

Electrochemistry on Mars

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More than 20 years ago, the only wet chemical experiments ever carried out on the surface of another planet took place. In 1976, the Viking I and II missions included biology experiments that revealed unusual chemical reactivity between water and Martian regolith (soil, sediment, and dust). The unexpected results of those experiments are still debated by planetary scientists.¹ New light may soon be shed on the peculiar chemistry of Martian soil. The Mars Environmental Compatibility Assessment (MECA), under development by the Jet Propulsion Laboratory (JPL) of the California Institute of Technology (Pasadena, CA), is scheduled to fly aboard the Mars Surveyor 2001 Lander. A key component of MECA is the Wet Chemistry Laboratory (WCL). The WCL is a set of four "beakers," each of

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which contains an integral array of electrochemical sensors. The beakers and sensor arrays were designed and supplied by **Orion Research, Inc.** (Beverly, MA), and are based principally on ion-selective electrode (ISE) technology developed at **Orion**.

Each beaker is capped by an actuator assembly which, with help from the Lander's robot arm, is capable of injecting an aqueous solution into the beaker, adding soil scooped at a controlled depth from the planet's surface, stirring the soil-water mixture, and adding solid reagent pellets. pH, redox potential, total ionic content, heavy metals, and specific cation and anion concentrations will be determined. The principal goal of the MECA experiment is to assess the hazardousness of Martian soil and dust to human explorers and equipment. The WCL promises also, however, to provide data relevant to basic scientific questions concerning the historical distribution of liquid water on Mars and the possibility of ancient life in addition to answering questions raised by the Viking missions.

WCL beaker design

Figure 1 is a schematic representation of the WCL beaker and actuator assembly. The electrochemical sensors are embedded in the walls of the beaker. The actuator assembly contains a sealed solution vessel with puncture valve and actuator, sample introduction drawer and actuator, stirrer motor and impeller, pressure and temperature sensors, and a solid pellet dispenser and actuator.

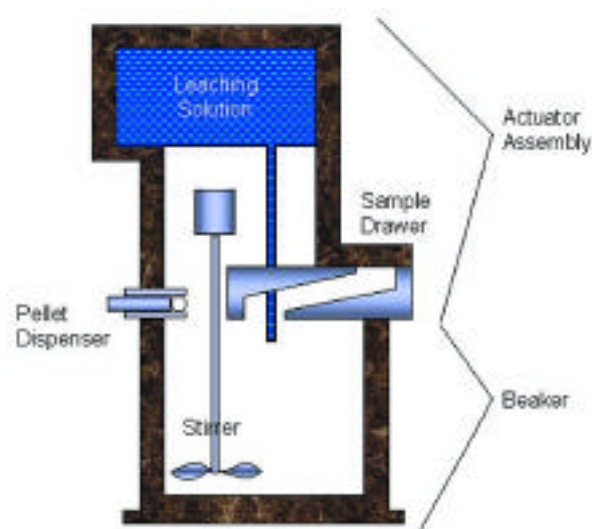


Figure 1 WCL beaker and actuator assembly.

Figures 2a-d detail the construction of the beaker. Housed in an anodized aluminum enclosure, an inner beaker of cast epoxy serves as reaction vessel and platform for the electrochemical sensors that populate all four walls. The sensors are fitted into machined holes such that the sensing surfaces face into the beaker and connection wires face out (*Figures 2c* and *d*). From a purely mechanical point of view, the sensors can be classified into two types: solid-state and polymer-membrane-based sensors (see *Table 1*). Solid-state sensors (in the form of chips, pellets, or wires) are bonded directly into the beaker walls, their sensing surfaces flush with the inner wall of the beaker. Polymer-membrane sensors (ISEs and gas sensors) require a means for mechanically retaining the membranes under an extreme range of pressure and temperature conditions. A

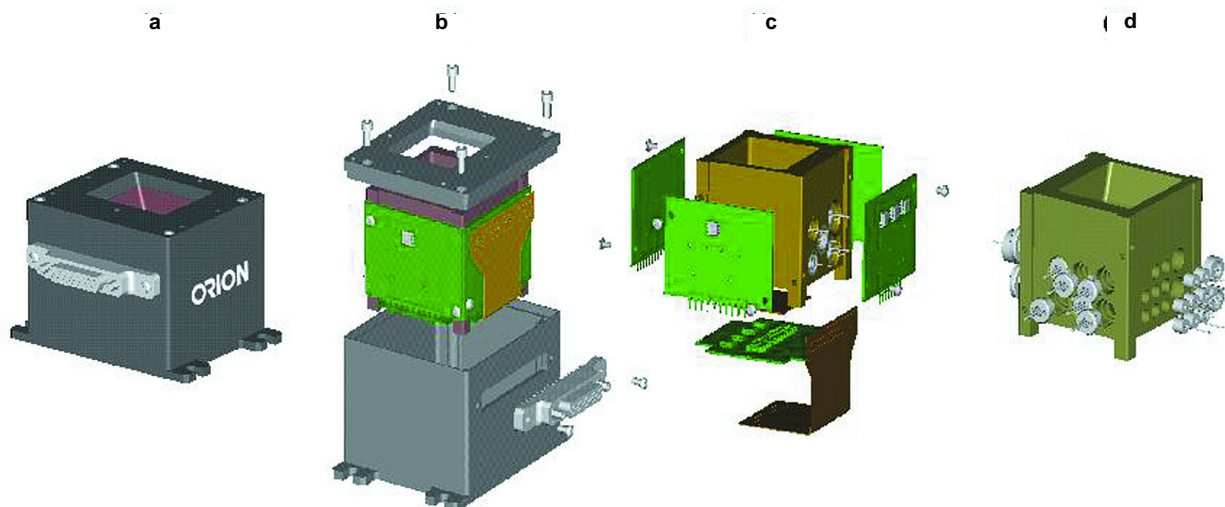


Figure 2 Beaker construction.

Table 1

WCL electrochemical sensors			
Sensor (quantity)	Type	Electrochemical technique	Analyte(s)
Conductivity cell	4-Electrode, planar chip	Conductimetric	Total ionic content
pH(2)	Polymer membrane	ISE(potentiometric)	pH
pH	Iridium dioxide	ISE(potentiometric)	pH
Membrane-covered CV electrode	3-Electrode, 0.25-mm gold cathode	CV	Oxygen; other volatile oxidants
Platinum macroelectrode	1.0-mm disk	ISE(potentiometric)	Oxidation-reduction potential
Gold macroelectrode	0.25-mm disk	CV	Oxygen; other oxidants or reductants
Gold MEA	Planar chip, 512 10- μ m elements	ASV	Heavy metals
Silver/sulfide	Solid-state pellet	ISE(potentiometric)	Silver or sulfide
Cadmium	Solid-state pellet	ISE(potentiometric)	Cadmium
Chloride (2)	Solid-state pellet	ISE(potentiometric)	Chloride
Bromide	Solid-state pellet	ISE(potentiometric)	Bromide
Iodide	Solid-state pellet	ISE(potentiometric)	Iodide
Lithium (3)	Polymer membrane	ISE(potentiometric)	None (added to leaching solution as reference ion)
Sodium	Polymer membrane	ISE(potentiometric)	Sodium
Potassium	Polymer membrane	ISE(potentiometric)	Potassium
Magnesium	Polymer membrane	ISE(potentiometric)	Magnesium
Calcium	Polymer membrane	ISE(potentiometric)	Calcium
Ammonium	Polymer membrane	ISE(potentiometric)	Ammonium
Nitrate	Polymer membrane	ISE(potentiometric)	Nitrate
Perchlorate	Polymer membrane	ISE(potentiometric)	Perchlorate
Carbon dioxide	Membrane-covered gas sensor	ISE(potentiometric)	Carbon dioxide or bicarbonate

threaded retaining ring compresses these sensor modules against a lip in the beaker wall resulting in sensing surfaces that are slightly recessed (see *Figure 3*).

Printed circuit (PC) boards are mounted outside each wall and the bottom of the inner beaker. Sensor leads are connected directly to the PC boards where preamplifiers are mounted for each ISE. A heating pad is located between the bottom of the beaker and the bottom circuit board. All sensor signals and heater connections are routed through the bottom PC board to a flex circuit that interfaces with a micro-D connector on the aluminum housing. All void

space between the inner beaker and enclosure is filled with a lightweight potting compound. An anodized aluminum cover completes the assembly. The beaker has overall dimensions of $4 \times 4 \times 5$ cm, an inner volume of 36 mL, and a mass of 250 g.

WCL sensor selection and design

Table 1 is a list of the WCL electrochemical sensors. In addition to potentiometric ISEs, a conductivity cell, bare and membrane-covered cyclic voltammetry (CV) electrodes, and microelectrode array

(MEA) for anodic stripping voltammetry (ASV) are included. Sensor selection in the WCL was driven by several considerations, discussed below.

Analytical goals of the MECA experiment

MECA has a primary goal to determine hazards to human explorers and equipment and secondary goals to contribute to the scientific knowledge of Mars. The most likely chemical hazards posed by the Martian soil and dust are corrosiveness and toxicity. The best indicators of corrosiveness are pH and oxidation-reduction potential (ORP); therefore, sensors for the direct determination of these parameters are contained

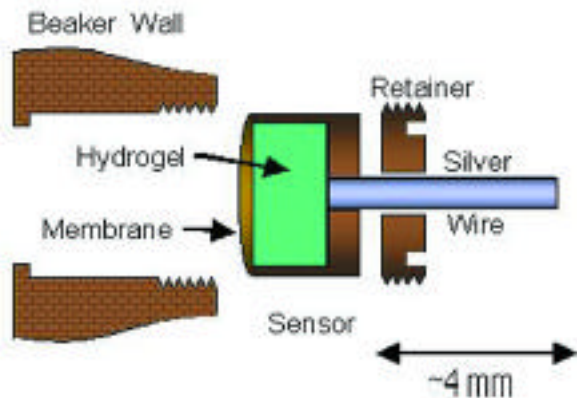


Figure 3 Polymer membrane sensor.

in the beakers. The most likely toxic substances to dissolve from an inorganic matrix are heavy metals; thus an electrode for heavy metal detection by ASV and ISEs for silver and cadmium are present.

Three areas in which the WCL may contribute to MECA's scientific goals are in helping to unravel the results of the Viking biology experiments, elucidating the history of water on Mars, and assessing the likelihood that Mars might have supported or may still support life. The Viking experiments indicated the presence of an oxidant or oxidants in the soil. The MECA beakers contain two types of CV electrode: a bare electrode, which may indicate the presence of any type of oxidant (or reductant) in the soil leachate, and a membrane-covered CV electrode that will only detect volatile substances such as oxygen. There is a great deal of evidence that liquid water once existed in abundance on Mars and may yet be found in underground aquifers. Models of the Martian environment during wetter periods in the planet's past may be enhanced by determining the soluble salt fraction of regolith at particular locations and depths. Conductivity measurement will indicate the total quantity of salts in the sample, while ISE determination of specific ions such as sodium, potassium, magnesium, calcium, and chloride may help to further refine historical models. Certain chemical species that can also

be measured with ISEs (i.e., carbonates, nitrates, sulfides, and ammonium) can sometimes, in combination with other types of evidence, serve as markers of past or present biological activity.

In some instances, the WCL sensors are redundant. Redundancy decisions were driven not only by the relative importance of the measured parameter, but also by the expected reliability of the sensors. Solid-state sensors proved extremely reliable, even after being subjected to numerous freeze-thaw cycles during qualification testing; therefore only one each of sensors for ORP, conductivity, CV, ASV, silver, and cadmium was included. Nevertheless, there is inherent redundancy in some of these parameters: Measurement of oxygen and other oxidants or reductants by the bare and membrane-covered CV electrodes supplements the assessment of ORP; heavy metals are determined by ASV as well as by silver and cadmium ISEs. pH sensors and reference electrodes are expected to be less reliable than solid-state sensors. Because these parameters are so important, three pH sensors and three lithium reference electrodes were selected. Reference electrodes are critical to every measurement in the WCL except membrane-covered cyclic voltammetry, carbon dioxide, and conductivity. The chloride ISE can serve as a back-up reference cell if the others fail; thus a second chloride ISE was included.

Expected composition of Martian regolith

Through a combination of three lines of evidence—direct analysis by the Viking X-ray fluorescence spectrometer, analysis of terrestrial meteorites believed to have originated on Mars, and simulations of Viking biology experiments—a proposed composition of Martian soil was developed and is presented in Table 2.² Based on cation concentrations, solubility models, supposed oxidation states, and geochemical evidence, the soluble fraction of Martian soil might be expected to be composed mainly of sodium chloride and magnesium sulfate,^{3,4} not unlike terrestrial seawater.

Reliable ISEs with good sensitivity and selectivity are available for sodium, chloride, and magnesium. Sulfate ISEs have been described in the literature and were evaluated, but could not be flight-qualified in time for MECA. However, measurement of conductivity and three of the four specific components is sufficient to characterize a soil conforming to this simple, four-ion model.

Availability, performance, and maturity of sensors

In keeping with NASA's "cheaper, better, faster" 1990s philosophy, it was desired to use off-the-shelf technology wherever possible in MECA. Sensors with proven heritages were preferred over those that may have been developed more recently. As described in the following section, a proven terrestrial heritage did not always qualify a sensor for the extreme environmental demands of a Mars mission.

continued

Table 2

Mars soil composition model	
Constituent (elemental composition expressed as oxides)	Concentration (%)
SiO ₂	43.8
Fe ₂ O ₃	18.2
Al ₂ O ₃	7.2
SO ₃	7.2
MgO	6.0
CaO	5.8
Na ₂ O	1.34
Cl	0.8
P ₂ O ₅	0.68
TiO ₂	0.6
MnO ₂	0.45
Cr ₂ O	0.29
K ₂ O	0.10
CO ₂	<2
H ₂ O	0–1

Survival and performance testing

No electrochemical experiment has ever needed to survive and operate under the conditions imposed by MECA—from the heat and humidity of the launch pad in Florida; through the cold, dry vacuum of space; and finally to the extreme diurnal temperature fluctuations on the surface of Mars. All of the MECA components have been subjected to a full regimen of shock, vibration, and environmental cycling tests. The glass pH electrode, a sensor with unparalleled heritage in terrestrial applications, was eliminated early in the program. Not surprisingly, temperature swings from -100 to $+40$ °C resulted in cracking in a few instances, but the real problem was degradation in insulation resistance. The relatively thin epoxy wall of the beaker could not prevent electrical leakage paths between the test solution and the wire lead of such a high-impedance sensor under repeated expansion and contraction. Polymer-membrane electrodes, on the other hand, survived temperature cycling despite fears at the outset that the membranes might undergo glass transition at low temperature and become brittle. Early plans for a thin-film polymer sensor design that could tolerate dehydration of the inner hydrogel and yet be quickly rehydrated on Mars had to be scuttled because of temperature hysteresis. A thick-film design proved stable and was chosen, but required changes to other aspects of the experiment to prevent drying, as discussed below. Solid-state sensors fared well in qualification testing.

Reference electrode selection

The Achilles' heel of many electrochemical analyses is the reference electrode. In a conventional reference electrode, ions are allowed to leak into the sample solution. Early in the program, it was determined that even the lowest attainable leak rate would compromise determination of some parameters, most ob-

viously conductivity. Performance of several no-leak reference concepts described in the literature could not be replicated. As the WCL concept matured, models for expected regolith composition were developed and qualification test results for various types of sensors became available. Armed with this information, the idea of using a polymer-membrane lithium ISE as a reference half-cell and maintaining a fixed level of lithium ion in the leaching solution was conceived, evaluated, and adopted. Several criteria had to be met. First, the lithium level in the leaching solution had to be high enough to 1) establish a

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stable lithium electrode potential, 2) swamp out any lithium native to the sample, and 3) swamp out the effect of any ions in the sample that might potentially interfere with the lithium electrode. At the same time, the lithium level had to be low enough to allow accurate measurement of the sample's contribution to the conductivity and low enough not to interfere with any other measurements. Leaching solution composition is discussed further below.

Experimental design

One morning near the beginning of Earth Year 2002, weak rays of sunlight will begin to evaporate CO₂ frost from the Mars 2001 Surveyor Lander. The Lander computer will have received the instruction from JPL in Pasadena to begin operation of the first of MECA's four WCL beakers. After a year-and-a-half of cold storage at JPL; three months of prelaunch integration at Cape Canaveral; launch; and nine months of cruise, orbit, and touchdown on Mars, the time will have come to wake up the WCL and carry out soil analysis. A sequence of steps, each one agonized over by the MECA team for four years, will finally be initiated. Although many details are still being worked out, the following is an outline of one possible experimental sequence.

Ready to begin

The ambient pressure will be about 7 torr, one-hundredth of Earth ambient and composed almost entirely of carbon dioxide. The temperature may be as low as -100 °C. The beaker and headspace in the actuator above it will have left Earth filled with an inert gas at 1 atm pressure. A few drops of water will

have been added to the beaker to provide a humid atmosphere for the polymer membrane sensors that could otherwise dry out. Those few drops of water, the hydrogels in the membrane sensors, and 30 mL of leaching solution in a sealed tank in the actuator assembly will have quickly frozen upon leaving the Earth's warmth.

Warmup

It will take a few hours for the sunshine to be strong enough to supply adequate energy to the solar collectors on the Lander (hopefully a dust storm will not be occurring). Then the day's activities can begin. Under control of the MECA electronics (which serves all four WCL systems), the sampling drawer will be opened for just a few moments to vent the beaker to Martian ambient pressure. Heating pads under the beaker and on the water tank will then be activated. The leaching solution and hydrogels in the membrane sensors will thaw. After about an hour, when temperature sensors indicate that the assembly is comfortably above freezing, an actuator will puncture the seal on the water tank and leaching solution will dribble into the partial vacuum of the beaker.

Leaching solution

The leaching solution plays two very important roles in addition to that of extracting the soluble components of the sample. It contains lithium ion to fix the half-cell potentials of the lithium reference

Table 3

Component	Proposed leaching solution composition	
	Concentration (m	M/L)
Li ₂ SO ₄	2.5	
NH ₄ NO ₃	0.01	
NaClO ₄	0.01	
CaCl ₂	0.01	
MgCl ₂	0.01	
KNO ₃	0.01	
K ₃ Fe(CN) ₆	0.01	

ISEs and low levels of other ions to serve as calibration values for other sensors. The approximate composition of the leaching solution is shown in *Table 3*. Specific calibration ion levels are as low on the response curves of the corresponding sensors as possible in order to provide useful calibration without overwhelming eventual contributions of those ions from the soil. Ferricyanide is included as calibration for the bare CV electrode. Because of mutual interferences and other incompatibilities, not all sensors can be calibrated. Characterization of those sensors on Earth will have to be relied upon for interpretation of the data they will provide.

Calibration

Once the leaching solution is in the beaker, the

stirrer will be turned on. The stirrer provides moderate agitation—a 0.8-mm-diam impeller rotating at 2 rps. Sensors will be interrogated sequentially by the MECA electronics board. Temperature, conductivity, and ISEs will require only a few seconds per reading and CV sensors only a few more. ASV takes several minutes because a long deposition time promotes low detection limits for metals. The reading of all sensors will be repeated several times to evaluate stability and allow a general assessment of the system's health before proceeding with sampling and analysis.

Sampling

Possibly at the same time that the first WCL system is warming up and undergoing calibration and health check, the Lander's robot arm will be selecting a scoop of soil for analysis. The scoop will be positioned just outside the sampling drawer and the robot arm camera will capture an image. For at least two reasons, however, the experiment will have to go on hold until the next day. Possibly, it will have become so late in the Martian day that solar power will be beginning to wane—the workday on Mars will only be six to seven hours' duration. More importantly, though, it is necessary to allow the leaching solution in the beaker to refreeze so that it will not boil off when the sampling drawer is opened. Depending on the exact orientation of the Lander, it may not be possible to freeze the solution while the

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sun is still bright. Therefore, the earthbound MECA team will have one sleepless Mars night to analyze the transmitted data and images before deciding to move on to the next step.

Analysis

The second and probably final day of the experiment will begin with the leaching solution frozen in the beaker. An actuator will push the sample drawer out into the Martian atmosphere. The robot arm will dump its contents through a coarse sieve into the extended drawer. The robot arm camera will capture an image of the soil in the drawer so that an estimate of the quantity of soil can be made. The drawer will then be retracted through a wiper seal, dumping the soil onto the frozen solution and resealing the beaker. The beaker and actuator assembly will now be heated to above freezing. Some or all of the sensors will be interrogated during the thawing of the leaching solu-

tion. One reason for this is that some components of the soil, the mysterious oxidant from the Viking experiments, for example, may be short-lived. The bare and membrane-covered CV electrodes will thus be very important during this early stage of analysis. Conductivity (and temperature, of course) will monitor the phase change from solid to liquid; ORP and pH changes may be of interest at this time. In order to obtain as many critical readings as possible during melting, it would not make sense to operate the ASV electrode, since the ASV analysis takes minutes, and heavy metals will be leached slowly and are not short-lived. Once thawing is complete, stirring will begin and complete cycles of sensor interrogation will be repeated throughout the leaching process. It may be desirable to repeat the analysis after addition of a second scoop of soil. If so, the second analysis would have to be carried out the following day after allowing the system to refreeze overnight.

Reagent addition

Once soil analysis is complete, a reagent pellet will be added to the mixture. Addition of a reagent can increase the amount or quality of information that may be obtained from the experiment. Various reagents were considered (e.g., an acid to digest more minerals, or potassium iodide to react with oxidants and allow a refined total oxidant determination), but most likely the reagent pellet will serve to effect a standard addition calibration of the sensors. Given the exotic nature of the analysis, minimization of the uncertainty inherent in all the measurements is probably the most effective enhancement to the experiment. Thus, either on the same day as the soil analysis or on the following day, a pellet containing quantities of analytes estimated to be approximately equal to the contributions from the soil will be added to the mixture. The cycle of sensor interrogation will be repeated continuously as the pellet dissolves with the aid of stirring.

Data analysis

Data from the first WCL experiment will be eagerly awaited. Decisions based on transmitted data must be made during the experiment (e.g., whether to proceed with soil addition after the initial health check and calibration are complete) and immediately afterward, so that any changes that are desired for the subsequent three experiments can be implemented. Some of the data will take considerable time to interpret. No one knows for sure what effect the prolonged cruise and other stresses will have on the sensors or what type of soil specimen will be obtained. Viking data are still being analyzed. Spare WCL beakers, stored on Earth under conditions simulating those of the flight beakers, may be resurrected in order to attempt duplication of the results obtained on Mars. It will be interesting to compare the WCL results to those obtained on returned samples, expected in the year 2007 or thereabout.

Additional experiments

Four WCL assemblies will be present on the Lander. At this time, it is still under discussion whether all four experiments will be the same. One possible scenario is that the experiments will be identical, but that two will analyze surface soil and two will take soil from depth. Certain aspects of MECA are still evolving. It has not yet been decided where on Mars the 2001 Surveyor Lander will touch down. At this very moment, the Mars Global Surveyor is orbiting Mars and photographing the planet's surface in unprecedented detail (see <http://mars.jpl.nasa.gov/mgs/index.html>). Will some newly discovered feature on the Martian surface be so compelling as to make the site selection easy?

Conclusion

NASA is planning Mars missions now at two-year intervals. The '05 mission includes provisions for returning samples to Earth. A manned mission could occur in less than 20 years. The MECA team hopes to refine remote, automated chemical analysis systems like the WCL, and fly them to Mars and elsewhere—Jupiter's satellite Europa and Saturn's Titan have intriguing surface chemistries. WCL-like devices have terrestrial applications as well. Multisensor arrays, so-called "electronic tongues," and the algorithms and know-how for interpreting the data they provide have great potential for future automated and remote monitoring and control applications.

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