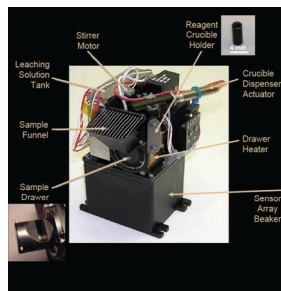


**MECA WET CHEMISTRY – THE NEXT GENERATION.** A.D. Aubrey<sup>1</sup>, M.H. Hecht<sup>1</sup>, F.J. Grunthaner<sup>1</sup>, S.P. Kounaves<sup>2</sup>, M.C. Lee<sup>1</sup>, G.D. O'Neil<sup>2</sup>, R.C. Quinn<sup>3</sup>, and L. DeFlores<sup>1</sup>. <sup>1</sup>Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, 91109 (Andrew.D.Aubrey@jpl.nasa.gov), <sup>2</sup>Department of Chemistry, Tufts University, Medford, MA, <sup>3</sup>SETI Institute, Mountain View, CA, 94043.

**Introduction:** During the summer of 2008, the Microscopy, Electrochemistry, and Conductivity Analyzer (MECA) operated on the Northern Plains of Mars as part of the Phoenix mission. From  $L_S = 76^\circ$  to  $147^\circ$ , Phoenix characterized the local terrain and atmosphere, and analyzed soil excavated by a robotic arm [1]. MECA combined three experiments in a single instrument suite (**Fig. 1**): The Microscope Station (MS); the Wet Chemistry Laboratory (WCL); and the Thermal and Electrical Conductivity Probe (TECP). While MECA was fully successful within the context of Phoenix, it was designed for a fixed lander and as such was constrained by consumables. Subsequent development has been aimed at extending those technologies to long-lived rover missions.



**Figure 1. Left: one of four MECA Wet Chemistry Laboratory (WCL) cells flown on the Mars Phoenix Mission. Bottom: The MECA enclosure on Mars. Shown in the middle of the picture are the four WCL cells. In the foreground is the soil inlet for the microscopes.**



The four cells in the Wet Chemistry Lab (WCL) performed solution chemistry on Mars for the first time [2]. Highlights of the WCL results included the finding that most of the soluble chlorine is in the form of perchlorate, and that the solution has a near-neutral pH due to buffering by carbonates [3,4]. WCL experiments were conducted over (at least) two days time, each of which began with thawing of the solution. Critical steps of the experiment were tank or beaker thaw, and additions of aqueous solvent, calibrant, sample, acid, and  $\text{BaCl}_2$  addition for sulfate titration [5].

Each WCL cell contained ion selective electrodes (ISE) for direct measurement of cations and halides ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{Cl}^-$ ), a  $\text{Ba}^{2+}$  ISE for the aforementioned sulfate titration, two polymer pH sensors, one iridium oxide pH sensor, and two  $\text{Li}^+$  sensors to serve as references against a calibrant added to the solution. Oxidation-reduction potential (ORP) was determined from the Pt ground wire [6]. WCL also measured electrical conductivity (EC), which is proportional to the total concentration of dissolved ionic species in the water and performed cyclic voltammetry (CV) scans in a tri-electrode configuration; a working electrode, a platinum ORP counter electrode, and a chloride ISE used as a reference electrode. Two Ag chronopotentiometry electrodes (measuring electrode potential (mV) as a function of current (nA) as the current is ramped upwards from 0V) recorded the concentration of  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ .

**The Next Generation:** From a scientific perspective, checking the global applicability of WCL findings and improving the quantitative determination of particular species are primary goals. From a technical perspective, two objectives have taken priority: Extending the analytical capability to dozens of soil samples while decreasing the demand on spacecraft resources, and extending the quantitative aspects of the experimental analyses.

The NERNST project (NASA ASTID funded) is focused on developing the next generation wet chemistry laboratory based on techniques employed during the Phoenix MECA-WCL *in situ* experiments. This project implements miniature chemical sensors on a microfluidic chip with channels widths of  $\sim 200 \mu\text{m}$ . This technical approach utilizes an aqueous extraction system to inject solutions into a simple microfluidic array (**Fig. 2**). The advantages of microfluidics for planetary science include significant reductions in mass/volume, much lower requirements for reagent volumes, reusability of flow channels for multiple measurements, and integrated fluidic handling capabilities implemented on-chip. The microfluidic array uses similar families of sensors as MECA, drawing largely on heritage as demonstrated by WCL during the Phoenix mission. For instance, an identical set of ISEs is currently used with this microfluidic system while CV tri-electrodes can be accommodated in identical locations. Thus the single 4" microfluidic device accommodates all WCL sensor capabilities in a single fluidic/sensing layer. The latest design of the microfluidic chip, currently utilized in the testbed setups, includes basic analytical chemistry capabilities including serial

dilution of standards and sample extracts, titration, and pH control of the solution [7]. This functionality is accomplished using the reagent input and dilution matrix (Fig. 2) and drastically improves on the accuracy and precision of these sensing techniques *via* runs after multiple dilutions.

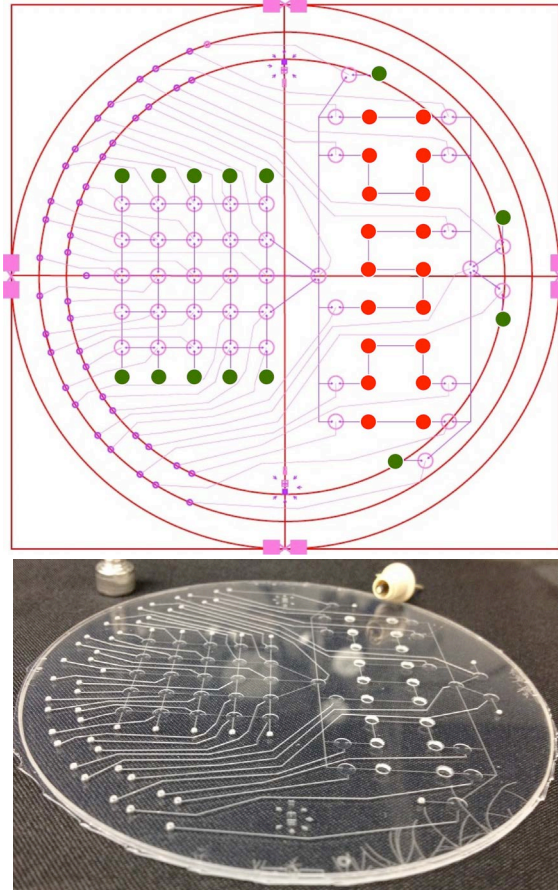


Figure 2. Top: Four-inch diameter NERNST microfluidic chip CAD photolithography mask design. Inputs / outputs (green) and dilution matrix is on the left hand side while sensors (red) are distributed on the RHS. Valves are actuated pneumatically by a low-pressure source – for Mars this could be ambient pressure. Bottom: Photograph of JPL-fabricated glass microfluidic device shown – miniature 2 mm ISE sensor also shown in photo.

Two parallel NERNST microfluidic testbeds are in operation at collaborating institutions, Tufts and JPL. The JPL microdevices laboratory (MDL) is responsible for design, fabrication, and test of the microfluidic devices used for the testbed setup. JPL capabilities for microfluidics have matured greatly over the past decade through collaboration with the Mathies Laboratory at Berkeley on the *Urey* project. The *Urey* instrument was pre-selected as a flight instrument for the ExoMars Pasteur payload until 2009 when the microfluidic system was descoped. However, NASA investment in MDL during these years has led to multiple spin off applications including NERNST, sample extraction

and processing technologies, and continuation of the *Urey* analytical concept which utilizes capillary electrophoretic (CE) separation and laser-induced fluorescence (LIF) detection. The NERNST technology is highly compatible as one of the layers in an end-to-end integrated microdevice for solid sample extraction and analysis. This is highly complementary to capabilities of CE separation devices for detection of organic and inorganic species on another fluidic layer. Thus the technologies demonstrated using the NERNST microfluidic setup, although highly capable as a stand-alone instrument, are desired for extract characterization in any CE separation device as ionic strength and pH are critical factors that may influence separation protocols.

Tufts is charged with miniature ISE sensor fabrication for NERNST and the metal electrochemical sensors for CV measurement are provided by SETI. The operational system integration, testing, and data acquisition is optimized by having independent functioning systems at Tufts and JPL. The new microfluidic chip design is being tested and characterized using complex standards (Fig. 3) – analyses of natural sample extracts analyses will follow suite in the ensuing months.

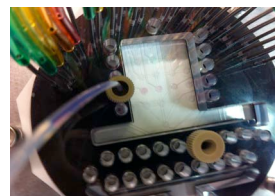
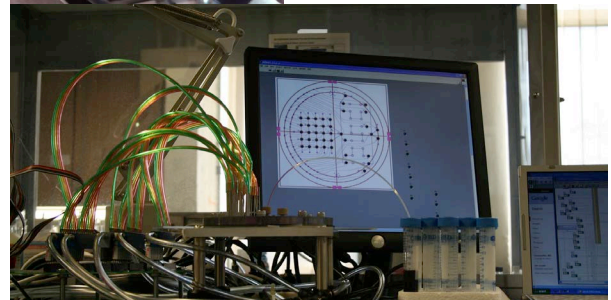


Figure 3. Left: NERNST testbed functional system demonstrating sample mixing / dilution using the new microfluidic chip. Below: NERNST testbed prototype setup.



**Conclusion:** With knowledge in hand about the expected range and distribution of key ions on mars, improvements to sensors are being implemented that will, for example, remove ambiguity from calcium, nitrate, and sulfate detections. In addition, NERNST incorporates a mechanism to weigh the soil samples in order to establish absolute composition within the low profile form factor achieved using microfluidics.

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**References:** [1] Smith, P.H. *et al.* (2009) *Science* 325, 58. [2] Kounaves, S.P. *et al.* (2009) *JGR* 114, E00A19. [3] Hecht, M.H. *et al.* (2009) *Science* 325, 64. [4] Kounaves, S.P. *et al.* (2010) *JGR* 115, E00E10. [5] Kounaves, S.P. *et al.* (2010) *GRL* 37, L09201. [6] Quinn, R.J. *et al.* (2011) *GRL* 38, L14202. [7] Jensen, E.C. *et al.* (2010) *Lab Chip* 10, 685.