acid separation of valine, leucine, and glycine was demonstrated using a  $\mu$ HPLC column packed with phenyl hexyl-functionalized silica beads. Note the enantiomeric separation for the case of valine.

## 5. ION SPRAY NOZZLE

The integration of a  $\mu$ HPLC column to a mass spectrometer requires that we bring the liquid analyte into the gas phase and form a molecular ion for MS analysis. The use of traditional electron ionization requires that the analyte be brought into the gas phase, typically by heating, and both the use of heat and excess energy imparted by the electron ionization process can produce considerable fragmentation of some important classes of organics. Electrospray ionization represents a soft ionization mechanism that nebulizes the analyte and carrier fluid. Residual charge on these droplets, owing to the presence of buffers or hydronium ions (in the case of positive ion electrospray ionization) gets transmuted to the molecular ion as the solvent evaporates.

Our design for an ion spray nozzle draws from recent prototype electrospray nozzles developed by co-author Ferrance [16]. The prototype device shown in Figure 5 has been shown to produce stable electrospray under atmospheric testing conditions. The design features a bonded glass-glass microchannel that is fed by a NanoPort fitting bonded to the inlet and exits the chip at a tapered location along the edge of the chip. The electric field is applied between an acetic acid

reservoir in the chip, which provides capacitive coupling to the buffered mobile phase, and a brass counterelectrode positioned within a few mm of the nozzle outlet. In recent testing, a voltage difference of 2400 V was applied between the nozzle and the counterelectrode, corresponding to an electric field of  $\sim 1$  V/ $\mu$ m. The time-resolved current data shown in Figure 6 show that applied voltage less than 2400 V (at  $t < 400$  s) produced current oscillations that are known to be characteristic of unstable spray conditions [17]. At  $t > 400$  s, stable electrospray current is recorded at the counter-electrode for the duration of the test.



Fig. 5. A tapered electrospray nozzle prototype has been fabricated in glass. Taylor cone formation is shown (right).

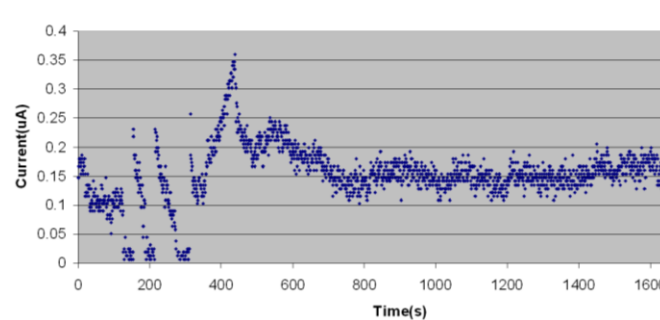


Fig. 6. A prototype electrospray ionization nozzle exhibits stable electrospray under atmospheric conditions.

We are currently designing a new generation of ion spray nozzles that will employ the tapered edge nozzle shown here, integrated with a microfabricated means of applying voltage to the tip. The ion nozzle design is also compatible with the Pyrex-silicon architecture used for the  $\mu$ HPLC columns.

## 6. TIME-OF-FLIGHT MASS SPECTROMETER

The OASIS TOF-MS [2] has two operational modes: high-sensitivity linear mode and high-resolution reflectron mode. The prototype measures approximately 30 cm x 18 cm x 13 cm and has been designed to be a compact, low power ( $< 2$ W), low voltage ( $< 1000$  V) instrument. The TOF-MS has been thoroughly tested using an electron ionization (EI) source for analysis of pyrolysis products, as a result of the VAPoR instrument development effort. In the near future, the electron ionization source will be replaced with an ion spray interface, to allow mass determination of chromatographically resolved analytes.

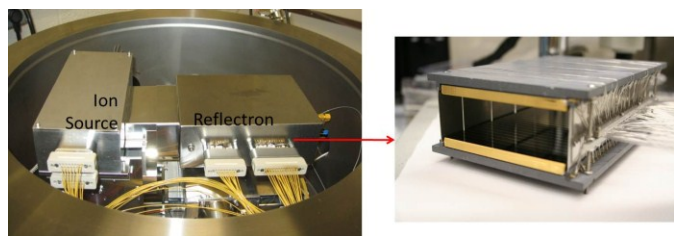


Fig. 7. The time-of-flight mass spectrometer comprises an ion source, reflectron, and linear and reflectron microchannel plate detectors.

The TOF-MS (Figure 7) presently consists of a carbon nanotube (CNT) field emission electron gun, NiCr ion extraction, steering, and focusing lenses, a monolithic three stage reflectron, and two microchannel plate (MCP) detectors (one each for linear and reflectron modes) operated in ion counting mode. During operation, ions are first generated by electron ionization within the ion source. High-speed electronics then pulse an ion lens voltage to release ionized sample into the TOF analyzer. The ions are then separated by mass and arrive as isomass packets at the detector. By measuring MCP voltage as a function of time, a mass spectrum is acquired.

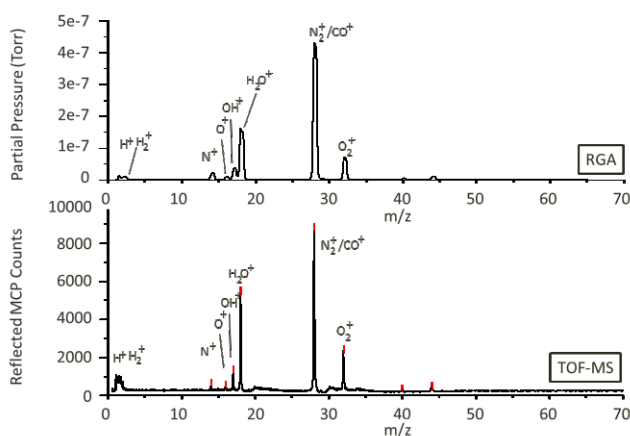


Fig. 8. Comparative mass spectra obtained for background chamber gases using a commercial RGA (SRS300) and the OASIS TOF-MS.

The signal is recorded using a time-of-flight board (P7887), and the instrument settings are recorded via a custom LabView interface. The voltages are applied using a series of eight-channel unipolar high voltage power supplies (EMCO High Voltage Corporation, Sutter Creek, CA). Voltage pulsing at a pair of push-pull electrodes within the ion source is provided by two high-precision pulsers (Model D-1040, Jordan TOF Products, Inc., Grass Valley, CA). The TOF-MS is housed in a high vacuum chamber pumped by an oil-free turbomolecular pump system. The chamber base pressure is  $2e-7$  Torr. A commercial residual gas analyzer (RGA300; Stanford Research Systems, Sunnyvale, CA) is also mounted to the main volume of the chamber, close in proximity to the ion source of the TOF-MS, for the purpose of corroborative measurements.

A comparison of the TOF mass spectrum with the commercial RGA mass spectrum collocated in the vacuum chamber is shown in Figure 8. These spectra were taken measuring the background gases in the chamber. The TOF spectrum is capable of reproducing the RGA spectrum with high fidelity, and with superior mass resolution. The TOF-MS mass resolution shown here is  $m/\Delta m$  170, but mass resolution exceeding 270 (at  $m/z$  18) has been demonstrated.

To guide the design and operation of the TOF-MS, we simulate the electrostatic profile and ion electrodynamics using SIMION (Version 8.1). An optimized TOF-MS configuration is shown in Figure 9, in cross-section. Systematic tuning of the voltage biases of key electrostatic elements and electric field profile optimization in the ion source (upper left) and reflectron (right) regions provide critical guidance for the experimental testing of the analyzer. A set of tunable parameters were optimized by iterative simulation and experimental testing, including push and pull electrode voltages during ionization and extraction modes, ion steering in the vertical dimension, relative dimensions of the first and second reflectron stages, and the values of the first and second stage electric fields in the dual-stage reflectron.

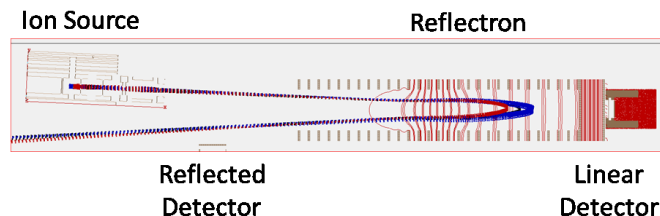


Fig. 9. SIMION simulations of the electric fields and ion trajectories show spatial and temporal ion packet focusing at the reflected detector. In this simulation, the detector position was adjusted for optimization purposes.

## 7. CONCLUSION

The development of OASIS will interface an on-chip microfluidic  $\mu$ HPLC analytical column to a time-of-flight mass spectrometer, previously developed for gas-phase analysis as part of the VAPoR instrument. Preliminary demonstration of the analytical separation of amino acids using a packed Pyrex-silicon column has been demonstrated. Refinements to the column chemistry selection and protocols are currently underway, with an emphasis on compatibility with future autonomous *in situ* operation. An ion spray interface to the TOF-MS is currently in design, based upon a successful electrospray device that generates spray at the tapered edge of a chip. The TOF-MS has been thoroughly tested and optimized using an electron ionization source, and iterative simulation and experiment have yielded a mass resolution approaching  $m/\Delta m$  300 and a sensitivity as high as  $1.3e-3$  counts/second/(molecule  $\text{Ar}/\text{cm}^3$ ). This development work targets a future landed astrobiology mission to a planetary surface that harbors water or water ice, such as a comet,

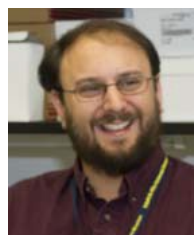
asteroid, or icy moon in the outer solar system.

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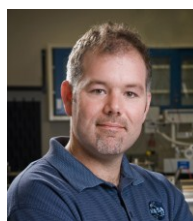
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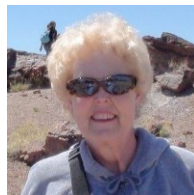
**Stephanie A. Getty** received her Ph.D. in physics from the University of Florida in 2001 and a B.S. in physics in 1998. She joined NASA Goddard Space Flight Center in Greenbelt, MD, in 2004. Prior to NASA GSFC, she held a DCI Postdoctoral Fellowship in the Physics Department at the University of Maryland, College Park. Her research and instrument development interests are in the area of scientific instrument development for *in situ* planetary science, particularly in the pursuit of understanding the origin, evolution, and processing of organic chemistry in our Solar System. She is currently serving as principal investigator of the ASTID-funded OASIS instrument development, as well as the PIDD-funded development of a two-step tandem laser mass spectrometer for the *in situ* investigation of refractory organics on planetary surfaces. Dr. Getty is a current member of the American Chemical Society and the American Society for Mass Spectrometry. She is a member of the session organizing committee of the IEEE Aerospace Conference, and she is a member of the steering committee of the Mid-Atlantic Micro/Nanotechnology Alliance.



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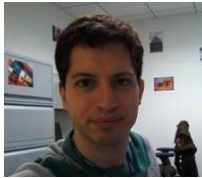
James Webb Space Telescope.

Dr. Ferrance is a member of the American Association for the Advancement of Science, The American Chemical Society, and the Royal Society of Chemistry.

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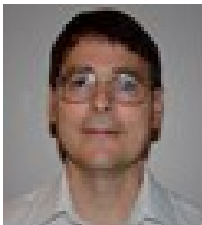
**Adrian Southard** received his bachelor of arts in physics from New College of Florida in 2000 and his Ph.D. in chemical physics from University of Maryland in 2009. His Ph.D. research focused on transport in organic semiconductors and novel device fabrication methods. He joined the VAPoR team at NASA

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**Jerome P. Ferrance** received his Bachelor of Engineering, Master of Science in Chemical Engineering, and Ph.D. degrees from the University of Pittsburgh, Pittsburgh, PA in 1985, 1987, and 1996, respectively. He completed post-doctoral work in coal liquefaction modeling at the Department of Energy as an Oak Ridge Associated University Fellow. His subsequent research at the

University of Pittsburgh and the University of Virginia as an Assistant Research Professor, focused on the design and fabrication of microfluidic devices for clinical, forensic, and homeland security applications. His work involved both instrument development for utilizing microchips, and integration of multiple processes on these devices. He has incorporated bioanalytical methods for DNA and protein analysis on microchips and his current work at J<sup>2</sup>F Engineering (Charlottesville, VA) is focused on the development of microfluidic devices and carbon nanotube sensors for biochemical analysis.