A MICROFLUIDICS-HPLC/MASS SPECTROMETER DETECTION SYSTEM FOR HUMAN AND ROBOTIC MISSIONS. R. D. Kidd[1], N. Scianmarello[2], E. Neidholdt[1], J. Simcic[1], S. Madzunkov[1] and Y.-C. Tai[2], [1]Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena CA, 91109, [2]California Institute of Technology, 1200 E. California Boulevard, Pasadena, CA, 91125.

Introduction: Our objective is to design, build and demonstrate a new miniaturized instrument for analysis of organic compounds in planetary materials with high sensitivity (parts-per-billion/trillion depending on target species) and accuracy, with a particular focus on detecting biomarkers previously extracted from crushed rocks, soils and ices. The ultimate goal of this research is to develop a miniaturized instrument for both robotic and human missions. The proposed work consists of the development and integration of two high TRL 3-4 instruments: a complete, microfluidic High Performance Liquid Chromatograph-on-a-chip (HPLC-chip) and a miniature Paul quadrupole ion trap Mass Spectrometer (MS) detector, based on flight heritage but modified for external ionization.

The objectives for the analyzer are to look for: (1) signs of extinct life by detecting carboxylic acids and lipids - the longevity and preservation of carboxylic acids and lipids offer a chemical insight into potential primordial biological activity; and (2) extant life by searching for peptides and proteins - macromolecules that strongly indicate a biotic origin.

High Performance Liquid Chromatography (HPLC) is one of the most widely used tools in analytical chemistry due to its sensitivity, accuracy and capability for identifying a wide range of organic compounds. Reverse-phase (RP) HPLC separation with C18 resin is a standard technique for separating compounds and is capable of identifying molecular structure preferences (e.g. stereoisomers), fatty acid molecular weight distributions, non-homologous series, and ether-bound isoprenyl lipids (Archaea biomarkers). RP-HPLC is a proven method for identifying organic biomarkers in ancient sediments on Earth and has been used to separate terpane, sterane, and alkane biomarkers from crude petroleums and bitumens [1-3].

Starting in 2004 the Caltech Micromachining Laboratory demonstrated the first complete microfluidic reverse-phase HPLC-chip instrument (pumps, injector, mixer, column), which is capable of separating a wide range of organic compounds based on their varying elution times through the separation column [4]. The HPLC-chip is based on Micro-Electro-Mechanical Systems (MEMS) technology and consists of a reusable microfluidic polymer chip with dimensions smaller than a quarter. The HPLC-chip integrates three electrolysis-based electrochemical pumps, one for loading the sample and the other two for delivering the solvent gradient; a static mixer; a column packed with silica-based reversed-phase support; and an electrospray nozzle directly on the polymer chip.

There are a variety of compact detectors commonly used for HPLC: UV/VIS, refractive index, fluorescence, electrochemical, conductivity, evaporative light scattering to name a few. However, none of these types of detectors can give a definitive identification of molecules nor can they identify, and in some cases, even detect unknown compounds. The coupling of LC to MS (via electrospray ionization, ESI) is recognized as the premier technique for any application, which requires high sensitivity, selectivity, and complete unambiguous identification of an unknown collection of chemical species. A further advantage for LC/MS is that the need for chemical labeling (for optical detectors) and/or derivatization (for gas chromatography) are eliminated. The uneven reliability of prior ESI efforts will be solved in the proposed work through the inclusion of a desalting mode/valve on the chip.

The principal advantages of a Paul quadrupole ion trap in chemical analysis can be summarized as follows: (i) high sensitivity, (ii) compactness and mechanical simplicity in a device which is nevertheless capable of high performance, (iii) MS^n mass spectrometry experiments are available by performing sequential mass analysis measurements, (iv) ion/molecule reactions can be studied for mass-selected ions, (v) high resolution <1 Da and 1000 Da), (vi) ions of high mass/charge are accessible using resonance experiments. QIT can be made into a compact or miniaturized device by suitable scaling of dimensions and potentials and this has been accomplished in the flight-proven QIT in the Vehicle Cabin Atmosphere Monitor (VCAM) recently flown on the International Space Station [5]. Under current NASA funding through the ASTID (and previously, PIDDP [6]) and Advanced Environmental Systems (AES) programs this QIT is undergoing further miniaturization to realize a total system mass of ~2 kg in total mass, including electronics and vacuum pumps.

References: [1] Simoneit B. R. et al. (1998) *Orig. Life Evol. Biosph., 28,* 475–483. [2] Brocks J. J. et al. (1999) *Science, 285,* 1033–1036. [3] Kawamura K. and Kaplan I. R. (1987) *Geochim Cosmochim Acta, 51,* 3201–3207. [4] Xie et al. (2005) *Anal Chem., 77,* 527–533. [5] Darrach M. D. et al. (2012) *J. Am. Inst. Aero. & Astro., Electronic* 2012–3432. [6] Madzunkov S. M. et al. (2013) *J. Am. Inst. Aero. & Astro., Electronic* 2012–3453.