



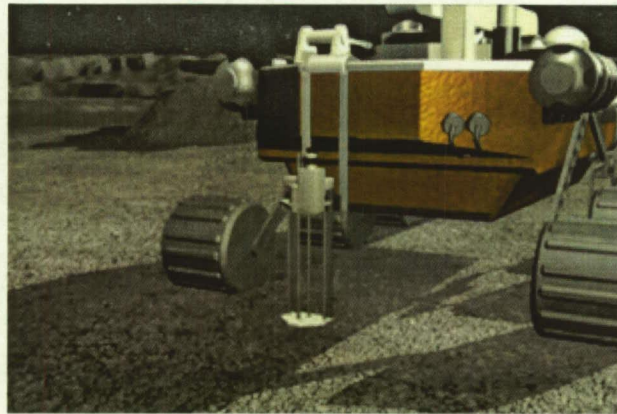
Selection, Development and Results for The RESOLVE Regolith Volatiles Characterization Analytical System

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RESOLVE:

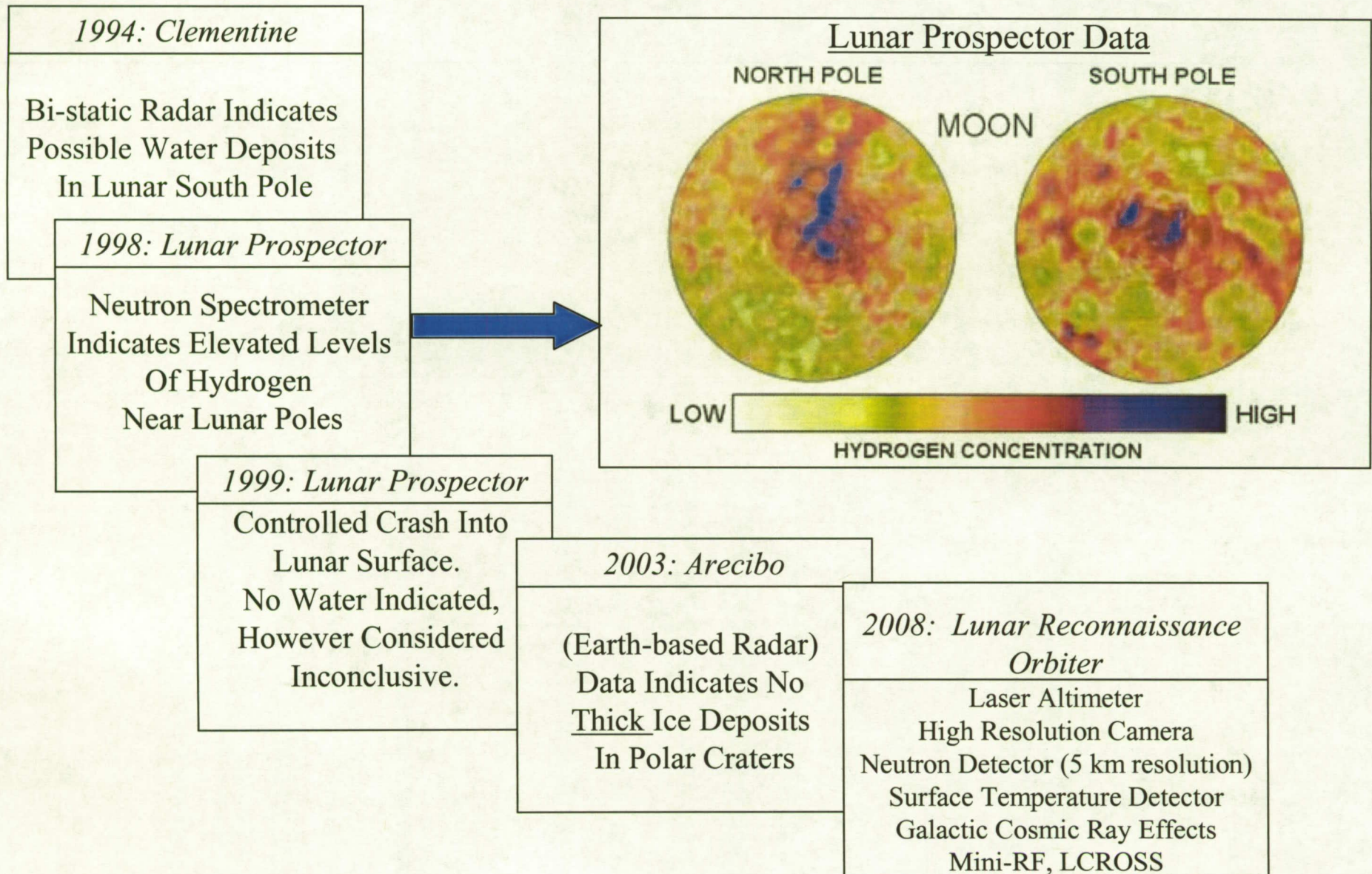
A Bridge Between Early Lunar ISRU & Lunar Science Objectives





Hydrogen or Water on the Moon?

RESOLVE: Regolith & Environment Science and Oxygen & Lunar Volatile Extraction

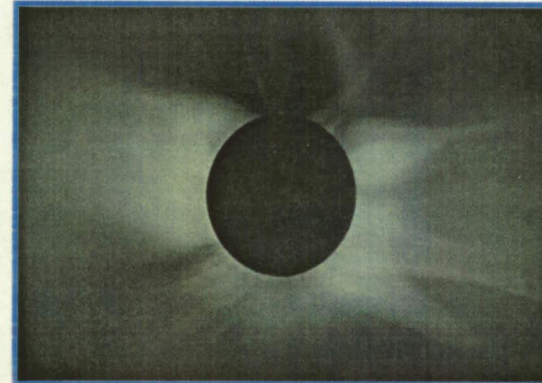




Sources of Polar Hydrogen

RESOLVE: Regolith & Environment Science and Oxygen & Lunar Volatile Extraction

- **Solar wind:**
 - Directly implanted H with preferential retention in cold traps
 - Released and transported from non-polar soil grains
- **Impact of wet objects:**
 - Hydrous meteorites (and micrometeorites)
 - Comets
- **Giant molecular clouds**
- **Planetary degassing**
 - Possible small contribution



Solar Wind



Comets



Giant
Molecular
Clouds



Distinguishing Sources of Volatiles

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Source	Properties
Solar Wind only	Solar D/H (25×10^{-6}) and C^{12}/C^{13} No or very little H_2O
Continuous delivery of solar wind-derived gases	Solar D/H (25×10^{-6}) and C^{12}/C^{13} (but chance of fractionation) Low concentrations of H_2O Possibly roughly uniform distribution of H_2O
Comets, carbonaceous asteroids	High D/H ($100-400 \times 10^{-6}$) (chance of fractionation) Patches of high H_2O concentrations Blocks of ice Other volatiles Organic compounds
Giant molecular clouds	Very high D/H ($10,000 \times 10^{-6}$) Organic compounds Likely to be in concentrated in thin layers?

Jeff Taylor, Univ. of Hawaii



Ground Truth Data Needed

RESOLVE: Regolith & Environment Science and Oxygen & Lunar Volatile Extraction

Gain knowledge to guide future mission architecture decisions to allow utilization of in-situ resources to their fullest extent and optimum benefit.

To do this we must:

- **Understand the resources** (Are there extant resources worth going after?)
 - What resources are there?
 - How abundant is each resource?
 - What are the real and vertical distributions and hetero/homogeneity?
 - How much energy is required to evolve/separate each resource?
- **Understand environment impact on extraction and processing hardware**
 - What is the local temperature, pressure, radiation environment?
 - What are the physical/mineralogical properties of the local regolith?
 - Are there extant volatiles that are detrimental to processing hardware or humans?
- **Design and utilize hardware** to the maximum extent possible that has **applicability to follow-on ISRU missions**
 - Can we effectively separate and capture volatiles of interest?
 - Can we execute repeated processing cycles (reusable chamber seals, tolerance to thermal cycles)?
- **Engage the public about lunar missions and 'living off the land'**



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RESOLVE

Regolith & Environment Science & Oxygen & Lunar Volatile Extraction



RESOLVE Design Working Assumptions

RESOLVE: Regolith & Environment Science and Oxygen & Lunar Volatile Extraction

Resource Working Assumptions

- Hydrogen-source (from satellite observations) shall be on the order of 1000 ppm of regolith mass.
- Chemical form of hydrogen is unknown
 - Estimated average concentration of hydrogen-source is 0.1% to 0.9% by weight in regolith
 - Hydrogen-source most likely hydrogen (H_2) or water (H_2O), but other possibilities include: NH_3 , CH_4 , H_2S , HCN , and CH_3OH , but these are expected to be less than 2% of the water conc.
- Several other volatiles are likely: CO_2 , CO , He , Ne , Ar , etc.
- Composition and concentration of volatiles in polar craters is unknown.
- Buried concentrations of ice to lightly held hydrogen gas is possible. System must handle all possibilities.
- Core drill will deliver 15mm x 25 cm $\frac{1}{4}$ cores for heating and analysis
 - Estimated volume of H_2 or H_2O is 1 liter + other volatiles
 - System should analyze, separate and capture H_2 & H_2O



RESOLVE Objectives

RESOLVE: Regolith & Environment Science and Oxygen & Lunar Volatile Extraction

*Resource
Characterization*

*In-Situ Resource
Utilization Demo*

*Additional experiment
goals if payload &
mission design allow.*

1	Determine form and concentration of hydrogen in permanently shadowed regions	Science - Resource Focused
2	Determine other volatiles available	
3	Determine grain size distribution and morphology of regolith	
4	Determine quantity of which volatile(s) are evolved by excavation & crushing	
5	Determine chemical/mineralogical properties	
6	Determine bulk excavation related physical properties of regolith	Engineering - Processing Focused
7	Demonstrate capture and separation of water	
8	Demonstrate oxygen extraction	
9	Engage & Excite Public/Education Outreach	
G1	Determine difference between sunlit and shadowed regions	Rover required
G2	Determine spatial distribution of resources	Rover required
G3	Demonstrate scalable extraction/processing techniques	
G4	Demonstrate scalable oxygen production technique	



Brief RESOLVE Overview

RESOLVE: Regolith & Environment Science and Oxygen & Lunar Volatile Extraction

- **RESOLVE - Regolith & Environment Science and Oxygen & Lunar Volatile Extraction**
- Goal – identify and quantify volatiles, demonstrate ISRU, engage the public interest in ‘living off the land’ technology
- RESOLVE incorporates 5 modules
 - EBRC (Excavation and Bulk Regolith Characterization)
 - Drill/crusher
 - ERPC (Environment and Regolith Physical Characterization)
 - camera/microscopy/RAMAN
 - ROE (Regolith Oxygen Extraction)
 - Oxygen production
 - RVC (Regolith Volatile Characterization)
 - Oven/GC
 - LWRD (Lunar Water Resource Demonstration)
 - Adsorption beds/droplet demo/electrolyzer



Comparison between GC and MS

RESOLVE: Regolith & Environment Science and Oxygen & Lunar Volatile Extraction

- Gas Chromatography with thermal conductivity detectors
 - (+) we expect large concentrations (% range) which work well with TCDs
 - (+) well established columns for separation and measurement of compounds that are expected
 - (+) measures water
 - (-) unknown compounds may co-elute and be misidentified
 - (-) very low levels of some compounds (He^3) cannot be detected, most compounds detectable down to 1000ppm in the vapor phase
- Mass Spectrometer
 - (+) Unique fingerprint when compounds are isolated
 - (-) Matrix effects
 - Pressure of sample
 - Viscosity of gas varies with composition and directly affects response
 - (-) difficult to interpret spectra with multiple compounds
 - (-) no industrial experience with water quantitation by MS
 - (-) attempts to use MS analysis with RWGS system never produced realistic mass balance
 - (-) cannot differentiate between same mass compounds (ex. N_2 and CO, or HD and He^3)



Selection of Carrier Gas

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- We would like a single injection and carrier gas to analyze H₂, He, and all the other gases of interest
- Whatever the carrier gas, that gas will NOT be analyzed!
- Neon appears to be a good choice, but H₂ & He peaks will be reversed from the other gases... No Problem!

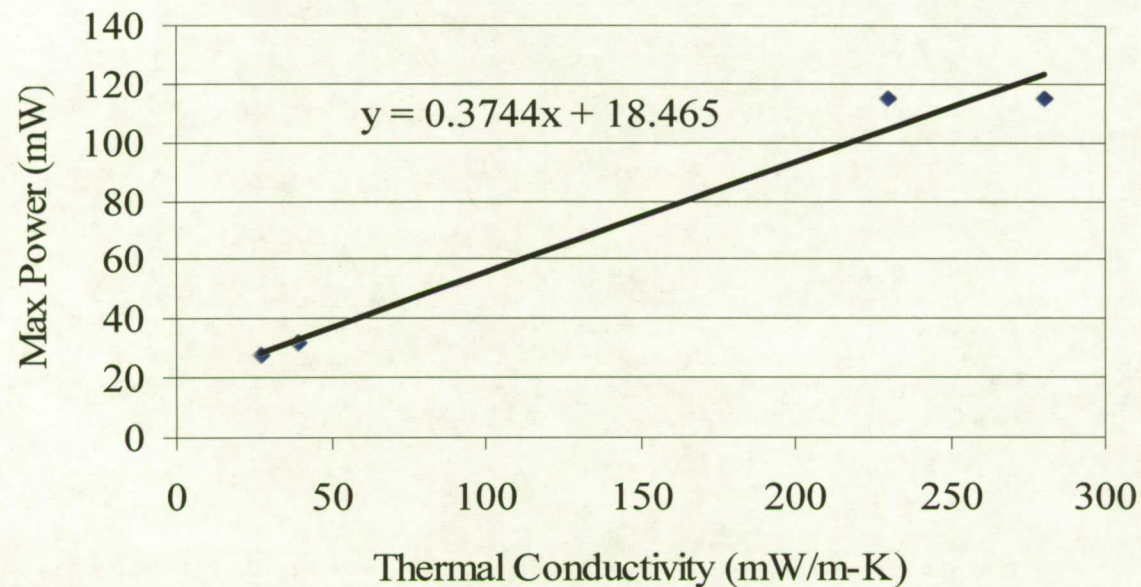
Molecular Formula	Name	Thermal Conductivity (mW/m K)
Ar	Argon	22.6
H ₂	Hydrogen	230.4
He	Helium	190.6
Ne	Neon	60.3
O ₂	Oxygen	33.7
N ₂	Nitrogen	32.3
H ₂ O	Water	27.1
CH ₄	Methane	49.1
CO ₂	Carbon Dioxide	25.1
CO	Carbon Monoxide	32.3



Adjusting Detector Power for Neon

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Gas Name	Maximum Power (mW)	Thermal Conductivity, mW/m K		
		500 K	523 K	600 K
Argon	28	26.8	39.6	44.0
Helium	115	222.3	230.0	252.4
Hydrogen	115	274.0	280.0	300.0
Neon	46	69.9	73.5	78.7





Engineering Breadboard Unit (EBU) 1 Accomplishments

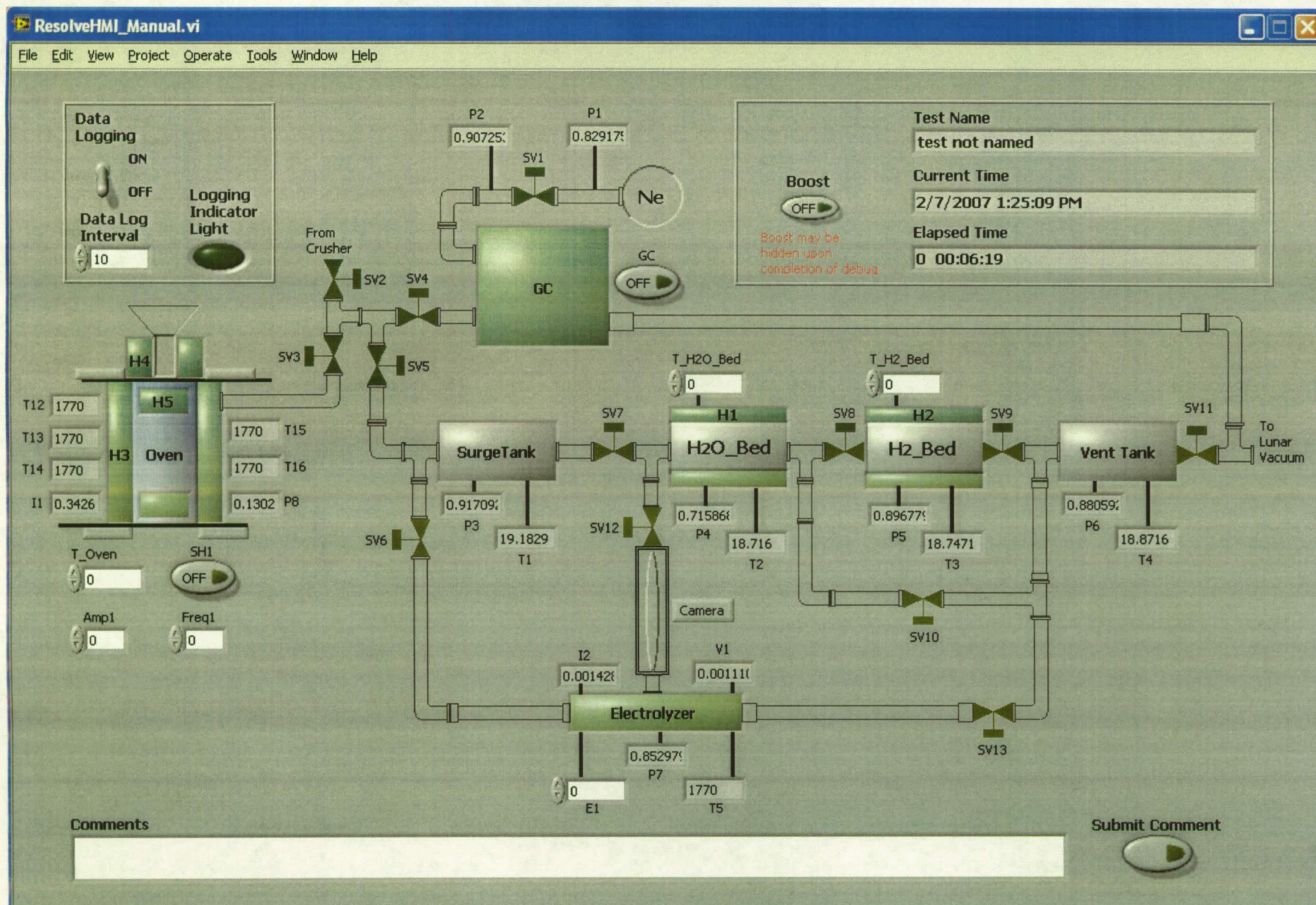
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- Regolith Volatiles Characterization
 - Regolith Oven Complete and Tested (150 C)
 - Oven is vibro-fluidized to ensure even heating (validated by testing)
 - Oven is heated in steps to provide data on release temperatures
 - Siemens Miniature Gas Chromatograph Modified and Calibrated to meet detection objectives.
 - Detection limits in vapor phase: 2-20% water, 1000 ppm – 100% H₂, He, N₂, O₂, CH₄, CO, CO₂.
 - H₂S separated but not calibrated.
 - NH₃, HCN, formaldehyde, and methanol not tested yet



Manual Control Interface

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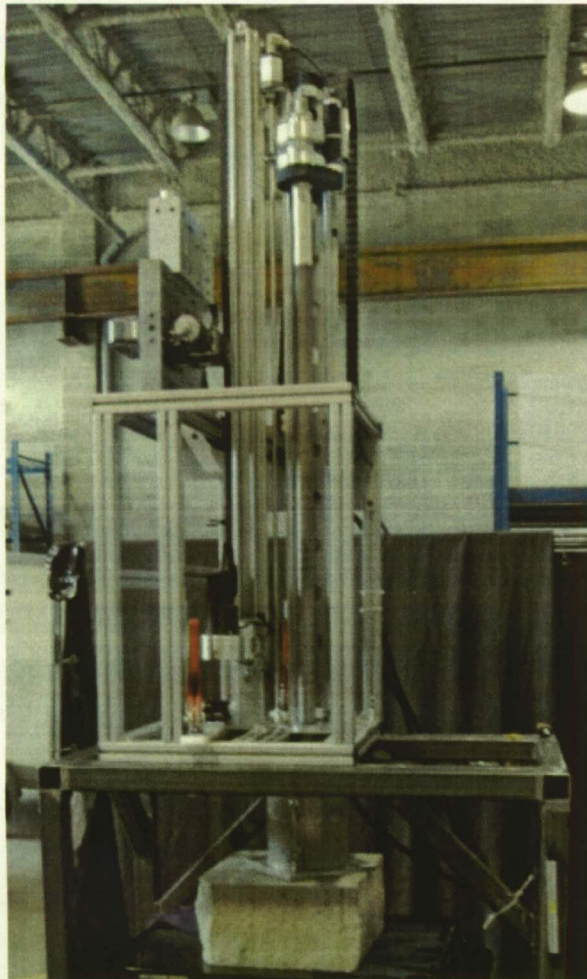




Drill & Regolith Volatiles Characterization Photos

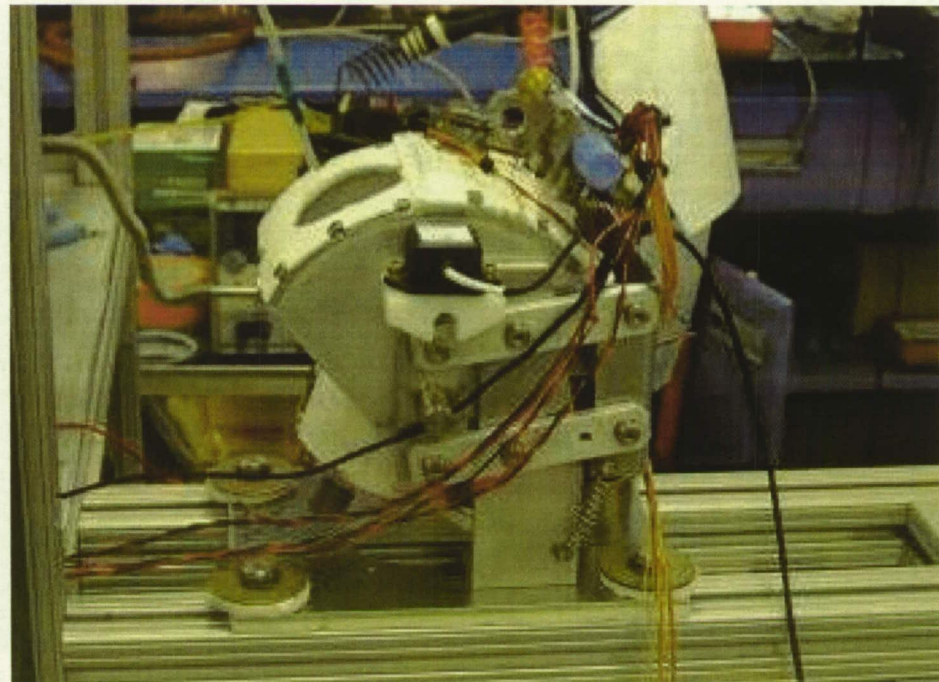
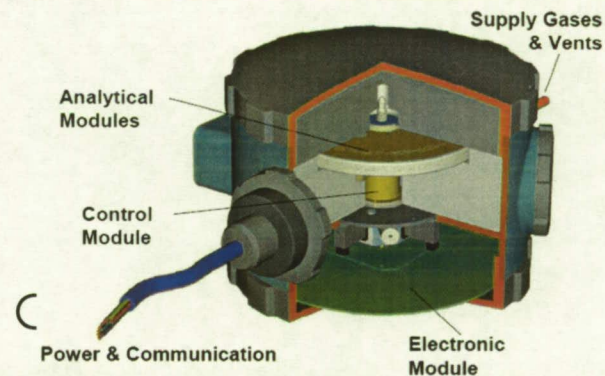
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Details of Siemens MicroSAM GC



Drill & Crusher
(Northern Center for
Advanced Technology)

Dale Lueck/ NASA Kennedy Space Center

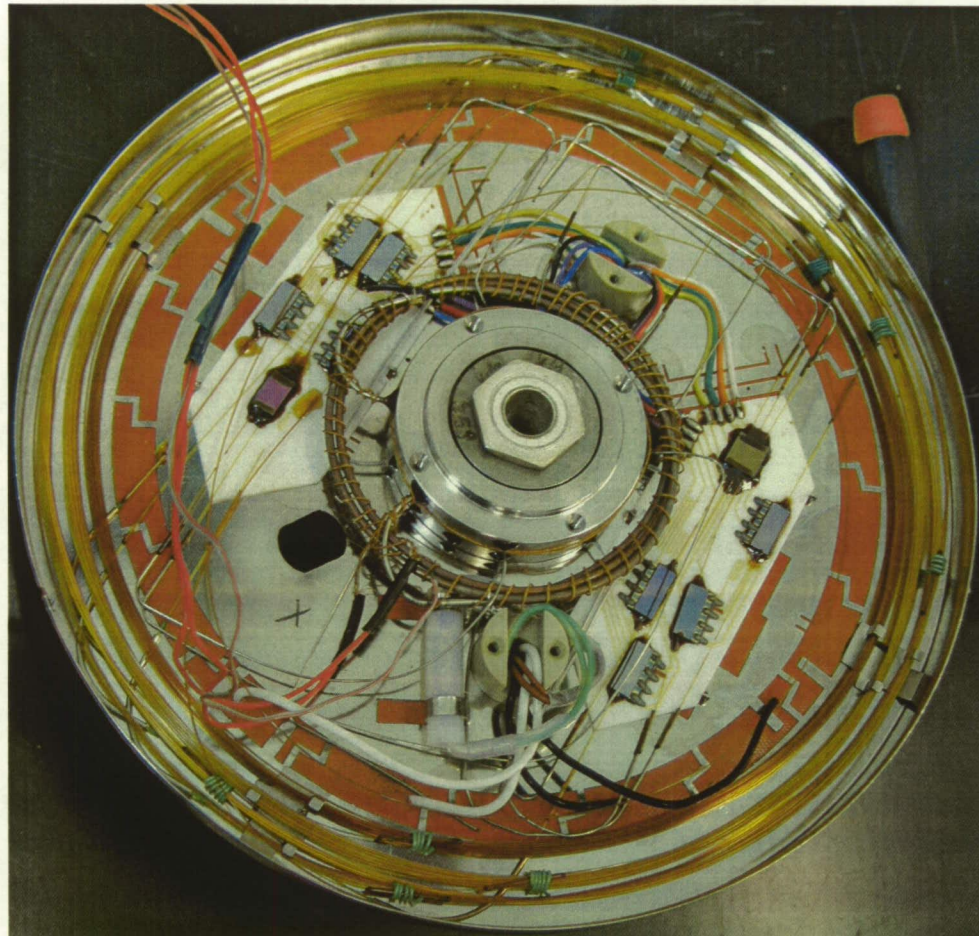


Regolith Volatiles Characterization Oven



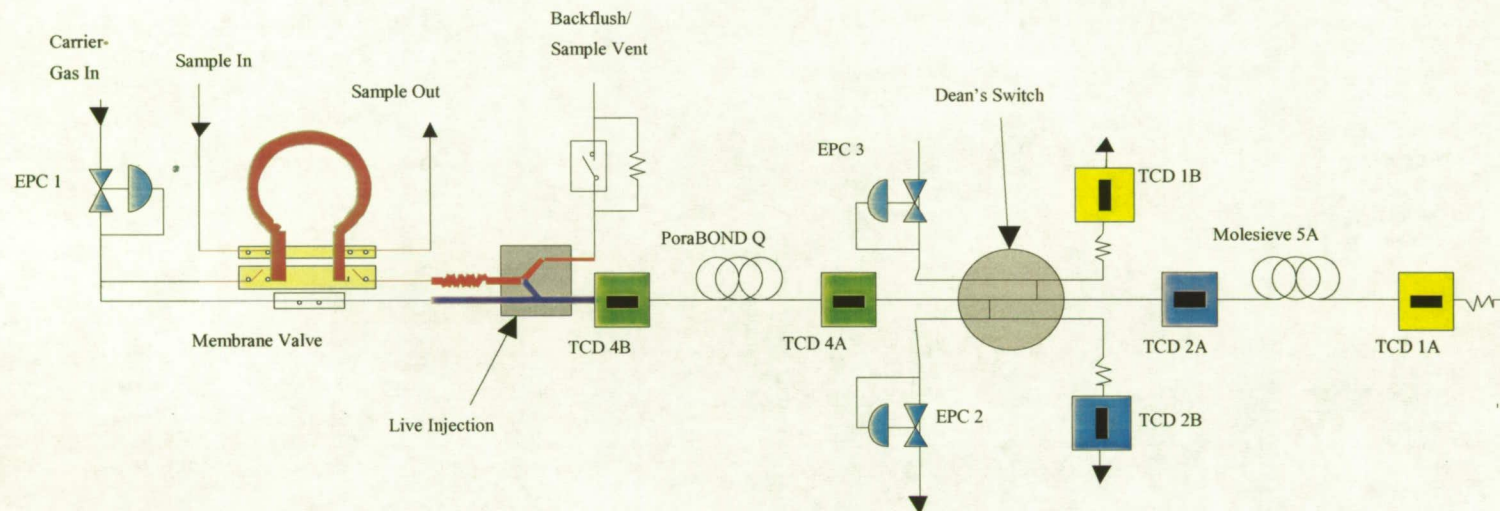
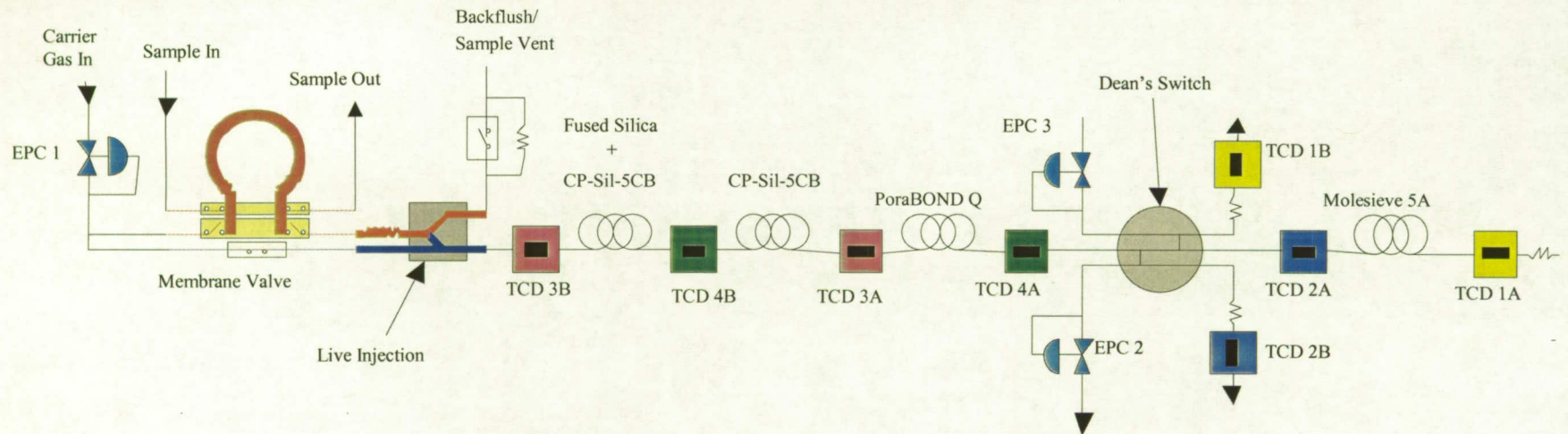
GC Application Module

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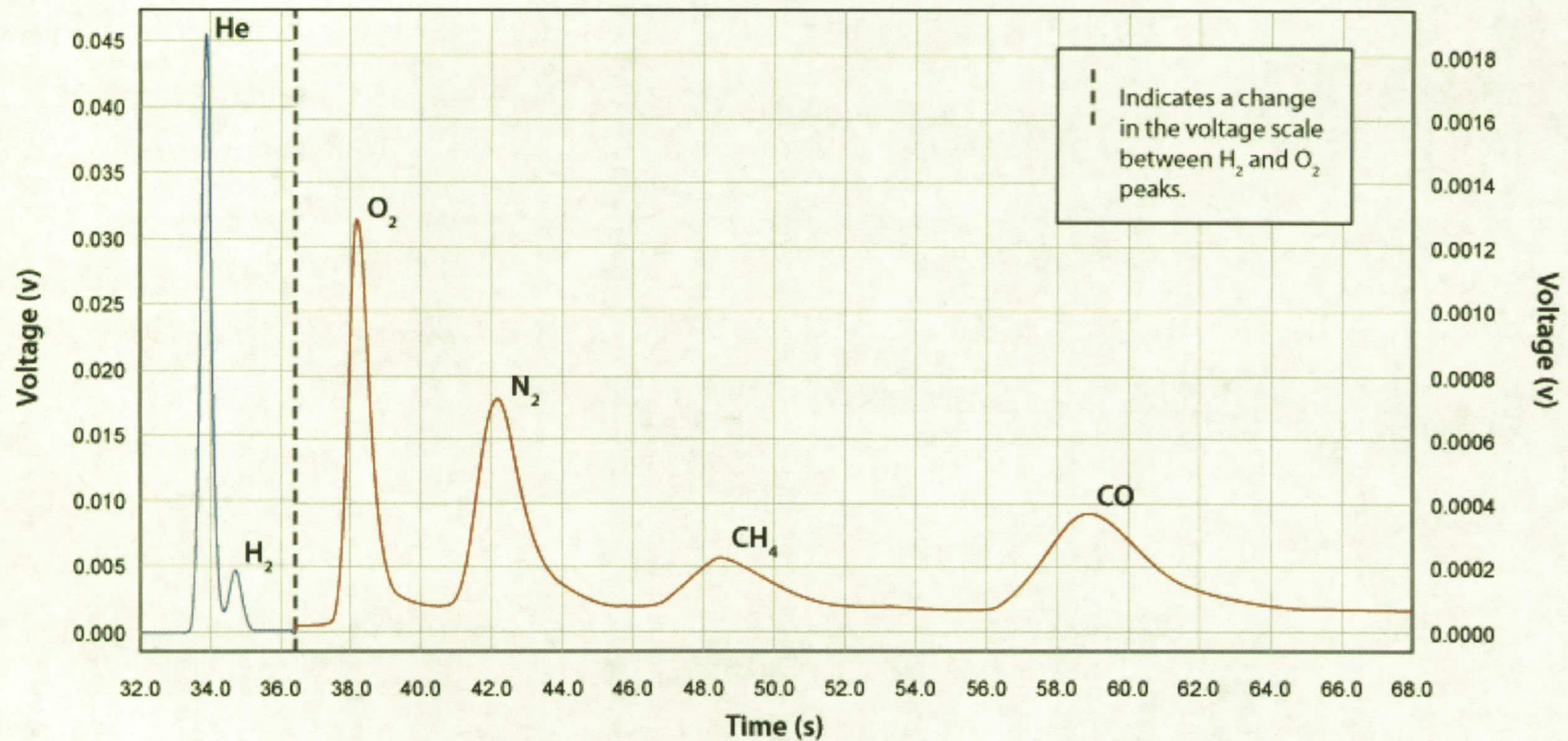
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Separation of Light Gases

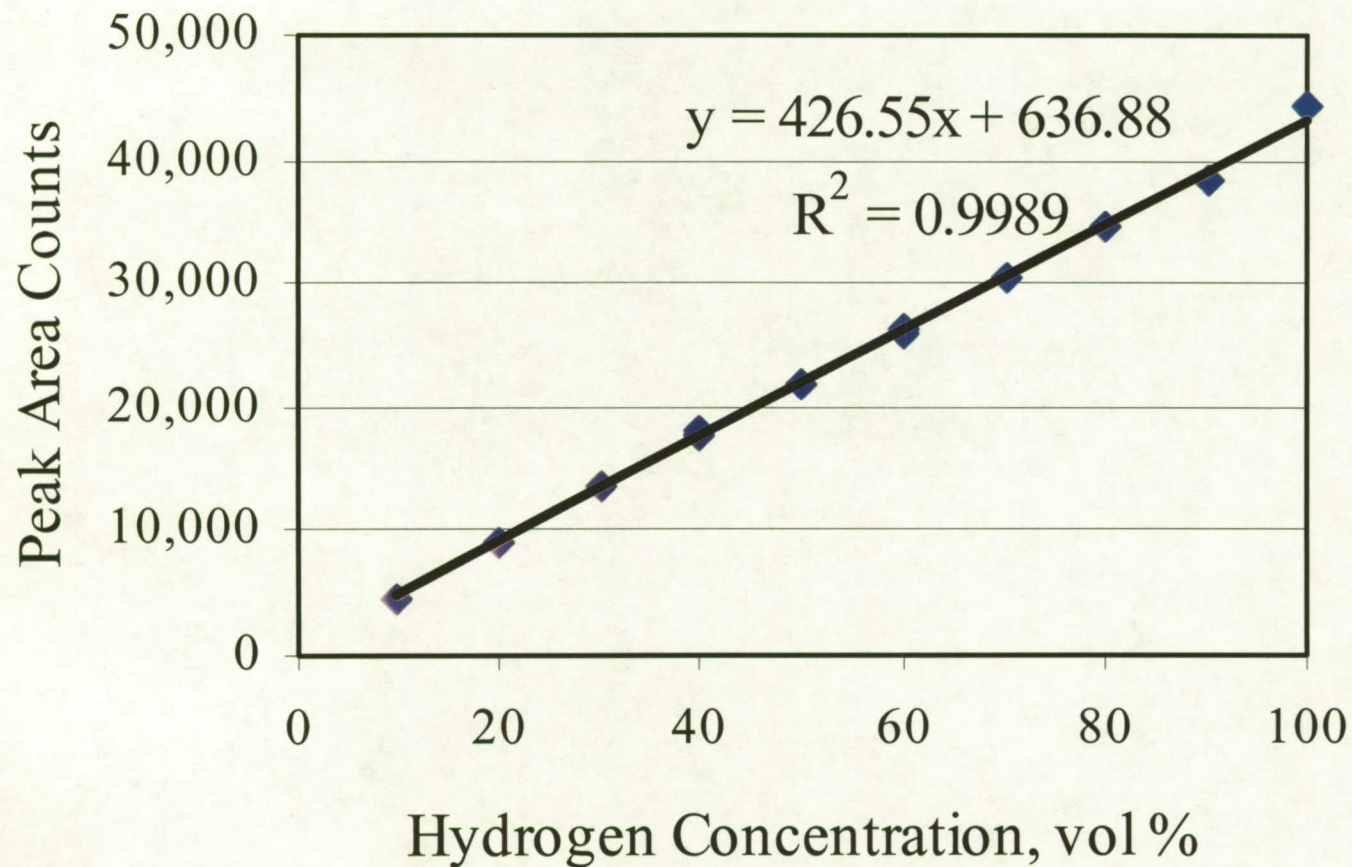
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EBU 2 Calibration Results Hydrogen

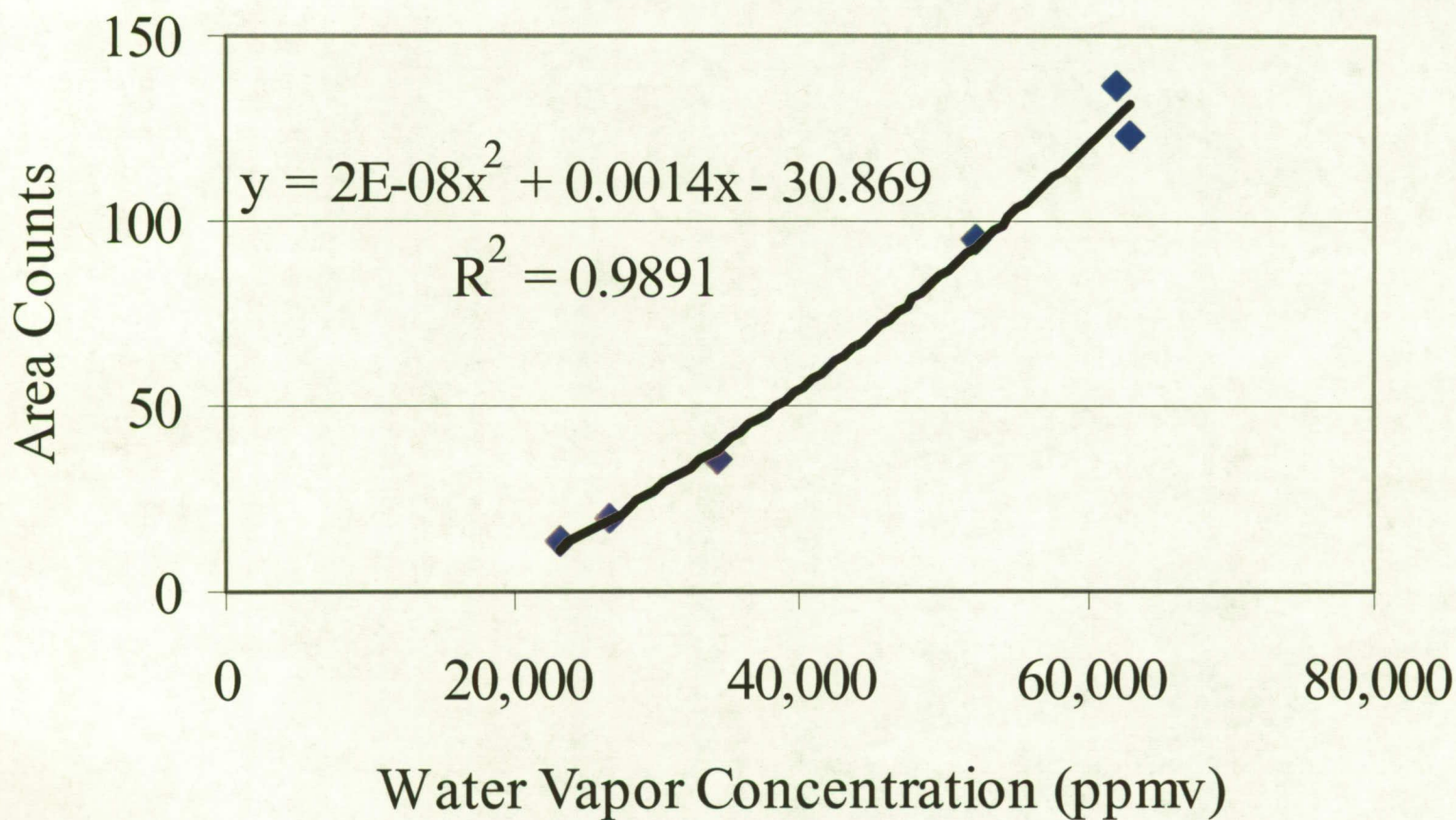
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EBU 1 Calibration Results Water

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The Path Forward

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- Engineering Breadboard Unit (EBU) #2 is under design.
 - This is a field prototype that is flight-like in size.
 - We would desire to add a Mass Spectrometer to the GC to allow GC/MS analysis which would allow greater sensitivity and the analysis of H₂/HD/D₂/He³/He⁴ mixtures.
 - Currently we have no good candidate MS which can scan at 20 hz over the range of 2-100 AMU to keep up with the GC separations.
- RESOLVE EBU2 field prototype will be completed in June of 2008
 - Laboratory tests will be conducted in July & August
- Field Test at a lunar analog location in November of 2008
 - Mauna Kea, Hawaii is likely location



Water Analysis on PoraBond Q Column

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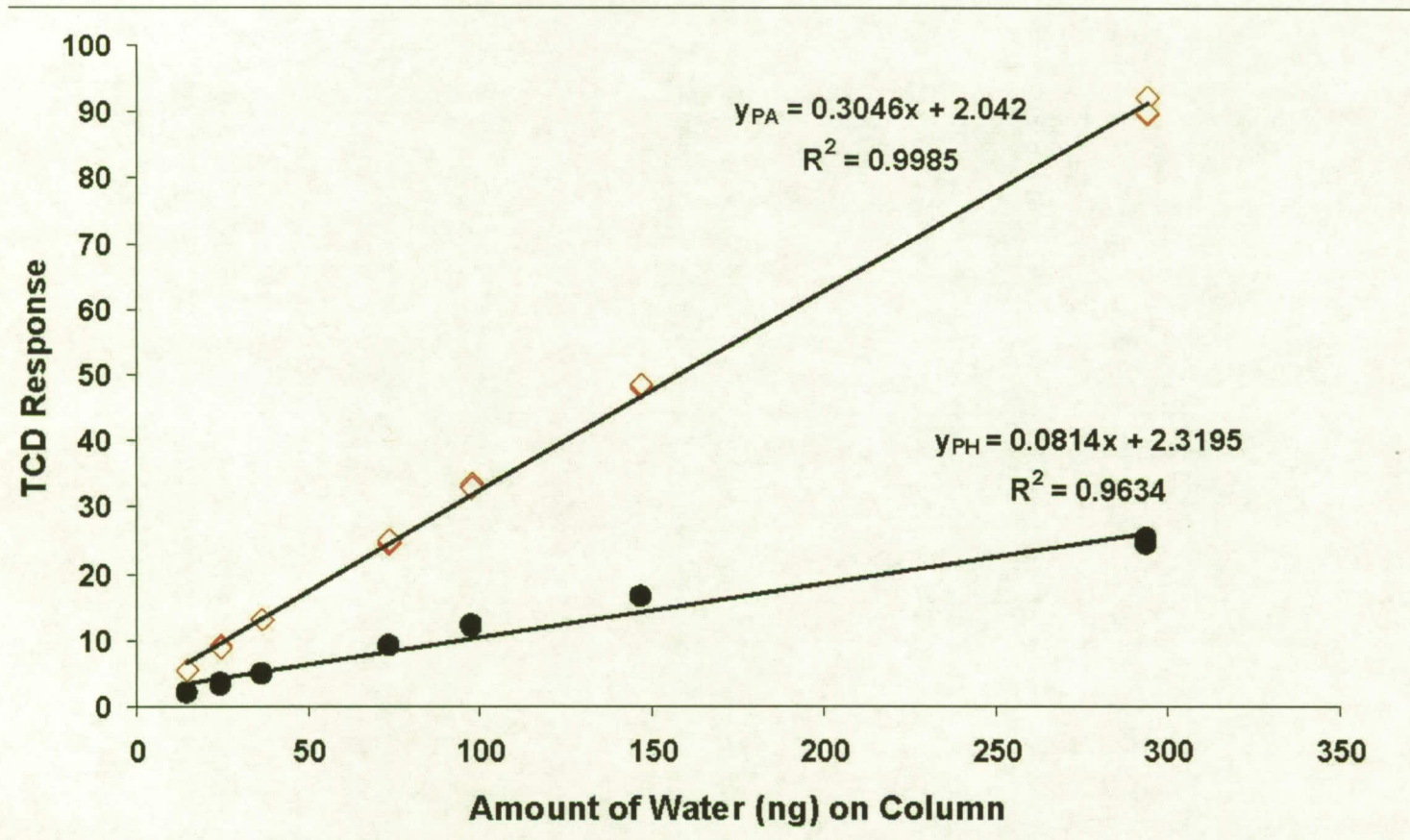
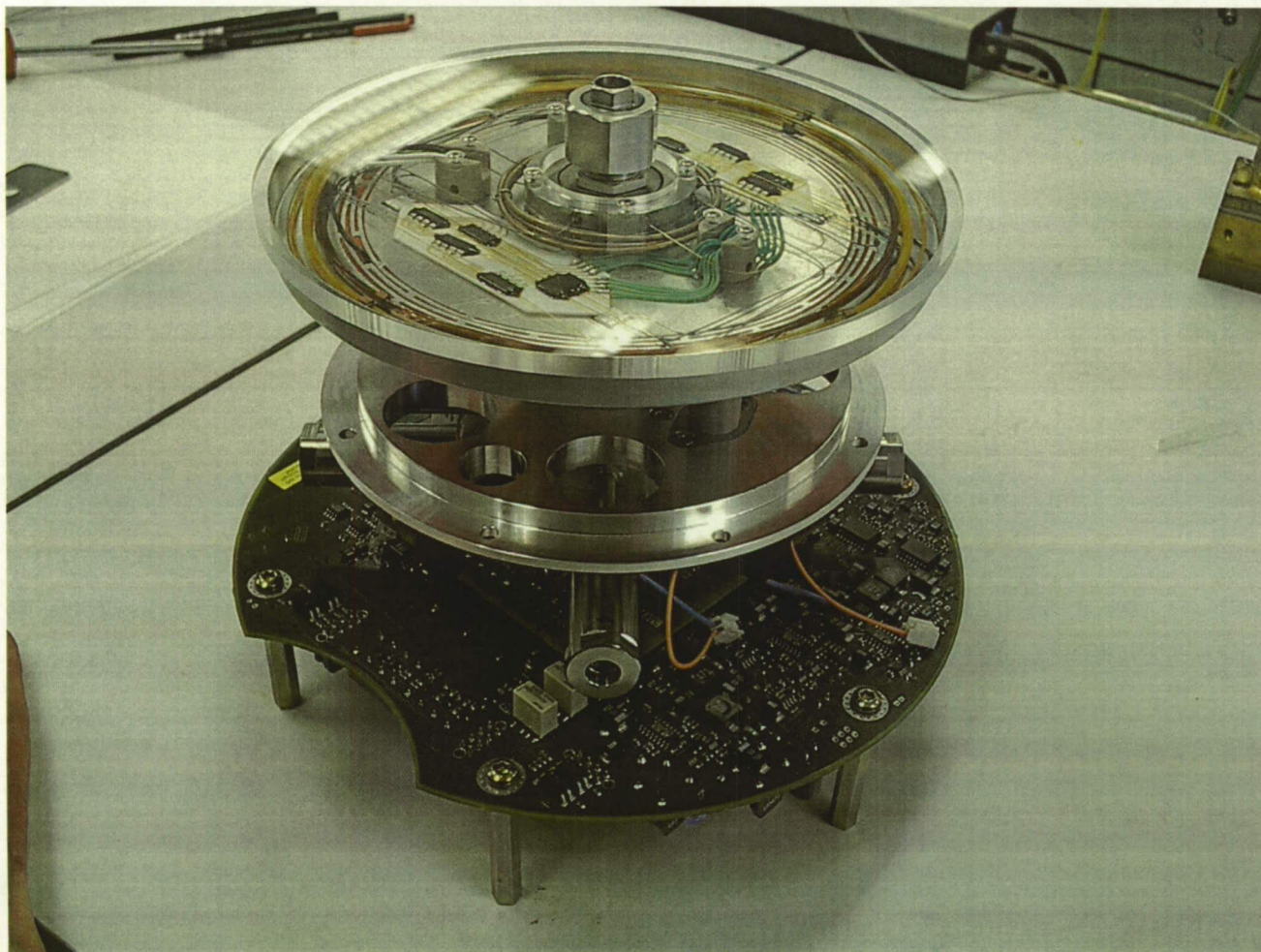


Figure 7. Calibration curve of water on CP-PoraBOND Q column



Gas Chromatograph Module

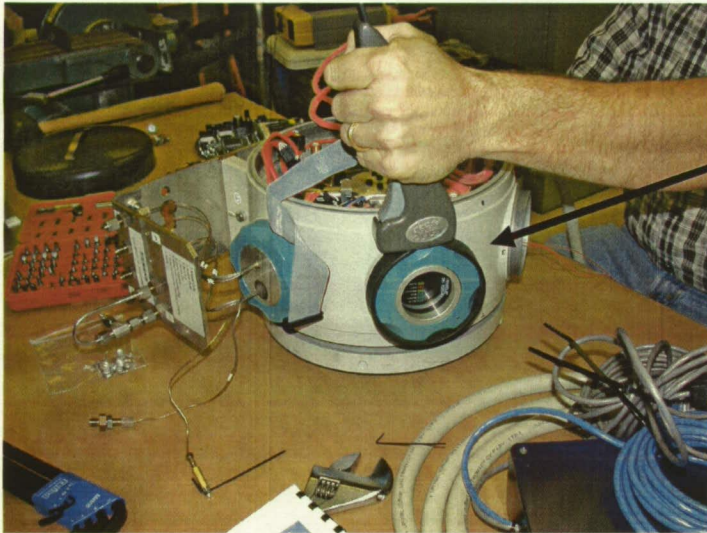
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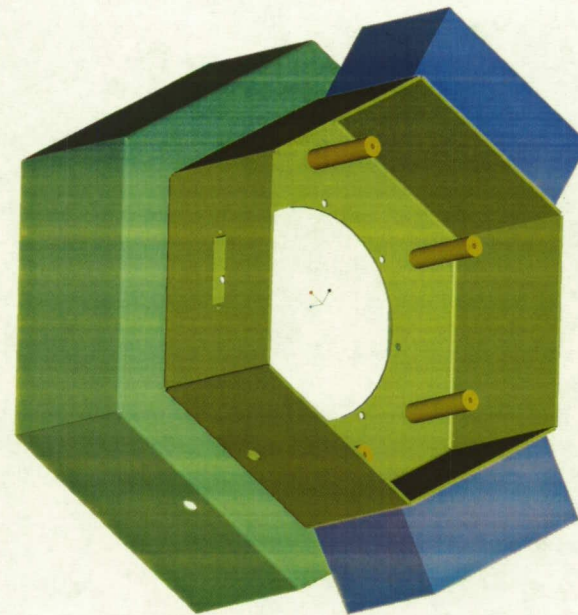
CAD Model of Light Weight GC Case Design

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Before: 42 lbs

After: 10 lbs





Near Term Plans

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- Fabricate Light Weight Enclosure
- Re-assemble MicroSAM
- Modify Application Module for Higher Water Concentrations and Lower Detection Limits
- Integrate with complete RESOLVE package and Rover (CMU)
- Integrated Testing begins in June
- Field Test and Demo on Mauna Kea ~ November, 2008
- **Future**
- Flight re-design and to the Moon: 20??

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Abstract. The RESOLVE project requires an analytical system to identify and quantitate the volatiles released from a lunar drill core sample as it is crushed and heated to 150°C. The expected gases and their range of concentrations were used to assess Gas Chromatography (GC) and Mass Spectrometry (MS), along with specific analyzers for use on this potential lunar lander. The ability of these systems to accurately quantitate water and hydrogen in an unknown matrix led to the selection of a small MEMS commercial process GC for use in this project. The modification, development and testing of this instrument for the specific needs of the project is covered.

Keywords: Gas Chromatography, GC, RESOLVE, Lunar Volatiles Analysis

PACS: 07.87.+v, 82.80.Bg, 95.55.Pe, 96.20.Dt

INTRODUCTION AND ANALYSIS REQUIREMENTS

The Clementine (Nozette, et al., 1996) and Lunar Prospector (Feldman, et al., 1998) missions to the Moon have returned data that has been interpreted as an indication of increased concentration of hydrogen bearing materials in and around the permanently shadowed craters of the lunar poles. While oxygen bearing minerals are abundant in the regolith, these hydrogen deposits are valuable for fuel and water resources if they are present in sufficient quantities for In-situ Resource Utilization (ISRU). The Regolith & Environment Science, and Oxygen & Lunar Volatile Extraction (RESOLVE) project is developing and testing the hardware needed to obtain "ground truth" for lunar resources at the lunar pole. The system includes a 15mm diameter x 1 meter deep core drill which will deliver the core in 25 cm sections to be crushed and heated in the Regolith Volatiles Characterization (RVC) oven. Samples of volatiles evolved from the crusher and oven must be analyzed for the presence of hydrogen bearing molecules, thought to be primarily hydrogen or water. The possibility that the volatile samples could contain other hydrogen bearing molecules (such as ammonia, methane, HCN, or H₂S) along with other volatiles (such as CO₂, CO, He, and Ar) from solar or cometary sources makes the analysis more complex as the pressure and matrix of the derived volatiles are unknown. Although the resolution of the data is poor (pixel sizes of 30 km or more), the estimated concentration of hydrogen (if the form is hydrogen) is estimated to be 1700 +/- 900 ppm (Feldman, et al., 2001). Whether this is hydrogen or water, the minimum amount of volatilized hydrogen would achieve a pressure of over 500 kPa at STP or 900 kPa at 150 °C inside a 0.2 L oven. If the maximum estimated hydrogen is present, pressures over 1700 kPa at STP and 2600 kPa at 150 °C would be derived. While this represents a large amount of hydrogen-bearing gas, the wide range of potential pressures presents an additional challenge to the analytical system. If concentrations below 100 ppm (hydrogen equivalent) are present, the resource is presumed to be too low in concentration to be of interest for ISRU. The performance of the analytical system is stated relative to the concentrations of the evolved vapors, and not to the concentrations in the lunar regolith. The goals for the vapor analysis are as follows.

Essential Compounds: H₂, H₂O

Secondary Compounds of Interest: CO₂, CO, NH₃, CH₄, H₂S, O₂, N₂, He

Detection Limits: Any compound under 100 AMU and present in the evolved gases at a concentration of at least 0.5% by volume shall be detected, identified, and quantitated.

Identification: All compounds deemed essential to detect by the Science Advisory Team shall be positively identified by the analytical system within a mixture of some or all essential and secondary compounds of interest.

Quantitation: Errors in the quantitative analysis of each compound shall not exceed 0.2% by volume of the total evolved gases or 10% relative of the specific gas identified, whichever is greater.

Gas Sample Contaminants. All gas samples are evolved from regolith that contains up to 10% of particulates < 10 μ in particulate size. These particulates are likely to travel with the gases into all collection beds, valves and analyzer sample inlet ports. Filtering to remove these particles will likely be only partially successful, allowing some particles of even smaller size to pass on through. Elimination of all fines is considered undesirable before analysis and capture of the adsorbed volatiles.

Thermal Location: The sample gas lines and all points the sample contacts will need to be warm enough to prevent condensation. For water, this would mean temperatures that are above 100°C.

This paper will outline the steps taken in choosing a commercially available instrument system suitable for the analysis requirements and its modification for our particular application.

ASSESSMENT OF VARIOUS ANALYTICAL SYSTEMS

The requirements for measuring both hydrogen and water as essential analytes limit the choices for the analytical systems. While infrared absorptions systems can measure many of the compounds of interest, H₂, O₂, and N₂ as well as any inert gases are not measured as they have no absorption bands in the infrared. Among general purpose systems that can measure all of the gases of interest, only gas chromatography (GC) and mass spectrometry (MS) appear to offer the detection limits and compound identification needed. The pros and cons of each technique are explored below.

Mass Spectrometry

In any mass spectrometer, the molecules to be analyzed enter into the evacuated spectrometer through an inlet; enter the ionization section where the molecules are, typically, bombarded with electrons to produce a series of ions typical of the molecules that entered and the energy of the electrons impacting them. These ions are then accelerated into the mass separation section where the various ions are separated based on their mass/charge ratios. The mass separation section operates on one of several principles for which the MS type is named.

Time-of-Flight MS

Time-of-Flight (TOF) MS has a flight tube through which the ions are accelerated through a fixed voltage to the detector. All the ions in each sample are analyzed sequentially, separated in time by the rate of acceleration through the fixed voltage. Arrival times are very short, requiring a very fast detector and A/D converter to separate the rapidly arriving ions.

Quadrupole MS

Quadrupole MS utilizes four rods with RF fields imposed on them to "tune" the mass separation to one specific mass at a time. The field can be rapidly tuned sequentially to each unit mass to obtain a separation spectrum of ions. Ions closer together than 1 unit mass will be read as the same mass. The RF field generators are fairly complex and require calibration in near real-time. Detector data rates are much lower than with TOF, since the total charge can be accumulated for a single mass and read out only once for each analysis.

Magnetic Sector MS

Magnetic Sector MS accelerate the ions through a constant voltage and then pass the ions into a magnetic field that causes each ion to follow a curved path based on its mass/charge ratio. Light ions curve more sharply than heavier ions, varying the detector position where they strike and are detected. A detector array separates the different

masses. Low data rates and a permanent magnet characterize a magnetic sector MS. Small size sectors can achieve separation with small, light-weight magnets.

Pros and Cons of Mass Spectrometry

MS requires no consumable gases for basic operation, unlike a GC. Each compound gives a specific pattern of ions that helps to identify the original molecule without specific calibration for that compound. IE, identification (but not quantitation) is possible without calibration. Since the major weight in a mass spectrometer is the vacuum pump system, we can lighten the system weight considerably for use on the Moon, where superior vacuum is available in abundance. Since the core MS detector operates at very low pressure, it is possible to sample from a variety of pressure sources if a variety of sample inlet restrictions are provided. This might allow a single instrument to sample the lunar atmosphere ($1\text{E-}10$ torr) as well as the high pressure (~ 5 atm) volatiles derived in the RVC. However, this range of pressures (over 13 orders of magnitude) would be a serious challenge for the sample inlet design.

The analysis of water vapor in a mass spec presents several challenges. Water vapor is very "sticky", leaving residues attached to various parts of the MS inlet and internal structures. At least one manufacturer suggested the problem is intrusion of ambient water vapor through the seals on a MS on Earth. If this is the true source of the problem, then the problem would not exist on the Moon or Mars. Clearly, the source and existence of this problem should be proven before a solution is implemented. These residues can persist for some time and give false signals or very high baseline concentration of water even when current samples have no water in them. Identifying that the background signal has changed would be a major problem in a continuous analyzer attached to the RVC oven exhaust. Without a known or low baseline, quantitative results would be difficult or impossible. This problem can be reduced by operating the MS at high temperatures where water can not condense and adhere to surfaces easily. The water itself is quite stable, but when ionized is very reactive, forming new compounds with other ions or compounds that may be present in the sample. Thus the signal for water may be matrix dependent in a MS. These effects are mitigated by operating the ionizer and separation sections at low pressures. Then the mean-free-path would make reactive collisions unlikely. But, this would also lower the signal levels and reduce the accuracy of the quantitation.

Ion masses can be populated by other molecules or ions of the same mass. This can cause some confusion in a complex matrix. This is not a new problem, and standard MS software can analyze these situations with multi-component simultaneous equations. However, the accuracy of the results suffers in such systems and can become the dominant source of errors in a complex system that has not been separated prior to the MS analysis. Manufacturers of Thermo-gravimetric Analyzers (TGA) have begun offering MS analyzers as an add-on to quantitate and identify the effluent gases. Attempts to use the MS signal for the quantitation of water evolved from the samples have not been very good. The use of signal integration techniques on single mass plots vs. temperature of evolution produced large errors even with known pure compounds as standards and known mixtures for samples. Results were typically low, compared to TGA weight losses, by up to 25%. In earlier work with a reverse water gas shift (RWGS) reactor at KSC, attempts to use MS for analysis of the recirculating gas stream were of limited success. Material balance calculations were typically off by 20 -30%. Our MS experts could only point to matrix effects that could be solved by better standards with compositions closer to the actual gas compositions. The experiences with the RWGS experiments are particularly troublesome, as the gases in the RWGS system include many of the same gases we are concerned with in the RESOLVE project: H_2 , CO_2 , CO , and H_2O in various concentrations. Indeed, the RWGS case is better defined and has less possible variations than the RESOLVE case. In the RWGS experiment we obtained excellent mass balances by switching our analytical system to GC.

Gas Chromatography

Gas Chromatography (GC) analysis is a method to separate a mixture of gases and then measure each separate component on a universal detector. The separation is done by passing the mixture of gases over a stationary coating or packing that attracts the differing molecules to a greater or lesser degree. The stationary phase is commonly contained in a long thin tube made of SS or fused silica, with the combination of the tube and stationary phase coating or packing known as a chromatographic column. The name is derived from early experiments in which the color components in mixtures were separated to produce a "color graph" or chromatogram of the separated dyes. In

gas chromatography, all the components to be separated must be in the gas phase to be carried through the column by a moving carrier gas stream, with each component being delayed (or "retained") in proportion to the attraction each molecule has to the stationary phase. GC systems have been in common use since the 1950's, with many advances in all facets of the system, including injection valves, column switching, column design, stationary phases, oven design, and detectors. The recent development efforts have been put into the design of miniature GC systems utilizing silicon chip detectors and valves to achieve very small systems with much faster separations. These systems typically use a thermal conductivity detector that employs a thin platinum wire or film suspended in a small channel in a silicon chip. By orienting the platinum wire coaxial with the gas flow, and heating the wire, the wire temperature responds primarily to changes in the gas stream's thermal conductivity, given careful control of the temperature and gas flow rates.

Pros and Cons of Gas Chromatography

GC has the advantage of separating the compounds to be measured, which greatly reduces the possibility of confusion over what compounds were present. This process is essential when the detector provides no identification information, which is the case with a TCD detector. In this case the sole means of identification is the elution time, which will require careful control of the column and inlet temperatures as well as carrier gas flow rates. Combining a GC with a MS as the detector yields a much more powerful tool than either technique done separately. GC systems require the use of a carrier gas. The containment tank and the flow controls add weight to the system. For long periods of operation, the carrier gas supply can become the major weight component of the analytical system. Samples containing many compounds can become difficult to analyze with a universal detector, as complete separation of many peaks is often not realized in practice, especially where an unknown compound might occur. In the case of an unknown compound, no data to aid in identification is obtained other than the retention time.

System Selection

GC was selected as the initial analytical system for several reasons. Since we were looking for a developed and affordable system that could analyze the gases of interest and several GC manufacturers had systems set up for those gases, it was a matter of finding an appropriately designed system for potential unattended operation. This led to a survey of automated miniature GC systems that could be fully automated. Three potential candidates emerged among the commercial miniature GC systems. The earliest system is currently marketed by Agilent and is the outgrowth of a MEMS GC first devised at Stanford in the 1970's. It has been well developed into a field portable system with up to 4 separate modules for various analyses. The second is from Varian, with a somewhat similar design with separate modules, each keyed for separate analyses using separate gas flows and injections for each module. The third is a MEMS design of a process GC from Siemens, intended for field mounting in a chemical plant. This system allows a single injection to be analyzed on multiple columns, a technique known as multi-dimensional chromatography. Since they already had an application module that would do all of our separations, including water and hydrogen separations along with most of our other gases, we elected to use this instrument as the start for our design. While the Siemens MicroSAM process GC had many of the attributes we were looking for, some of the things we wanted would require modification of their standard application.

SYSTEM DESCRIPTION

The application module of the MicroSAM contains all of the active components of the GC. It has 8 thermal conductivity detectors (TCD) arranged in 4 pairs, a multi-port diaphragm valve used for sampling and backflush operations, a programmable on-column fluidic injection system, up to 4 columns, and a dean's switch for doing a heart cut onto the last analytical column, a molecular sieve column in our case. All of these components are contained in a single temperature controlled module 1.1 cm thick by 16.1 cm in diameter. This application module is attached to the electronic controls through 3 multi-pin connectors and a series of spring loaded pneumatic connections in the central hub that lead to 3 programmable electronic pressure controllers (EPC). During operation, the application module is operated isothermally to eliminate the cool down period associated with temperature programming. The third EPC is programmed to allow only the permanent gases to enter the mole sieve column. As received, all peaks have eluted and the back flush is completed in 220 sec. With a 10 second sample flush time

before the next injection, a complete cycle time of 240 sec is achieved on a continuous run basis, including the data transfer to the host computer. As received, the module could analyze all the permanent gases: H₂, He, O₂, N₂, CH₄, and CO along with CO₂, H₂O, and H₂S. Also included, but not of interest to us, were light hydrocarbons up to C₄. The module is normally operated on Helium carrier gas except for H₂ and He analysis, which can be run on argon or nitrogen.

SYSTEM MODIFICATION

While the module as shipped can separate all of the gases we want, the use of helium as the carrier gas precludes a helium analysis. Also, the detection limits for hydrogen would be poor with a helium carrier gas and the response at high concentrations of hydrogen is often reported as non-linear using a helium carrier gas. Since we want all of our analytes quantitated on a single run and a single carrier gas, we decided on a neon carrier gas because its thermal conductivity is intermediate between H₂/He and most of the other gases. Neon is somewhat close to the thermal conductivity of methane, so we expected a decreased signal for methane, one of our secondary analytes. The thermal conductivity of several gases of interest at 400K is shown in Table 1 below.

TABLE 1. Thermal Conductivity of Selected Gases at 400K (Lide, 1998-9).

Molecular Formula	Name	Thermal Conductivity (mW/m K)
Ar	Argon	22.6
H ₂	Hydrogen	230.4
He	Helium	190.6
Ne	Neon	60.3
O ₂	Oxygen	33.7
N ₂	Nitrogen	32.3
H ₂ O	Water	27.1
CH ₄	Methane	49.1
CO ₂	Carbon Dioxide	25.1
CO	Carbon Monoxide	32.3

Since the thermal conductivity of neon is quite different from helium or argon, the two carrier gases typically used on this GC, the settings for the power level for the TCD detectors would have to be derived from the settings used for these gases versus their thermal conductivity. The gas properties immediately adjacent to the detector filament (a thin platinum film) are the most important factor in preventing detector burn out. The maximum power levels for the TCD's were published for Ar, N₂, He, and H₂ carrier gases. Since the filament is much hotter than the detector body (about 400 K), we selected thermal conductivity data in the range of 500 – 600K for determining the interpolated power level for neon carrier gas. Since complete data was not readily available for all the gases at all the temperatures, some of the data was calculated as indicated by values in italics. Table 2 and Figure 1 show the data, curve fit, and results (Lide, 1998-9).

TABLE 2. Maximum Allowable Power vs. Thermal Conductivity for Carrier Gases in MicroSAM GC.

Gas Name	Maximum Power (mW)	Thermal Conductivity, mW/m K		
		500 K	523 K	600 K
Argon	28	26.8	39.6	44.0
Helium	115	222.3	230.0	252.4
Hydrogen	115	274.0	280.0	300.0
Neon	46	69.9	73.5	78.7

The curve fit in Figure one was used to calculate maximum power value shown in Table 2 for neon. With the estimated maximum bridge power in hand, we proceeded to set the TCD bridge voltages to 900 mV, giving a typical bridge power of 35 mW on neon. Using this setup, we injected a 6 component calibration gas mixture (Table 3) to test the system.

TABLE 3. Six-Component Calibration Gas Mixture.

Gas	H ₂	CH ₄	O ₂	N ₂	CO	CO ₂	He
Conc., Vol %	4.00	4.00	5.00	5.00	5.00	5.00	Bal

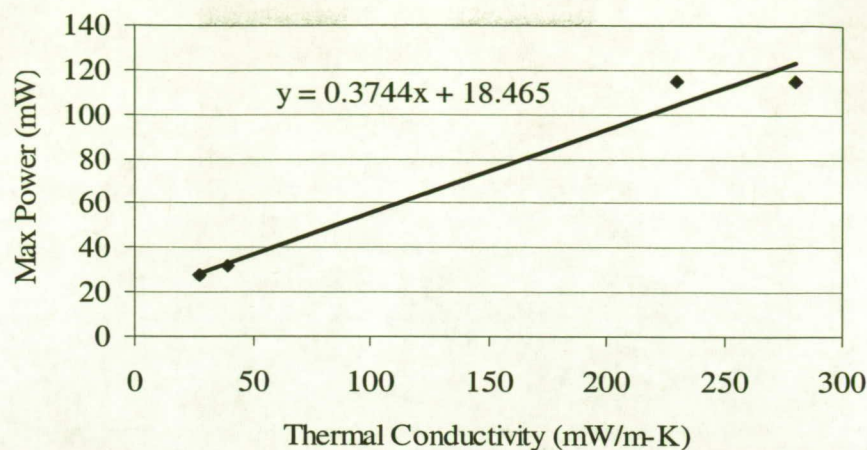


FIGURE 1. Maximum TCD Bridge Power vs. Thermal Conductivity of Carrier Gas at 523 K.

For water calibration we built a custom 2-pressure humidity generator from spare parts, a purchased consumer cooler, and a precision thermistor temperature probe. This system worked well, but the water analysis on the GC had a few problems. With the as-shipped application software, the column temperature was only 333K, too low for even moderate water vapor concentrations. As problems persisted even at a column temperature of 383K, we determined that the inlet lines and sample loop inside the application module needed additional heat to ensure that condensation of the water vapor did not occur. We wrapped the critical areas with insulated nichrome wire, and silanized the inlet tubing using dimethyl ethoxy silane (DMES) the Shuttle tile waterproofing agent, which is a vapor at the temperatures in this GC module. We were limited to a maximum temperature of 383K by the loss of separation on the mole sieve column at higher temperatures. The application for our analysis includes columns for the higher hydrocarbons and a pre-column that might adsorb injected water vapor. The flow schematic as received is shown in Figure 2. By bypassing the first two columns and detector pair 3A & B, we achieved the schematic shown in Figure 3. A photo of the inside of the application module, Figure 4, gives some idea of the difficulty in modifying a MEMS assembly with no fittings and only cemented joints on 0.25 mm fused silica tubing.

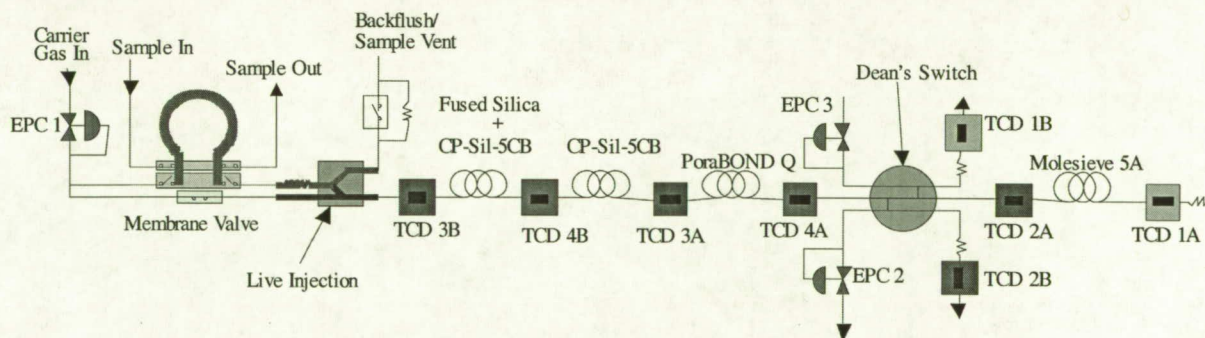


FIGURE 2. As Received Application Module Flow Schematic

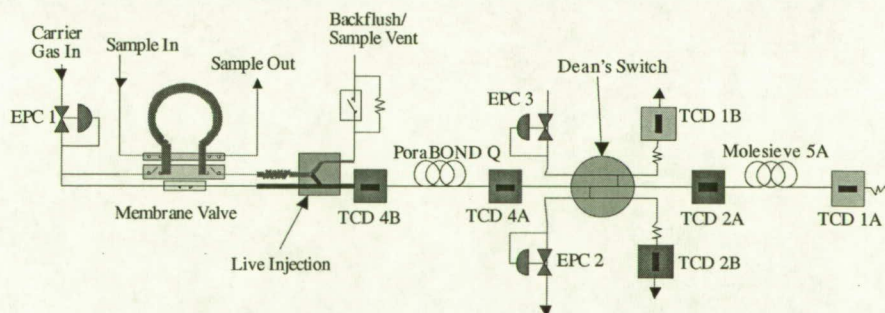


FIGURE 3. Modified Application Module Flow Schematic

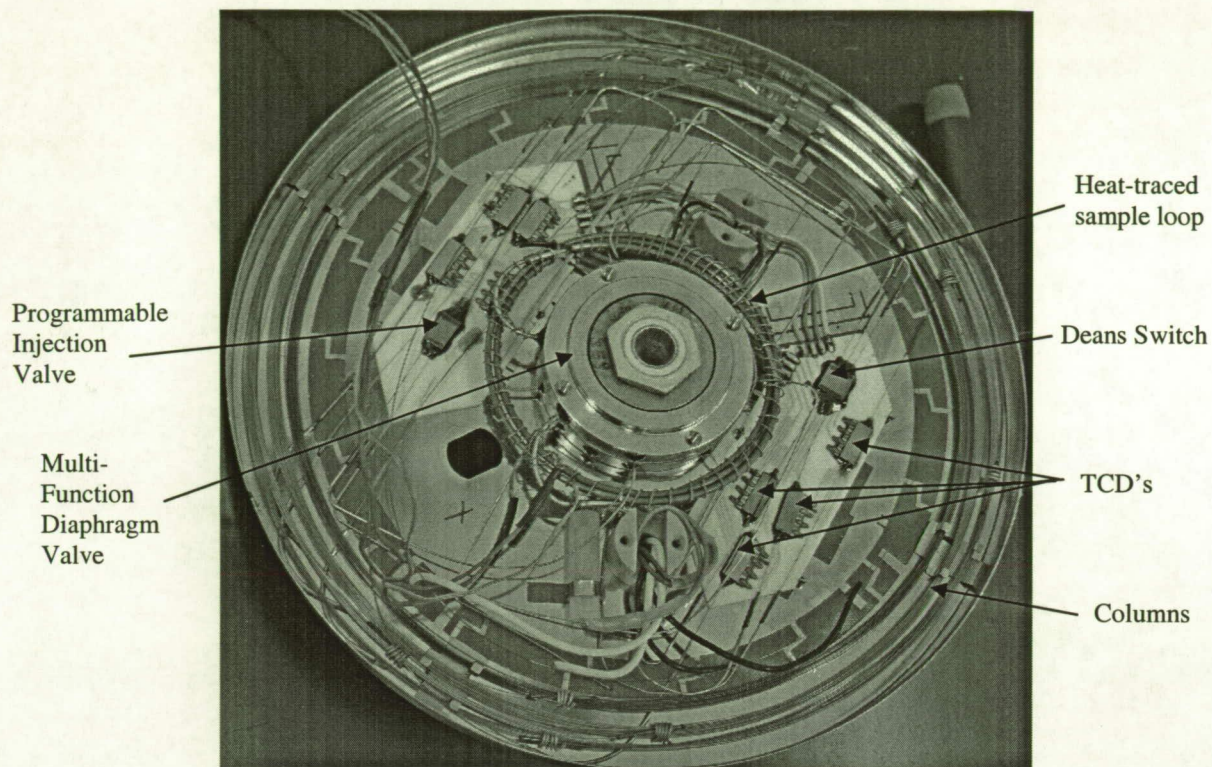


FIGURE 4. Modified Application Module with Cover Removed, ~90% of Actual Size

RESULTS

After completion of the modifications described, we proceeded to test the GC system and integrate it with the RESOLVE oven (designed by John H. Glenn Research Center) and the Lunar Water Resource Demonstration led by J. Captain at KSC. Some typical calibration results and a sample chromatogram are shown. Mass balances with the known contents of the oven were good during the initial integrated testing.

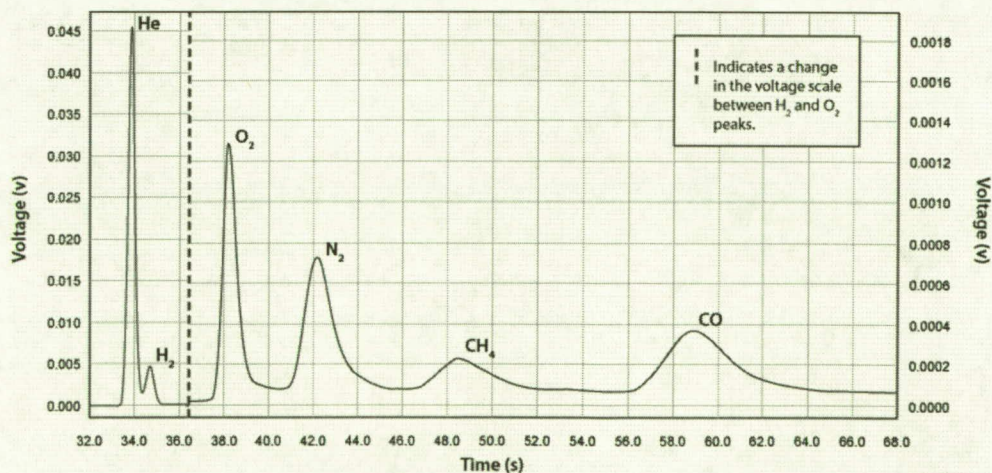


FIGURE 5. Chromatogram of 6 Gas Standard, CO₂ Not Shown.

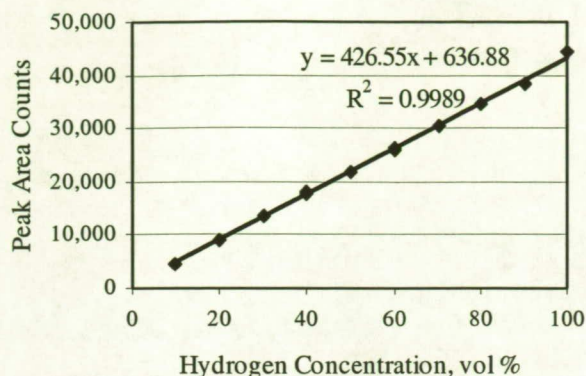


FIGURE 6. Hydrogen Calibration Curve, High Range.

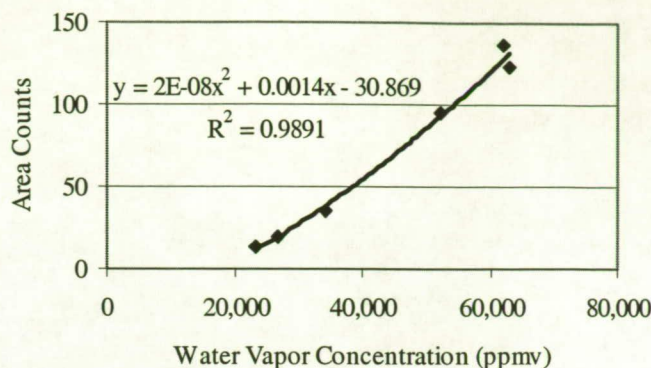


FIGURE 7. Water Vapor Calibration Curve, Low Range.

CONCLUSIONS AND FUTURE WORK

The water calibration curves continue to show a non-zero intercept at about 15,000 ppm water vapor concentration. This is marginally acceptable for our use and we hope to achieve improved results with the changes planned for the second breadboard version, EBU2. The changes that would address the water detection limit problem include mounting the mole sieve column into a new lower temperature oven and the testing of other porous polymer columns than the presently used PoraBond-Q column supplied by Siemens. The separate oven will allow higher temperatures for the injection and water separation. At least 420K is needed for the higher water concentrations from the RVC oven. A better column would have less of a polar character than the PoroBond-Q. Coupled with the higher column temperatures, improved performance is expected on both the high and low water vapor concentrations. The removal of the outer explosion proof case will lower the weight of the GC assembly below 5 kg. Lastly, we would still like to find a miniature MS with 2-100 AMU capability and a fast scan rate (~10 scans/sec or higher) to couple with this GC. The combination of the two analyzers would allow the determination of H₂/HD/D₂ and He³/He⁴ as well as any unknowns that may be encountered.

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