Full Paper

Analysis of Simulated Martian Regolith Using an Array of Ion Selective Electrodes

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Abstract
A prototype miniature array of polymer membrane and solid state ion selective electrodes was developed for the purpose of performing an in-situ analysis of the soluble ionic species in Martian regolith (soil). The array contains a total of 27 electrodes for K^+, Na^+, Ca^{2+}, Mg^{2+}, NH_4^+, Ba^{2+}, NO_3^-, Cl^-, and Li^+, each in triplicate. Barium electrodes were used to indirectly monitor sulfate through precipitation by the addition of barium chloride while the lithium electrodes served as a reference for the array by having a constant lithium concentration as a background for all solutions. The array was tested with several types of simulants, soils, and sawdust from a Mars meteorite, all with varying salt content, meant to approximate the various hypotheses regarding the ionic composition of the Martian soil. The activities of anions and cations determined with the array were compared to ion chromatography data.

Keywords: Ion selective electrode, Array, Mars, Regolith, Meteorite, Soil, Ion chromatography, Geochemistry, Electrochemistry

Devoted to the Memory of Professor Robert (Bob) Osteryoung

1. Introduction

The primary application of ion selective electrodes (ISEs) is arguably in the field of clinical chemistry [1–3]. However, instances of ISEs used for analysis for environmental purposes, specifically of soil samples, are also prevalent [4–6]. For samples where multiple ionic concentrations are desired, such as in a soil/water mixture, using an array of ISE sensors can provide unique and advantageous analytical data. The choice of sensors to include in an array is dependent upon on the assumed ionic content of the sample. For our application, it was critical that the ISE array contain sensors selective for the major ions found in a soil/water mixture. For terrestrial soils, these ions include Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, Cl^-, NO_3^-, SO_4^{2-}, and HCO_3^-/CO_3^{2-} [7]. Currently, selective ionophores for all these ions, except sulfate, exist and are widely used [8, 9].

Using ISEs to measure terrestrial soil samples can be difficult since there may be unknown interferents present, but at least the ionic concentrations will generally be known or reasonably estimated to within a certain range beforehand. However, measuring the ionic content of a totally unknown regolith sample on the surface of Mars presents some very unique challenges. Among these are; fabricating ISEs rugged enough to survive a journey through space lasting nearly a year, extreme temperature variations, radiation, enduring the ambient Mars conditions upon arrival and several month afterwards, and the requirement of being of very small in mass and volume since both are at a premium on planetary missions.

In previous Mars missions, such as Viking and Pathfinder, X-ray fluorescence (XRF) analysis was performed on various rocks and soils [10, 11]. While the XRF data have proved invaluable, they do not provide direct evidence for the presence of soluble inorganic species, particularly salts. The most recent missions, the 2003 Mars Exploration Rovers (MER) Spirit and Opportunity, have returned data strongly confirming that the Martian surface had at some point been exposed to liquid water. Through the detection of minerals such as jarosite and hematite, which on Earth are typically are formed by prolonged exposure to aqueous environments [12, 13], it is a reasonable assumption that Mars once possessed a far different climate that allowed for large standing bodies of water. The primary conclusion that can be drawn from this new MER evidence is that there should be a relatively high salt content in the soil leached and deposited by the once freely flowing water on the surface. However, knowledge of the elemental (XRF) composition of the soil and the fact there was water on the surface at some point, does not necessarily allow us to accurately predict the ionic content of a regolith/water mixture. All that can be assumed is the probable existence of salts as extrapolated from the XRF data of the most recent missions [14, 15]. The returned data shows upper and lower limits for elements such as chlorine and sulfur in amounts of 0.1 to 0.7% and 1 to 25% by weight, respectively. Assuming these two forms are completely found as chloride and sulfate, the upper and lower bounds of the salt content in the soil can be estimated. However, there is currently no way to know the actual chemical form of these elements. Therefore,

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an ISE array is ideally suited to determining the ionic concentrations of evaporite salts left behind from this ancient Martian surface water.

The 2001 Mars Surveyor mission included an instrument package designated as the Mars Environmental Compatibility Assessment (MECA). Included as part of MECA were four Wet Chemistry Labs (WCL), with each WCL containing an array of ISEs [16, 17] mounted within the walls of a beaker having a 25 mL volume. Four WCLs, built to print, are now part of the 2007 Phoenix Mars Scout Mission. The ISE arrays in the MECA-WCL performed very well under all environmental and physical tests. They were characterized and tested with several soil simulants and desert soil samples meant to simulate a possible Martian regolith. However, the WCL design would allow only one sample to be measured with each array. It was felt that for future missions, more samples were needed in order to provide a more accurate overall chemical composition of the soil. In Addition, the ISE sensor arrays for the current MECA-WCL, with the exception of the reference electrodes, have no redundancy, nor did they have any capability for measuring sulfate, an anionic species of great geochemical interest . The concept of redundancy in the electrodes has two important implications. First, having multiple electrodes of each type allows averaging of the electrode responses and rules out the possibility of a faulty measurement. Secondly, if one or more of the electrodes should fail at any time, the redundant electrodes are still operable, resulting in no sacrifice in measurement.

In an attempt to improve upon the design of the WCL ISE arrays, we proposed the development of a miniature ISE array that could function as a "dip probe", allowing multiple soils to be measured with the same probe. The goal was to have a functioning array capable of measuring a soil sample in a test tube having an overall volume of 10 mL. In order for this to work, the array itself could be no larger than roughly 1.25 cm in width and 5 cm in length. We present here the initial results of an ISE array with a total of 27 electrodes, triplicates of K^+, Na^+, Ca^{2+}, Mg^{2+}, NH_4^+, Ba^{2+}, NO_3^-, Cl^-, and Li^+. The described array not only has a greatly reduced mass/volume compared to the WCL array, largely due to its planar configuration, but also redundancy in all sensors, and the capability to measure sulfate indirectly through the use of a barium ISE.

2. Experimental

2.1. Chemicals

Valinomycin (potassium ionophore I), 4-*tert*-butylcalix[4]-arene-tetraacetic acid tetraethyl ester (sodium ionophore X), ETH 5234 (calcium ionophore IV), ETH 5506 (magnesium ionophore VI), Nonactin (ammonium Ionophore I), Barium ionophore I, Lithium ionophore VI, dioctyl sebacate (DOS), *ortho*-nitrophenyl octyl ether (*o*-NPOE), potassium tetrakis(4-chlorophenyl) borate, (KTpClPB), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), tridodecylmethylammonium nitrate (TDMAN), high molecular weight poly(vinyl chloride) (PVC), and tetrahydrofuran (THF) were all Selectophore grade from Fluka. Chlorides of potassium, sodium, barium and lithium were puriss from Fluka. Ammonium nitrate, calcium chloride and magnesium chloride were ACS reagent grade from Aldrich. The monomer 2-hydroxyethyl methacrylate (HEMA) and photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPAP) were from Acros. Minerals used as geochemical simulants were obtained either from the Tufts geology department or from Ward's Natural Sciences (Rochester, NY). All solutions were made using 18 MΩ Nanopure water. When the lithium ISEs were used as the reference electrodes, all solutions contained a background of 5 mM lithium acetate.

2.2. Ion Selective Electrodes

Due to the unusual application of these electrodes, their design and fabrication differs significantly from conventional ISEs. The classical liquid inner filling solution was impractical due to the extreme temperature fluctuations. By substituting a poly(HEMA) hydrogel for the inner reference solution, the electrodes can be fabricated with much smaller dimensions and are far more rugged when faced with sub 0 °C temperatures [17]. Figure 1 shows a cross section view and dimensions of one of the electrodes used in the array.

The individual ISEs were machined from a 3.2 mm thick PVC sheet into square housings having a length and width of 3.5 mm. The appropriate diameter wells for the silver wire and poly(HEMA) hydrogel were then milled. A silver wire (1 mm diameter, 99.999% purity) was then epoxied into the rear of the housing. The Ag/AgCl internal reference element was electrochemically generated using 0.1 M NaCl and applying a potential of +0.5 V vs. Ag/AgCl reference for three minutes using a EG&G263 potentiostat. Once the Ag/AgCl layer was washed and dried, the HEMA monomer solution (containing both an organic and aqueous phase) was pipetted into the well until it was flush with the outside of the housing (10 μL). The organic phase contained the HEMA monomer with 2% wt DMPAP photoinitiator. The aqueous phase was a 10^{-3} M solution of the primary salt. In all cases, except NO_3^-, this was a metal chloride. For the NO_3^- ISE, a mixture of 10^{-3} M NaCl and NH_4NO_3 was used. The organic and aqueous solutions were mixed together in a 56:44 weight ratio and UV cured for 7 minutes. Lastly, the PVC membrane was applied on top of the poly(HEMA) layer.

The compositions of the polymer membranes are listed in Table 1. For a given membrane, a total component weight of 250 mg was dissolved in 2.5 mL of THF. The cocktail was poured into a glass ring (2.54 cm inner diameter) fixed to a glass plate and the solvent was allowed to evaporate overnight. This master membrane was then kept in a Petri dish until needed. Individual membranes were bored from the master membrane with stainless steel tubing having a

Table 1. Ion-selective polymer membrane compositions in weight %.

Ion	Ionophore	KTpClPB [a]	NaTPFB [a]	TDMAN	PVC	DOS	*o*-NPOE
K^+	1.1	–	55	–	32.5	65.8	–
Na^+	0.9	65	–	–	32.9	–	65.9
Ca^{2+}	1.3	–	51	–	32.8	–	65.2
Mg^{2+}	1.0	150	–	–	32.9	–	65.4
NH_4^+	1.0	–	46	–	32.9	65.4	–
Ba^{2+}	1.2	–	75	–	32.7	–	64.8
Li^+	1.0	–	53	–	32.5	–	65.2
NO_3^-	–	–	–	6.0	29.0	–	65.0

[a] mol % relative to ionophore

3 mm inner diameter. This membrane was then glued to the PVC housing with 10 µL THF and allowed to dry. All electrodes were conditioned overnight in a solution identical to the aqueous component of the hydrogel.

For the chloride electrodes, the ISE housings were similar to Figure 1. However, the silver wire was extended all the way through the housing and epoxied. The face of the wire was sanded with 240 and 500 grit sandpaper to form a smooth 1 mm diameter Ag disk and then anodized to form a Ag/AgCl electrode. All individual ISEs were calibrated several times prior to incorporation into the array to ensure proper response.

In the early attempts to combine the electrodes in an array format, THF was used to glue the ISEs together with no spacing between neighboring electrodes. The result was massive cross contamination of dissimilar neighboring PVC membranes with inevitable electrode failure. To prevent this, similar neighboring ISEs were separated by a 0.3 mm thick PVC film and dissimilar ISE neighbors were separated with a 0.5 mm thick PVC film. Although this added to the already restrictive size of the array, the separators greatly reduced cross-contamination and allowed the array to be fabricated within the required tolerances. When fully assembled, the array measured 11.5 mm in width and 36 mm in length. All ISEs and separators were glued together with small aliquots of THF and allowed to dry. Since all ISEs in the array had previously been calibrated, no further pretreatment of the electrodes was necessary. The array was stored in a sealed hydrated environment and frozen for several days at −20 °C to simulate Martian ambient conditions.

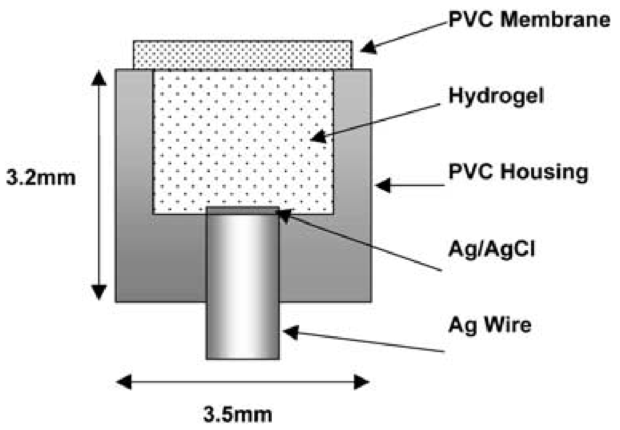

Fig. 1. Cross section of a hydrogel-based ion selective electrode. The length of each electrode is identical to the given width.

2.3. Sample Preparation

To properly characterize the array, we chose to divide the samples into three categories: aqueous simulants, geochemical simulants, and soil (regolith) samples. In all, five aqueous, nine geochemical, and seven soil samples were analyzed with the array. For brevity, we report the findings of two of each type.

The composition of the two aqueous simulants were based on the work of Clark & VanHart [19] and are tabulated in Table 2. Both were dilutions of concentrated stock solutions meant to simulate a Martian soil leachate. The first is a dilution of a highly concentrated New Mexico brine. The brine (hereafter called AQ1) is unique in that it contains a sulfate concentration that is nearly five times that of chloride, the opposite typically found in brines. The second (AQ2) is a less concentrated sample composed of magnesium sulfate and sodium chloride.

The geochemical simulants were composed of a mixture of natural minerals and were formulated to be chemically identical to several literature Martian soil estimates based on the results of the XRF data from past Mars missions. XRF analysis has returned elemental data only, thus the concentration of ionic compounds believed to be present in the Martian soil varies widely in the literature. One geochemical simulant (GEO1) was modeled after Viking XRF data and is composed of minerals and a high concentration of salts [20]. The other, GEO2, modeled after the same data,

Table 2. Chemical composition aqueous simulants (mol/L).

Salt	AQ1	AQ2
$MgSO_4$	6.4×10^{-2}	1.9×10^{-2}
NaCl	2.0×10^{-2}	5.1×10^{-3}
Na_2SO_4	2.8×10^{-2}	–
$KHCO_3$	8.0×10^{-4}	–
KNO_3	1.2×10^{-3}	–
$Ca(NO_3)_2$	1.2×10^{-4}	–

Table 3. Geological composition of geochemical simulants.

GEO1			GEO2		
Mineral	Description	% wt.	Mineral	Description	% wt.
Quartz	SiO_2	23	Orthoclase	$KAlSi_3O_8$	8
Feldspar	$KAlSi_3O_8$	16	Albite	$NaAlSi_3O_8$	8
Diopside	$CaMgSi_2O_6$	7.8	Diopside	$CaMgSi_2O_6$	26
Hypersthene	$(Mg,Fe)_2Si_2O_6$	17.2	Hypersthene	$(Mg,Fe)_2Si_2O_6$	53
Hematite	Fe_2O_3	18	Olivine	$(Mg,Fe)_2SiO_4$	1
Ilmenite	$FeTiO_3$	3	Magnetite	Fe_3O_4	2
Halite	NaCl	1	Ilmenite	$FeTiO_3$	2
Thenardite	Na_2SO_4	14			

has an assortment of minerals, but no soluble salts [21]. It should be noted that the two simulants have the same overall elemental makeup but are chemically very different. Their geochemical compositions are listed in Table 3.

The first of the two soil (regolith) samples was provided by NASA's Johnson Space Center, and consisted of a volcanic salt-rich Palagonite collected from South Point Hawaii (HWSP352). The second consisted of "sawdust" from the SNC class Shergottite Martian meteorite EETA79001 [18]. This is the meteorite that, via chemical and isotopic analysis of gases trapped in glass inclusions, has provided the conclusive evidence that SNC meteorites are from Mars.

To avoid possibly damaging the PVC membranes with mineral particles, all simulant samples were filtered and only the leached solution was exposed to the array. The geochemical simulants and soil samples were weighed out in amounts (Table 3) that assumed 1.5 g of soil would be added for every 25 mL of water. The final mixture was then added to the appropriate volume of deionized water and stirred for one hour to leach the ionic content of the sample. The sample was then gravity filtered with Whatman #1 paper into a clean polypropylene bottle and kept at 4 °C until needed. For all samples, separate aliquots were obtained for pH and conductivity measurement utilizing Orion probes 92–72 and 13005D, respectively (Thermo Electron Corporation). A second aliquot of the sample was reserved for ion chromatography (IC) analysis. Depending on the magnitude of the conductivity measurement, appropriate dilutions were made. The remaining portion of the sample was used for the ISE array measurement.

2.4. Potentiometric Measurements

All data obtained from the ISE array was acquired with a 16-channel electrode monitor (Lawson Labs Inc., Malvern, PA) connected to a laptop. To accommodate the number of electrodes in the array, the number of outputs from the electrode monitor was doubled with the use of a homemade switchbox using four 4-pole double throw switches. During a given experiment, the potentials were monitored from the first 16 ISEs for two minutes per spike, the switches were thrown, and the potentials from the remaining ISEs monitored for an additional two minutes. The data were acquired at two second intervals and averaged during the last 60 seconds of the measurement. Activities for all ISEs were calculated according to Nikolskii-Eisenman equation.

$$E_M = E^o + \frac{2.303RT}{z_I F} \log\left(a_I(aq) + \sum K_{IJ}^{pot} a_J(aq)^{z_I/z_J}\right) \quad (1)$$

Here, E° and E_M are the standard potential and the measured potential, R, T, z, F, and K are the gas constant, absolute temperature, ionic charge, Faraday's constant, and selectivity coefficient, respectively. The subscripts I and J refer to the primary and interfering ions respectively. This equation has long been known to inaccurately predict EMF values for ions of varying charge [1]. However when the results were compared with a more recent equation reported to more accurately model any number of mono and divalent ion interferences [22], the results were no different. The lack of discrepancy between the two equations was attributed to the relatively high concentrations of all ions measured and the excellent selectivity coefficients obtained. Additionally, Microsoft Excel's Solver was used to minimize the sum squared error between the observed potentials and those predicted with Equation 1 by using an iterative optimization method [23]. Following analysis of the sample, two spikes of barium chloride of 5 and 50 mM were added to precipitate all sulfates (volume/mass restrictions allowed only one reagent tablet to be added to the WCL in the 2001 mission. The 2007 mission will have the capability to add up to three reagent tablets). For sulfate quantification, the barium activity was determined alongside the other five cations. This value was compared to the predicted activity of barium given the volume and concentration of the spikes. The difference between the two values was assumed to be equivalent to the activity of the sulfate in the sample. This method takes into account the selectivity of the barium electrode which other methods such as titrations and standard subtraction methods overlook.

A ThermoOrion 90-02 double junction reference electrode, filled with either 1 M lithium acetate or 0.1 M sodium chloride, was used for calibration and selectivity coefficient determination purposes. Corrections for junction potentials using the Henderson equation were only deemed necessary when the reference electrode was filled with sodium chloride. For any experiment other than calibration, one of the three lithium ISEs was used as the reference electrode. In order to calibrate all the ISEs simultaneously, a multi-ion stock solution was used containing 10^{-1} M NaCl, KCl, $CaCl_2$, $MgCl_2$, $BaCl_2$, NH_4NO_3 and 5×10^{-3} M LiAc. Using this solution, calibration curves for all cations and nitrate could be obtained from 10^{-4} to 10^{-2} M with simple spikes (the concentrations for chloride were somewhat higher). The multi-ion calibrations were performed regularly to verify the working condition of all electrodes in the array. All activity coefficients were calculated according to the Debye-Hückel equation.

2.5. Ion Chromatography

All samples containing particulate matter were analyzed using ion chromatography (IC). A Dionex ICS-2000 instrument was used with potassium hydroxide eluent and an AS18 column for anion analysis and methanesulfonic acid eluent and a CS12A column for cation analysis. Calibration standards of eight common cations and eleven anions were made using 1000 ppm standards (Absolute Standards Inc. Hamden, CT). To prevent particulates from entering the instrument lines, all samples were injected with the use of Anotop IC syringe filters (Whatman). All samples were run in triplicate and the results averaged. In order to allow accurate comparisons between the activities determined by the ISE array and the concentrations found using IC, an ionic strength was calculated based on the sum of concentrations for all ions, and activities then calculated.

3. Results and Discussion

3.1. Calibration of the Array

After the array was assembled, each electrode type was calibrated in respect to its primary ion from 10^{-8} to 10^{-1} M. All ISEs responded rapidly, with Nernstian behavior, and nearly all displayed a linear range to 10^{-5} M. All ISEs were monitored during the calibrations to provide qualitative information on selectivity. Additionally, all ISEs were calibrated simultaneously with the use of the multi-ion stock solution. Figure 2 shows the results of one electrode per species of this multi-ion calibration. The EMF response for each electrode is plotted versus the individual ion activity. For comparative purposes, the Li-ISE response is plotted at three concentrations values, even though its concentration was constant, as a check on any effects due to increases in ionic strength with each successive spike. This plot demonstrates the effectiveness of using lithium as a reference system. While all other electrodes displayed Nernstian slopes over the three order of magnitude calibration, the lithium ISE experienced a total EMF change of < 1 mV.

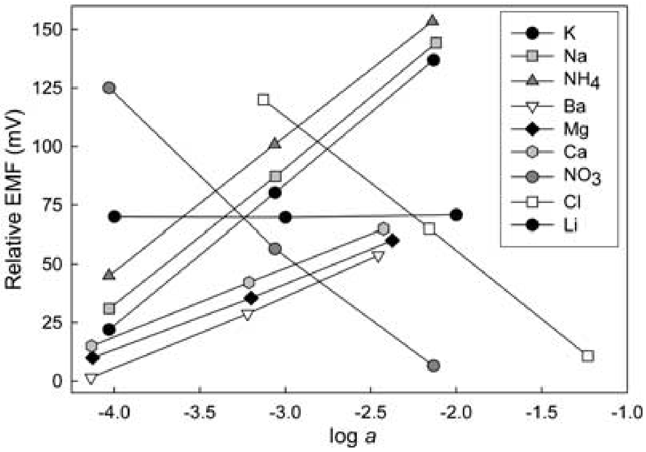

Fig. 2. Resulting plot of a multi-ion calibration in which one electrode per species is shown for clarity. Potentials are normalized for clarity.

3.2. Selectivity Coefficients

Unbiased selectivity coefficients were determined using the separate solution method (SSM) for all polymer membrane ISEs according to a well established procedure [24]. Separate electrodes were made for each species so the poly(HEMA) hydrogel could be filled with an interfering salt. In all cases except for the sodium ISE, the hydrogel contained 10^{-3} M NaCl; for sodium, KCl was used. EMF values were obtained using the ThermoOrion 90-02 with 1 M lithium acetate for all electrodes except lithium which used 0.1 M sodium chloride. For all species, the results of three electrodes were averaged. Nernstian slopes were observed for all interfering as well as primary ions as seen for one of the lithium ISEs in Figure 3. Selectivity coefficients of the solid state chloride ISE were obtained by the SSM method as well. However, the potential of the electrode was only measured in 10^{-1} M solutions. Table 4 displays the log

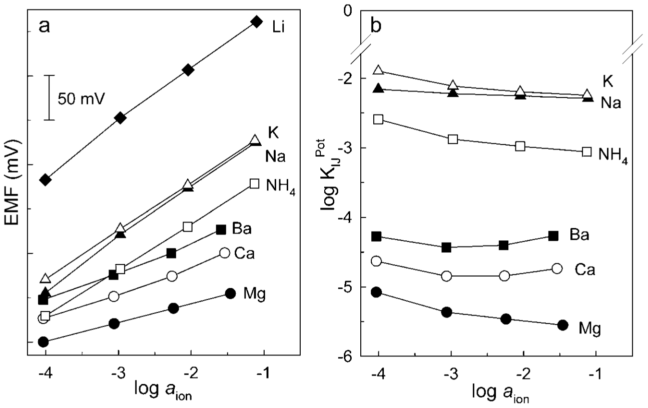

Fig. 3. a) Resulting Nernstian slope responses of lithium ISE to primary and interfering ions accomplished with NaCl filled hydrogel. b) Selectivity coefficients obtained from data in (a). Because of Nernstian response, selectivity is largely independent of sample activity.

Table 4. Determined log K_{IJ}^{pot} values for cation and anion ISEs.

	Interfering Ion, J						
Primary Ion, I	K^+	Na^+	Ca^{2+}	Mg^{2+}	NH_4^+	Ba^{2+}	Li^+
K^+	–	−4.9	−7.0	−7.5	−1.9	−6.6	−6.1
Na^+	−2.4	–	−5.0	−5.7	−4.8	−5.2	−3.2
Ca^{2+}	−8.2	−6.6	–	−8.2	−7.6	−3.1	−6.4
Mg^{2+}	−3.0	−4.3	−1.4	–	−3.4	−2.3	−4.4
NH_4^+	−0.8	−2.9	−5.7	−5.9	–	−6.0	−4.7
Ba^{2+}	−3.4	−3.1	−1.7	−8.1	−3.9	–	−4.2
Li^+	−2.3	−2.3	−4.7	−5.6	−3.1	−4.3	–
	Cl^-	NO_3^-	Ac^-	SO_4^{2-}	HCO_3^-	Br^-	
Cl^-	–	−3.6	−3.5	−3.9	−3.5	2.6	
NO_3^-	−2.0	–	−3.1	−3.0	−2.9	−0.8	

K_{IJ}^{pot} values obtained for all ISEs. For the cation ISEs, the selectivity coefficients have been well established [8] and the values obtained were as expected. However, the results did prompt some concern for the samples to be analyzed. Accurate detection of ammonium would be very difficult owing to its poor selectivity over potassium. The reverse is not necessarily true since in soils, potassium is almost always much more concentrated than ammonium. Likewise, magnesium, and to a lesser extent barium, would pose some difficulty if there is an excessive calcium content, which may be very likely. The values obtained for the lithium ISE reveal that this electrode is well suited as a reference. All selectivity coefficients were such that no significant interferences were predicted. The nitrate ISE is selective over all tested anions, but is known to suffer drastic interferences from highly lipophilic anions [25]. The chloride ISE showed very little interference except from bromide. Owing to the greater insolubility of silver bromide over silver chloride, this electrode displays a preference for the bromide anion [26]. Given the selectivity coefficient, an accurate chloride measurement is possible assuming that the chloride concentration is in excess of bromide roughly three orders of magnitude, which is the case for Earth's oceans.

3.3. Ion Chromatography of Simulants

The analyses of the samples using IC resulted in major peaks for sodium, potassium, calcium, magnesium, chloride, and sulfate in all samples. Other ions were also detected but all were at trace levels (< 1 ppm) and did not pose any interference to the ISEs. Unidentifiable peaks were observed in only a small number of the samples, but due to their small size they were ignored. A carbonate peak was seen in all anion runs, but due to the limitations of the instrument, this ion was not quantified. Bromide was observed in most samples with low ionic strength. However, the chloride concentration was in excess by at least three orders of magnitude, putting to rest any concern about interferences with the solid state chloride ISE. The IC results demonstrated that the ISE array contained all the electrodes required to provide an accurate description of a leached soil sample.

The span of ionic strengths estimated from the ion concentrations was quite large. GEO1, with its high sulfate concentration resulted in a calculated ionic strength of 0.18 M, while the meteorite sample EETA79001 had a value of only 0.8 mM. The ionic strengths are likely very accurate since they were calculated based on all observed ion concentrations. It is possible that ions were present in the samples that the IC columns were not able to detect, such as very lipophilic anions (e.g., iodide and perchlorate) and transition metal cations, but it is unlikely they were present in high concentrations and thus would not have affected ionic strength significantly.

3.4. Sample Data

To simulate an experiment on Mars, the array was calibrated using the multi-ion approach prior to each sample analysis. By beginning at the lowest concentration in the Nernstian range of each electrode and spiking to a slightly higher level, the slope and intercept of each electrode could be determined. These pre-sample calibration data could be compared to the corresponding overall multi-ion calibration of that day to ensure all electrodes were behaving according to theory at lower levels. The multi-ion stock solution had to be modified to account for the limited linear range of some ISEs. Following the pre-sample calibration step, the array was inserted into a sample having a background identical to the final concentration of the pre-sample experiment. Once the potentials of all electrodes were read, the barium chloride spikes were added and activities calculated.

When multiple samples were read in sequence, this pre-sample calibration step decreased in effectiveness, i.e. the detection limit of the electrodes increased. Although the array was rinsed several times with deionized water between samples, there was undoubtedly some memory effect in the PVC membranes, especially when the previous sample was highly concentrated. In these cases, the slopes of the multi-ion calibration were used and a new intercept was calculated. Before any activity calculations were attempted, a nearly identical change in the potential from the final pre-sample calibration measurement to the sample measurement was confirmed with the three replicate ISEs of each species, indicating the resulting activities would be very precise.

It was expected that the aqueous simulants would provide the most accurate results of all the three types of samples due to the simplicity of their composition and absence of unknown species. The resulting activities determined with both the ISE array and IC analysis are shown in Table 5 with pH and conductivity data also included. For AQ1, the high magnesium content versus the much lower calcium concentration resulted in little interference for the magnesium electrode. The activity was determined with less than 20% error, which is acceptable. Other ions were determined with similar, if not much less, error. The ammonium was grossly underestimated. The error associated with this species was likely due to the high interfering concentration of potassi-

Table 5. Comparison of actual aqueous simulant activities (mmol/L) and those determined by the ISE array. Standard deviation given for ISE measurements ($n = 3$).

	AQ1		AQ2	
Ion	Actual	ISE	Actual	ISE
K^+	1.34	1.41 ± 0.20	0.02	0.03 ± 0.003
Na^+	52.05	50.09 ± 5.11	4.08	5.10 ± 1.15
Ca^{2+}	0.04	0.03 ± 0.001	0.01	0.01 ± 0.001
Mg^{2+}	21.21	17.37 ± 5.15	8.86	10.13 ± 4.77
NH_4^+	0.02	0.001 ± 0.001	0.02	0.02 ± 0.003
Cl^-	12.97	11.86 ± 0.79	4.14	3.71 ± 0.36
NO_3^-	0.98	1.65 ± 0.27	0.02	0.28 ± 0.05
SO_4^{2-}	18.73	> 13.5	7.10	7.48 ± 1.21
pH	7.63	–	5.72	–
Conductivity	13.0 mS/cm	–	3.29 mS/cm	–

um. Such errors with ammonium were also seen in other samples using simulants as well as soils. The sulfate content of the sample was not quantifiable since the potential of the barium electrode was unchanged after the final spike of barium chloride, indicating that all the spiked barium was precipitated as barium sulfate leaving no ionic barium for potentiometric detection. This illustrates a shortcoming with the standard subtraction sulfate determination method. In instances such as these, only a qualitative statement can be made regarding the sample sulfate content (Table 5). However, when dealing with an unknown sample such as Martian soil, where only the elemental sulfur abundance is known, this type of response would prove quite valuable since it would constrain the sulfur speciation.

Sample AQ2, having a much lower conductivity, had a sulfate content lower than the most concentrated barium spike and thus it was possible to calculate the its concentration, using the above described method, to within a 5% error. Although this method is not ideal, it is the best technique involving only one or two reagent additions that we have tested. A better method would be to use a multi-point titration, or to utilize a selective sulfate ionophore. However, given the circumstances and limitations, this method is quite sufficient. For other ions in this simulant, the activities determined with the ISEs were largely within one standard deviation of the IC values.

While the mineralogical composition of the geochemical simulants was known, it was not known what soluble ions would be present. Aside from the sodium sulfate content of GEO1, it was predicted that small amounts of calcium, magnesium, potassium, chloride, and sulfate would be seen in both simulants, mostly arising from impurities in the minerals used. IC data revealed between 1–5 ppm for all the ions listed above in both samples. The chloride, sulfate, and sodium in GEO1 were several orders of magnitude higher, as would be predicted from the compositions given in Table 3.

Table 6 gives the results of the combined data for these two simulants. All ions, except sulfate, in GEO1 were determined accurately even though there was enormous variation in its chemical composition. Similar to AQ1, the sulfate content of GEO1 exceeded the highest barium spike concentration. It should be noted that out of the 21 samples tested, GEO1 and AQ1 were the only two that had excessive sulfate levels; all others were within the upper limits of the barium additions. GEO2 was initially chosen to see how the array would fare with a less conductive sample. Surprisingly, this was overall one of the most accurate samples. Since the potential changed little for nearly all species from the pre-calibration potentials, there was a high degree of accuracy in the resulting activities. Potassium, calcium, nitrate, and chloride agreed with the IC data to within 10% while ammonium, magnesium, and sodium were all within 30%. The sulfate concentration was overestimated by a factor of fifty due to the inability of the barium electrode to detect such a small change in concentration. The poor sulfate determination in low conductivity samples led to the inclusion of a third spike to be utilized in all subsequent samples. The addition of a 0.5mM barium chloride spike would allow lower sulfate concentrations to be more accurately determined. Most of the geochemical simulants had high concentrations of sulfate and did not require this additional spike of barium. However, it was assumed that

Table 6. Comparison of activities (mmol/L) determined by ion chromatography and the ISE array for geochemical simulants (standard deviation, $n = 3$).

	GEO1		GEO2	
Ion	IC	ISE	IC	ISE
K^+	0.08 ± 0.005	0.05 ± 0.01	0.05 ± 0.0001	0.05 ± 0.01
Na^+	95.93 ± 0.061	74.96 ± 8.84	0.22 ± 0.001	0.17 ± 0.03
Ca^{2+}	0.05 ± 0.005	0.03 ± 0.001	0.05 ± 0.0002	0.05 ± 0.002
Mg^{2+}	0.03 ± 0.002	0.05 ± 0.03	0.06 ± 0.001	0.04 ± 0.01
NH_4^+	0.08 ± 0.005	0.004 ± 0.001	0.05 ± 0.003	0.03 ± 0.005
Cl^-	7.59 ± 0.023	9.57 ± 0.62	0.37 ± 0.001	0.40 ± 0.01
NO_3^-	0.03 ± 0.002	0.07 ± 0.08	0.03 ± 0.0001	0.03 ± 0.01
SO_4^{2-}	15.14 ± 0.077	> 13.5	0.03 ± 0.001	1.42 ± 0.90
pH	6.69	–	7.24	–
Conductivity	12.0 mS/cm	–	36.5 μS/cm	–

Table 7. Comparison of activities (mmol/L) determined by ion chromatography and the ISE array for soil samples (Standard Deviation, $n = 3$, [a] result of 1 electrode).

Ion	EETA79001		HWSP352	
	IC	ISE	IC	ISE
K^+	0.03 ± 0.0001	0.02 ± 0.01	1.44 ± 0.04	1.51 ± 0.27
Na^+	0.26 ± 0.001	0.20 ± 0.02	58.80 ± 0.076	61.17 ± 7.07
Ca^{2+}	0.12 ± 0.001	0.08 ± 0.01	0.09 ± 0.004	0.03 ± 0.01
Mg^{2+}	0.16 ± 0.001	0.13 ± 0.01	0.44 ± 0.014	0.30 ± 0.18
NH_4^+	0.03 ± 0.0003	0.01 ± 0.01	0.02 ± 0.00	0.001[a]
Cl^-	0.36 ± 0.0001	0.35 ± 0.01	52.43 ± 0.048	62.12 ± 14.26
NO_3^-	0.03 ± 0.0001	0.15 ± 0.19	0.04 ± 0.003	1.37 ± 2.36
SO_4^{2-}	0.03 ± 0.0002	0.09 [a]	1.04 ± 0.002	1.34 ± 0.19
pH	8.61		8.32	
Conductivity	83.9 μS/cm		7.99 mS/cm	

the soil samples would require the additional spikes based on their lower conductivity values.

The meteorite sample, EETA79001, was slightly more conductive than GEO2, but was still low in overall ionic content (Table 7). All ions except for ammonium were determined within a 25% error. Considering this sample originated from Mars, this could be seen as a true test of the array's abilities to describe the activities of a totally unknown extraterrestrial sample. Although the error was slightly higher than other samples, the activities of potassium, sodium, calcium, magnesium and chloride were all determined within one standard deviation of the mean activity. Nitrate and ammonium returned values with greater error, attributed to interferences from other ions at high concentrations. Nitrate may have been influenced by an undetected lipophilic anion while ammonium was likely influenced by potassium. However, the sulfate information was far more accurate with the addition of the third barium spike. Here, the sulfate concentration was slightly higher than that of GEO2, but was found within a factor of 2.5. For comparison, the determined sulfate concentration with GEO2 was overestimated by a factor of fifty. If the EETA79001 sample used the same barium spike for its sulfate concentration, the error would have been similar. During the measurements, two of the three barium ISEs began to respond with anionic slopes and only the remaining ISE could used, illustrating further the importance of having redundancy in a senor array.

The high conductivity of the HWSP352 sample was shown by IC to be almost entirely due to sodium chloride, with moderate concentrations of potassium and sulfate. All other ions were nearly the same concentration as found in EETA79001. Here, the errors for potassium and sodium were below 5%, with higher errors for calcium, magnesium, and chloride. Not surprisingly, the ammonium electrodes resulted in high errors due to the relatively high potassium content. Although there was ammonium in the sample, it was negligible when compared to other cations. The measurement of the nitrate in this sample provided a reasonable value, although the error was large possibly due to high chloride concentrations. The sulfate was moderately concentrated so the additional barium spike was not necessary, resulting in an error slightly less than 30%.

Initially, it was thought that when compared to the stimulant samples, the soil data would show a higher overall error due to its unknown composition and undetected ionic interferences. However, the overall results of these samples show that they are not prone to any more error than the simulant samples, indicating that the array can adequately handle samples of unknown composition.

4. Conclusions

The fabrication and characterization of an ion selective array, designed for durability, measurement in extreme environments, and analysis of widely diverse soil samples has been described. The array was fully characterized and tested with multiple simulants and soil samples modeling the salt content of the Martian regolith as presently understood. The analytical errors in using the ISE array, when compared to ion chromatography, were within acceptable limits and were usually within one standard deviation of the IC value. With errors often below 5% and rarely exceeding 30%, the array accurately describes the soluble composition of soils ranging from high ionic strength samples to soils with minor ionic content. Overall, the lithium reference system showed excellent stability. Using ion chromatography, no significant lithium concentration was found in any soil or simulant indicating that this reference system would be applicable for most environmental applications. The use of the barium ISE for sulfate determination was also successful. Under the worst conditions, the sulfate was only able to be inferred qualitatively, but still provided useful information. However, it was observed that some foreknowledge of the sulfate sample concentration is required in order to spike an appropriate amount of barium.

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