MEMS LIQUID AND GAS CHROMATOGRAPHY FOR MINIATURIZED PLANETARY IN SITU INSTRUMENTS. R. D. Kidd[1], B. Bae[1], P. A. Willis[1], A. C. Noell[1], N. Scianmarello[2] and Y.-C. Tai[2], Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena CA 91109, Richard.D.Kidd@jpl.nasa.gov, [2] California Institute of Technology, Pasadena, CA 91125.

Introduction: Our objective is to design, build and demonstrate a miniaturized instruments for analysis of organic and inorganic compounds in planetary materials with high sensitivity (parts-per-billion/trillion depending on target species) and accuracy, with a particular focus on detecting biomarkers extracted (or direct entry) from rocks, soils and ices. The ultimate goal of this research is to develop a miniaturized instruments for both robotic and human missions.

We have been using Micro-Electro-Mechanical Systems (MEMS) technology to reduce the size, mass and power of the three classical chromatographic technologies (Fig. 1): gas chromatography (GC), capillary electrophoresis (CE) and high performance liquid chromatography (HPLC) [1-4]. Both CE and HPLC are liquid chromatographic (LC) technologies.

SMD (Science Mission Directorate) Goals. Our instruments are meant to address two fundamental questions in astrobiology, namely, "how does life begin and evolve?" and "does life exist elsewhere in the universe?" For these reasons, the science objectives for instruments 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; (2) extant life by searching for amino acids, peptides and proteins - molecules that strongly indicate a biotic origin; (3) provide organic molecular detection and life detection capabilities for future landed missions to Mars, Europa, Titan, Enceladus, and other planetary bodies; (4) astrobiology field research on Earth.

HEOMD (Human Exploration & Operations Mission Directorate) Goals. Our instrumentation is cross-cutting with the human program and, in fact, we have already flown a GC system to the International Space Station for environmental monitoring [5] and will fly a MEMS-GC in 2018 [1]. HEOMD goals include (1) experiments on ISS (2), astronaut health monitoring, (3) environmental monitoring, (4) field laboratory.

Detectors: There are a variety of compact detectors commonly used for GC: mass spectrometry (MS), flame ionization detection (FID), and thermal conductivity detection (TCD). For a compact system, such as for cubesat-sized instruments, a MEMS-TCD would be preferred. For all else, our preferred detector is an ion trap MS [1,5].

For LC, UV/VIS absorption or fluorescence, refractive index, electrochemical, conductivity, evaporative light scattering are few common detectors in use. 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 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. These are exactly the requirements and conditions found in a planetary robotic exploration. The coupling of LC to MS via electrospray ionization (ESI) is the terrestrial standard and is especially useful in producing ions from macromolecules because it overcomes the propensity of these molecules to

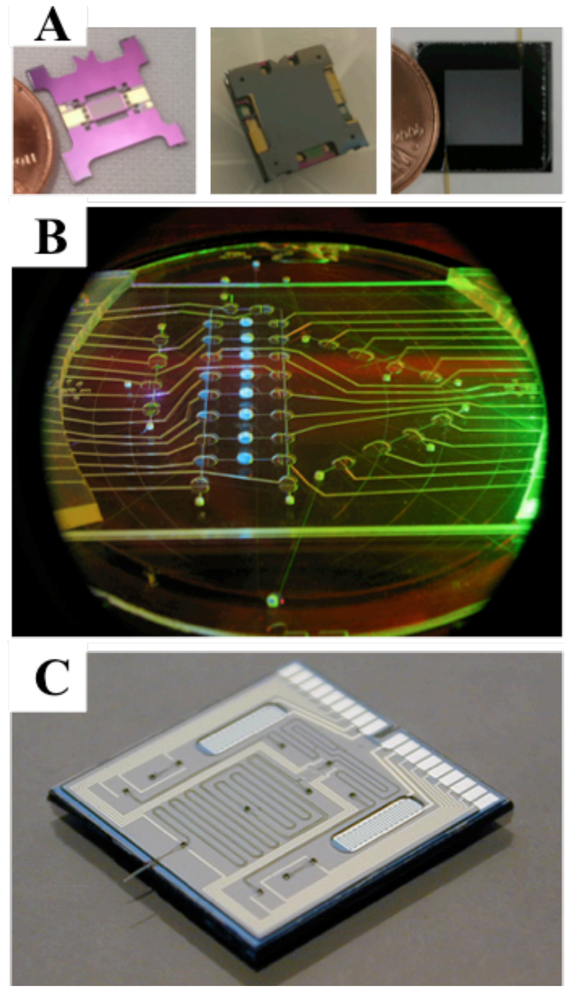

Fig. 1: Photographs of our MEMS-based chromatography chips. (A) left-to-right, MEMS-GC preconcentrator, 4-electrostatic valve array, 1 m column; (B) CE-chip; (C) HPLC-chip.

fragment when ionized through other methods (e.g. electron impact, laser ionization). A further advantage for LC/MS is that the need for chemical labeling (for optical detectors) and/or derivatization (for gas chromatography) are eliminated.

Until recently, HPLC systems have been considered to be unsuitable for *in situ* planetary applications due to their large mass and operational complexity. However, 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 [6]. 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. The technology eliminates many of the traditional fittings and connections associated with traditional HPLC systems, dramatically reducing the possibility of leaks and dead volumes and significantly improving ease of use, sensitivity, and reliability during analysis.

Ion Trap Mass Spectrometer: The Planetary Surface Instruments Group at JPL is drawing upon its experience in successfully developing and constructing MS flight instruments for the MEMS GC, CE, and LC systems. Our group has been responsible for the original research and flight development of several different miniature mass spectrometers including a Paul quadrupole ion trap (QIT) MS that was used in the Vehicle Cabin Atmosphere Monitor [5] and will be used in the Spacecraft Atmosphere Monitor (Fig. 2) [1].

Value-Added Sensors - Ion Selective Electrodes: Although we have been developing ion chromatographs on a chip [4], for inorganic measurements (inorganic ions, conductivity, pH, etc), simpler technology can be added on to LC-based systems.

The identification of perchlorates on Mars, one of the most notable instance of sample matrix effects in planetary science, was made possible by a wet chemistry instrument, JPL's Wet Chemical Laboratory (WCL) [7] onboard the Phoenix Lander. Using ion selective electrodes (ISEs) as part of its suite of soluble ion electrochemical sensors, WCL made the surprising discovery of perchlorate salts in the Martian regolith. This discovery helped explain how reactions between perchlorate and organics in the pyrolysis oven during sample volatilization had prevented every gas chromatograph-mass spectrometer instrument sent to Mars since Viking from conclusively detecting organic molecules.

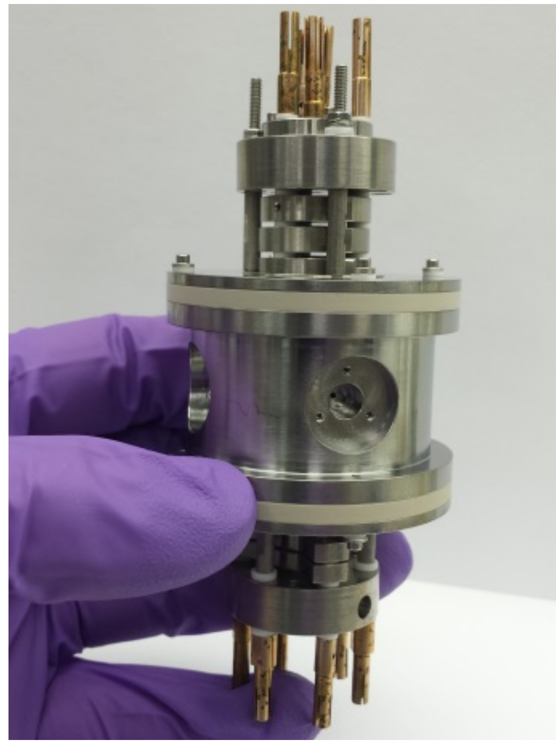

Fig. 2: Photograph of our 10 mm Paul ion trap mass spectrometer. This is the axial ionization version of our MS.

The clear success of the WCL instrument makes it, or a subset of its electrochemical sensors, a natural choice for future missions that will benefit from inorganic ion analysis such as the Europa Lander or a New Frontiers mission to Enceladus. However, the ISEs that were the main class of sensors in WCL are currently not robust enough to avoid drying out during a long duration mission to the outer planets. JPL is working to address that issue by developing solid contact ISEs (SC-ISEs) that no longer rely on a wetted hydrogel material in order to function. Taking advantage of the switch to SC-ISEs and advances in the technology since WCL was built will also allow reductions in sensor size and improvements in the limits-of-detection.

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