Introduction: Sulfate is of paramount importance in understanding both Mars’ geochemistry and its ability to support past or present microbial life. Elemental sulfur has been detected on Mars using a variety of X-ray methods, both in situ by Viking [1], Pathfinder [2], and the two MERs [3,4], and most recently from orbit by OMEGA [5]. From the returned data it has been hypothesized that that the predominated form of sulfur is sulfate. These X-ray methods though are not able to resolve whether sulfur exists in its elemental form or as sulfide, sulfate, sulfite, or any other form. Thus, it is important to ground truth the existence of sulfate and also determine which cations are associated with the it. Carrying out such wet chemical analyses on Mars is challenging and no landed mission to date has attempted to determine soluble ionic species in the Martian regolith.

The Wet Chemistry Lab: The 2007 Phoenix includes, as part of the Microscopy, Electrochemistry, and Conductivity Analyzer (MECA), four Wet Chemistry Labs (WCL) [6]. Each WCL is composed of an upper and lower assembly. The lower “beaker” consists of an array of sensors for measuring pH, Eh, conductivity, redox species via cyclic voltammetry, halides via chronopotentiometry, heavy metals via anodic stripping voltammetry, and dissolved ions via ion selective electrodes (ISE). The ionic species to be determined include Ca²⁺, Mg²⁺, K⁺, Na⁺, NH₄⁺, Cl⁻, Br⁻, I⁻, NO₃⁻, and SO₄²⁻. The upper assembly consists of a leaching solution reservoir (water and the first calibrants for the sensors), a 1cc sample drawer, and a reagent dispenser that holds five crucibles, including one for a second calibrant, another for an acid, and three with barium chloride for determination of sulfate.

During the first sol, the analysis consists of the WCL receiving a sample of regolith (soil) from the robotic arm, adding the initial leaching solution, taking data, adding a second calibrant, taking data, then adding the soil sample. After equilibration and data collection, the sample will freeze overnight. On the second sol, the acid will be added, data collected and then the sulfate will be determined.

Sulfate Analysis: Design and fabrication of the WCL posed many challenges, but the lack of a viable sulfate specific sensor introduced even greater complications. While a couple of sulfate ISEs have been described in the literature, their responses in solutions other than where all anions are either absent or chemically or physically removed, have been dismal. Thus, it would be difficult to obtain a reliable sulfate analysis of a regolith sample with such sensors. The WCL overcomes this analytical problem by exploiting the fact that, even under acidic or basic conditions, barium and sulfate form an insoluble precipitate of barium sulfate. Thus, following the extensive analyses of the leached regolith sample, the final phase of the analysis will determine sulfate via a barium titration using the Ba²⁺ ISE. Via the last three crucibles, measured amounts of BaCl will be added to the sample. The Ba²⁺ will react with any dissolved SO₄²⁻ and precipitate as BaSO₄. The Ba²⁺ sensor will measure the barium remaining in solution, and by simple subtraction, provide how much precipitated with the sulfate, i.e. how much sulfate was present. With respect to the 1 gram sample of Mars regolith, the first barium addition can precipitate up to 6% sulfate, the second addition extends the measurement to 12%, and the third to about 18%.

In preparation for the Phoenix mission, we are currently characterizing all the sensors, including the complete electroanalytical method for determining sulfate via the barium standard subtraction method using the Ba²⁺ ISE. Characterization will include a variety of standard solutions, geological Earth samples, Mars simulants, and sawdust from the EETA79001 Martian meteorite. We will be determining a variety of Ba²⁺ sensor response characteristics such as the limits of detection, interferences, and other constraints imposed by the Martian environmental conditions. In addition, we will also develop a response library to aid in the interpretation of the data.