THE IN-SITU WET CHEMICAL ANALYSIS LABORATORY AND SENSOR ARRAY (CHEMSENS): THE NEXT GENERATION MARS SOIL CHEMISTRY ANALYZER. K. McElhoney[1], N. Chaniotakis[1,2], G. D. O'Neil[1] , J. Bauer[3], D. Harjes[3], D. Traviglia[3], M. H. Hecht[4] and S. P. Kounaves[1*], [1]Department of Chemistry, Tufts University, Medford, MA, 02155, USA (*samuel.kounaves@tufts.edu), [2]Department of Chemistry, The University of Crete, Iraklion, Crete, 710 03, Greece, [3]Draper Laboratory, 555 Technology Drive, Cambridge, MA, 02139, USA, [4]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, 91109, USA.

Introduction: The 2007 Phoenix Mars Scout Lander [1] contained several instrument payloads, including the Wet Chemistry Laboratory (WCL), which consisted of four electroanalytical cells to analyze martian soil for soluble inorganic salt species and other parameters [2]. In addition to wet chemical analyses that identified and measured the soluble concentrations in the soil of K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, $SO_4^=$, the pH, electrical conductivity, the unexpected presence of ClO_4^- at almost 1% [3-5], and reduction-oxidation potential (E_h) [6], there were several lessons learned for instrument development for future analytical payloads.

The four WCL cells provided the first wet chemical analysis of a soil on another planet. It would have been advantageous to perform more analyses, but since limitations for payload space and weight were present the number of cell was limited to four. Including a similar or improved WCL on a future rover mission would require that it be able to provide the ability to perform such wet chemical analyses at multiple locations over the rover's lifetime. In addition to the capabilities of the original WCL on Phoenix, the next generation WCL must include improved calibration, reagent addition, and additional sensors for wider selection chemical species and conditions. For example, instead of using calibration pellets composed of pressed salts as the Phoenix WCL did [2], it should also allow for addition of liquid reagents to ensure rapid dissolution and equilibration of any added reagent.

The ion selective electrodes (ISE) contained in the WCL analyzed for the ionic species that included: Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Cl^-, Br^-, I^-, NO_3^-/ClO_4^-, pH and Li^+ (used as a reference) as well as other sensors for conductivity, the reduction-oxidation potential (Eh), chronopotentiometry (CP), cyclic voltammetry (CV) and anodic stripping voltammetry (ASV) [2]. Few of the sensors included any redundancy except for: Li^+, Cl^-, pH and halides (CP). Future WCL type instrument payloads should contain both a greater number of sensors as well as increased redundancy to provide more accurate and reproducible results.

To address the above issues, a new instrument based on the successful Phoenix WCL is under development: the *In-Situ* Chemical Analysis Laboratory & Sensor Array (CHEMSENS). Incorporating the above changes, as well as improved versions of the electrochemical sensors, CHEMSENS will provide remote chemical analysis in both terrestrial and extraterrestrial environments. Presented here, is the development of CHEMSENS and the improvements that were made over previous instruments.

Experimental: The development of CHEMSENS can be divided into two parts: instrument hardware development and sensor development. Both parts are critical to success of a future payload.

Instrument hardware development. The CHEMSENS hardware is built based on a "modular" concept so that it can be expandable or contractible to facilitate the specifications set by a future payload (Figure 1). For this reason, CHEMSENS is built in a grid system that can be anything from a 1 x 4 grid (similar to WCL) to, for example, a 10 x 10 grid, where 100 individual units can be present. Each CHEMSENS unit consists of a beaker where the sensors are housed and can hold 1 cc of soil and 5 mL of a leaching solution, as well as an "actuator assembly" which incorporates the leaching solution tank, sample and liquid calibration delivery mechanisms (Figure 2). Above the grid of beakers will be a gantry system for sample delivery from an external sample mechanism. Each beaker will contain three walls of ISEs and reference electrodes (RE) in a 4 x 4 grid and a fourth beaker wall reserved for other sensors (i.e. conductivity, pH, Eh, CP, CV, ASV) to be determined at a later date.

Sensor Development. In order to increase the number of sensors while decreasing the overall size of the unit, the sensors themselves needed to be miniaturized. Several iterations of sensors were fabricated, and

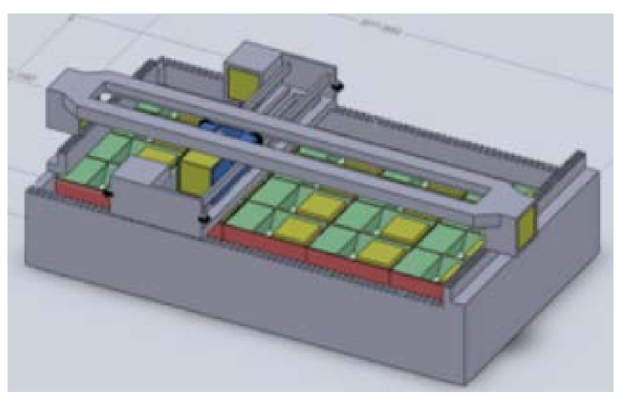

Figure 1. The overall configuration of CHEMSENS.

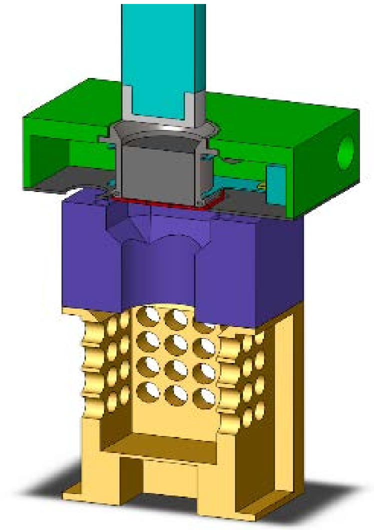

Figure 2. Rendering of a CHEMSENS unit showing the lower beaker and upper actuator assembly.

ultimately the use of nanoporous carbon as a replacement to the hydrogel used in the Phoenix WCL [2] yielded sensors that were at a size of approximately 3mm while having stable potentials, increased lifetimes and sensitive responses to increases in ionic activity.

Results and Discussion: To increase sampling, the grid system of the modular concept and individual CHEMSENS units provides the ability to customize the payload mass/size and the number of maximum number analyses that can be performed. This allows for the adaptability of CHEMSENS to a variety of future missions, both terrestrial and extraterrestrial, when payload specifications become available. Upon decreasing the size of the sensors, the overall beaker and ultimately the entire payload size can be decreased. The number of sensors is also customizable. At this time there is space reserved across three beaker walls for a total of 48 sensors (ISEs and REs). At the current configuration the ISE to RE ratio is 1:1, wherein this ratio provides space for 24 ISEs and 24 REs. Upon continued improvements in RE development the number of ISEs will only increase. This is an improvement upon the number or physical sensors, and continued development will replace some REs and allow for increased redundancy of the sensors.

In order to increase the stability and lifetime of the ISEs used for the CHEMSENS instrument, the hydrogel, which served as an electrolyte reservoir for the internal reference element in the WCL sensors, was replaced with a solid nanoporous carbon support. The configuration of the potassium SC-ISE is referred to as a symmetric membrane SC-ISE (SM-SC-ISE). Currently the SM-SC-ISE serves as the best sensor for the analysis to be performed using the CHEMSENS. A prototype potassium SM-SC-ISE was fabricated and has been shown to be stable with a lifetime of greater than 30 days, while exhibiting a calibration slope value of 54 ± 4 mV/decade (Table 1). All tests were performed in a background solution of 0.1 M NaCl, showing that the sensor was also selective towards potassium.

The development and testing of these types of ISE sensors was originally performed for potassium, but continued research, development, and testing, will be carried out for multiple chemical species until the entire sensors array locations on each cell wall are populated. Although the SM-SC-ISE has proved to be the best sensor for the chemistry to be performed, further investigations will ensure that CHEMSENS has the best available sensors for the most probable species expected in the martian soil.

Table 1. Potassium SM-SC-ISE Characteristics

Time Period	Avg. Potential ± σ (mV) (a_{K+} = 7.53 x 10^{-4}M K^+)
Days 0-2 (n=3)	323 ± 19
Days 5-15 (n=4)	260 ± 20
Days 12-29 (n=7)	241 ± 3
Days 0-29 (n=12)	267 ± 37
Calibration Slope (n=12)	54 ± 4 mV/decade

Summary: The next generation WCL type instrument (CHEMSENS) currently being developed at Tufts University and Draper Laboratory will build on the heritage and demonstrated success of the Phoenix wet chemistry laboratory. It will provide the ability to perform wet chemical analyses over a wide variety of geological surfaces, materials, soil chemistries, and over the lifetime of a long term rover or lander mission. It is being developed with the view to allowing a scalable payload that will match a variety of requirements and possess the flexibility for use on any type of future mission, from Earth, to Mars to Europa.

References: [1] Smith P. H. et al. (2009) *Science, 325*, 58-61. [2] Kounaves S. P. et al. (2009) *JGR, 114*, E00A19. [3] Hecht M. H. et al. (2009) *Science, 325*, 64-67. [4] Kounaves S. P. et al. (2010) *JGR, 115*, E00E10. [5] Kounaves S. P. et al. (2010) *GRL, 37*, L09201. [6] Quinn R. C. et al. (2011) *GRL, 38*, L14202.