Mars Surveyor Program '01 Mars Environmental Compatibility Assessment wet chemistry lab: A sensor array for chemical analysis of the Martian soil

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[1] The Mars Environmental Compatibility Assessment (MECA) instrument was designed, built, and flight qualified for the now canceled MSP (Mars Surveyor Program) '01 Lander. The MECA package consisted of a microscope, electrometer, material patch plates, and a wet chemistry laboratory (WCL). The primary goal of MECA was to analyze the Martian soil (regolith) for possible hazards to future astronauts and to provide a better understanding of Martian regolith geochemistry. The purpose of the WCL was to analyze for a range of soluble ionic chemical species and electrochemical parameters. The heart of the WCL was a sensor array of electrochemically based ion-selective electrodes (ISE). After 20 months storage at $-23°C$ and subsequent extended freeze/thawing cycles, WCL sensors were evaluated to determine both their physical durability and analytical responses. A fractional factorial calibration of the sensors was used to obtain slope, intercept, and all necessary selectivity coefficients simultaneously for selected ISEs. This calibration was used to model five cation and three anion sensors. These data were subsequently used to determine concentrations of several ions in two soil leachate simulants (based on terrestrial seawater and hypothesized Mars brine) and four actual soil samples. The WCL results were compared to simulant and soil samples using ion chromatography and inductively coupled plasma optical emission spectroscopy. The results showed that flight qualification and prolonged low-temperature storage conditions had minimal effects on the sensors. In addition, the analytical optimization method provided quantitative and qualitative data that could be used to accurately identify the chemical composition of the simulants and soils. The WCL has the ability to provide data that can be used to "read" the chemical, geological, and climatic history of Mars, as well as the potential habitability of its regolith. *INDEX TERMS:* 6225 Planetology: Solar System Objects: Mars; 6297 Planetology: Solar System Objects: Instruments and techniques; 5470 Planetology: Solid Surface Planets: Surface materials and properties; *KEYWORDS:* Mars, chemical analysis, electroanalysis, sensors, ISE

1. Introduction

[2] Even though the two Viking missions, operating from 1976 to 1982, and the Pathfinder mission in 1997, established the bulk elemental composition of the Martian soil (regolith) using X-ray fluorescence techniques, we have no direct analyses which provide the identity, ionic character, or solubility, of any compounds or salts. To date, the composition of the Martian soil has only been inferred through close examination of several SNC and the ALH84001 meteorites, generally accepted as having originated from the Martian surface. Traces of several salts have been found including, CO_3^{2-}, SO_4^{2-}, halides, and several cations, indicating aqueous interaction in the past. Because of the form of the carbon and sulfur species found, the Martian environment required alkaline and oxidizing conditions. Given these conditions and the overall composition

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of the meteorites, calcium sulfate, calcium carbonate and sodium chloride are thought to exist on the Martian surface [*Gooding*, 1992; *McSween*, 2002].

[3] From the three Viking and Pathfinder sample locations, the soil was found to be composed predominately of silicon and iron with significant levels of chlorine and sulfur, as well as smaller fractions of elements that are commonly found in terrestrial soils [*Clark et al.*, 1977, 1982; *Rieder et al.*, 1997]. Using mineralogical data taken by the Viking and Pathfinder, it has been hypothesized that 8–25% of the Martian soil may be composed of evaporites containing predominantly sodium chloride and both magnesium and calcium sulfates [*Clark and VanHart*, 1981; *Catling*, 1999].

[4] The Mars Environmental Compatibility Assessment (MECA) payload was designed, built, and flight qualified for the now canceled MSP (Mars Surveyor Program) '01 Lander. MECA was commissioned by NASA's Human Exploration and Development of Space enterprise to evaluate physical, chemical, and electrostatic hazards that might be associated with the Martian soil. The integrated MECA payload contained the following: a microscopy station to inspect particles with both an optical microscope and an Atomic Force Microscope (AFM) [*Akiyama et al.*, 2001]; an electrometer, located in the Lander's robotic arm, to characterize the electrostatics of the soil and its triboelectric charge [*Buehler et al.*, 1999]; an array of material patches to monitor characteristics of the soil such as hardness and adhesion and to study the abrasive and adhesive properties of soil grains; and a wet chemistry laboratory (WCL).

[5] The WCL was intended for in situ measurements of cations, anions, dissolved gases (CO_2 and O_2), oxidation/reduction potential (ORP), and conductivity in the Martian soil. The sensor array included the following ISEs: K^+, NH_4^+, Na^+, Li^+, Ca^{2+}, Mg^{2+}, Cd^{2+}, NO_3^-, Cl^-, ClO_4^-, I^-, Br^-, and Ag^+/S^{2-}. ISEs are a well-established method for determining the concentration of individual ions in solution. When multiple electrodes are combined in an array, they form a powerful analysis tool. Most array ISEs are PVC-based, but a large number have been fabricated using alternative materials including graphite, photocured coated wires, and chalcogenide glass.

[6] In principle, an array of ISEs can be used to monitor several analytes simultaneously, although this approach is infrequently used. Since these electrodes are selective and not specific, extensive modeling must be performed to account for any and all interfering ions present in solution. As the number of electrodes in the array increases, the model required to determine ionic concentrations increases in complexity. Generally, such ISE arrays are used when the overall composition of a sample is reasonably well known, such as for sodium and potassium in blood. The MECA-WCL sensors were composed of both solid state and PVC membrane ISEs specifically designed to perform chemical measurements of the Martian regolith. Electroanalytical devices are well suited for analysis in such extraterrestrial environments and are compatible with the severe mass and power constraints. In addition, since a Mars soil analysis is a "one shot" experiment, an ISE array allows maximum data return and minimizes the complexity of the sampling process. The WCL has the ability to provide data that can be used to "read" the chemical, geological, and climatic history of Mars, as well as the potential habitability of its soil.

[7] To successfully accomplish an analysis of the Martian regolith, the MECA-WCL and its sensors had to withstand shock and vibration, subfreezing temperatures, and the 7 torr CO_2 atmosphere during operation. Leak rates on the sample introduction device were sufficiently large to subject the array to vacuum conditions on its journey to Mars. Survivability of the sensor array under all anticipated conditions was demonstrated at NASA's Jet Propulsion Laboratory (JPL) prior to delivery using standard environmental test methodology. We describe here the extensive preflight and postcancelation study undertaken to determine in detail the ISE resiliency and analytical viability after extended low-temperature exposure and repeated temperature cycling.

[8] The WCL was stored frozen over two 8-month periods, approximately twice the exposure during the journey to Mars. It was then subjected to a series of freeze/thaw cycles, such as would be experienced during a Martian day. Knowing that the storage procedure for the WCL was not seriously affecting the sensor responses, further experiments were carried out to fully characterize several ISEs. The response of each electrode toward interfering ions required quantification through values known as selectivity coefficients. These values can be determined through any of several well-documented methods [*Bakker et al.*, 2000]. In this work a fractional factorial calibration method was chosen and applied to five cation and three anion ISEs (NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, and ClO_4^-). The fractional factorial calibration method measures the effect that various concentrations of several interfering species have on the response of a given electrode [*Saez de Viteri and Diamond*, 1994; *Forster et al.*, 1991]. For a given calibration electrode, a predetermined number of solutions are prepared that will systematically vary the concentrations of all interfering ions while maintaining the concentration of the calibrant ion [*Box et al.*, 1978]. The calibrant ion concentration is then changed, and the process of altering the interfering ion concentrations is repeated. The output of the calibrant ion electrode for each solution is then compared to results predicted by a model describing the response of the calibrant ISE. The model used in this work accounts for the presence of an unlimited number of mono and divalent interferents [*Naegele et al.*, 1999]. This model equation extends the classical Nickolskii equation which has been used extensively in the past to model ISE responses in the presence of interferences. However, it has been shown that this equation is inferior when ions of various charge are present [*Bakker et al.*, 1994]. The current model contains variables for slope, intercept, and primary ion concentration as well as a summation term incorporating all selectivity coefficients and concentrations of interfering ions.

[9] The output of the model is generated by inserting initial guess values for the variables (slope, intercept, and all selectivity coefficients). The known concentrations used from the factorial experiment for all ions are also entered. The output is provided as the predicted voltage response (mV) for the ISE. The error between the model-predicted output and the actual response of the calibrant ISE is then minimized for each solution by allowing the variables to vary within wide predetermined ranges. The values generated when the error reaches a global minimum can then be

Figure 1. The Mars Environmental Compatibility Assessment wet chemistry lab ion-selective electrode (ISE) sensor array cell showing the internal placement of individual sensors. Inset shows a typical individual ISE sensor.

used for subsequent soil analysis. The low optimization errors that were observed are indicative of accurate results. In this work we have used the Microsoft Excel® add-on Solver as the optimization program. Solver has previously been shown to return results for ISE data comparable to other well-established optimization methods such as genetic algorithms and simplex optimizations [*Walsh and Diamond*, 1995].

[10] The resulting values were subsequently used to determine concentrations of several ions in two soil leachate simulants based on terrestrial seawater and hypothesized Mars brine as well as four actual terrestrial soil samples. The concentrations determined by the array were compared to actual values for the simulant and soil samples using ion chromatography (IC) and inductively coupled plasma optical emission spectroscopy (ICP).

2. Instrument Description

2.1. Wet Chemistry Lab

[11] The MECA Wet Chemistry Laboratory (WCL) consists of four thermally insulated, single-use, independent analysis cells (Figure 1) designed and built by ThemoOrion Research, Inc. (Beverly, Massachusetts) and capped with a water reservoir/actuator assembly (Figure 2) designed and built by Starsys Research Corporation (Boulder, Colorado). The actuator assembly consists of a sealed water tank with a puncture valve, a sample loading drawer, a stirrer motor with impeller, and a solid pellet dispenser. The pressurized tank can hold 30 mL of a "leaching" solution containing several ions at $10^{-5}M$ concentration levels. It serves both to leach the soluble components from the soil and as a calibration standard for the reference and ion-selective electrodes. The sample loading "drawer" was designed to receive the soil from the Lander robotic arm, remove excess soil, deposit it in the chamber, and provide a crude chamber seal. The sample drawer seals with enough force to maintain a chamber overpressure sufficient to prevent boiling at 27°C and <25 torr. The drawer loading compartment holds ~1.0 cm³ of sample, and the base is a spring-loaded flap which will retract to allow the soil to fall into the cell as the drawer is closed. A sieve or screen prevents particles

>0.5 mm from falling into the receptacle and space is provided to allow excess soil to fall off. A brush removes excess soil as the drawer is closed.

[12] Each rectangular cell, fabricated from an epoxy resin and designed to be inert in a range of environments, is 3 × 3.5 cm wide and 3.5 cm deep, with an internal volume of about 35 mL. The cells are designed to lose <0.5 thermal watts of power against a 40°C temperature gradient. A Viton® sealing surface insures a leak rate of <0.1 cm³/min of water vapor at 30 torr (corresponding to 4 μg/min) against an outside pressure of 5 torr over the operating temperature range, despite contamination with dirt and dust. This leak rate corresponds to a partial pressure of water
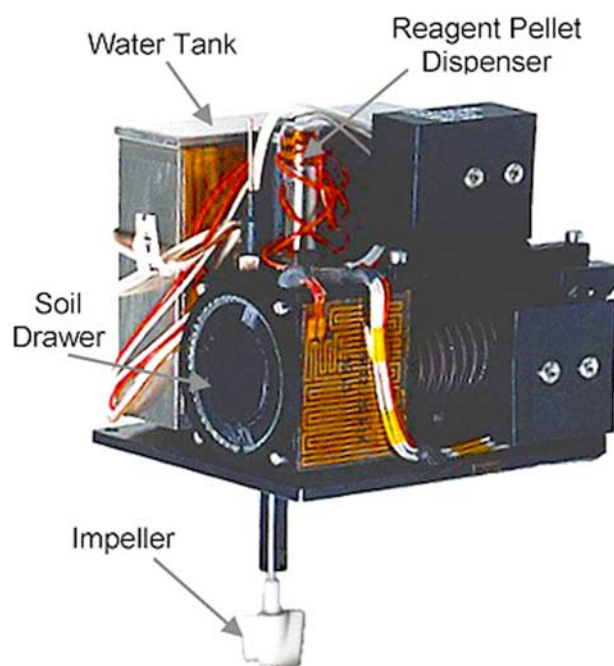

Figure 2. The actuator assembly consisting of a sealed water tank with a puncture valve, a sample loading drawer, a stirrer motor with impeller, and a solid pellet dispenser.

10 times lower than that of the Mars ambient contribution at 1 cm from the leak. As a result, leakage would not cause any noticeable frosting or other disturbance of adjacent instruments.

[13] To initiate a chemical analysis, the Lander's robotic arm places soil in the sliding drawer scoop, the drawer is closed, and the chamber and cell are resealed at the ambient Martian pressure of ~7 torr. The water reservoir is heated to melting and the metal seal on the water tank is punctured. Head gases intentionally sealed into the water tank force the water to flow into the instrumented cell, where it mixes with the soil. The temperature inside the WCL is maintained at $20 \pm 0.5°C$ during the analysis and monitored throughout as an additional indicator of any vigorous reaction. The atmosphere above the liquid consists of a mix of water vapor, the inert head gases from the water tank, and any gases evolved from the soil and should be in the vicinity of 50 torr. Note that the measurement temperature is above the external boiling point. Subsequent additions of soil were not planned but could be performed if the water were first allowed to cool or freeze.

[14] Since some chemical reactions may occur almost instantly upon addition of the water to the soil, data from as many of the sensors as possible is immediately collected. Thereafter they are read serially and repetitively at discrete intervals. The stirring impeller homogenizes and drives the solution toward equilibrium in the shortest possible time. A small reagent pellet, introduced near the conclusion of the experiment, provides an end point calibration of the sensors.

2.2. ISE Sensor Array

[15] As shown in Figure 1, a total of 26 sensors are embedded in the four walls of an inner beaker constructed of cast epoxy, and capable of holding 35mL of solution. Printed circuit boards surround the inner beaker and contain preamplifiers for each of the sensors. These in turn are surrounded by an anodized aluminum casing. Additional information regarding construction and design of the beaker has been published previously [West et al., 1999]. Several of the sensors are duplicated to ensure accurate measurement for those ions of particular interest. Since a pH measurement of the Martian soil is exceedingly important, three pH ISEs using two different transductions mechanisms are installed. Redundant ISEs are also included for Li^+ and Cl^-. The extra Li^+ ISE is necessary since it serves as a reference electrode half-cell. It was chosen because only a low concentration of Li^+ is expected in the Martian regolith. Thus the lithium potential should remain unchanged upon soil addition. However, if both Li^+ ISEs fail, the redundant Cl^- ISE would assume the role of reference. Table 1 shows the sensors included in the array and the species and parameters measured. Specially configured metal electrodes measure conductivity and redox potential. Gold microelectrode arrays are used for cyclic voltammetry (CV) and for anodic-stripping voltammetry (ASV) in order to determine reversible and irreversible oxidants present and the concentrations of heavy metals, including lead, copper, mercury, and cadmium at ppb levels, respectively.

[16] The WCL was designed to meet often-conflicting needs for sterility, hydration, storage, transport in dry, airless environments, and good sealing after introduction of sample. Some compromises were accepted, including the

Table 1. Species and Parameters Measured by the Mars Environmental Compatibility Assessment Wet Chemistry Lab Sensors[a]

Species Parameter	Sensor Type or Method
Total ionic content	Conductivity cell, 4-electrode planar chip
H^+	pH, polymer membrane, potentiometric
H^+	pH, iridium dioxide, potentiometric
Dissolved O_2	Au electrode 0.25-mm, membrane-covered, Au cathode, using CV.
Dissolved CO_2	ISE gas permeable membrane, potentiometric
Redox potential	Pt electrode, 1.0-mm disc, potentiometric
Oxidants and Reductants	Au electrode, 0.25-mm disc, using CV
Cu^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}	Au MEA, chip, 512 10-μm elements, ASV
Ag^+/S^{2-}, Cd^{2+}, Cl^-, Br^-, I^-	ISE, solid-state pellet, potentiometric
Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, NO_3^-, ClO_4^-	ISE, polymer membrane, potentiometric

[a]Definitions are as follows: CV, cyclic voltammetry; ISE, ion-selective electrode; ASV, anodic-stripping voltammetry; and MEA, microelectrode array.

risk of sensor dehydration. The expected ambient Martian pressure at the anticipated landing site is $6-7$ torr, with the surface temperature ranging from $25°C$ to $-100°C$. To mitigate the effects of such risks, the most crucial sensors were designed to suffer minimal effects from inadvertent exposure to a dry evacuated environment. Several of these, the solid-state ISEs, ORP, and conductivity sensors, contain no fluid and can tolerate the vacuum environment well. Glass electrodes, commonly used for pH and reference electrode measurement, were found to crack and were discounted as sensor candidates. The polymer ISEs contained a hydrogel inner reference system and were chosen for their large dynamic range, rapid equilibration times, and excellent selectivity [Bakker et al., 1997]. These sensors are able to withstand the necessary temperature cycling and are even tolerant of complete dehydration if sufficient rehydration time is allowed. The flight hardware passed all acceptance tests designed to simulate mission conditions using conventional ''accelerated lifetime'' protocols. Extended low-temperature exposure, however, is not amenable to such acceleration techniques. Accordingly, for this study, we investigated the performance of the PVC membrane ISEs after two 8-month exposures to low temperatures.

[17] An unusual aspect of the ISEs is their unconventional positioning in the walls of the WCL. Because their sensing surfaces are all oriented vertically, a hydrogel inner layer proved optimal, whereas a classical liquid inner reference solution would not have been feasible. The hydrogel layer was thicker than typically used in order to prevent premature drying of the gel.

[18] Three of the ISEs in the cell, a Li^+ and Cl^- reference, and the dissolved oxygen sensor, could not be used because of excessive electronic noise. This was determined to be caused by a problem with the electronics board and not the

sensors themselves. Thus only one Li^+ ISE served as the reference for all measurements in this work.

3. Experimental Details

[19] The Li_2SO_4, NH_4NO_3, KNO_3, $CaCl_2$, $MgCl_2$, Na_2SO_4, and $KHCO_3$ were American Chemical Society reagent grade from Aldrich. The $NaClO_4$, $(NH_4)_2SO_4$, $Ca(NO_3)_2 \bullet 4H_2O$, and NaCl were from Fisher Scientific, and $MgSO_4 \bullet 7H_2O$ was from Acros Organics. All solutions were prepared with 18 MΩ deionized water from a Barnsted NANOpure system. The WCL assembly, ISE sensors, conductivity cell, and other voltammetric electrodes were designed and fabricated by ThermoOrion. Development and fabrication of the gold microelectrode array (AuMEA) has been previously described [*Feeney and Kounaves*, 2000]. Conductivity measurements were made using a Thermo-Orion four-cell probe (model 13005D).

[20] Primary ion calibration solutions between 10^{-6} and $10^{-1} M$ were prepared by serial dilution of 1 M stock solutions and each spiked to give $2.5 \times 10^{-3} M$ Li_2SO_4. All solutions were stirred with a ThermoOrion stirrer equipped with a 1 cm diameter impeller. Each run lasted 10 min, during which time the ISE potentials were initially acquired every 10 s. However, this time interval was later reduced to 2 s. All experiments were conducted in a Faraday cage to eliminate noise. After each run, the WCL was washed twice with deionized water to prevent any cross contamination. All potentials were referenced to the lithium ISE potential and averaged over the last 8 min of the run. When all calibrations had been completed for a given ISE, the values were averaged and plotted versus the concentration of the primary ion.

[21] Electrode potentials were measured via LabView using a data acquisition program and an analog circuit board designed and fabricated by JPL. The ISE data were multiplexed through the board and acquired with the aid of a National Instruments DAQCard-1200. Acquired potentials were exported to a Microsoft Excel spreadsheet for further calculations.

[22] Prior to these measurements, the WCL used in this study (Flight Unit 6) had been assembled in August of 1999 and placed in cold storage at $-23°C$ between September 1999 and May 2001 (20 months). During the ensuing 6 months of evaluations and calibrations, the sensors were thawed and frozen numerous times. Between uses, the beaker was sealed, after the addition of 2–3 drops of deionized water to provide a humid atmosphere for the hydrogels, and stored at approximately $-20°C$. After freezing, the beaker was allowed to thaw for 1 full day before resuming calibrations. This calibration process was carried out over a period of time incorporating six freeze/thaw cycles.

[23] Prior to running experiments on Mars, the ISEs were to be calibrated with a leaching solution containing a dilute mixture of $2.5 \times 10^{-3} M$ Li_2SO_4 and $1.0 \times 10^{-5} M$ of $NaClO_4$, $MgCl_2$, $CaCl_2$, NH_4NO_3, and KNO_3. The relatively high concentration of Li_2SO_4 is required to prevent other cations from interfering with the Li^+ reference potential. After calibration, soil addition, and measurement, a solid reagent pellet may be added as a final calibration point. In this study, the original leaching solution formulated for Mars is used as one of three calibration solutions. The other two calibration solutions are simple modifications of this original solution containing the same concentration of Li_2SO_4 but with the other salts at 10^{-4} and $10^{-3} M$ rather than $10^{-5} M$. Periodically, the response of all electrodes was tested simultaneously by running this leaching solution calibration, generally immediately after the beaker had thawed.

3.1. ISE Calibration

[24] Aside from the ISEs calibrated with the fractional factorial method, these same ISEs were also calibrated in a more traditional manner without interferences. These primary ion calibrations were used to determine the slopes and intercepts of each ISE. These data could then be compared to the results of the fractional factorial to ensure accuracy. Each calibration was repeated 5 times.

[25] For the fractional factorial experiments, the same solutions were used for both cation and anion calibrations. As with all solutions exposed to the ISE array, all contained $2.5 \times 10^{-3} M$ Li_2SO_4 to serve as a reference half-cell. Solutions were monitored for 3 min with a 2 s data acquisition window. The Li^+ reference potential was subtracted, and the last 60 points were averaged to obtain one potential for each electrode. The beaker was rinsed twice between samples with deionized water to prevent cross contamination.

[26] Solver was employed to determine individual electrode characteristics using initial guess values for slope, intercept, and selectivity coefficients. The anion full factorial required only 24 solutions since there were only three electrodes involved, whereas the cation calibration required 80 solutions.

[27] The Li^+ reference ISE was calibrated separately from the other electrodes in order to establish the concentration range that would not disrupt the reference potential. Because the Li^+ ISE served as the reference, slope and intercept were not as great a concern so a primary ion calibration was not conducted. Rather, the selectivity that this electrode displayed over interferents was sought. Therefore only a factorial experiment was performed. The Li^+ ISE was calibrated with the aid of an external double junction Ag/AgCl reference electrode. This reference, containing a 2 M $(NH_4)_2SO_4$ inner electrolyte, was connected to the analog circuit board, allowing the lithium reference ISE potentials to be monitored.

3.2. Soil Leachate Simulants and Samples

[28] Two soil leachate simulants were prepared and used to determine the accuracy of the fractional factorial method and the ability of the array to provide the concentration of the ions in the samples. Since the ISE array measures only ionic species, the simulants were formulated to imitate the dissolved constituents resulting from the leaching of a Martian soil sample. Thus the leachates contained no particulate matter. The first simulant of Mars soil leachate (MSL 1) (Table 2) contained the major components of terrestrial seawater at 10, 20, 40, 80, and 100-fold dilutions. The second simulant (MSL 2) was based on a terrestrial evaporite brine from New Mexico that was dominated by $MgSO_4$ rather than NaCl and has been proposed as an analog of the evaporites on the Martian surface [*Clark and*

Table 2. Original Molar Composition of Mars Soil Leachate Simulants With Concentrations Measured by the ISE Array

	MSL 1 Simulant				MSL 2 Simulant		
Species	Original Concentration, M	Measured Concentration, M	Error, %	Species	Original Concentration, M	Measured Concentration, M	Error, %
Na^+	4.70×10^{-1}	4.44×10^{-1}	5.3	Na^+	1.90	1.45	23.7
K^+	9.30×10^{-3}	9.25×10^{-3}	0.7	K^+	5.00×10^{-2}	5.40×10^{-2}	8.0
Ca^{2+}	1.00×10^{-2}	4.44×10^{-3}	56.9	Ca^{2+}	3.25×10^{-3}	3.06×10^{-5}	99.1
Mg^{2+}	5.30×10^{-2}	5.76×10^{-2}	8.7	Mg^{2+}	1.60	7.38×10^{-1}	53.8
NH_4^+	–	9.40×10^{-6}	–	NH_4^+	–	2.32×10^{-5}	–
Cl^-	5.47×10^{-1}	3.11×10^{-1}	45.1	Cl^-	5.00×10^{-1}	6.38×10^{-1}	27.6
NO_3^-	–	3.48×10^{-5}	–	NO_3^-	3.7×10^{-2}	3.25×10^{-2}	12.1
ClO_4^-	–	6.45×10^{-7}	–	ClO_4^-	–	1.46×10^{-6}	–
SO_4^{2-}	2.80×10^{-2}	–	–	SO_4^{2-}	2.30	–	–
HCO_3^-	2.30×10^{-3}	–	–	HCO_3^-	2.0×10^{-2}	–	–

VanHart, 1981]. Since its total salinity exceeded even that of seawater, the most concentrated solution used in our experiments was a 25-fold dilution from the initial brine composition. The four other dilutions from the original brine were 50, 100, 200, and 250-fold. Each simulant was run in triplicate, and the results were averaged.

[29] For concentration determinations, the same model was used as for the selectivity coefficient determination. In a similar fashion, the slopes, intercept and all selectivity coefficients determined from the previous experiment were entered into the model equation for each electrode. However, the concentrations were now treated as variables. Here multiple initial guess values were used to ensure a global minimum in the error between the model-predicted and actual potentials was reached. The values used were (1) the minimal value of $10^{-10}M$ for all concentrations; (2) an upper value of $10^{-3}M$; or (3) the concentration determined using the primary ion calibration curves (neglecting any effects of interfering ions). The initial value that returned the lowest error was used for comparison with actual concentrations. Each simulant was run for 10 min with data acquired every 2 s. The last 8 min of data were averaged to obtain one potential for each ISE.

[30] Four soil samples were obtained though JPL from arid desert locations at Red Rock, Nevada, and Rio San Salvador, Chile. The two samples from Nevada were red sandstone (Red Rock 1) and yellow sandstone (Red Rock 2). The Chilean samples (Chile 1 and Chile 2) appeared similar in composition but were taken at different elevations with respect to the local river water level, with Chile 2 being the higher of the two. Soils taken from dry desert locations were used since they are more likely to approximate the regolith of the dry Martian surface.

[31] After the soils were leached in deionized water for 1 hour with constant stirring, they were filtered with Whatman #1 filter paper to remove particulates, and the soluble fraction was placed in the WCL beaker. Once the initial measurement was made, the sample was then spiked to give additional concentrations of 1.0×10^{-4}, 5.0×10^{-4}, and $1.0 \times 10^{-3}M$, of each ion in the leaching solution. The measurements were duplicated using Na_2SO_4 because of an incompatibility of Ca^{2+} ISE with ClO_4^-. The anion data were obtained from soils using the ClO_4^- salt, while the cation data were obtained from the SO_4^{2-} salt measurements. Each soil measurement was run in triplicate, and the Solver results were averaged.

4. Results and Discussion

[32] After nearly 2 years of subzero temperature storage and 18 weekly freeze/thaw cycles, the initial results of the primary ion calibration studies were very encouraging. Nearly all ISEs displayed ideal behavior and excellent reproducibility, response time, and endurance, with no embrittlement or cracking. Table 3 summarizes the results for the ISE primary ion calibrations. A confirmation that the ISE sensors were functioning correctly was the similar responses obtained from the three pH sensors. The membrane-based pH electrodes (pH 1 and 2) gave similar slopes and intercepts, as expected, because of their identical composition. The intercept of the iridium oxide pH sensor was offset considerably from the other two sensors, but its slope was similar. All ISEs exhibited Nernstian behavior (59 mV/decade slopes for monovalent species and 29 mV/decade for divalent) and excellent linearity. The slope for the NO_3^- ISE was slightly less than

Table 3. ISE Response to Primary Ion Calibrations

Electrode	Salt/Reagent Used	Linear Range, M	Slope, mV/decade[a]	Intercept, mV[a]
K^+	KNO_3	$10^{-1}-10^{-5}$	60.45 ± 2.06	120.51 ± 4.53
NH_4^+	NH_4NO_3	$10^{-1}-10^{-5}$	61.28 ± 0.79	132.55 ± 1.17
Na^+	$NaClO_4$	$10^{-2}-10^{-5}$	55.82 ± 3.52	121.94 ± 8.90
Na^+	Na_2SO_4	$10^{-1}-10^{-5}$	57.44 ± 2.03	128.54 ± 5.80
Ca^{2+}	$CaCl_2$	$10^{-1}-10^{-5}$	30.76 ± 1.89	101.61 ± 4.38
Mg^{2+}	$MgCl_2$	$10^{-1}-10^{-5}$	30.16 ± 0.30	100.61 ± 1.46
NO_3^-	NH_4NO_3	$10^{-1}-10^{-5}$	-47.72 ± 1.96	58.01 ± 5.99
Cl^-	$CaCl_2$	$10^{-1}-10^{-4}$	-56.62 ± 0.48	7.79 ± 3.16
ClO_4^-	$NaClO_4$	$10^{-1}-10^{-5}$	-59.55 ± 2.06	-202.44 ± 2.58
IrO_2 pH	pH 4,7,10 buffer	$10^{-4}-10^{-10}$	58.08 ± 0.43	614.92 ± 5.58
pH 1	pH 4,7,10 buffer	$10^{-4}-10^{-7}$	52.85 ± 0.32	339.42 ± 6.01
pH 2	pH 4,7,10 buffer	$10^{-4}-10^{-7}$	52.98 ± 0.22	338.75 ± 4.60

[a]Average of five calibrations; standard deviation given.

theoretical, but was reproducible and thus not a major concern. Intercepts were prone to minor shifting, but given the operating conditions, they are not significant. It should be noted that the intercepts shifted randomly without any systematic bias. Only the Na$^+$ sensor was unable to maintain a linear response for concentrations $>10^{-2}M$. NaClO$_4$ was used initially since this was the sodium salt used in the leaching solution. At the highest concentration ($10^{-1}M$), however, the Na$^+$ ISE response was compromised by the lipophilic perchlorate ion and an upper limit of detection was reached. Thus, for calibration purposes only, Na$_2$SO$_4$ was chosen as the calibrant salt for the Na$^+$ sensor. The linearity of the Na$^+$ ISE improved with the change in the calibration salt from ClO$_4^-$ to SO$_4^{2-}$. For the pH calibrations, ThermoOrion pH buffers 4, 7, and 10 spiked with $2.5 \times 10^{-3}M$ Li$_2$SO$_4$ were used. The iridium oxide pH sensor maintained a linear response throughout all standards. However, both of the PVC membrane ISEs were linear only to $10^{-7}M$ H$^+$. The pH 10 buffer had such a low hydrogen concentration that any buffering agents in the solution dominated the response. Consequently, the ionophore in the pH PVC membrane did not have adequate selectivity for hydrogen over other buffer components to enable a linear response down to this level.

[33] In general, the level of reproducibility was excellent. Each ISE was calibrated during a period in which it was exposed to at least three freeze/thaw cycles. Had these sensors been calibrated once per week for 3 weeks and had never been exposed to $-20°C$ temperatures, these results would have been typical. However, given the experimental conditions, the results are very promising for using such ISEs in cold, harsh environments. The calibration data clearly show that the extended cold storage period and several freeze/thaw cycles have little effect on the analytical response of these sensors. The standard deviations were often less than 1 mV and rarely exceeded 5 mV in the linear dynamic range of a given sensor.

[34] A concern in calibrating the ISEs in high concentration standards was that with a $10^{-1}M$ solution, the Li$^+$ ISE potential would be dominated by the primary ion. If this occurred, the reference potential would be compromised and the overall potential would not maintain a linear relationship. Except for Na$^+$, the calibration curves were linear up to the highest concentration standard. Despite the high concentrations of primary ions, the Li$^+$ ISE provided a stable reference potential.

[35] Overall, the primary ion calibration results confirmed a number of items. First, the Li$^+$ half-cell reference system performed as well as a traditional reference electrode. Had it not, Nernstian slopes and high levels of reproducibility would not have been obtained. Second, the hydrogel internal reference layer for the ISEs functioned properly and is equally as stable as the classical liquid internal reference. Third, the PVC membrane ISEs were much more robust and analytically reproducible than one would have expected after experiencing such harsh conditions.

[36] The values obtained from the primary ion calibrations and those from the leaching solution calibrations were remarkably similar for most of the ISEs. Even though the solution contained all ions in the leaching solution at similar concentrations, thus introducing interference effects, the similarity was expected since most ISEs were fabricated
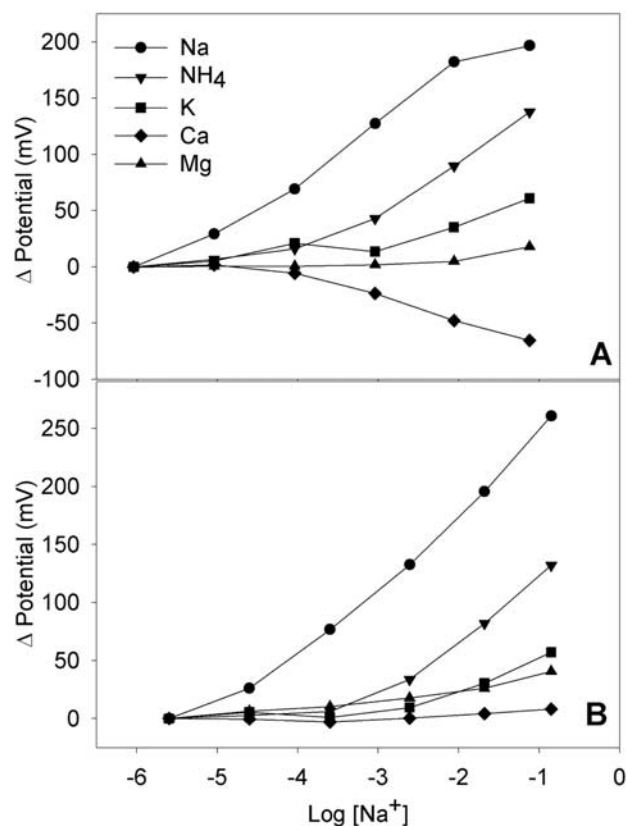

Figure 3. Responses of relevant cation ISEs to the calibration of the sodium ISE illustrating the effect of ClO$_4$ on the Na$^+$ linear range and on the overall response of the Ca^{2+} ISE. Potential changes are given for the addition of (a) sodium perchlorate and (b) sodium sulfate.

with ionophores that exhibit excellent selectivities for their primary ions. The cations were largely unchanged except for Ca^{2+}. This electrode gave an overall slope of slightly less than 16 mV. This value is about 14 mV less than expected for a divalent ion. Closer analysis of the data revealed that the response from 10^{-5} to 10^{-4} m was Nernstian. However, from 10^{-4} to 10^{-3} m the response was negligible. Therefore the assumption was made that some ion(s) in the leaching solution interfered with the Ca^{2+} ISE. Typically, ionophores for Ca^{2+} are very selective [*Bakker*, 1997], and an interference of such magnitude as was observed here would be unlikely. A theoretical slope for Ca^{2+} was obtained when a preliminary version of the leaching solution was run that did not contain NaClO$_4$ and KNO$_3$ but KHCO$_3$ and NaCl. This result seemed to indicate the interference was anionic rather than the expected cationic interference. The interferent was determined through the primary ion calibrations. The software used enabled all electrode responses to be monitored while calibrating a single electrode. When the Na$^+$ ISE was calibrated with NaClO$_4$, the expected response was for the cation ISEs to increase in potential with concentration. However, the Ca^{2+} ISE responded in a negative manner after 10^{-4} m Na$^+$. Once the calibration salt was changed to Na$_2$SO$_4$, the Na$^+$ calibration yielded predicted responses from all cations as shown in Figure 3. It was concluded that ClO$_4^-$ interfered with the

Ca^{2+} ISE response. Although anions interfering with cation ISEs is not common, it has been documented with Ca^{2+} ISEs and the perchlorate ion [*Hulanicki et al.*, 1981; *Lee et al.*, 2002].

[37] The slopes and intercepts of the three anions incorporated in the leaching solution varied more than their cation counterparts. The slope for the Cl^- sensor decreased from the primary ion calibration to the leaching solution calibration because the linear range of this sensor only extended to $10^{-4}M$ and the least concentrated leaching solution contained $4 \times 10^{-5}M$ Cl^-. The ClO_4^- sensor was virtually unchanged indicating that it had excellent selectivity over both NO_3^- and Cl^-. The nitrate sensor, however, differed greatly between the two calibrations. The slope increased over 10 mV/decade, and the intercept decreased by over 200 mV. This large difference can be attributed to a drastic interference from either of the two remaining anions in solution. The typical PVC-membrane NO_3^- ISE is widely known to suffer from severe interferences because of ClO_4^- but is selective over Cl^- [*Wegmann et al.*, 1984]. Therefore the changes between the two calibrations were the result of ClO_4^- presence.

4.1. Factorial Determination of Ionic Selectivities

[38] Using the factorial method, in conjunction with Solver optimization, provided the best possible fit of the model parameters and resulted in selectivity patterns similar to those reported in the literature [*Bühlmann et al.*, 1998] when the K^+ ISE is susceptible to NH_4^+ interference but able to discriminate against Ca^{2+} and Mg^{2+}. Although these patterns are correct, the actual values are inferior those commonly found with identically constructed ISEs. This lowered selectivity is likely due to the environmental conditions these electrodes have faced combined with their age. These results produced low errors for nearly all ionic species calibrated. The error for a given calibration was determined by the sum of the square of the error between the actual potential and the model predicted potential for all solutions of a given calibration.

[39] The slopes and intercepts determined though the factorial calibrations were close to those values seen with the primary ion and leaching solution calibrations. Although some minor discrepancies were observed, the data sets complemented each other well. Given that all three different calibrations returned similar slopes and intercepts, it is logical to assume that the selectivity data obtained with the factorial method is accurate for these ISEs.

[40] With a few minor exceptions, the ISEs gave stable and predictable responses for all solutions. It was previously observed that the Na^+ ISE response was affected by noise that could not be eliminated by any attempts including a Faraday cage. Although the electrode's potential seemed erratic, it responded theoretically when sampled at 2 s intervals. The relatively high error value obtained from its calibration was attributed to the noise specific to this electrode and present when initially tested after its fabrication 2 years earlier.

[41] It had also been suggested by previous data that the Ca^{2+} ISE experienced severe interferences when used with ClO_4^-. Because of this incompatibility, Na_2SO_4 was used for the Ca^{2+} selectivity determination. The presence of ClO_4^- also appeared to strongly influence the NO_3^- ISE by its preferential detection of ClO_4^- over NO_3^- by a factor of nearly 1700, a behavior that is common with PVC-membrane-based NO_3^- ISEs.

[42] The selectivity coefficients obtained during the Li^+ ISE optimization were used to calculate the theoretical change in potential that would occur if the Li^+ ISE were exposed to a solution containing $10^{-1}M$ cation interferents. The K^+ ion presented the greatest interference and hence the greatest shift of ~6 mV. However, since K^+ never reaches such concentrations in either the simulants or calibration solutions, we can conclude that the lithium reference is indeed stable in solutions as those used here.

4.2. Soil Leachate Simulants

[43] The two leachate simulants (MSL 1 and MSL 2) were composed largely of ions previously modeled by the fractional factorial method (Table 2). Also shown are the concentrations determined by the ISE array for each species. Since measurements were made in multiple dilutions of the values listed in Table 2, the measured concentrations listed are average values extrapolated to the higher original concentrations to display the capability of the array to describe complex samples. Generally, error values were not significant in either simulant. Here a 50% error indicates that the measured versus actual concentrations differed by a factor of 2. Considering ISEs have a linear range of 5 orders of magnitude, measurement within a factor of 2 is reasonably accurate.

[44] Both SO_4^{2-} and HCO_3^- ions were included in these simulants but were not modeled. Also, the composition of both was such that at least two of the eight modeled ions were absent. Rather than omit these ions from the concentration determination, they were included primarily to approximate real world samples where not every ISE is necessarily represented by its primary ion in a given sample. The optimizations of both simulants resulted in concentrations approximating those expected. It was encouraging to see such good correlation for such varied matrices as represented by MSL 1 and MSL 2. For ions that were not present, calculated concentration values were generally either at or below the detection limit of that sensor. Ideally, their concentrations should have been calculated as $10^{-10}M$ (optimization minimum), but any value $<10^{-6}M$ was acceptable.

[45] The results for simulant MSL 1 are plotted in Figure 4. All five dilutions of each ion are plotted on a normalized 60 mV potential scale with a +5 mV offset. The excellent correlation between the true concentrations and the Solver optimized concentrations can easily be seen. Aside from the Ca^{2+} and Cl^- results, the percent error was always <30%. For K^+ and Mg^{2+}, the error was <5%. For the ions that were modeled but not present in MSL 1 (ClO_4^-, NO_3^- and NH_4^+), the optimized values were as expected. Both NH_4^+ and NO_3^- were at the optimization minimum, but some values extended into the $10^{-4}M$ range. Although these latter values coincide with other ionic concentrations in the simulant, the erratic pattern of responses from both sensors confirmed that those ions were indeed absent. The ClO_4^- values were mostly unchanged at $<10^{-6}M$ for all five dilutions, which represents an ideal response for a nonpresent ion.

[46] Similar results were obtained for MSL 2. This simulant had identical ionic species as MSL 1 with the
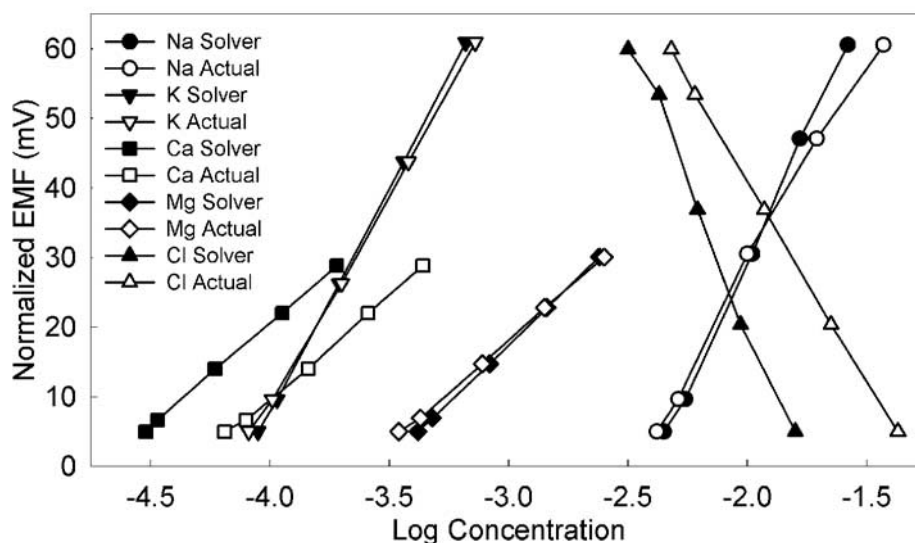
Figure 4. Comparison of the true concentrations and the array-determined concentrations for the ions in simulant Mars soil leachate (MSL) 1. All potentials are normalized to a 60 mV range offset by 5 mV.

addition of nitrate. However, the individual concentrations were significantly altered. The correlations between the actual and optimized concentration values were less accurate than those found with MSL 1. The most obvious changes were those found for Mg^{2+} and Ca^{2+}. While the MSL 1 optimization returned precise concentrations for Mg^{2+} and acceptable values for Ca^{2+}, MSL 2 returned acceptable values for Mg^{2+} and was barely able to track the Ca^{2+} response. The optimized Mg^{2+} response was in error by as much as 50–60%, whereas the Ca^{2+} optimization returned the minimal value for all but one of the dilutions. The Cl^- response was tracked very well, while that for the NO_3^- was acceptable. For ClO_4^- and NH_4^+, the only two ions not present in the simulant, the values returned were very low. The optimized ClO_4^- concentrations, as in MSL 1, did not vary to a large degree about the $10^{-6}M$ point through all five solutions. The NH_4^+ response was mostly kept at the minimum level, and as with MSL 1, the two most dilute solutions returned values approaching $10^{-4}M$.

[47] Since both simulants were composed of only ions that had been previously modeled, it was assumed that the correlation between the optimized results and the actual concentrations would be closer. In the case of the Ca^{2+} sensor in MSL 1, the average error was 55%. An error of this magnitude accounted for roughly a factor of 2 difference between the actual and the optimized concentration. The results with the two simulants show that the ISE array is capable of accurately describing samples of diverse composition and concentration.

4.3. Soil Samples

[48] Prior to any analysis, leached and filtered samples of all soil cations, except for NH_4^+, were analyzed with inductively coupled plasma optical emission spectroscopy (ICP). All anion concentrations, including SO_4^{2-}, were determined with ion chromatography (IC). The NH_4^+ analysis was performed using EPA method 350.7.

[49] Conductivity measurements were performed in order to estimate the amount of dissolved material that originated from each soil sample. The Chilean desert samples, Chile 1 and Chile 2, were the most conductive at 767 μS/cm and 2.02 mS/cm, respectively. The Red Rock samples, Red Rock 1 and Red Rock 2, had significantly lower conductivities of 15.8 μS/cm and 21.3 μS/cm, respectively. The composition of the soils was generally as expected, with the highest ionic concentrations resulting from Na^+ and Cl^-. Other ions such as Ca^{2+} and SO_4^{2-} were present in significant but not high concentrations. The ions NH_4^+ and ClO_4^- were not found in any soil tested except Chile 2 where ClO_4^- was detected. The ICP results showed Li^+ to be present only in the Chile samples at levels of about $10^{-5}M$. This value is not significant enough to alter the spiked concentration necessary for the reference measurement. The Li_2SO_4 concentration was originally chosen as $2.5 \times 10^{-3}M$ as to be sufficiently low not to interfere with other cation ISEs but high enough to swamp any Li^+ in the sample. Sulfate, which was present in all four soils, exceeded the Cl^- concentration in both of the Red Rock samples and produced roughly half the anionic concentration in both Chile samples. Even though no SO_4^{2-} ISE was included in this sensor array, it is common to both terrestrial soils and evaporites, and the inclusion of a SO_4^{2-} electrode would be crucial for elucidating Martian geochemistry (assuming of course use of a different lithium salt in the leaching solution).

[50] Comparisons between the actual concentrations and those determined by the ISE array show that, after the spikes were added, the correlation was excellent with some values improving upon the correlation of the soil simulants to the true concentrations. Since these samples were analyzed without prior knowledge of their composition, it was assumed that the correlation between the determined and actual concentrations would be worse than for the leachate simulants. This was assumed because the presence of a high concentration of unmodeled species was possible. However,
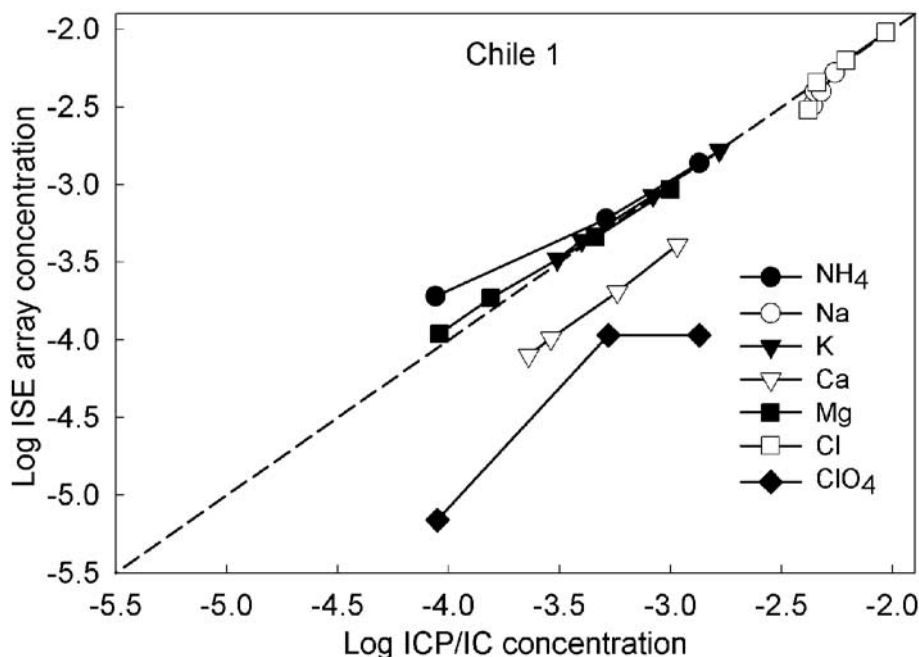
Figure 5. Logarithm of the soil concentration as measured by the ISE array versus the concentration determined from ICP and IC concentrations for the Chile 1 soil sample. Four points are plotted for each ion, composed of the unspiked soil followed by three spikes.

it was found that the actual concentrations were determined very accurately. There were instances where certain ISEs displayed errors, but these values were still accurate to within a factor of 3 or less.

[51] The errors for the unspiked soil samples for all ions were comparable to the simulants, where most determinations fell within roughly 20–30% of the true values. With the spike additions, the error between the actual and array-determined values decreased significantly, with the error often falling to <5% by the second or third spike. It is possible that the spiked soil samples provided more accurate concentrations than the simulants because the spikes contained all the ions that were modeled as part of the array. The soil samples only contained, at most, six of the eight ions. The ions not present in the simulants produced low concentrations and also sporadic responses, sometimes reaching as high as $10^{-4}M$. Thus it is clear that both the array and optimization process poorly describe ions not found in the soil. By spiking with all ions modeled, stable potential responses for all species can be ensured.

[52] Two examples of the soil analysis results are shown in Figures 5 and 6. The log(concentration) determined by the ISE array is plotted versus the log(concentration) as determined by ICP and IC. Ions that were not found native to the soil sample (NH_4^+ and/or ClO_4^-) show only three data points reflecting the three spikes added. For all soils, the initial measurement, prior to spike additions, returned various concentrations for NH_4^+ but were all $<10^{-5}M$. When ClO_4^- was not present in the soil, concentrations lower than the detection limit of $10^{-6}M$ were returned. Nitrate does not appear in any of the plots since the values measured by the sensors were overestimated by as much as 3 orders of magnitude. The presence of ClO_4^- dominated

the NO_3^- response, and no useful information regarding its presence was obtained.

[53] Chile 1 and Chile 2 showed the highest concentration of Na^+ and Cl^- found in the soils. The initial soil readings prior to spike additions show relatively high errors in the concentration determinations for most ions. However, with progressive spikes, these errors decrease significantly and are especially noticeable for the Mg^{2+} and NH_4^+ ISEs. The two Red Rock samples were significantly lower in overall ionic concentration as predicted by the conductivity values. However, their correlations were much more accurate compared to the Chile samples. This was unexpected since it was assumed that the samples with higher concentration would return lower errors. The same trend of increased accuracy with spike addition was seen in these samples as well. However, it was also noticed that the initial soil measurements were also more accurate.

[54] An observation made for all the soils was the consistent error between the true and experimental values of the ClO_4^- and Ca^{2+} ISEs. The Ca^{2+} response was identical to that of the MSL 1 simulant in that it was the only ion to respond linearly, yet have consistent errors of 50–60%. Either the initial factorial calibration was in error or the electrode's response was drifting over time. Initially it was believed that because the simulant and soil sample analyses were performed one month after the factorial calibration, electrode drift could not be ruled out. However, these electrodes were previously shown to withstand freezing temperatures with minimal drift for over 2 years. Therefore it is more likely that the initial calibration was in some way at fault. Individual ISE check calibrations identical to previous primary ion calibrations were carried out to ensure that the intercepts had not shifted. At the time
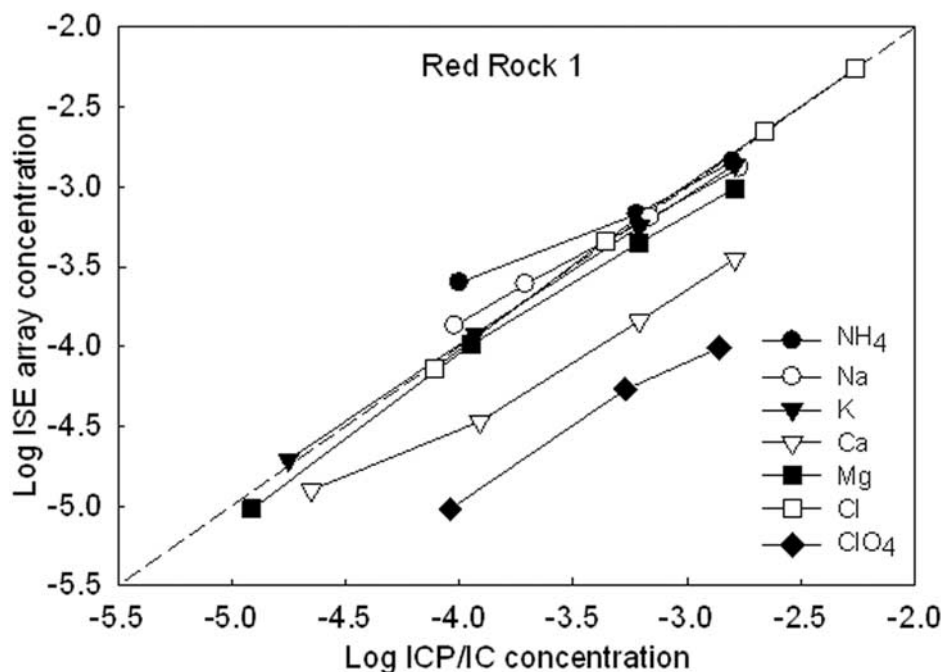
Figure 6. Logarithm of the soil concentration as measured by the ISE array versus the concentration determined from ICP and IC concentrations for the Red Rock 1 soil sample. Four points are plotted for each ion, composed of the unspiked soil followed by three spikes.

of these calibrations, the WCL sensor array had not been used for nearly 6 months and it had been nearly ten months since the last of the individual ISE calibrations were performed. The check calibration results showed that all ISEs exhibited similar responses as obtained with prior calibrations. Minor intercept and slope shifts were encountered but were within 1 standard deviation of the average. Since neither the slope nor the intercept of Ca^{2+} shifted significantly, the consistent errors seen in the concentration values cannot be explained by this a shifting. Rather, it is more likely that the error in the Ca^{2+} fractional factorial calibration was the main contribution to the poor results. The only exception to small shifts was ClO_4^-, which exhibited a negative intercept shift of over 30 mV.

[55] The response of the ClO_4^- sensor to the Chile 2 soil was accurate to within 17%. However, the error progressively increased with each spike and a non-linear response developed. The same was true for the soil samples. The inability to track the potential response of ClO_4^- sensor was surprising since it is selective over all other anions modeled and has been proven to be quite selective over SO_4^{2-}, the only other high concentration anion identified. When the intercept and slope of the ClO_4^- sensor was altered to match those obtained with the check calibration, the results were far more accurate, indicating a shifted intercept was to blame for the poor ClO_4^- performance. This was confirmed by reoptimizing the anion data with the ClO_4^- intercept obtained with the check calibration. The error was greatly reduced.

[56] Since the NO_3^- results were irrelevant because of the presence of the ClO_4^-, the anion concentrations were reoptimized using the data set intended for the cations using Na_2SO_4. This eliminated the effects of the ClO_4^- on the optimization. The NO_3^- response after this alteration was, on average, accurate to within a factor of 4 of the true value.

Although this is a significant improvement on the 3 orders of magnitude overestimation, it still presents a large error. However, given the performance of the NO_3^- sensor and the sub-Nernstian response to primary ion calibrations, this degree of accuracy is not unexpected.

5. Conclusion

[57] The PVC-based membrane ISE sensors were shown to be remarkably robust. Having been stored at $-23°C$ for over 2 years, repeatedly frozen and thawed, calibrated and tested for 6 months, this array has shown that such sensors are suitable for geochemical measurements in harsh terrestrial and extraterrestrial environments. It appears evident that the response of these ISE was not degraded by the prolonged storage at such low temperatures. Although not routinely recommended, cold storage had several advantages over conventional liquid or dry storage for these ISEs. The lifetime of an ISE is related to the amount of contact with aqueous solutions since the ionophore and plasticizer membrane components slowly leach out into solution rendering the ISE less and less reliable over time; therefore dry storage is typically recommended for prolonged periods. However, the hydrogels would quickly dry out in this case. Thus it appears that storage at subzero temperature is actually preferable for the WCL ISEs in that the hydrogels are frozen in a humid atmosphere ensuring hydration and the PVC membrane components will not leach during storage.

[58] Both primary ion and leaching solution calibrations displayed excellent reproducibility over several freeze/thaw cycles. Our studies found interferences due to ClO_4^-, most notably that it altered the overall slope of the Ca^{2+} sensor, the linear range of Na^+, and dominated the NO_3^- response. Thus, for future designs, it would be optimal to replace the ClO_4^-

ISE with a SO_4^{2-} ISE. In terms of overall design, the MECA-WCL was only intended for a one-time measurement, and thus it is not optimal for dealing with multiple solutions.

[59] Because of the soil measurement sequence listed in section 2.1, and the poor slope of the Ca^{2+} ISE during the leaching solution tests, it is unlikely that this ISE's poor response would have been noticed. This would have certainly resulted in an inaccurate determination of the Ca^{2+} concentration. However, had a simple two point calibration been implemented prior to soil addition (i.e., leaching solution addition followed by a reagent pellet addition), this situation would have been identified, and corrections to subsequent soil data would have been attempted. Similarly, the consistent errors observed from the Ca^{2+} ISE for the simulant and soil sample results would have not been detected until after the experiment was concluded. The cause of the errors may lay in a flawed factorial calibration or a temporary intercept shift. However, both explanations can be rendered invalid because of the low error value associated with the factorial calibration and the similar slope and intercept values obtained with check calibrations, respectively. However, a simple two-point precalibration procedure prior to soil analysis would have identified the issue, and appropriate measured to rectify the situation could have been taken.

[60] The use of the fractional factorial calibration coupled with Solver successfully described the slope, intercept, and selectivity coefficients of eight ISEs. These results were used to determine the concentrations of these eight ions in complex samples of soil leachate simulants and soil samples. Although errors were encountered in the determining the concentrations, the overall conclusion is that the sensor array successfully predicted the concentrations of the constituent ionic species.

[61] The simulants and samples exposed to this array consisted of several salts within a large concentration window. The selectivity issues, sensor noise, and incompatibilities that were experienced are not unlike what might occur if this array was performing an extraterrestrial chemical analysis. The 8-month journey to Mars would affect the sensors in unknown ways and the current operating condition of this array reflects the possible difficulties that might be encountered. The optimization shows that the soils and simulants can be chemically characterized reasonably well using an array of carefully selected ISE sensors.

[62] The ISE sensor array used here was effectively a prototype and can undoubtedly be improved upon by better selection of the individual array members and by improving the composition of the active ISE components. Because the WCL was designed for only one measurement, we can confidently predict that for its primary mission the MECA-WCL would have most likely survived the journey to Mars and would have been able to carry out geochemical analyses on the Martian surface for several days.

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