

Design of an Integrated LC-MS Prototype for an *in situ* Mission to an Icy Body in the Solar System

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Introduction: Future high-priority planetary exploration will target destinations that are likely host to a broad diversity of inorganic and organic composition. Primitive bodies, such as comets and carbonaceous asteroids, are thought to have contributed an inventory of prebiotic chemistry to the early Earth, and cataloging their present-day, cryo-trapped organic diversity can offer details about the breadth of organic astrochemistry that is representative of the Solar System's origins and evolution. Major classes of organics likely to be present on these primitive, small bodies include polycyclic aromatics, carboxylic acids, alcohols, aldehydes and ketones, amines, nucleobases, and amino acids. The diversity of organic material on these primitive bodies can be challenging to fully characterize by mass analysis alone; liquid chromatography can offer additional discrimination based on functional group chemistry and/or size effects to alleviate ambiguity. Liquid chromatography-mass spectrometry (LC-MS) has enabled detailed and sensitive terrestrial investigations of meteoritic materials, interplanetary dust, and returned cometary particles[1]. It has been used to detect extraterrestrial amino acids in meteorites [2]–[4] and to quantify enantiomeric excess [4]. LC-MS is a sensitive, versatile approach to analyzing non-volatile organics with little to no degradation of the analytes.

The development goal of the OASIS instrument (Organics Analyzer for Sampling Icy Surfaces) is to implement LC-MS in a spaceflight-compatible package [5]. We estimate that an eventual flight-ready OASIS Instrument could weigh as little as 5 kg and consume only 3 W of power, even for the case of a cold surface of an icy satellite or comet. While separations of a range of molecular classes relevant to life could be performed, here we discuss results achieved for amino acids and nucleobases using the analytical column of the OASIS instrument.

Design: The OASIS instrument utilizes a four stage vacuum interface (Figure 1) designed to transmit ion current from a spray tip at the outlet of an LC analytical column into a prototype time-of-flight mass spectrometer [7], measuring 8x30 x 4 cm³.

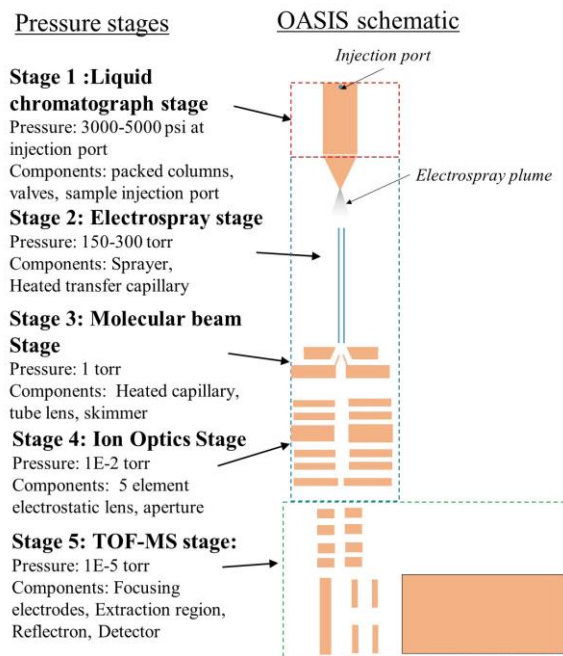


Figure 1 Schematic of the multi-stage interface between the OASIS microchip and a custom time-of-flight mass spectrometer

The LC analytical column and spray tip are integrated into a custom microchip (2 cm x 3 cm x 0.1 cm) with integrated heaters. The microchip was designed to sustain high delivery pressure (>5000 psi), minimize background contamination, and integrate the LC column to a spray tip with minimal dead volume, which can lead to degradation in the chromatography.

Results: Electro spray ionization (ESI) of a mixture of adenine and phenolphthalein standards was demonstrated from the nozzle component of a microchip using a commercial Waters TOF-MS for detection[6]. For this component-level demonstration, no chromatography was performed.

A packed column on a precursor microchip (without nozzle) is shown in Figure 2. For analytical testing, the 8 cm long, 75 micron inner diameter microchip column was packed with a commercial chiral stationary phase and connected to a 20 micron inner diameter commercial ESI tip (Waters). Separations of the chiral forms of four amino acids using the microchip column are shown in Figure 3. Resolution of the microchips with integrated spray tips is expected to surpass that

achieved here due to the reduced dead volume in the integrated microchips.

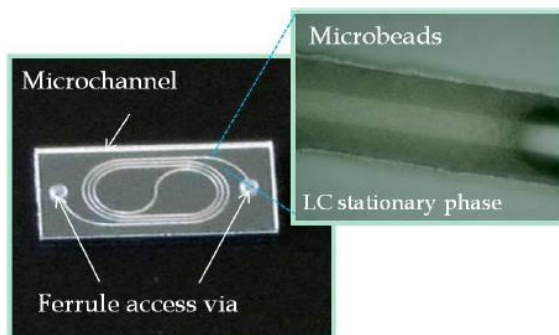


Figure 2 OASIS microchip without integrated spray tip (left) and picture of packed stationary phase (right)

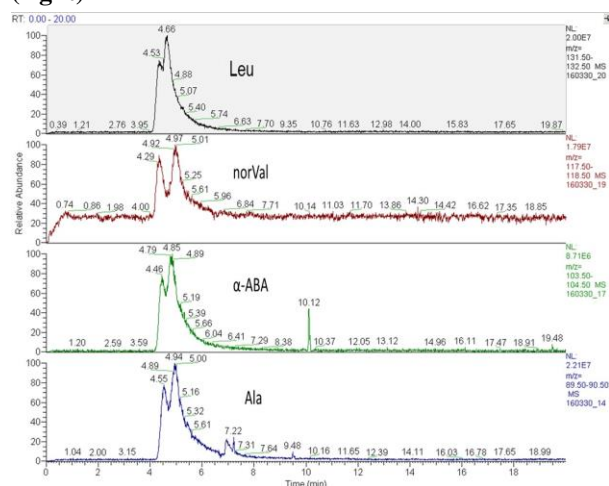


Figure 3 The amino acids leucine(Leu), norvaline(norVal), homoalanine(α -ABA), and alanine(Ala) in a 95:05 methanol:water 1% formic acid solution were separated by an OASIS microchip analytical column and detected using a commercial mass spectrometer (Thermo LTQ orbitrap XL)

A challenging aspect of the microchip to TOF-MS interface (Figure 1) is the efficient transfer of analyte from stage 1 where pressures are greater than the vapor pressure of the sprayed solvent, as required by ESI, to the fourth stage where pressures are in the microtorr regime. This transfer is dominated by gas flow at higher pressures, but the second stage is characterized by sufficiently low pressure for electrostatic forces to steer and focus the charged analytes. The second stage uses a ring electrode to direct ions through a skimmer opposite the capillary. A multi-element electrostatic lens in the third stage (Figure 4) is then used to focus ions through a second skimmer (not shown) into the final (fourth) TOF-MS stage.

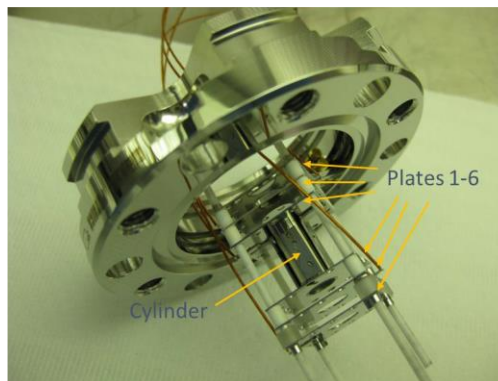


Figure 4 A five element electrostatic lens built from plates, with apertures, and a hollow, cylindrical element (Kimball Physics eV parts)

We monitored transfer efficiency through the various lens elements by examining the currents reaching the transfer capillary, skimmer, and the plates in stages 2 and 3. Currents intercepted by the heated transfer capillary are readily measurable in the tens of nanoamp range at flow rates of 0.5 $\mu\text{L}/\text{min}$ (80:20 methanol:water, 10% formic acid, 0.5 mM adenine). Currents transmitted through the ion optics stage are in the tens of picoamps. Most of the losses appear to be within stage 2; however, characterization of currents at the spray tip is underway to also assess losses in the capillary transfer region. While the transmission of current does not guarantee a proportionate response in isolated, charged analyte[8], it represents practical way to insure good mechanical alignment and allows for optimization of focusing of the electrostatic lens of stage 3.

References: [1] Burton *et al. Chem. Soc. Rev.*, vol. 41, no. 16, pp. 5459–5472, Jul. 2012. [2] M. P. Callahan *et al. Meteorit. Planet. Sci.*, vol. 48, no. 5, pp. 786–795, May 2013. [3] Elsila *et al. Meteorit. Planet. Sci.*, vol. 44, no. 9, pp. 1323–1330, 2009. [4] Glavin *et al. Meteorit. Planet. Sci.*, vol. 41, no. 6, pp. 889–902, 2006. [5] Getty *et al. (2013) IEEE Aerospace Conference*, 2013, pp. 1–8. [6] Southard *et al. (2014) IEEE Aerospace Conference 2014*, pp. 1-7. [7] Glavin *et al. Aerospace Conference, 2012 IEEE*, 2012, pp. 1–11. [8] Page *et al. (2007) J. Amer. Soc. Mass. Spec.*, vol 18, no. 9, pp. 1582-1590, Sep. 2007