Part 1 Environmental Analysis

Chapter 6 Extraterrestrial

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6.1 Introduction

Humans have observed the stars and planets since prehistoric times and wondered about their significance and composition. After observations and conjectures by early philosophers such as Democritus in the 4th century BCE, understanding of our solar system rapidly accelerated during the 16-19th centuries starting with Copernicus' discoveries of Jupiter's four largest moons and the rings of Saturn, followed by Galileo's study of lunar mountains and his suggestion that other worlds may also have Earth-like surfaces. These initial observations were astronomical, made by optical and later radio telescopes. In the mid-twentieth century though, the politically driven "Space Race" accelerated the quest to physically reach these other worlds. Following those successes, human and robotic missions to the Moon as well as robotic missions to other planetary bodies have revolutionized our understanding of our solar system. Starting with the first successful rendezvous with another planet (Mariner 2 at Venus in 1962) and first successful landing (Venera 7 on Venus in 1970), robotic landed missions have provided a great deal of knowledge about these nearby but alien environments through a combination of visual images and physical measurements, supporting a variety of geological, chemical and meteorological investigations.

The first successful landing on Mars was made by the two NASA Mars Viking 1 & 2 landers in 1976. Included in the payload were a gas chromatograph, mass spectrometer, x-ray fluorimeter, and three life detection instruments. Additional surface missions in 1997 (Pathfinder/Sojourner Rover) and 2004 (Opportunity and Spirit rovers) included mainly x-ray spectrometers and imagers. It was not until 2007 with the launch of the Phoenix Mars lander mission that the first electroanalytical measurement system was delivered to the martian surface. Here we present the historical context of the first electroanalyses on Mars, an overall description of the electrochemically-based sensors that were part of the Phoenix Wet Chemistry Laboratory (WCL), the results of the martian soil analyses and their implications, the most recent Earth-based experiments, and a preview of the next generation electroanalytical instruments currently in development for upcoming missions to Mars and beyond.

6.1.1 Historical Development of Electroanalytical Instruments for Mars

By the early 1990's the evidence pointed to a Mars that was most likely wet and warm sometime in its past history. Though much data had been collected by previous missions via elemental analyses using either X-ray and optical spectroscopy, little or nothing was directly known about the soluble salts in the soil or such parameters as pH or conductivity. Such knowledge is critical in understanding the biological potential of Mars for supporting indigenous life in the past or present, and also for assessing hazards that might be encountered by future human explorers. This prompted proposals to develop instrumentation that could investigate the aqueous geochemistry of the martian soil. The idea was to reconstitute the ancient wet environment by adding water to the soil and measuring the ionic species in the solution. The limitation was that whatever technique was to be used had to be preferably rugged, and of low mass, volume, and power. Electrochemical sensors appeared ideal for such an endeavor.

The first reported development and demonstration of an electrochemically-based analyzer for martian regolith (soil) was as part of the Mars Aqueous Chemistry Experiment (MACE) program at Lockheed Martin Astronautics (LMA) in Denver, Colorado, as an in-house study of the feasibility of a chemical

reaction investigation for future Mars missions [1]. Among its goals were; to determine the reactions between Martian surface materials and liquid water; investigate the unusual oxidation capabilities of Martian soil discovered by Viking; and explore for evidence of chemical and physical modifications of the surface to understand weathering processes. To accomplish its goals, MACE included ion-selective electrodes (ISE) for a variety of cations/ions (e.g., Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , Br^- , NO_3^-) and electrodes for redox potential and conductivity.

The Wet Chemistry Laboratory (WCL) was first proposed in 1997 to NASA's Office of Human Exploration and Development of Space as a payload on the 2001 Mars Surveyor Program (MSP'01) Lander, as part of the Mars Environmental Compatibility Assessment (MECA) instrument package. The purpose of the MSP'01 WCL was to determine the total dissolved solids, redox potential, and pH, and to detect potentially dangerous heavy metal ions, emitted hazardous gases, and the soil's corrosive potential. The WCL was chosen by NASA in 1998 to be designed, built, and flight qualified for the 2001 mission [2]. The MSP'01 Lander was canceled in May 2000 due to the loss of NASA's two 1998 Mars-bound spacecraft, the Mars Climate Orbiter and Mars Polar Lander. In the summer of 2002 the WCL was proposed as part of the Microscopy, Electrochemistry, and Conductivity Analyzer (MECA) instrument package for the 2007 Phoenix Mars Scout Lander (MECA). The Phoenix, including WCL, was selected by NASA on August 4th, 2003 as the first Mars Scout Mission. It was launched August 4th, 2007 and landed on the northern polar plains of Mars on May 25th, 2008 [3,4].

6.2 The Phoenix Wet Chemistry Laboratory (WCL) Electroanalytical Sensor Array

The MECA instrument package on board the Phoenix lander included four identical Wet Chemistry Laboratories (WCL), whose objective was to address the mission goals of understanding the aqueous chemical reactivity of the soil and identify potential chemical energy sources available to support past or present life. The WCL has been previously described in detail [2,5] and is only briefly reviewed here. Figure 1 shows an individual WCL unit and as part of the MECA package on Mars during its first sol (day) of operation. To accomplish its objectives, each WCL was comprised of an upper "actuator" and a lower "beaker" assembly. The actuator consisted of a 25mL titanium tank that contained deionized water plus ionic species at $\sim 10^{-5}$ M concentrations for the initial sensor calibrations, a drawer that would accept $\sim 1 \text{ cm}^3$ of soil through a screened funnel from the robotic arm, and a stirrer motor for stirring the soil/solution mixture. The actuator also included a reagent dispenser that held five "crucibles" for a second calibration reagent, an acid, and three crucibles packed with BaCl_2 for the titrimetric determination of SO_4^{2-} .

The lower "beaker" contained an array of sensors in that included: ion-selective electrodes (ISEs) for the determination of Na^+ , NH_4^+ , K^+ , H^+ , Mg^{2+} , Ca^{2+} , SO_4^{2-} (via Ba^{2+} titration), and $\text{NO}_3^-/\text{ClO}_4^-$; solid pellet ISEs for the determination of Cl^- , Br^- , and I^- ; an iridium oxide electrode and two H^+ ISEs for the determination of pH between 0-12 with an accuracy of ± 0.5 pH units; a 564 element 12- μm Au disk microelectrode array (MEA) for anodic stripping voltammetry (ASV); a set of 1 mm Ag disk electrodes for the determination of halides by chronopotentiometry (CP); a 1 mm Pt disk electrode for redox acid/base chemistry by CP; a concentric two-carbon-ring electrode for solution electrical conductivity; a 250 μm Au disk electrode for cyclic voltammetry (CV), within a potential window of ± 1000 mV and accuracy of ± 1 mV, to identify and analyze for possible reversible and irreversible redox couples; and a 1 mm Pt disk electrode for determination of the oxidation-reduction potential (E_h) between ± 1000 mV with an accuracy of 20 mV [5]. Each beaker also contained two Li^+ ISEs that served as reference electrodes. The only electrodes present in duplicate were the, the solid pellet Cl^- electrode, along with a set of Ag electrodes for CP halide determination and the Li^+ electrodes for a total of 23 electrodes in each beaker.

Fig. 1 An individual Wet Chemistry Laboratory (WCL) (a) and as part of MECA on Mars (b). *Courtesy of NASA JPL and S.P. Kounaves*

The most important consideration for the WCL beaker assembly was to ensure that all of the electrochemical sensors would arrive on Mars in the same condition they left Earth. The sensors had to survive: a prolonged pre-launch stay on the flight-deck at Cape Canaveral, Florida; significant physical stress during launch; a nine month cruise to Mars at subzero temperatures; entry to the martian atmosphere; landing on the surface; and exposure to extreme temperature swings and radiation during the time on the planet. Prior to launch significant pre-flight characterization and testing were performed in order to understand the demands of spaceflight on the WCL and each of the sensors [5]. Each sensor was rigorously characterized before and after the series of stress tests, which included operation at ~ 7 mbar (the expected pressure at the landing site), standard accelerated aging cycles, shock and vibration tests, and long periods (>8 months) of cold storage.

Using elemental analyses to determine that the surface materials contain elements such as sulfur, chlorine, magnesium, or calcium, provides little or no information about the identity of ionic species, especially their oxidation state. Using a simple array of electrochemical sensors, the Phoenix WCL analyses on the other hand made startling new discoveries providing new scientific insights into the aqueous geochemistry and history of the Mars, its potential for supporting microbial life, its chemistry, and its atmospheric chemistry. An instrument which can easily identify and quantify ion components in an aqueous solution is the only way to fully understand the geochemistry, habitability, and potential human toxicity, not only of Mars, but of other planetary environments, including the oceans of Europa.

6.2.1 Ion-Selective Electrodes

Ion-selective electrodes are potentiometric sensors which are routinely used on Earth for a variety of laboratory, environmental, and clinical analyses [6, 7]. ISEs are sensitive, selective, inexpensive, have dynamic ranges that are typically greater than five orders of magnitude, are robust enough for field-based research, and are available for nearly 100 cations and anions [8]. ISEs are prepared by separating two solutions (an internal reference and the external sample) by a chemically selective membrane. These membranes were traditionally made from glass, but are now commonly constructed from plasticized polyvinyl chloride (PVC). The potential difference measured across the PVC membrane originates from selective partitioning of an ion from the sample solution into the membrane via a complexing ligand referred to as an ionophore [9]. This partitioning results in a potential gradient across the membrane that is measured by the internal and external reference electrodes. Its magnitude is given by the Nernst Equation:

$$E = E_i^o + \frac{2.303RT}{zF} \log(a_i) \quad (1)$$

where E is the measured potential, E^o is a collection of potentials relating to the various electronic connections within the sensor, reference electrode and voltmeter, R is the ideal gas constant, T is absolute temperature, z is the charge of the ion involved in the complex, F is Faraday's constant and a_i is the activity of ion i in solution. Note that this equation is only valid for a solution containing only ion i . When multiple ions are present in solution, the measured potential is a function of both logarithmic activity of the primary and interfering ions, and can be described by the Nikolskii-Eisenman equation.

$$E = E_i^o + \frac{2.303RT}{zF} \log \left(a_i + \sum K_{i,j}^{pot} a_j^{z_i/z_j} \right) \quad (2)$$

The subscripts i and j in equation 2 refer to the primary and interfering ions, respectively, and $K_{i,j}^{pot}$ is the potentiometric selectivity coefficient. $K_{i,j}^{pot}$ varies for each interfering ion, and depends upon the precise membrane composition. The lower the value of $\log K_{i,j}^{pot}$, the more highly the interfering ion is discriminated. (For a detailed review of ion-selective electrodes, including selectivity theory and a detailed account of ISE response, see Bakker et al. in this volume).

For the WCL Mars data the following equations were used in order to account for temperature differences between Earth and Mars during calibration and use:

$$S_M = S_E (T_M/T_E) \quad (3)$$

$$E_i = E_C - S_M \log(a_i) \quad (4)$$

where S_M and S_E are the calibration slopes determined on Mars and Earth, respectively; T_M and T_E are the temperatures at which the calibration was carried out on Mars and Earth, respectively; E_i is the calibrant intercept, E_C is the stable calibrant potential; and a_i is the activity of the calibrant ion. The validity of the above relationships was confirmed during preflight characterization of the electrodes.

The ISEs deployed on Phoenix were designed to cope with the difficult conditions associated with remote long-term analysis on at a harsh and remote location. The sensors were required to: be robust; have long lifetimes; survive pre-flight testing and characterization; and have large dynamic ranges suitable for analysis of an environment that had yet to be studied. For these reasons, a configuration was chosen where the aqueous inner-filling solution was replaced by the polymeric hydrogel poly (hydroxymethyl acrylate) (poly-HEMA) (Fig. 2), as described by Cosofret et al [10]. The hydrogel was

Fig. 2 (a) Schematic of a hydrogel ion-selective electrode used onboard NASA's 2007 Lander Phoenix. (b) Placement of electrodes along the WCL beaker wall. *Courtesy of NASA JPL and S.P. Kounaves*

conditioned in an electrolyte solution containing a chloride salt to complete the interface with a Ag|AgCl electrode placed in contact with the gel. The hydrogel enabled extremely robust sensors because the material is able to freeze/thaw without large physical deformations, and can be effectively rehydrated given enough conditioning time.

6.2.2 Other Electroanalytical Electrodes

The electrodes used for electrical conductivity (EC), oxidation-reduction potential (E_h), cyclic voltammetry (CV), chronopotentiometry (CP) and anodic stripping voltammetry (ASV) were all solid state, and thus did not require the same design considerations as the membrane ISEs. The electrodes were polished and tested after fabrication, then calibrated and characterized, and remained as is until their use on Mars [5].

Electrical conductivity is a measure of how well a solution is able to carry charge. This is largely a property of the dissolved ionic species in solution and temperature. The EC probes onboard Phoenix consisted of two concentric activated carbon electrodes, separated by a layer of insulating epoxy. The inner electrode was a 3 mm diameter disk, while the outer electrode was a 0.7 mm thick ring. EC was used to estimate the ionic strength (μ) of the solution and to calculate activity. Prior to flight, the EC of solutions, which were of varying ionic strengths and made from ionic species assumed to be present in the martian regolith, was measured and the resulting calibrations were used to calculate ionic strength using the relationship:

$$\mu = 7 \times 10^{-6} EC^{1.0733} \quad (5)$$

This was an empirically derived relationship, and assumed that the species present in the pre-flight calibrations solutions were similar to those found on Mars.

The results of the 1976 Viking biology experiments suggested that the martian soil probably contained one or more oxidants and thus might result in water/soil solutions with high oxidation-reduction potentials (E_h). The E_h was measured using a 1.0 mm Pt disk electrode. When a normal hydrogen reference electrode (NHE) is used, positive potentials correspond to the presence of oxidizing species (electron donors), while negative potentials are related to reducing species (electron acceptors).

In cyclic voltammetry (CV) a triangularly changing potential is applied to an electrode while the current is monitored. CV can be used to identify redox couples and, depending on conditions, can sometimes be used to constrain the identity of the redox species by using the peak potential (E_p) [11]. On Phoenix, the potential was scanned between ± 1 V. In the WCL a standard three-electrode cell was employed, with a 250 μ m Au disk serving as the working electrode, a Cl⁻ ISE as the reference and a 1.0 mm Pt disk as the counter. A gold working electrode was selected based on its broad applicability towards organic and inorganic redox active compounds. The minimum scan rate achievable was 333 mV/s due to constraints caused by the large scan window and the hardware buffer limit of 4094 bytes, which ultimately limited the number of data points to 2015. In order to accommodate all possible current windows, each experiment needed to be run 6 times at different gain settings.

Anodic stripping voltammetry (ASV) is primarily used for the detection of heavy metal ions in solution. ASV is performed by applying a cathodic potential for a fixed amount of time and reducing a metal ion onto the working electrode surface. The deposited heavy metal is then oxidized during an anodic potential scan. The resulting peak current is proportional to both the metal ion concentration and the deposition time. Very low detection limits can be achieved using ASV because the effective preconcentration of analyte on the electrode. The WCL contained a 564-element array of 12 μ m Au microelectrodes for ASV. The array of microelectrodes are attractive for remote analysis due to their very low capacitive charging currents, small size, rugged construction, low noise, and spherical diffusion with increased current signal. Unfortunately, just before launch the ASV software was found to be problematic and thus ASV was never successfully performed for any martian soil samples.

Chronopotentiometry is the measurement of the potential at a working electrode as a function of applied current. The current can be applied as a step or a ramp (both of which were used on Phoenix). A

three-electrode cell was employed in WCL, with a 1.0 mm Ag disk as the working electrode. The reference and counter were the same as used for CV. The CP was primarily used for the determination of halides present in the soil. In the presence of halides, the silver surface will oxidize to form an insoluble salt at the surface of the electrode. The reaction at the silver electrode is:

where X^- is a halide anion (Cl^- , Br^- or I^-). The concentration of X^- (C^*) in solution can be determined using the Sand equation:

$$C^* = \frac{2i\tau^{1/2}}{nFAD^{1/2}\pi^{1/2}} \quad (7)$$

where i is the applied current, τ is the transition time, n is the number of electrons transferred, F is Faraday's constant, A is the electrode area, and D is the diffusion coefficient of X^- . When the current applied to the working electrode is sufficient to cause a redox reaction at the surface, the potential will adjust to maintain the applied current. As the concentration of X^- at the electrode surface decreases, the potential required to drive the reaction will increase. When the concentration of X^- at the electrode surface drops to zero, the potential will rapidly decrease causing an inflection point in the E vs. t curve.

For mixtures of halides the measured potential and transition time can be used to determine the identity of the species in solution. The measured potential is related to the standard potential of the redox couple, while the transition time indicates concentration. In the Phoenix experiments the transition order was iodide, bromide, and chloride, which is inversely related to the K_{sp} of each silver salt.

6.2.3 The WCL Custom Reference Electrode Configuration

The typical reference electrode serves two main functions in electrochemical cells: it produces a constant potential independent of ions in the sample; and, along with the working electrode, completes the flow of current in the electrochemical circuit [11]. Conventional reference electrodes based on liquid-junctions are able to accomplish these functions by separating the sample solution from a reference solution. They rely on slow leakage of ions from the inner solution into the sample in order to complete the circuit. This type of arrangement has several drawbacks, which make their use for long-term remote monitoring impossible: the slow diffusion of ions from the inner solution would cause sample contamination and an increase in conductivity; liquid junctions typically require frequent maintenance; inner solutions need to be changed and refilled; and can only be used in an upright position in situations where bubbles might form internally and block the junction.

Two Li^+ ISEs were used as reference half-cells in the WCL to mitigate the risks of the unknown composition of the martian soil and the need for stability. To maintain their potential, the leaching solution contained 1 mM LiNO_3 as a reference electrolyte [5]. This choice assumed that there would be significantly less than 1 mM Li^+ present in the martian soil and that interfering cations would not be a problem due to the high selectivity of the lithium ionophore. However, the presence of 1mM NO_3^- limited its detection to levels >1 mM. In the case that both Li^+ ISEs failed, a solid-pellet Cl^- ISE would then act as the reference electrode. Since the concentration of Cl^- in the regolith could be significant, a correction could be made using the Cl^- concentration obtained from the CP experiments, which can measure Cl^- concentration without calibration.

6.3 Results from the Phoenix WCL

After landing successfully on Mars, the Phoenix payload underwent a series of system checks to ensure all of the instrumentation had arrived in proper working order [12]. Before any electrochemical analyses could be performed, the beaker chamber needed to be equilibrated with the martian atmosphere by repeatedly opening and closing the sample drawer (referred to as “burping”). Once the pressure was equilibrated, the first leaching solution (TS20) was added to the beaker. TS20 contained 10^{-5} M of Na^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , HCO_3^- , 5×10^{-5} M Cl^- , and 1×10^{-3} M NO_3^- . A simple two-point calibration

was subsequently performed by adding a solid-pellet of salts, which increased the concentrations to 3×10^{-5} M, 1.5×10^{-4} M, and 1.09×10^{-3} M, respectively. After about an hour the potential of the electrodes had stabilized and $\sim 1 \text{ cm}^3$ of martian soil was then delivered to the beaker. Figure 3a shows the real-time monitoring of the ISE potentials during the analysis sequence. In total, three samples, one from the surface (Rosy Red) and two from the top of the ice table approximately 5 cm in depth (Sorceress 1 and Sorceress 2), were successfully added and analyzed in three of the four WCLs.

The wet chemistry laboratory onboard Phoenix provided the first wet chemical measurement of soluble species the martian soil [12,13]. The ionic species and their concentrations in the soil were found to be similar to those generally observed on Earth, thus the martian soil at the Phoenix site is considered to be habitable for any putative martian microbes [14]. Preliminary data analyses showed the monovalent cations, Na^+ and K^+ , to be present at relatively low concentrations: ~ 1.4 and ~ 0.4 mM, respectively. The concentrations of the Ca^{2+} and Mg^{2+} ions at 0.75 and 6.4 mM were consistent with a saturated Ca/Mg carbonate-buffered system [12]. Chloride was also measured, and was found to be present at 0.40 mM.

Fig. 3 (a) Potential vs. time traces recorded for the ISEs for the Sol-30 (Rosy Red) sample on Mars. The two vertical lines indicate the addition of the calibrant crucible and the sample (b) Concentrations of cations and anions in solution containing 25mL leaching solution and 1 g of martian regolith for three of the WCL units. *Reprinted with permission from [12]*

6.3.1 The Discovery of Perchlorate and its Parent Salts Using the Perchlorate and Calcium ISEs

One of the most significant discoveries made by Phoenix was the high concentration of perchlorate (ClO_4^-) in all three of the soil samples analyzed, roughly 2.5 mM in the 25 mL solution, equivalent to ~ 0.6 wt% in the soil [12,13]. The ClO_4^- was measured by the ISE originally intended for NO_3^- , but whose membrane actually responds selectively according to the Hofmeister lipophilicity series ($\text{ClO}_4^- > \text{I}^- > \text{Br}^- > \text{NO}_3^- > \text{NO}_2^- > \text{HCO}_3^- > \text{Cl}^-$). Thus, the 3 orders of magnitude response can only be due to ClO_4^- . Perchlorate is a strong oxidizing agent, and is used on Earth in a variety of products, including solid rocket propellants, fireworks, explosives, and automotive air bag systems. It also occurs naturally and has been found in a variety of arid regions, though its discovery in the McMurdo Dry Valleys of Antarctica has provided conclusive evidence that its terrestrial presence is ubiquitous [15, 16]. On Mars, the presence of ClO_4^- is a tracer for liquid water because the ClO_4^- ion is highly soluble and relatively unreactive at ambient temperatures. The presence of ClO_4^- has widespread implications for Mars' geological history and future human exploration. In addition, the identity of the ClO_4^- parent salt cation has significant implications for the planet's ancient and modern history of water [17].

The initial findings from the WCL had suggested that the ClO_4^- was likely present as either Ca- or $\text{Mg}(\text{ClO}_4)_2$ [12, 13]. The ISE data has been recently reanalyzed and indicates that the parent salts include a major fraction of $\text{Ca}(\text{ClO}_4)_2$ [17]. The signal from the Ca^{2+} ISE for Sol 30 (Fig. 4a) shows a negative exponential response after addition of the soil sample, in contrast to the expected positive exponential

response given the amount of CaCO_3 in the soil [18]. However, due to the presence of ClO_4^- in the sample, the Ca^{2+} sensor suffers from anion interference, resulting in a negative bias of the signal [19].

Fig. 4 Determination of perchlorate parent salts using Ca^{2+} ISE response. (a) Data from WCL on Sol 30. (b) Ca^{2+} ISE response with various ratios of Ca/Mg. Reprinted with permission from [17]

Laboratory experiments using various ratios of $\text{Ca}(\text{ClO}_4)_2$ to $\text{Mg}(\text{ClO}_4)_2$ in a Mars simulant shows that when the ClO_4^- parent salt is 100% $\text{Ca}(\text{ClO}_4)_2$, an initial potential spike is observed (Fig. 4b, light blue open circles), mainly due to the rapid detection of Ca^{2+} by the Ca^{2+} selective ionophore. After a short time, the potential decreases to an equilibrium value ~ 23 mV below the calibration standard. When the ClO_4^- parent salt is 100% $\text{Mg}(\text{ClO}_4)_2$ (Fig. 4b, dark blue closed circles), the potential shows a sharp decrease immediately after soil addition followed by a subsequent stabilization to the equilibrium value. In order to match the curve observed with WCL on Mars, a $\sim 3:2$ mixture of Ca/Mg is necessary. The existence of a soluble Ca^{2+} salt means that there has not been sufficient liquid water for the Ca^{2+} to react and precipitate with the known higher levels of sulfates that are globally present. The implication of this is that the Phoenix landing site (and most likely all of the martian surface) has been severely arid for perhaps for the past 3 billion years [17].

6.3.2 Determination of Soluble Sulfate by Titration Using a Barium ISE

Another goal of the Phoenix WCL was to determine the presence and levels of soluble sulfate that had been suggested by previous Mars missions. Because no suitable ISE was available for the direct determination of SO_4^{2-} , the detection of SO_4^{2-} was accomplished by using a Ba^{2+} ISE to monitor the concentration of Ba^{2+} (added as BaCl_2) used to precipitate the SO_4^{2-} in the soil/solution mixture [20]. In the presence of sulfate, the soluble Ba^{2+} immediately precipitates due to the highly selective and rapid formation of BaSO_4 . As the precipitation occurs there is a decrease in the measured amount of Ba^{2+} and increase in the amount of Cl^- .

The slow and more accurate determination of the sulfate by titration was fortuitous. It was noticed early on that the Cl^- in the first two WCL units slowly increased during the analysis. Initially this was thought to be due to a slow release of Cl^- from the added soil. However, during the sol 96 analysis no sample was added to the WCL, but the same increase in Cl^- was present. It thus became clear that there was a slow and constant titration of the solution with the barium in the reagent crucibles. The increase in Cl^- was also independently confirmed by chronopotentiometry. Figure 5 shows the results of this unintended titration.

Fig. 5 Determination of SO_4^{2-} by the Ba^{2+} ISE (▲), Cl^- ISE (■) and CP electrode (●). Response of the Ba^{2+} and Cl^- ISEs in; (a) Cell 0 to the soil sample on Sols 30 and 34; (b) Cell 2 to the soil sample on Sols 107 and 116; and (c) to the failed soil delivery on Sol 96 in Cell 3 (i.e., the blank). Reprinted with permission from [20]

The amount of SO_4^{2-} in solution was determined by taking the change in Cl^- concentration and dividing it by 2, or:

$$[\text{SO}_4^{2-}]_T = \frac{1}{2} \Delta[\text{Cl}^-] \quad (8)$$

where $[\text{Cl}^-]$ is taken immediately after the sample addition response until an increase is seen in the Ba^{2+} , indicating that no more SO_4^{2-} is being precipitated by the Ba^{2+} .

The results from the Ba^{2+} and Cl^- electrodes in the two working WCL units indicated that there was $4.8 (\pm 1.5)$ mM (equivalent to $1.2 (\pm 0.5)$ wt% soluble SO_4^{2-} in the soil) for the Rosy Red sample, and $5.9 (\pm 1.5)$ mM SO_4^{2-} (equivalent to $1.4 (\pm 0.5)$ wt% soluble SO_4^{2-} in the soil) for the Sorceress-2 sample [20].

6.3.3 Determination of pH for the Soil/Water Mixture

The pH of the martian regolith was measured using two polymer-based membrane ISEs and an iridium oxide electrode. Measurement of pH of the Martian regolith was seen as a critical objective for the mission, which is why this measurement was performed in triplicate. The dynamic range of the polymer based pH ISEs as determined pre-flight was $1 < \text{pH} < 9$, while the dynamic range of the iridium oxide electrode was $1 < \text{pH} < 12$ [5]. Here, we discuss the pre-flight calibration and how the measurement was obtained on the surface of Mars.

Prior to flight each pH sensor was calibrated with four standard pH buffers saturated with ambient air as well as with 0.5% CO_2 . In order to correctly identify the contributions of the martian soil apart from the atmospheric contributions towards pH, the leaching solutions were pH buffered by equilibration with a gas that was predicted to be similar to the martian atmosphere (0.8% CO_2 , 94.2% N_2 and 5% He at 1000 mbar pressure). The leaching solutions delivered on Mars to each WCL were expected to have a pH of 5.06 ± 0.04 at the analysis temperatures expected on Mars [5].

Figure 6 shows the response of a polymeric membrane pH electrode towards the Sorceress-1 sample. The early part of the green curve confirms that after equilibration with the martian atmosphere the pH was indeed within the expected range. This measurement served as the initial calibration point for the pH sensors. As the cell was burped, the pH increased to 6.4, in line with the P_{CO_2} of 8.4 mbar as measured by the Meteorological Station (MET) aboard Phoenix. When the calibration standard was added, the pH decreased to 3.9, confirming that the pH electrodes were functioning properly. Accounting for atmospheric P_{CO_2} and the a temperature of approximately 8°C (Rosy Red) and 6°C (Sorceress 1), at the time of sample delivery, the pH was determined to be $7.7 (\pm 0.3)$ for the pH1 sensor for the Rosy Red sample, and $7.6 (\pm 0.3)$ and $7.6 (\pm 0.3)$ for pH 1 and 2 for the Sorceress 1 sample. An average of these values yields a pH for the Martian soil/solution mixture of approximately 7.7 [12]. This was a major finding, showing that the martian soil was alkaline and would be a habitable soil for Earth-like organisms.

Fig. 6 Determination of the pH of the Martian soil (Sorceress 1). Pairs of dashed blue lines represents opening and closing of sample drawer. Orange line represents addition of calibrant acid. Blue boxes represent intervals used for the determination of pH before opening of the sample drawer (~LMST 10:35) and after sample delivery (~LMST 12:50). LMST is the local mean solar time. *Reprinted with permission from [12]*

6.3.4 Determination of the Redox Potential

The oxidation-reduction potential (E_h) was measured to determine the presence of any species capable of oxidative electron transfer. In general, the redox potential of a solution can be calculated using the Nernst equation:

$$E_h = E^o - \frac{RT}{nF} \ln \frac{a_{red}}{a_{ox}} - \frac{mRT}{nF} \ln [a_{H^+}] \quad (9)$$

where E^o , R , T , n , F , and a all have their usual meanings and m is the number of moles of protons transferred. As equation 9 predicts, at constant pH the measured E_h is a function of the relative amounts of reduced and oxidized species present in solution.

The E_h of martian soil as measured in the Rosy Red beaker was 253 ± 6 mV at $\text{pH } 7.7 \pm 0.1$, which suggests a slightly oxidizing environment [21]. The plausible identity of the oxidizing species was investigated using laboratory measurements of martian simulants. Figure 7 shows the overlay of E_h measured in WCL (black circles) compared with simulant data with added 16 ppm oxygen (as calcium peroxide – grey triangles) and 10 ppm ferrous iron (as ferrous sulfate – grey crosses). The ferrous iron was found to be thermodynamically unstable at pH 7.7, so thus any iron was likely present as a near-insoluble ferric species. The data suggests that the measured E_h may be due to low levels of oxidants such as metal peroxides [21].

6.4 Future Directions for Planetary Electroanalytical Instrumentation

Currently on Mars, the rover Curiosity (also known as the Mars Science Laboratory, MSL) is busy refining our understanding of the Martian surface. Although there are several complex science instruments aboard the rover, there are no electrochemical sensors. Future characterization of Martian chemistry and geochemistry requires in-situ wet chemical analysis of the regolith. Currently under development in our group with the support of NASA and JPL are two instrument payloads that build upon the successes of the Phoenix mission, while incorporating new sensor technologies and measurement protocols. A discussion of these instruments is presented below with a focus placed on the electrochemical sensors that are under development.

Fig. 7 E_h of Mars simulant salt mixtures containing 10 ppm ferrous iron (grey crosses) and 16 ppm peroxide (grey triangles). The data is overlaid with the measured WCL data collected from the Rosy Red beaker. *Reprinted with permission from [21]*

6.4.1 The Next Generation WCL - CHEMSENS

The NASA supported development of the *In-situ Chemical Analysis Laboratory and Sensor Array* (CHEMSENS) is based on the Phoenix WCL and will provide for real-time investigation of the soil on Mars and similar planetary settings. Though the Phoenix mission is viewed as highly successful and is still providing results years after the end of the mission, it was clear that improvements could be made for future missions. These included: (1) the number of individual WCL units; (2) an increased number of sensors in the array; and (3) sensor redundancy. Incorporating these improvements resulted in a scalable payload of "mini-WCL" units with a movable gantry for sample delivery and various actuator assemblies. This will allow for a payload of a few or a hundred WCL units to be incorporated into a lander or rover.

While decreasing the overall size of the WCL unit from accommodating 1 cc of soil and 25 mL of leaching solution to 1 cc of soil and roughly 8 mL of leaching solution, the number of sensors was increased by a factor of greater than 3. In order to achieve this goal while increasing the number of sensors, the overall size of the sensors needed to be miniaturized. ISEs in the WCL beaker had an outer diameter (O.D.) between 6-7 mm. Along with the conductivity sensors (O.D. ~10 mm) the ISEs took up the greatest amount of space in the WCL sensor. Figure 8 shows a prototype of the CHEMSENS beaker where there is room for 15 sensors per beaker wall and the actuator assembly and delivery is accomplished by the XY gantry above the beaker.

The main task and challenge of the sensor development was the miniaturization of the ISEs. When the active area of the internal reference element reservoir (pHEMA) was decreased, the sensors lost their ability to operate for more than a few days, if at all. Keeping the reservoir O.D. of ~3 mm, the membrane diameter was then decreased from 6-7 mm to ~4 mm (Fig. 9). When performing studies with the pHEMA, leaching of the electroactive components occurred much faster than for the large O.D. ISEs. To counteract the loss of ionophore, a previous method incorporating porous carbon was utilized [22]. Doping the porous carbon with a plasticized ionophore mixture allowed any ionophore that leached out of the ion-selective membrane (ISM) to be replaced from the reservoir, driven by the equilibrium between the two phases. This allowed for continuous monitoring of solutions in constant contact with solution for > 50 days [23].

Fig. 8 Prototype of the CHEMSENS beaker and actuator assembly (a). Each beaker has been fabricated to accommodate 15 sensors per wall across 3 walls and an empty wall for the incorporation of other electrochemical sensors such as pH, conductivity, CV, CP, etc. The actuator assembly is on an XY gantry that will deliver sample (after external delivery to sample cup), dispense calibration solutions and weigh samples. A close up of the beaker (b) shows the leaching solution reservoirs, with four equal volume reservoirs (larger circles). *Courtesy of Draper/Tufts*

Fig. 9 A comparison of the sensor housing used in WCL and developed for CHEMSENS. The sensor housing on the left is similar to that used during the Phoenix mission housed in the WCL beakers. The middle housing was an initial prototype, and the housing on the right is the current housing used for the ISEs for the CHEMSENS project. *Courtesy of McElhoney/Tufts*

6.4.2 A Microfluidic Wet Chemical Analysis System - NERNST

Another approach being developed in our laboratory in collaboration with researchers at NASA's Jet Propulsion Laboratory is a microfluidic total analysis system for analysis of martian regolith (Fig. 10). The system, called NERNST, provides a more detailed chemical picture of the martian surface material by allowing the manipulation of reagents and increasing the number of measurements. A microfluidic system offers several very attractive advantages for *in-situ* planetary analysis: it requires very little power; can be effectively miniaturized to have a small footprint; and uses extremely small amounts of reagents. In addition, the analyses generally do not suffer as a result of miniaturization.

Fig. 10 The NERNST setup showing full assembly and chip. *Courtesy of NASA JPL*

The NERNST concept applies several lessons learned from the Phoenix mission in order to provide a more robust, sensitive and accurate measurement of the martian regolith. With NERNST, a sample of martian soil is first mixed with water off-chip in a sample extraction hub, then the sample leachate (the water separated from the soil-water mix) is pumped on-chip for analysis. The sample can then be manipulated (with acid/base, BaCl_2 , etc.) and measured multiple times with multiple electrodes in order to provide a deeper understanding of the soluble chemistry of the soil sample.

The advantages of using this microfluidic configuration lies in the ability to more closely perform a classical laboratory-based wet chemical analysis. For instance, with NERNST the electrodes can be calibrated over their entire dynamic range prior to sample analysis, and then spot-checked randomly throughout the analysis time. This is typical laboratory procedure, but was not available on Phoenix due to the beaker and experiment design. A second advantage is that reagents can be added to small aliquots of the sample solution without permanently altering the stock sample.

Automated wet chemical analysis systems such as CHEMSSENS and NERNST can be used in conjunction with electroanalytical sensors, not only to reduce the mass, cost, and power consumption of the instrument, but to provide very a detail picture of the aqueous geochemistry of sample in remote extreme environments. The direction of such devices points to ever more sophisticated robotic systems that could one day provide basically the same chemical analyses as a sophisticated terrestrial analytical laboratory.

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