DEVELOPMENT OF IN SITU MICROCHIP-BASED LIQUID CHROMATOGRAPHY FOR TITAN LAKE SAMPLES P.A.Willis[1], H.F. Greer[1], A.M. Fisher[1], R.P. Hodyss[1], F.J. Grunthaner[1], H. Jiao[2], D. Mair[3],and J. D. Harrison[4], [1]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, Peter.A.Willis@jpl.nasa.gov, [2]Los Gatos Research, Los Gatos, CA, [3]Fluigence, Santa Clara, CA, [4]University of Alberta, Edmonton, AB, Canada.

Introduction: A chemical analysis of the organic inventory of compounds present in Titan's lakes is a crucial component of the investigation into the planetary chemistry of Titan. This contribution will describe the initial stages of a new ASTID-funded research program initiated in Fall 2009 aimed at lab-on-a-chip (LOC) system development for astrobiological investigations on Titan. This technology development builds off related work at JPL and Berkeley [1-3] on the ultrasensitive compositional and chiral analysis of amino acids on Mars in order to search for signatures of past or present life.

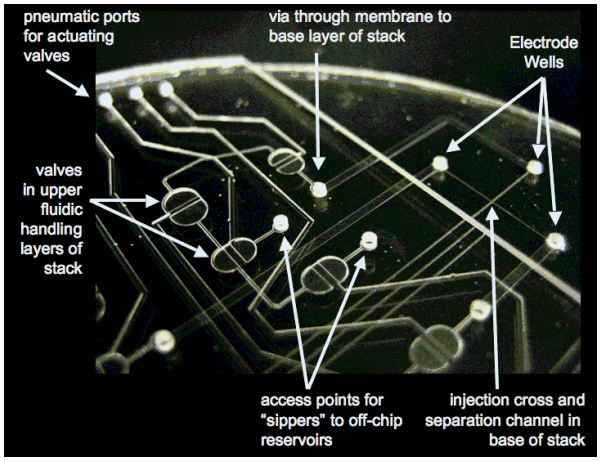

Figure 1. Photograph of a Mars-specific lab-on-a-chip capillary electrophoresis system.

The Mars-focused instrument system utilizes a microcapillary electrophoresis (µCE) system integrated with on-chip perfluoropolyether (PFPE) membrane valves and pumps for automated liquid sample handling, on-chip derivitization of samples with fluorescent tags, dilution, and mixing with standards for data calibration (see Figure 1). It utilizes a four-layer wafer stack design with µCE channels patterned in glass, along with a PFPE membrane, a pneumatic manifold layer, and a fluidic bus layer. Three pneumatically driven on-chip diaphragm valves placed in series are used to peristaltically pump reagents, buffers, and samples to and from capillary electrophoresis electrode well positions. Electrophoretic separation occurs in the all-glass channels near the base of the structure and picomolar level detection of amino acids is performed via laser induced fluorescence under 405 nm illumination.

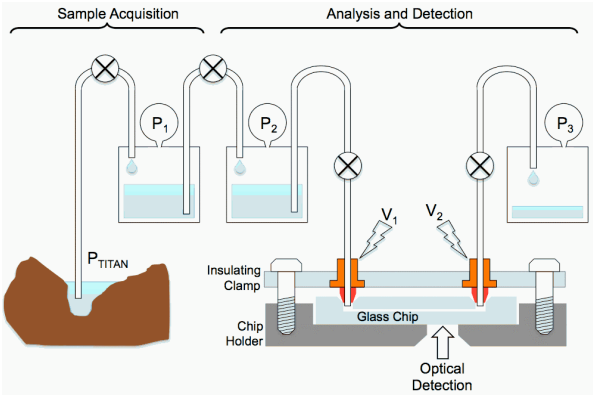

Figure 2. Schematic cross-section of a Titan-specific LOC system.

Next Generation Instrument Development for Titan Exploration: The Titan-specific lab-on-a-chip system under development here focuses its attention on the unique organic chemistry of Titan. In order to chromatographically separate mixtures of organics such as polycyclic aromatic hydrocarbons (PAHs), the Titan-specific microfluidic platform utilizes the related technique of microcapillary electrochromatography (µCEC). This technique differs from conventional µCE in that microchannels are filled with a porous stationary phase that presents surfaces upon which analyte species can adsorb/desorb. It is this additional surface interaction that enables separations of species critical to the understanding of the astrobiological potential of Titan that are not readily separated by the µCE technique.

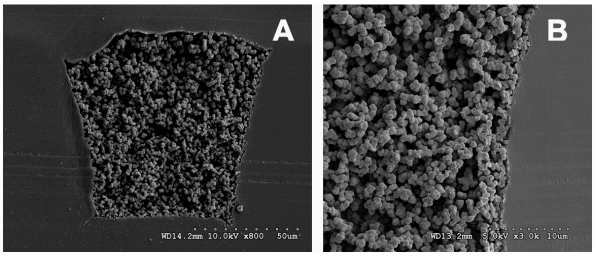

Figure 3. Scanning electron micrograph images of cross-sections made from porous polymer monolith filled microchannels.

We have developed two different approaches for the integration of these stationary phases into microdevices, both by the packing of submicron-sized beads,

and by the growth of porous polymer monoliths inside empty channels via a photoinitiated chemical polymerization process [4] (see Figure 3). By utilizing different acrylate monomer mixtures of varying functionalities and compositions, microchannels tailored for separations of all classes of organic species relevant to the planetary chemical dynamics of Titan can be produced. Over the course of our research in the time period 2009-2012, we will characterize electrochromatographic separations of different organic molecular classes, utilizing laser induced fluorescence as the detection technique. Our 2012 mid-TRL instrument concept will be ready for higher-level system integration, with the ultimate goal of providing a liquid chromatography instrument system available for Titan lake lander missions in the 2018-2022 launch timeframe. This chromatography instrument would be available for interface to mass-spectrometric detection, enabling an extremely versatile LC-MS instrument for Titan *in situ* exploration.

References:

[1] P.A. Willis et al. (2008) *Lab Chip, 8*, 1024-1026. [2] A. Aubrey et al. (2008) *Astrobiology, 8,* 583-588. [3] A.M. Skelley (2005) *PNAS, 102*, 1041-1048. [4] Ngola et al. (2001) *Anal Chem, 73*, 849-856.