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MARS AQUEOUS CHEMISTRY EXPERIMENT

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ANNUAL TECHNICAL REPORT
YEAR 2

FOR THE

MARS AQUEOUS CHEMISTRY EXPERIMENT

JUNE 1994

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FOREWORD

This document was prepared in accordance with the requirements of NASA Contract NASW-4698, Section F.4(a), Annual Progress Reports.

Introduction

This report details the interim progress for contract NASW-4698, the Mars Aqueous Chemistry Experiment (MACE), an instrument being developed under the Planetary Instrument Definition and Development Program (PIDDP). The progress reported is for the period from June 1993 through May 1994. The second year of the MACE project has shown significant progress in two major areas:

•MACE Instrument concept definition:
A baseline design has been generated for the complete MACE instrument, including definition of analysis modes, mass estimates and thermal model. The design includes multiple reagent reservoirs, 10 discrete analysis cells, sample manipulation capability, and thermal control.

•MACE Measurement subsystems development:
Progress is reported regarding measurement capabilities for aqueous ion sensing, evolved gas sensing, solution conductivity measurement, reagent addition (titration) capabilities, and optical sensing of suspended particles.

MACE Instrument Concept Definition

Table 1 summarizes the capabilities and functionality of the MACE baseline concept. The estimates and capabilities listed are derived from detailed analysis of existing systems, and predicted from the mechanisms detailed in the following sections.

Table 1 MACE Baseline Concept Summary

MACE Instrument Parameter	Baseline Concept Specification	Comments
Total Instrument Mass	2.50 kg	Based on detailed estimates for over 200 individual line items
Total Instrument Dimensions	14.93x11.17x13.86 cm	Cube shaped
Total Instrument Volume	2.3 liters	Instrument bulk density ~ 1.1 g/cc
Analysis Capability (Sample Cells)	10 individual cells, 0.3 cc sample each	Mounted on carousel for random access to sample loading and analysis stations
Transport Mechanisms	Shaped Memory Alloy (SMA) driven, 1 Carousel Motor	•High reliability, low power, simple mechanisms, reduced electronics. •Motor used for random access capability
Analysis Water Reservoir	80 cc	6 cc per analysis + 2 cc for rinse
Liquid Analysis Reagents	5 liquid reservoirs	Micropump used to meter liquid reagents
Powdered Analysis Reagents	2 Porous Wheel Particle Dispensers (PWPD)	PWPD's used to meter powdered reagents into test cell for a variety of analyses
Thermal Control	2 RHU's Shaped Memory Alloy (SMA) thermal switches	Configuration maintains internal instrument temperature above freezing, even in 150K ambient conditions
Aqueous Solution Sensors and Mechanisms	(ISE) array Redox potential temperature conductivity titration & decomposition analyses particle size distribution solution stirring	•12 distinct ions measured in solution •Oxidation reduction electrochemical pot. •heats of solution measurement •solution total ionic strength •metered reagent addition using micropumps and powder dispensers •light scattering from insoluble particles •required to suspend particles, mix ions
Evolved Gas Sensors	chamber pressure Gas Selective Electrodes	•gas evolution events measurement •Partial pressure of specific evolved gases
XRF interface	Kapton window in MACE sump	Interface for x-ray fluorescence measurement of elemental composition of soluble regolith components

The sequence for a MACE aqueous dissolution analysis has been defined. The scenarios for sample acquisition and fluid management refer to Figures 1 and 2, showing detailed drawings of the MACE baseline instrument concept from the top and side views. The figures show the instrument at full scale, with all mechanisms and actuators having full functionality.

Sample Acquisition and Preparation

A stationary Sample Inlet Cone covered by a Coarse Screen is accessible from the outside of the instrument housing. Soil samples to be analyzed by MACE are delivered to the Sample Inlet Cone of the instrument by a robotic arm, or perhaps a small rover. The Coarse Screen prevents oversize particles from entering the instrument while the 45° mounting angle serves to deflect the larger particles away from the Sample Inlet Cone. Soil sample particles small enough to pass through the Coarse Screen and fill the cavity within the Sample Volume Control plate. This volume essentially defines the sample volume: about 0.3 cubic centimeters (cc).

A Shape Memory Alloy (SMA) activated mechanism moves the Sample Volume Control plate from the position directly beneath the Sample Inlet Cone to the Fill Position aligning with the inlet to the Sample Test Cells. The inlet to the Sample Test Cell is kept free of sample particles that could degrade or prevent proper sealing by use of a stationary O-Ring Guard located directly above the Sample Test Cell fill position. When in the position to fill the Sample Test Cells, the Sample Volume Control plate also allows excess sample material to be discarded through the Excess Sample Exit in preparation for a receiving a new sample. Immediately after the sample material has been deposited into the Sample Test Cell, the Sample Volume Control plate is returned to the original position beneath the Sample Inlet Cone. This scenario results in minimal cross contamination between samples.

To rotate the carousel to another position, the SMA Clamping System of the Analysis Chambers must first be energized. Applying power to the SMA Clamping System causes the Analysis Chambers to move away from the Sample Test Cell, and frees the carousel to rotate to the next position via random access. The SMA mechanism of the Clamping System must be activated to release the Sample Test Cell any time the carousel rotates. When power to the SMA mechanism of the Clamping System is removed, the conventional compression springs apply sufficient force to the upper and lower O-Ring Seals of the Sample Test Cells to create a gas tight seal around the Analysis Chamber.

After the sample material has been deposited into the Sample Test Cell, the random access carousel supporting the 10 individual Sample Test Cells can be rotated. The rotation may move the test cell directly to the Analysis Chamber, or alternately position the test cell to align with the outlet of either Porous Wheel Particle Dispenser (PWPD). The PWPD is used to dispense a metered quantity of powdered reagent into the test cell. The PWPD is driven by a SMA mechanism that rotates the PWPD central shaft to deliver a metered quantity of powder for the analysis. After the desired quantity of powder has been added, the carousel is rotated to the Analysis Chamber position.

Fluid Management

Water for the aqueous dissolution experiments is stored in a 100 ml reservoir, filled with 80 ml of water. The remaining volume within the reservoir is used to provide pressurization to transport the analysis water to the lower portion of the analysis chamber and the Sample Test Cell. The reservoir contains enough water to conduct experiments on 10 different soil samples, with adequate reserve to allow rinsing of the lower Analysis Chamber between analyses. I a titration or decomposition analysis is to be performed, liquid reagents are added to the water within the lower portion of the Analysis Chamber by

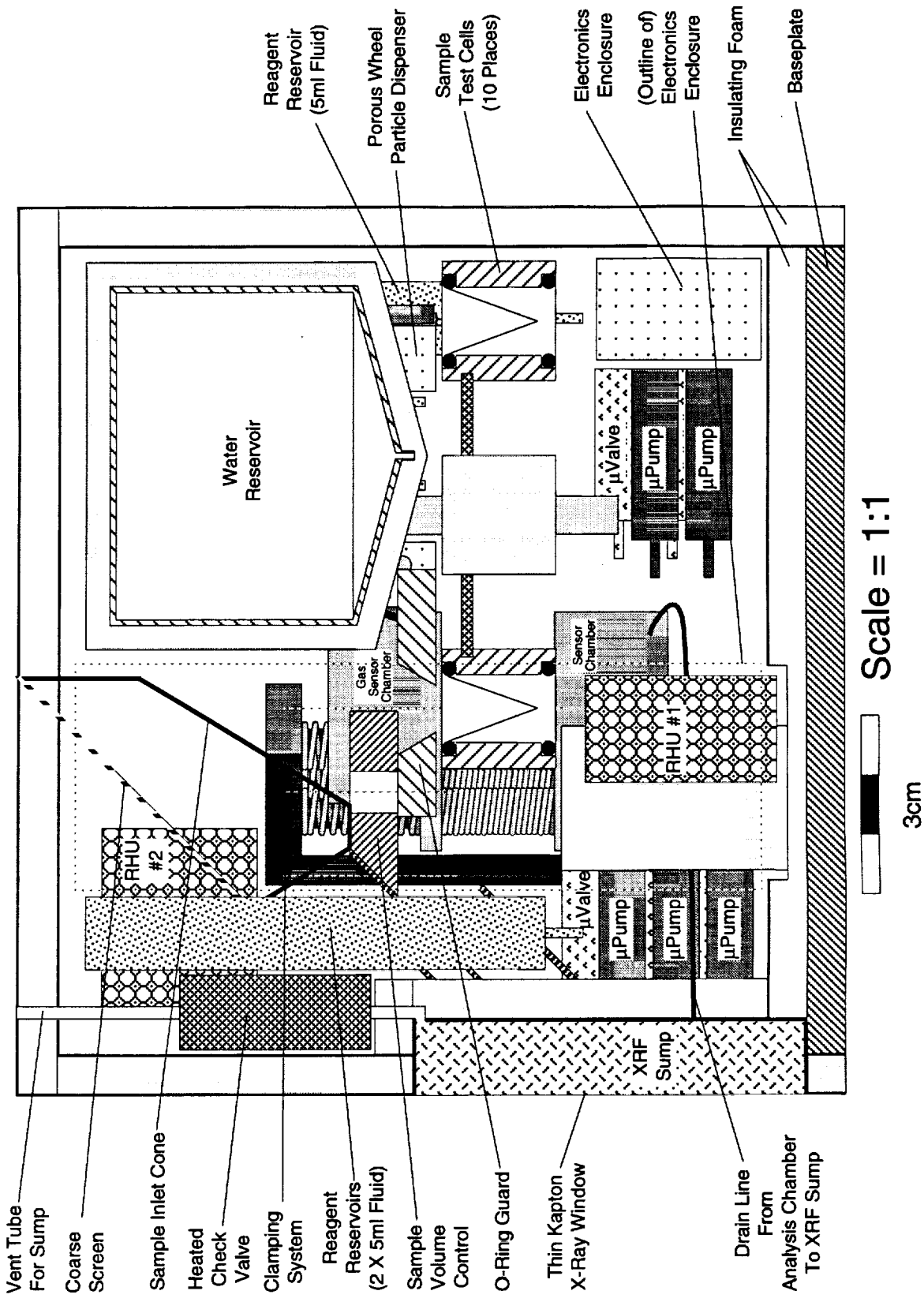

Figure 1 MACE Baseline Concept Side View

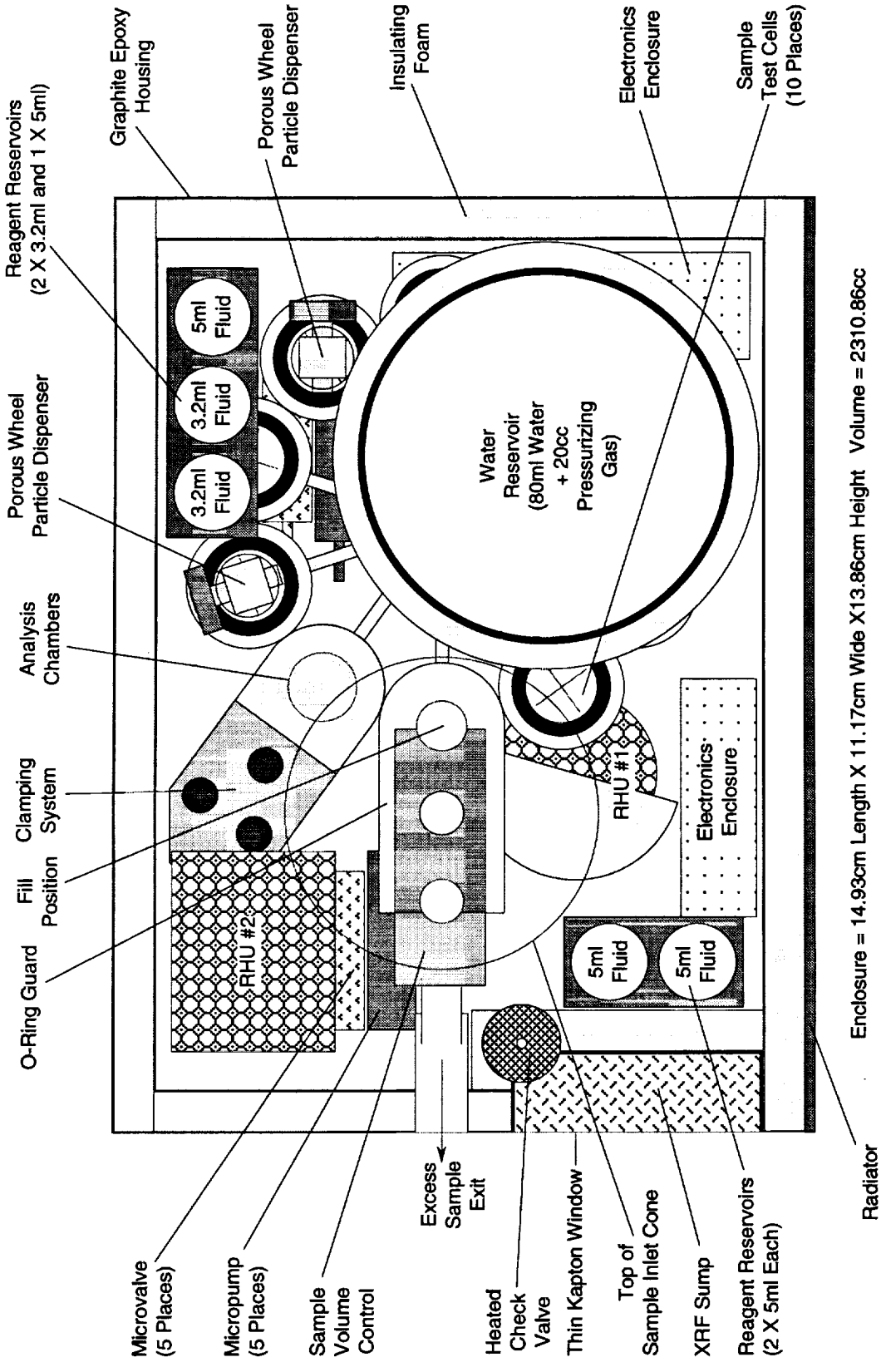

Figure 2 MACE Baseline Concept Top View

first opening the appropriate Microvalve and activating a Micropump. The micropump is an implantable miniaturized solenoid activated pump developed for *in vivo* insulin addition in diabetic patients. The reagent may be added to the analysis chamber in precise increments of 0.5 µl, enabling titration and controlled decomposition analysis scenarios to be performed. Our baseline concept includes three separate Reagent Reservoirs having 5 ml fluid capacity each, and two additional Reagent Reservoirs with 3.2 ml fluid capacity. Each Reagent Reservoir has its own Microvalve and Micropump for independent operation. The choice of chemical reagents (liquid and powder) to be used within these reservoirs is TBD, but will likely include acid, alkaline, and surfactant reagents.

When the analysis of a sample is completed, all fluids are drained into the XRF Sump. A heated valve and vent tube connected to the upper portion of the Analysis Chamber is opened and the liquid remaining in the soil sample is allowed to sublimate to the low pressure ambient environment of Mars. This is done before opening the Analysis Chamber to avoid a build up of water vapor on the inside of the instrument enclosure that could degrade the emissive nature of the thermal surfaces and affect the stability of the instrument. A Heated Check Valve and vent tube attached to the XRF Sump performs a similar function to remove the liquid from the waste received from the Analysis Chamber. After the liquid portion of the waste has evaporated, the residue deposited on the Thin Kapton Window of the XRF Sump can be analyzed by an external X-Ray Fluorescence (XRF) spectrometer to qualitatively and quantitatively identify elements leached from the soil sample. This will reveal the water soluble elements contained in the Martian soils. Table 2 summarizes the MACE operational modes and analytical measurement capabilities.

Table 2 MACE Instrument Modes of Operation

Mode	Physical Operations	Analytical Measurements
Sample Loading, & Transport	receive regolith sample transport sample to reaction chamber seal sample chamber (hermetic)	bulk volume used to meter sample
Sensor Calibration	seal chamber (hermetic) meter cal sol'n(s) to sensor chmbr flow cal gas past gas sensors chamber rinse & unseal	ISE calibration gas sensor calibration temperature sensor calibration
Humidification	meter water into sensor chmbr so only vapor contacts sample	evolved gases comp. (superoxides) ΔP from gas evolution ΔH of humidification sample bulk conductivity
Aqueous Dissolution	meter water into sample chamber to wet sample	ionic dissolution species/kinetics sol'n calorimetry, ΔH of hydration freezing point depression evolved gases composition/kinetics ΔP from gas evol. & decomposition solution conductivity/kinetics oxidation reduction potential
Acidification	addition of acid reagent(s)	acid soluble species sol'n calorimetry, sample bulk Cp evolved gas ΔP, composition
Post Analysis Activities	neutralization of analysis water transport of anal. water to sump sensor chamber cleanup spent sample transport	pH titration/buffering capacity particle size/settling kinetics
Water Evaporation	water evaporation to ambient atmosphere	freezing point depression XRF of soluble sample fraction

MACE Instrument Thermal Model

The thermal model of the MACE instrument was developed using Systems Improved Numerical Differencing Analyzer (SINDA), which analyzes resistor-capacitor network representations of thermal systems. Figures 3 and 4 show drawings of the MACE instrument with numbers identifying the locations of the thermal nodes. Conduction, radiation, and RHU heating thermal transport modes were modeled within the instrument enclosure. The current analysis does not include heating from the electronics assemblies.

Thermal Model Description

The thermal interactions of the MACE instrument enclosure with the Mars environment include: solar heating, free convection, radiation to the environment, and conductive and radiant exchange with the spacecraft baseplate. The solar heating is modeled as a solar constant (dependent on the Mars location) multiplied by the solar absorptance of the instrument enclosure and a factor to account for sun angle. The solar absorptance used in the thermal model is 0.85, based on the Viking thermal model. Lower solar absorptance than this was assumed to be unobtainable due to the frequent dust storms on Mars, which would degrade the emissive nature of any optical coating. Three Mars locations were modeled to evaluate the range of heating conditions. These cases are identified as hot, nominal and cold. The hot case is representative of -30° latitude, the nominal case +30° latitude, and the cold case +60° latitude, each taken at the latitude specified while Mars is at perihelion. The thermal design for the MACE instrument was optimized for each of these cases based on the temperatures achieved during the daily solar cycling. Table 3 summarizes the thermal design and environmental conditions for each case.

Table 3 MACE Thermal Design and Environmental Conditions

Environment Case	Latitude at perihelion	Solar Constant	Temperature Range	Thermal Design features
Nominal	+30°	550 W/m^2	155 - 220 K	2 RHU's Internal emissivity: 0.05 Baseplate emissivity: 0.03 Reservoir emissivity: 0.2 Polyurethane foam: 0.25"
Cold	+60°	0 W/m^2	150 K	2 RHU's Internal emissivity: 0.03 Baseplate emissivity: 0.02 Reservoir emissivity: 0.2 Polyurethane foam: 0.25"
Hot	-30°	700 W/m^2	188 - 293 K	2 RHU's Internal emissivity: 0.05 Baseplate emissivity: 0.05 Reservoir emissivity: 0.2 Polyurethane foam: 0.25"

The MACE design incorporates 2 RHU's (each generating 1W) for heating the instrument enclosure. 0.1 W from one RHU is conductivly coupled to the water reservoir, and the remaining 1.9 W is radiated to the enclosure interior. Both RHU's include variations of a specially developed Martin Marietta Shape Memory Alloy (SMA) actuated Thermal Switch mechanism to allow for the heat to be routed to the instrument radiator from either RHU, and also for the water reservoir RHU to break thermal contact with the reservoir in the event of high ambient temperature.

Note: Boldface type identifies thermal node numbers

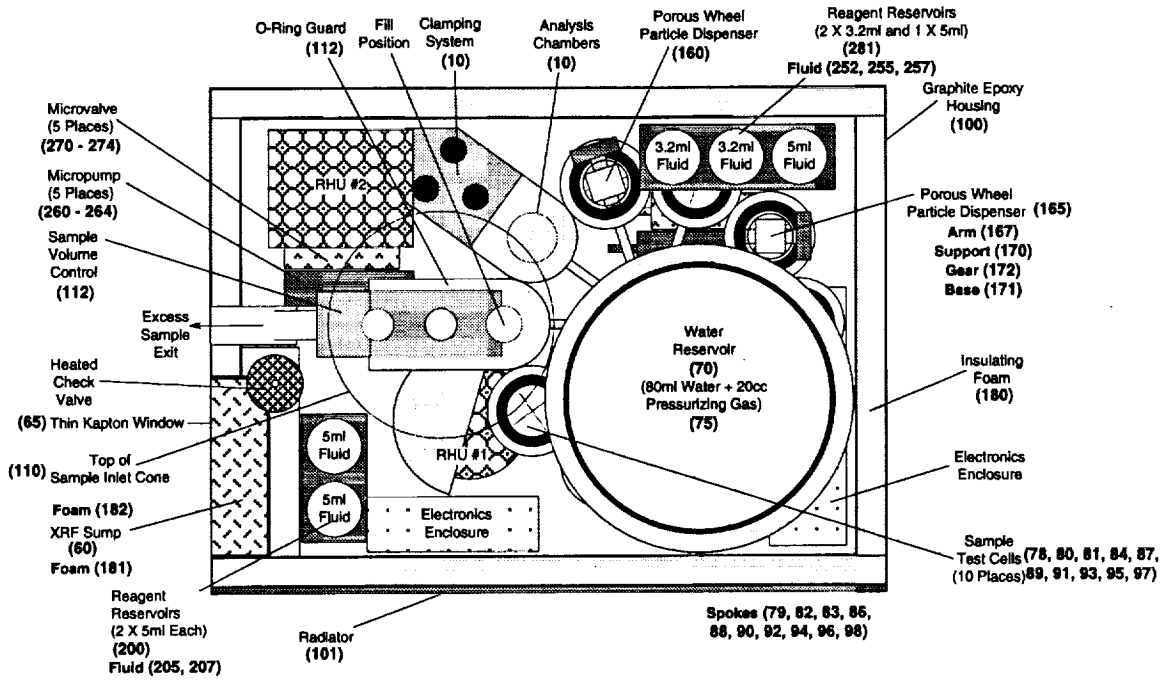

Figure 3. Top View of MACE Baseline Concept Thermal Model

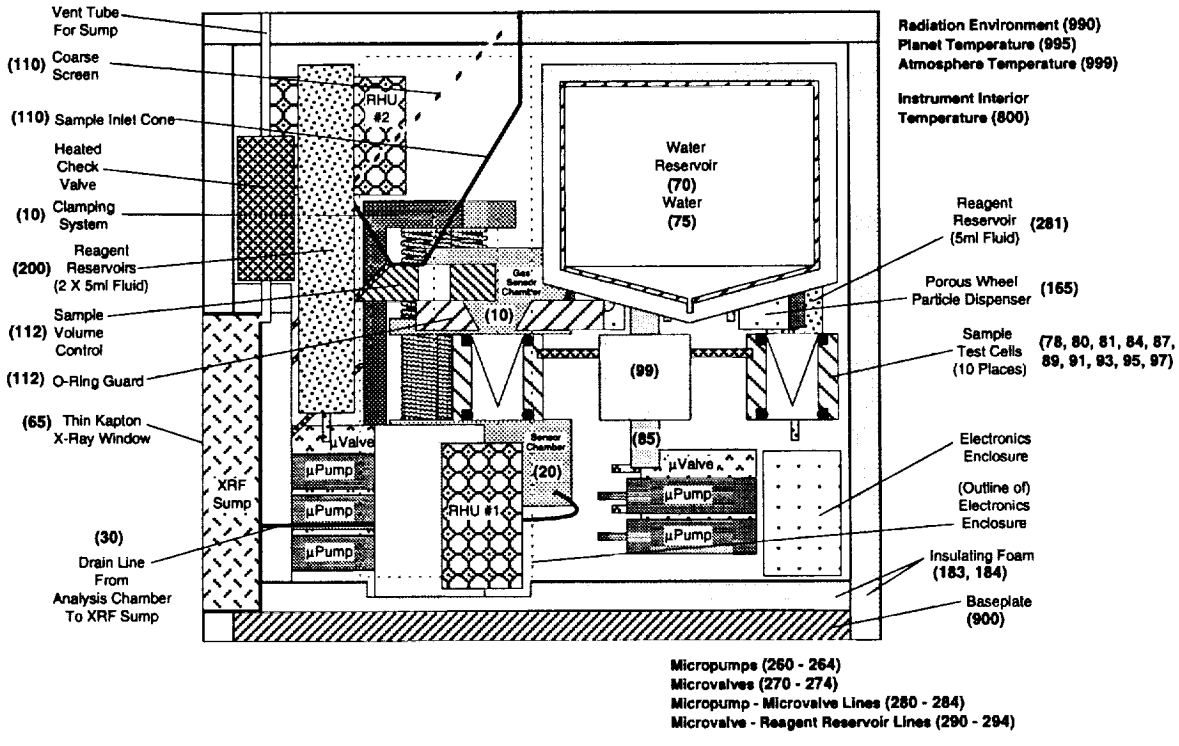

Figure 4 Side View MACE Baseline Concept Thermal Model

Foam insulation (6 mm Confor polyurethane foam) is used around the inside of the instrument enclosure, sump sample inlet and the spacecraft baseplate to provide thermal isolation from the Mars environment. The insulating foam isolates the instrument interior from the ambient environment and acts to stabilize the interior temperature. Low emissivity surfaces are provided by single or possibly multiple layers of coated Kapton films. The specific coating used on the Kapton is dependent on what emissivity is required to stabilize the enclosure temperature, and is dependent on the ambient conditions. Higher values for the emissivity provide a more flexible design which is better able to withstand the effects from contamination. The contamination will be minimized within the enclosure by venting the enclosure to the exterior environment following each analysis.

Temperatures on Mars vary as a function of latitude, season, and time of day. The ambient temperature profiles used in the thermal model are based on the 1972 JPL Mars Environment Model by Kieffer, which was derived from Mars planetary temperature data. The thermal model was run for three ambient temperature cases: Nominal, Hot, and Cold, representing the hot and cold extremes, and an average. The MACE instrument enclosure radiation is modeled as a cube that radiates to a constant 100K thermal sink (Mars sky) through the upper surface, and radiates to a sink at the planet temperature through the sides of the enclosure. For free convection calculations, the air temperature was set equal to the planet temperature. This approach is consistent with previous Viking thermal analyses.

Thermal Model Results

Figures 5 through 7 show plots of the sump, water reservoir, enclosure, and environment temperatures over two days of solar cycling. For each case the water reservoir was thermally isolated from the instrument enclosure to maintain the reservoir temperature stable to within ±0.5 K. In every case (nominal, cold, & hot) the instrument enclosure remains above 278 K (+5°C) to prevent freezing of the analysis water. In the event that the enclosure temperature rises above an acceptable nominal temperature (from solar input or high ambient temperature), the SMA thermal switch shunt is actuated to thermally connect the RHU's to the instrument radiator plate, reducing the heat load within the enclosure.

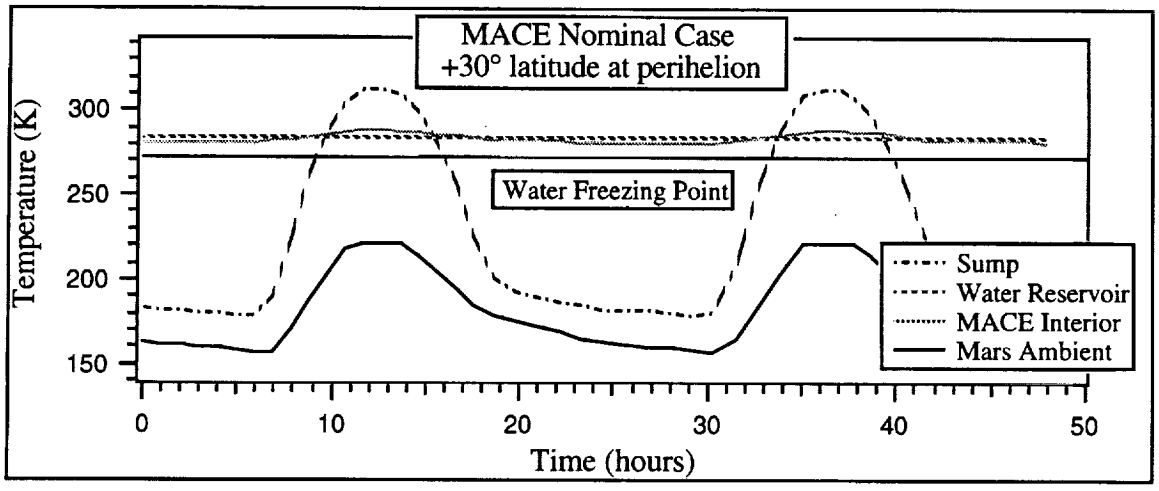

Figure 5 Thermal Model Nominal Case Temperature Profiles

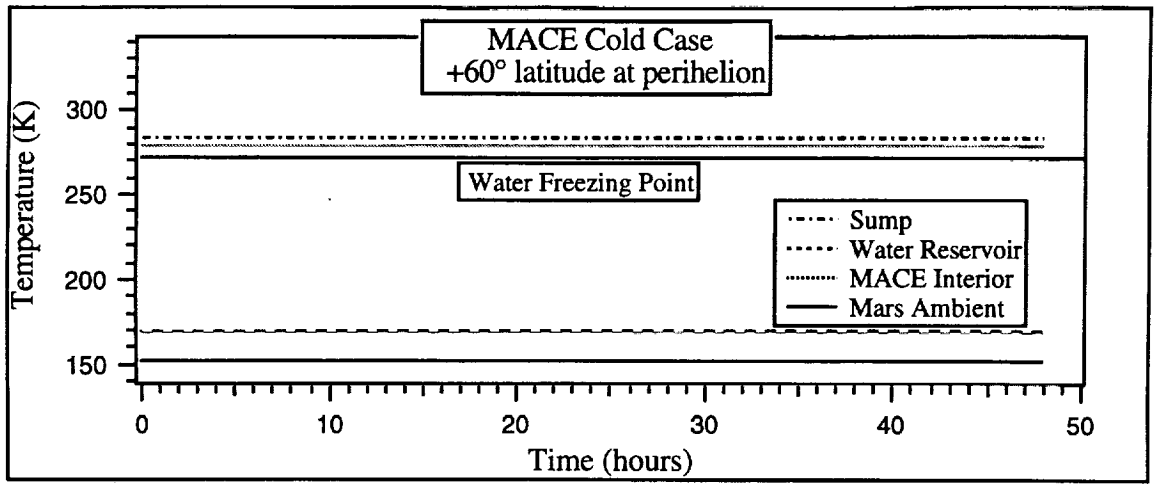

Figure 6 Thermal Model Cold Case Temperature Profiles

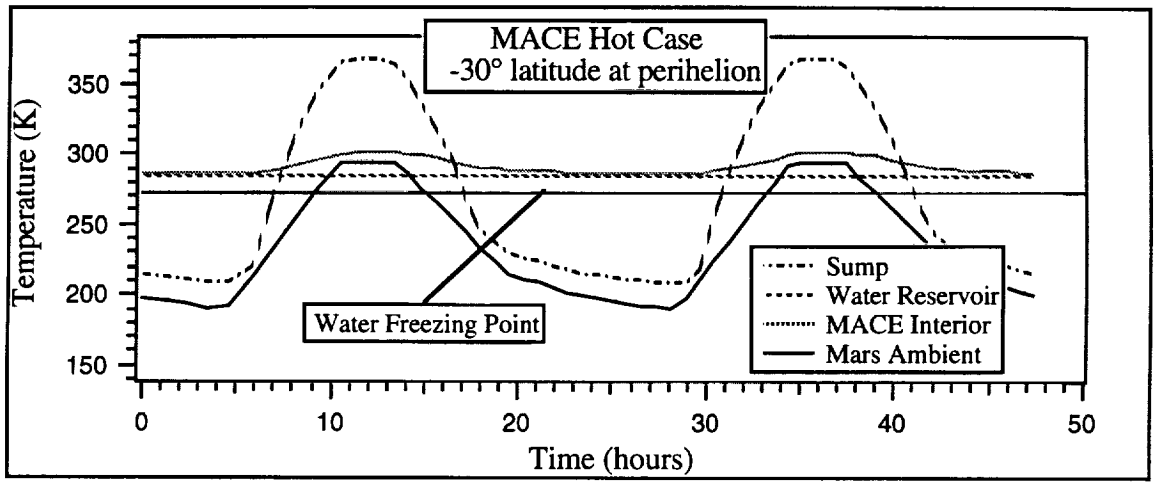

Figure 7 Thermal Model Hot Case Temperature Profiles

The launch and prelaunch environments have not yet been analyzed, but environmental conditions and instrument conditions were assumed. For prelaunch, a constant purge of dry, inert gas is used to keep everything cool. This is to remove RHU heating using convection, without benefit of a cool radiator to remove the heat from the enclosure. There is also the option to pre-cool the entire instrument to some low temperature immediately before launch. During launch there is no gas purge, and no opportunity for cooling until the spacecraft is in orbit. This interval is on the order of 5 to 10 minutes during which the instrument will self heat. The thermal inertia of the MACE instrument is high enough to minimize the temperature rise during this period. The time interval associated with launch to orbit is short enough that no thermal problems are anticipated. Once the orbit is achieved and during the cruise, the temperature within the spacecraft is assumed to be -60 to -80 °C. This is sufficient to provide a good thermal sink for the MACE radiator to dump any excess heat and maintain the instrument at nominal temperature.

MACE Measurement Subsystems Development

Ion Selective Electrode (ISE) survey

A relationship has been established with the Stanford Research Institute International (SRI International, Menlo Park, CA) to begin development activities associated with miniaturized aqueous ion sensors. The Physical Electronics Laboratory (PEL) at SRI routinely fabricates miniaturized devices with micrometer to nanometer dimensions. The personnel at SRI have a high degree of expertise and direct experience in fabrication of a wide variety of microsensors.

A subcontract to SRI was initiated, using MACE PIDDP funds, to perform a survey of current technology appropriate for use in sensing ions in aqueous solution consistent with the goals of MACE. Dr. Jose P. Joseph (Microsensors Program Director at PEL) performed the technology survey and reported the results. The survey report included mostly solid state electrolyte ISE's, but also addressed other technologies where appropriate. The survey considered the state of current technology, interference and selectivity estimates, recommendations for Ionic Strength Adjustment solutions, and estimates of the development effort required to miniaturize the sensors for use in MACE. The ions/sensors of interest for the purposes of the survey included: Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, H^{+}, Fe^{2+}, Fe^{3+}, SO_4^{2-}, PO_4^{2-}, HCO_3^{-}, NO_2^{-}, Cl^{-}, Br^{-}, oxidation reduction potential, conductivity, and solid electrolyte reference electrodes. SRI was provided with estimates of nominal and extreme case ion concentrations for each of the ions of interest. Table 4 lists the ISE's considered in the survey, the sensing material, theoretical detection limit, and major interfering ionic species.

Table 4 Summary of Ion Selective Electrode Technology Survey for MACE

Ion of Interest (ISE)	Sensing Material	Detection Sensitivity (μM)	Potential Interfering Ions
Potassium (K^{+})	valinomycin	16	Li, Na, Mg, Ca
Calcium (Ca^{++})	(R,R)-N,N'-[Bis(11-ethoxycarbonyl)undecyl]-N,N',4,5-tetramethyl-3,6-dioxaoctnediamide	0.04	Na, K, Mg
Hydrogen (pH)	IrO_2	pH 1 to pH 13	Na, K, Ca
Sodium (Na^{+})	Bis[12-crown-4-methyl]dodecylmethyl malonate	20	K, Mg, Ca, Li
Magnesium (Mg^{++})	N-heptyl-N',N'-bis {8-[[3(heptylmethylamino)-1.3-dioxoproply]amino] octyl}-N-methyl-propanediamide	10	H, Na, K, Ca
Iron (Fe^{++}, Fe^{+++})	dithia-12-crown-4	10	alkaline earth metal ions
Bromide (Br^{-})	bis(diethyldithio carbamato)mercury (II)	10	SO_4, NO_3, Cl
Carbonate (CO_3^{-})	Aliquat 336 dissolved in trifluoroacetyl-p-butylbenzene	10	Cl, SO_4, NO_3
Chloride (Cl^{-})	quaternary chloride salt	10	Br, NO_3, SO_4
Nitrate ($NO3^{-}$)	Orion 92-07 nitrate selective membrane	10	Cl, SO4, CO3, Br
Sulfate (SO_4^{--})	$PbSO_4/PbS/Ag_2S$	50	CO_3, NO_3, Cl
Phosphate (PO_4^{--})	dibenzyltin chloride derivative	80	Cl, Br, NO_3
reference electrode (Fl- or H+)	solid state electrolyte	n/a	n/a
Oxidation - Reduction (redox)	platinum electrodes	n/a	n/a

A wide variety of chemical sensor was considered in the survey, and the conclusion stated that Ion Selective Electrodes (ISE) have sufficient selectivity for the measurement objectives in the MACE instrument. The ISE's listed in Table 3 represents the best candidate sensor based on survey results, with the problematic interfering ions are shown in bold typeface. In most cases the selectivity of the ISE listed was high enough that even in the presence of moderate amounts of potentially interfering ions, the measurement could be performed with an accuracy better than 2%, and precision less than 6%. The main exception to this was the sulfate ISE, where the carbonate ion represents a major interference with measurement of the sulfate ion. This interference may be reduced if pre-treatment of the sample is performed, or if multiple sensors for the same ion are used. The sensors for a particular ion would be fabricated using different sensing materials, and thus have different selectivity patterns. This multiple sensor technique allows independent estimates to be generated for ionic activities based on pattern recognition technology, or neural network analysis. Figure 8 shows a schematic representation of a hybrid sensor structure that may be used in the MACE ISE array. The structure includes high impedance electronics to process the raw signals generated by the sensors directly on the array silicon substrate, minimizing both mass and power.

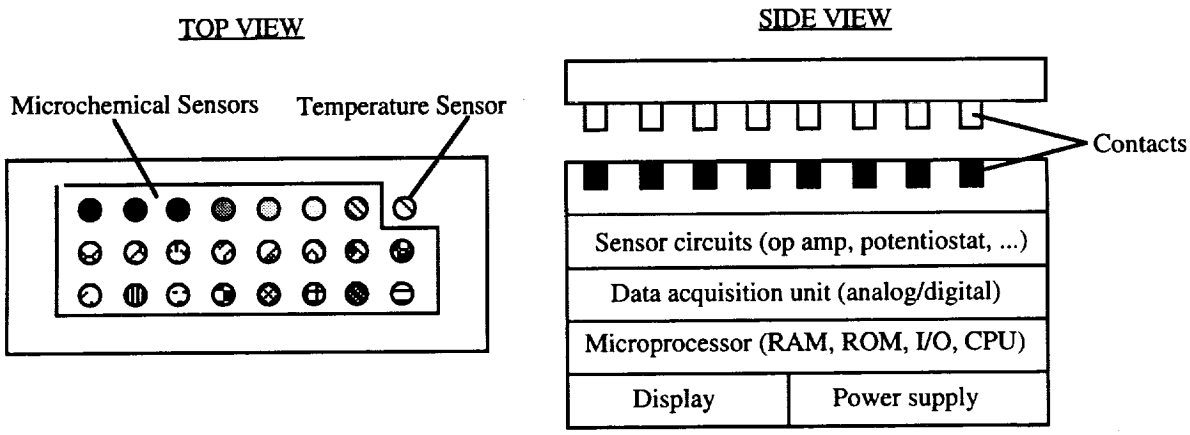

Figure 8 Schematic diagram of Hybrid ISE Structure

An additional task in the survey included a Rough Order of Magnitude (ROM) estimate for development and fabrication of an array of micro-sensors on a single structure. For the purposes of estimation it was assumed that the array included electrodes for each of the ions of interest to MACE, with spacing between adjacent electrodes (center to center) on the order of 300 μm. The sensor area and configuration in each case were determined by the ease of manufacture and maturity of technology. It is difficult to estimate exact development costs without further definition regarding membrane materials, multiple sensing strategies for particular ions, and sensor redundancy issues. At this point in time, the development cost estimate is in the range from $400 to $600 k for an array of sensors that includes capabilities for measuring each of the ions of interest to MACE.

It is possible to utilize the ISE sensors in a dual capacity in the MACE instrument. The physical layout of the sensors on the ISE array will permit the sensors to also be used as water level sensors. When water is introduced into the analysis chamber, contact with each electrode sensor produces a distinct change in the electrical signal produced by that sensor. Aligning the sensors in a linear array in the analysis chamber will enable the water level to be sensed directly in the chamber. The reference electrode must be at the chamber bottom, and the first electrode to be contacted by the water. As the water level rises in the analysis chamber, contact with each ISE completes an electrochemical cell, and allows ion measurement and level sensing operations to commence.

Mg++ ISE development

Development activities have been initiated to fabricate a miniature Mg++ ISE using Martin Marietta Internal Research and Development (IRAD) funding. No commercial ISE is currently available (using liquid or solid electrolyte materials) for sensing Mg^{++} ions in aqueous solution. Mg^{++} ions that are thought to be important constituents in the Martian regolith, and are included in ions of interest for the MACE instrument. The development is intended as an ISE technology proof of concept demonstration for MACE instrument feasibility. The sensors will be of miniature size in a wire configuration (1 mm diameter by 2 mm length), and have full functionality over the concentration range from 0.01 to 1000 mM. The ISE selectivity and response characteristics will be fully documented when the sensors are completed in July 1994.

Evolved Gas Sensors

Work has begun on development of miniaturized solid state sensors for gases of interest to MACE. Gas may primarily be evolved from superoxide and carbonate mineral decomposition, but other reactions may also evolve gases of interest. The two major gases of interest are oxygen and carbon dioxide. The following sections describe the development activities associates with the gas sensing technologies appropriate for the MACE application. The sensors described utilize solid state electrolyte materials, and are readily amenable to miniaturization. The major problem associated with sensors of this type in the MACE application is the high operational temperature requirement (≈500°C), however a miniaturized array of sensors should require minimal power to operate.

CO2 Sensor Development, Testing, and Apparatus

A prototype solid electrolyte potentiometric CO_2 sensor of miniature size was developed for proof of concept studies. The sensor is configured in a planar geometry, with solid state reference and measuring electrodes co-located on one side of a beta alumina electrolyte substrate. A thick film platinum heater on the opposite side of the alumina allows operation at high temperatures.

Experimental Apparatus

Figure 9 shows the laboratory setup used to evaluate the sensor performance at reduced pressures. The vacuum sensor chamber has a volume of about one liter. It is connected to various test gas cylinders at the inlet, and to a large vacuum chamber capable of attaining sub-millitorr pressures on the outlet. Gas flow metering valves on the inlet and outlet ports allow the gas composition and total pressure in the sensor chamber to be varied over a wide range during the experiments. Data regarding the chamber pressure is monitored using an electrical strain-gauge pressure transducer interfaced to the data acquisition computer. Calibration and verification of the electrical pressure gauge were performed using a mechanical absolute pressure gauge that is traceable to a NIST standard. The sensor and heater temperatures were determined by measuring the resistance through the platinum heater element. Prior to these experiments the heater element resistance was correlated to the melting points of various pure materials. The experiments consisted of systematically varying the total pressure, gas composition, and sensor heater voltage and current while acquiring voltage data from the sensor electrochemical potential. The total pressure in the sensor chamber ranged from 50 to 130 mbar, and covered a variety of gas compositions using Argon, Oxygen, and Carbon Dioxide. The post test data analysis involved correlation of the sensor output data to the gas composition, thermal, and total pressure environments. Figure 2 shows a schematic diagram of the sensor, including dimensions, measurement interfaces, and environmental influences on the sensor output.

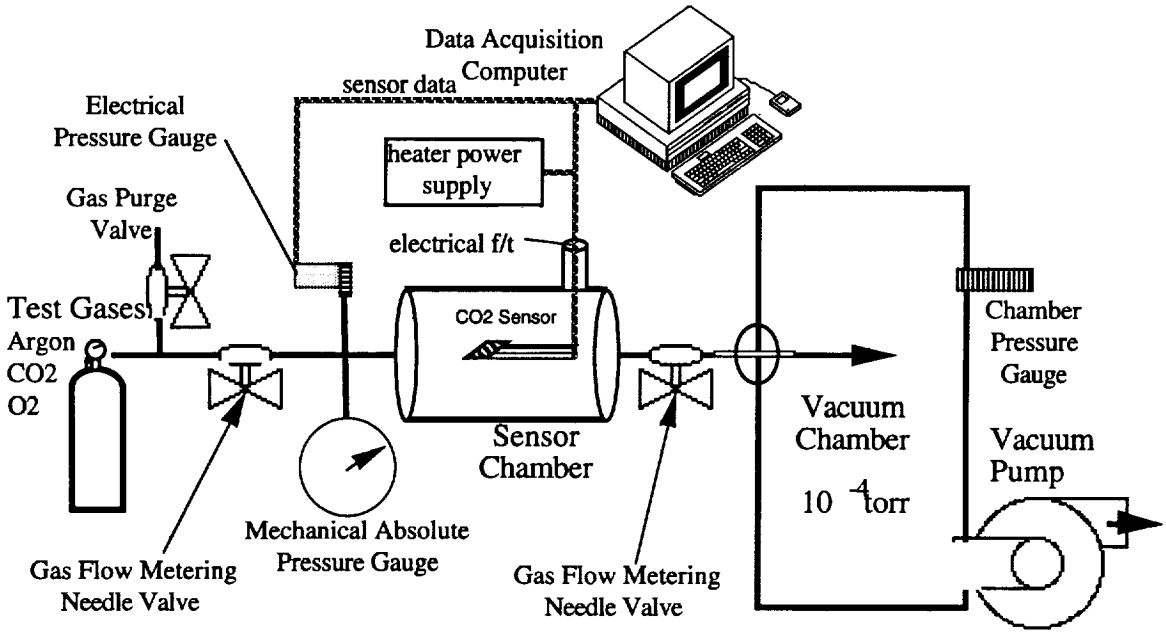

Figure 9 Experimental Setup for Solid State CO2 Electrochemical Gas Sensor Reduced Pressure Tests

Carbon Dioxide Sensor Test Results

The sensor response was found to be a complex function of the total pressure, sensor temperature, gas composition, and CO_2 partial pressure. Analysis of the data has shown that the thermal and gas composition environments influence the output sensor electrochemical potential through separate mechanisms. Figure 10 shows the **Thermal Influences** in bold, and the *electrochemical influences* in italic.

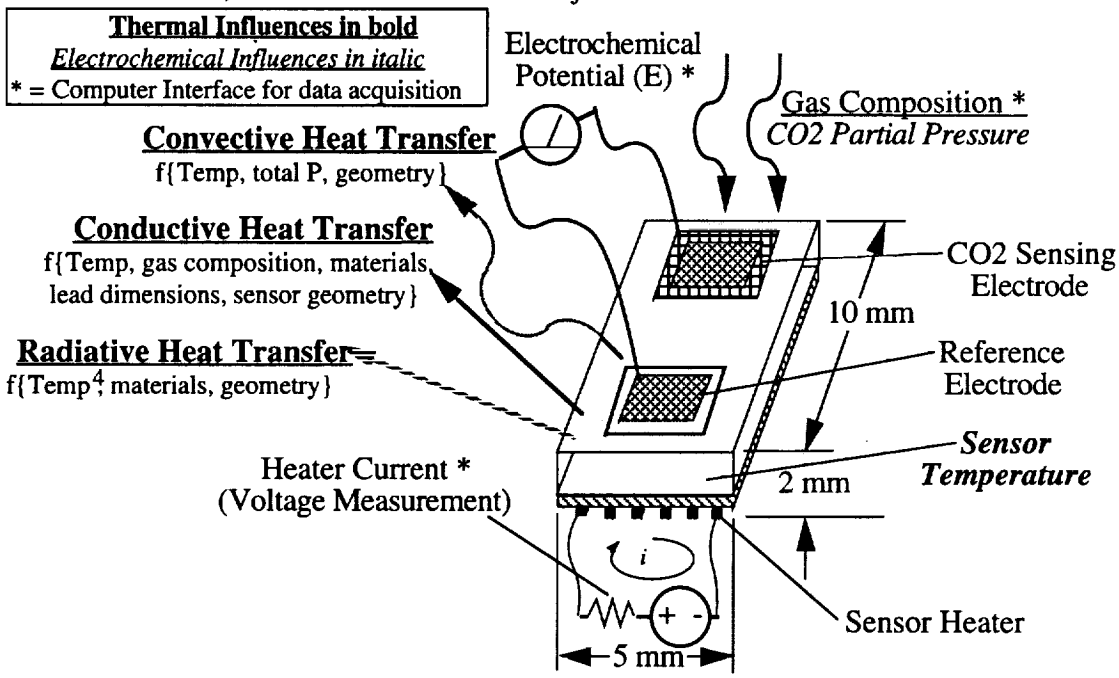

Figure 10 CO2 Solid State Electrochemical Gas Sensor Schematic Showing Measurement and Environmental Interfaces

The parameters and mechanisms that correlated with the thermal performance of the sensor include heater temperature, sensor materials (emissivity, conductivity), sensor geometry (surface area, view factors, lead dimensions), total pressure (convective heat transfer), and gas composition (gas conduction heat transfer). These factors will change upon further sensor miniaturization. The electrochemical factors associated with the sensor performance include the sensor temperature, gas composition (CO_2 partial pressure), and the total pressure. The electrochemical effects are essentially independent of the sensor size.

Figure 11 shows results for the reduced pressure Nernst response for a family of sensor temperatures. The minimum detectable limit of CO_2 under the test conditions (50 mbar Ar and 1 mbar O_2) is shown to be less than 1 mbar CO_2 partial pressure, determined from the Nernst plot intercept with the 0 mbar CO_2 partial pressure condition. The figure also shows the variation of Nernst slope with temperature.

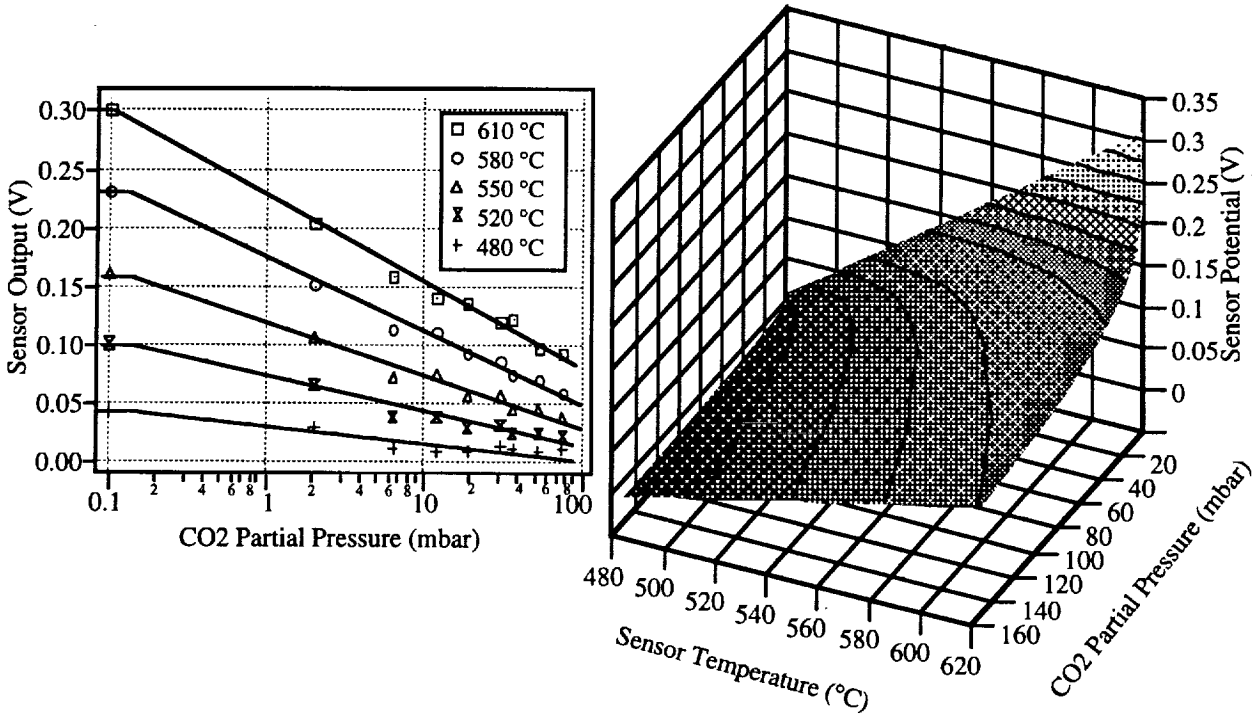

Figure 11 Reduced Pressure Nernst Response for Sensor Temperature Family of Curves

Sensor selectivity studies were also performed using variable oxygen partial pressure in reduced pressure environments of constant CO_2 and Argon gas compositions. The results show that the Nernst slope for oxygen response passes through zero, and that selection of an appropriate sensor temperature will result in sensor operation that is completely independent of the oxygen partial pressure. The Nernst slope coefficients for O_2 and CO_2 were seen to follow similar functions of temperature, with the O_2 coefficients of much lower magnitude than the CO_2 coefficients.

CO2 Sensor Experiment Summary and Conclusions

The solid state electrochemical gas sensor concept has been proven for operation in reduced pressure environments. The sensor thermal performance was found to be a function of materials, geometry, and pressure environment, and nearly independent of gas composition. Further miniaturization of the sensor will improve the thermal performance while preserving the CO_2 selective electrochemical response. Gas sensors of this type are ideal candidates for use in planetary and space flight instruments. Their rugged nature, small size, low mass and power consumption, and demonstrated reduced pressure performance satisfy the rigorous MACE instrument performance requirements.

Solution Electrical Conductivity Sensor

The salts likely to be present within a Martian regolith sample will alter the electrical conductivity of the analysis water during aqueous dissolution. Measurement of the kinetics of the solution electrical conductivity will yield insight into the total ionic content, while the ISE's will measure specific ion content. The nature of the measurement requires that electrical current be passed through the solution, but the quantity should be minimal to avoid any unintentional electrochemistry from occurring. The total ionic content of the aqueous solution could be quite high, and the measurement should be able to cover several orders of magnitude to provide functionality over the full dissolution range from deionized water to saturated salt solutions. A measurement concept was developed using a single constant current (DC) pulse of short duration. Integration of the voltage waveform required to maintain the constant current pulse yields information regarding the solution resistivity and conductivity. A prototype sensor and electronics assembly has been fabricated, and preliminary tests performed.

A parallel wire conductivity cell was fabricated from 0.020 inch diameter platinum wire, inert epoxy and acrylic plastic. The two electrode wires in the cell are each 5 mm long, spaced 5 mm apart and set into a ~7 mm dia acrylic puck that is about 15 mm long. This configuration allows readings to be taken from standard solutions in test tubes, rather than dispensing the standard solutions and rinsing with deionized water in a full MACE like arrangement. The sensor was couped to the electronic conductivity measurement circuit that to supplies a 20 msec constant current DC pulse. The circuit includes a switched bank of resistors set at multiples of 10 x so that the current pulse between the electrodes can be adjusted between 1μA and 10 mA in factors of 10. An operational amplifier drives the DC pulse, and the conductivity is read as the voltage waveform integrated over the pulse duration. It was observed that after the current pulse was applied, the ground reference showed a voltage offset for tens of seconds, an effect analogous to the charging of a battery. To minimize this problem the pulse duration was reduced to 2 msec. Circuitry was also installed to allow the circuit to be read automatically with a computer rather than through the oscilloscope that had been used during development. Work has been started on the next generation system that will utilize a constant voltage - variable current operation mode to minimize the electrochemical effects and simplify the data acquisition interface.

Aqueous Solution Stirring Mechanisms

A mechanism is required to agitate the analysis chamber during dissolution experiments. The stirring facilitates the distribution of ions throughout the aqueous solution, impedes the formation of an ion depletion layer around the ISE's, and allows measurement of a homogeneous solution. If stirring were not used the ISE array measurements would be subject to uncertainties associated with differential ion diffusivities and solubilities, and depletion boundary layer formation. Additionally, the particle settling experiment requires that particles be initially suspended in solution to enable the kinetics of particle settling to be measured. Three methods were investigated for agitating the soil sample and analysis water in the MACE instrument analysis chamber. These methods include a magnetic

stirring bar (Teflon coated), a vibrating whip, and a piezoelectric transducer, each of which is described in the following paragraphs.

The magnetic stirring bar method is commonly used in analytical laboratories, and is available as a commercial unit. The mechanism is easily made and effective as long as the material being stirred isn't too thick, or contains any magnetically affected particles. In a laboratory setting power, mass, and space are not usually a consideration. This is not the case in the MACE instrument, and special mechanisms must be designed to minimize the mass and power associated with the stirring mechanism. There is also a high probability that the soil sample will have particles that are magnetically affected, such as iron oxides in the clay fines. For these reasons the magnetic bar stirring method is not considered appropriate at this time.

The second option evaluated consisted of an oscillating paddle mechanism, constructed using Kynar piezoelectric material. The paddle was constructed from a "bimorph", that is, a laminated composite of two piezoelectric layers bonded together. The paddle measures 8 mm wide at the base, tapers to 3 mm width at the tip, and is 25 mm long. To mechanically drive the "bimorph" paddle requires a voltage source of about 260 volts to be alternately applied to each layered surface. Since this paddle will be in contact with the conductive aqueous solution, it was coated with a thin layer of insulating silicone rubber to keep from shorting the power supply. The vibration at the paddle tip was measured to be about 15 mm in air when driven at its resonant frequency, and about 6 mm maximum when not at resonance. In water, the mechanical action was damped to about 4 mm. The larger degree of motion at resonance was not observed when in the water. The stirring action that resulted from the paddle movement in water was minimal. If the frequency of motion was set too high, the paddle action went into a harmonic mode where the agitation produced was not very effective. The advantage to this method is the low power consumption ($\approx$200 mW), but the stirring action produced was not very effective.

A third mixing mechanism that utilized a sonic transducer was fabricated and evaluated, also made of piezoelectric Kynar. The mechanism was driven by a signal generator through an amplifier circuit to supply a voltage to the transducer of about 90 volts. Again, since the transducer was in intimate contact with a conductive solution, it was coated with a thin layer insulating silicone rubber. Agitation from this unit was observed to be even less effective than the vibrating paddle. It may be that the amount of power required for effective agitation was beyond what the transducer can couple to the solution, or that the amplifier output rolls off before an appropriate frequency is reached. Further tests and mechanisms are planned to devise a mechanism to enable stirring and agitation within the MACE analysis chamber.

Optical Sensing of Suspended Particles

One or more of the ten test cells in MACE is planned to be equipped with instrumentation to measure the kinetics of particle settling using optical techniques. This haws been termed the Particle Settling Experiment (PSE), and will yield information relating to particle size and distribution of the insoluble portion of the Martian regolith. The settling rate of particles suspended in solution is known to be proportional to the particle size distribution, and measurement of a regolith sample on Mars should provide an *in situ* estimate of the size distribution of insoluble particles. A test system is currently being designed to investigate how light transmission and scattering can be used to perform this measurement. This includes various light sources (LED, laser diodes, laboratory lasers) and detectors (single and arrays of photodiodes). The detector and cell geometries are being developed to enable the use of both forward and side scattering to maximize the measurement sensitivity. During the initial portion of the experiment, when particles have just been suspended via the stirring mechanism, forward scattering (or transmission) will provide the highest

sensitivity to particle settling. Small changes in the optical density of the suspended solution will be manifest as large differences in optical transmission, providing a high signal to noise ratio on the measurement. Conversely, at the end of the experiment when particles have settled out, scattered light will be highly sensitive to suspended particles.

There are many variables to consider in the development of this analysis, including: reduced gravity effects, irregularly shaped particles, anisotropic light scattering, and optical cell geometries. The initial effort is directed toward proving the measurement concept. Once a system has been developed, measurements will be performed using a variety of mono- and poly-disperse particle size distributions. The fidelity of the measurements acquired will determine the efficacy of this type of experiment. The amount of scattering depends upon the number of suspended particles, their size, shape, and composition. For a suspension of identical spherical particles of diameter D and index of refraction η, Mie scattering theory predicts that the ratio of the optical power scattered into a detector at angle ϕ and θ to the power in the incident beam is given by equation (1):

$$\frac{\Phi(\theta,\phi)}{\Phi_0} = \frac{nL}{k^2}\{[\int i_p(x,\theta,\eta)\cos^2\phi d\Omega]^2+[\int i_s(x,\theta,\eta)\sin^2\phi d\Omega]^2\}^{1/2} \quad (1)$$

where:

$\Phi(\theta,\phi)$= power scattered into detector in direction (θ,ϕ) [W];
Φ_0= power in incident beam [W];
$d\Omega$= solid angle subtended by detector at scattering center= $\sin\theta d\theta d\phi$ [sr];
n= number density of suspended particles [cm^{-3}];
L= length of the scattering volume [cm];
k= magnitude of incident light wavevector =$2\pi/\lambda$ [cm^{-1}];
$i_p(x,\theta,\eta)$= parallel component of the Mie scattering function [sr^{-1}];
$i_s(x,\theta,\eta)$= perpendicular component of the Mie scattering function [sr^{-1}];
x=particle size parameter=$2\pi D/\lambda$ [dimensionless].

Figure 12 shows the geometry of the scattering measurement. This equation assumes single scattering only. If the particle cloud is dense enough to produce multiple scatter, the situation is far more complex.

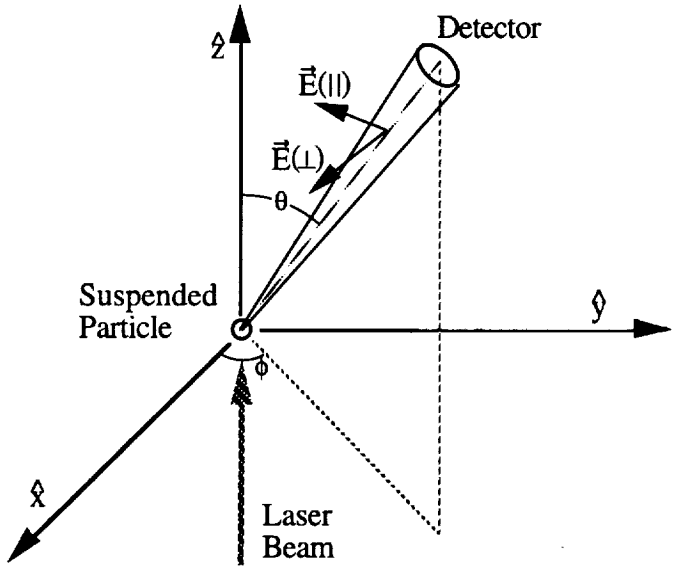

Figure 12 Geometry of the Suspended Particle Light Scattering Experiment

Equation (1) can be used to solve for the particle number density, n, if the particle size and index of refraction, η, are known from a single detector measurement of the scattered power. In a realistic experiment there will be particles of different sizes, shapes, and compositions. The total scatter will be a combination of the right hand side of equation (1) for many particle species. The accuracy with which n can be determined, if at all, will depend on the number of scattering angles which are taken as well as *a priori* knowledge of the nature and types of particles in the soil sample.

A proof of concept experiment has been performed to investigate the efficacy of making such measurements over a period of time which allows the particles to settle. A laser beam is directed into a water filled optical cuvette (1 cm path length) and a soil sample introduced. Small detectors such as silicon photodiodes and phototransistors were placed around the test cell to enable measurement of the scattered light resulting from the suspended particles in the water. The rectangular optical cell was constructed using a plastic cuvette, blackened on its interior surfaces to reduce internal reflections from the walls. A Helium Neon (HeNe) laser operating at 630 nm was used to provide the incident beam. Available sensors were used (a Newport silicon diode sensor and a Hamamatsu lateral effects sensor), and set up to monitor transmitted (straight through position) and scattered light (at a right angle to the incident beam). Photodiodes and phototransistors with matching preamplifiers are planned to replace these larger detectors in later versions of this experiment. The smaller the detector, the more refined the angular location for the scattered light measurement.

The straight through position is essentially an optical transmission measurement. The more particles in suspension, the more light is scattered, and the less light transmitted. The scattering measurement at a right angle to the incident beam varies in the opposite way: the more particles, the more laser light scattered into the detector. As the particles settle out with time, the transmission detector registers more and more light while the scattered registers less and less. Pure water (*i.e.*, no suspended particles) provided the calibration reference point for both measurements. The initial experiments were performed using sand (SiO_2) particles that had been sieved through 230 mesh screen, resulting in a particle distribution having diameters less than 63 μm.

The results of the initial proof of concept experiments show that multiple scattering occurs within the suspended particles during the first hours of settling. The narrow incident laser beam blossoms into a cloud of radiance which nearly fills the cell, and results in multiple scattering. Later, as more particles settled out, fewer particles (the smaller ones and the ones with large settling times) remained in suspension in the laser optical path, and single scattering dominated. The experiments were successful in demonstrating the light scattering concept, and showed that this technique will be useful for measurement of particle settling times in the MACE instrument. Further experiments are required to determine how the detected scattered and transmitted light profiles can be used to measure the particle size distribution, and in turn used to calculate the number density as a function of particle size. It also remains to be determined how the reduced gravity of Mars will affect the settling time on known particle size distributions.

Plans for the Remainder of the MACE contract

There are several sensor and interface issues that remain to be resolved for the MACE instrument. These sensors and issues are detailed in the following sections.

Amperometric Ion Sensor for Fe^{2+} & Fe^{3+}

A custom miniature sensor (≈1 cm2) has been acquired for sensing Fe ions in aqueous solution. No sensor for this application is commercially available. The Edison Sensor Technology Center at Case Western Reserve University (Cleveland, OH) has developed the thick film metallization technology for fabrication of these sensors that respond to both Ferric and Ferrous ions in solution. The sensor has three electrodes, and operates in an amperometric mode, where the current flowing through two of the sensors electrodes is measured at a given bias on the third electrode. Sensor interface electronics are required to supply the bias voltage and measure microamp scale currents are required for sensor operation. The electronics is termed a "potentiostat", that functions to apply a bias voltage to reference and counter electrodes while measuring the current through working electrode. The measured current signal is proportional to the activity of Fe ions in solution.

A computer interface to a potentiostat circuit will be developed to allow parametric evaluation of the sensor characteristics as a function of Ferric and Ferrous ions concentration, bias voltage, and solution temperature.

Miniature Solid State Oxygen Gas Sensor

A custom miniature amperometric solid state oxygen sensor has been acquired from the Edison Sensor Technology Center at Case Western Reserve University. The sensor operational characteristics will be evaluated and characterized in a low pressure environment, and the interferences and limitations measured.

Carbon Dioxide Gas Sensor Activity

A new version of the CO_2 sensor described in the Evolved Gas Analysis section is currently being fabricated at SRI International using Martin Marietta Internal Research and Development (IRAD) funds. The new version is based on different solid electrolyte materials in the measuring electrode that are non-hydroscopic. The use of these materials should result in a gas sensor that is more immune to H_2O vapor interference effects. The sensor will be characterized under low pressure conditions, and the effects of water vapor documented.

Titration Test Cell (TTC)

A micropump of the type described in the MACE Sample Acquisition and Preparation section of this report in currently being procure from the Wilson Greatbatch Company. This micropump was developed for *in vivo* insulin delivery in diabetic patients. It is a solenoid based pump, with the capability to deliver 0.5 µl of chemical reagent with each actuation.

The micropump will be incorporated into the Titration Test Cell (TTC) to demonstrate its performance. The TTC will be dimensionally similar to the MACE analysis chamber, and will provide a test bed to develop analysis protocols associated with titration and decomposition reactions. The cell will be interfaced to a computer to provide capabilities for sensing one or two ions in solution, chamber gas pressure, and direct control of the micropump operations. Titration analysis will involve measured addition of a chemical reagent(s) while measuring the effect on specific ions in solution. For example the buffering capacity of a solution can be measured by monitoring the solution pH during acid or base reagent addition. Decomposition reactions that are associated with gas evolution events may also be monitored. Carbonate minerals readily decompose upon acidification,

evolving CO_2. The kinetics of this reaction can be controlled using the micropump for acid addition, allowing the evolved gas to be measured using the chamber pressure gauge. Demonstrations of this type are planned for the TTC.

The demonstrations described above may be documented using a video system that is interfaced through the computer. This system includes a video character generator that provides capability for real time display of acquired data. The data is interfaced through a character generator, and superimposed over the actual test images, allowing the planned proof of concept demonstrations to be unambiguously documented. The data that may be displayed includes ISE measurements, solution temperature, conductivity, chamber pressure, and reagent addition equivalent values.

Fabrication of the MACE Sample Transport Model

An actual size model having some working mechanisms is planned to demonstrate the MACE instrument sample handling and analysis concepts. The model will include physical representations of all major subsystems, and demonstrate the functionality and layout of the sample transport systems. Shaped memory actuated mechanisms will be used in appropriate subsystems to provide functionality and demonstrate the applicability.

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16. Abstract

MACE is designed to conduct a variety of measurements on regolith samples, encompassing mineral phase analyses, chemical interactions with H2O, and physical properties determinations. From these data, much can be learned or inferred regarding the past weathering environment, the contemporaneous soil micro-environments, and the general chemical and physical state of the Martian regolith. By analyzing both soil and duricrust samples, the nature of the latter may become more apparent. Sites may be characterized for comparative purposes and criteria could be set for selection of high priority materials on future sample return missions.

The second year of the MACE project has shown significant progress in two major areas:

•MACE Instrument concept definition: A baseline design has been generated for the complete MACE instrument, including definition of analysis modes, mass estimates and thermal model. The design includes multiple reagent reservoirs, 10 discrete analysis cells, sample manipulation capability, and thermal control.

•MACE Measurement subsystems development: Progress is reported regarding measurement capabilities for aqueous ion sensing, evolved gas sensing, solution conductivity measurement, reagent addition (titration) capabilities, and optical sensing of suspended particles.

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