MINIATURE MAGNETIC RESONANCE SPECTROMETERS

Soon Sam Kim, Narayan R Mysoor, Steve Carries
Jet Propulsion Laboratory
4800 Oak Grove Drive, Pasadena, CA 91109
Christopher T. Ulmer
Ulmer Systems, Inc, Pasadena, CA 91106
Klaus Halbach, Consultant
Berkeley, CA 94708

ABSTRACT

For the purpose of in-situ planeatry exploration, such as chemical characterization of Martian surface materials by miniature instruments, . we have developed ~ miniature Magnetic Resonanoe Spectrometers (MRS) namely, Nuclear Magnetic Resonance (NMR) and Electron Paramagnetic Resonance (EPR) spectrometers at JPL. They are; Proton-NMR spectrometer for the detection of various forms of water, i.e., free water or adsorbed water in soil or rock pores, or chemically bound water in minerals; Iron-NMR (^{57}Fe-NMR) for the characterization of magnetic phase minerals; EPR spectrometer for the detection of oxidant radical species in the soil, oxidation states of paramagnctic ions and chemical characterization of volatiles e.g., carbonates, sulfates, by detection of color centers in solid or icy matrices.   For the miniature MRS, resonance was observed by scanning radio (NMR) or microwave (EPR) frequency at a fixed magnetic field provided by a small permanent magnet assembly. Each of the MRS is developed in two configurations; the conventional configuration with samples placed inside the MRS (internal detection mode), and the other by placing the MRS over a sample surface (external detection mode). The external detection mode does not require complex sample handling procedure and it is particularly suitable for selection of samples by a rover for planned Mars sample return missions. The miniature MRS are powered by 9 V batteries, and operated by a lap-top PC.

INTRODUCTION

For the next ten years, NASA will be actively pursuing planetary exploration programs with particular emphasis on Mars, with general plans for launching orbiters and landers every 26 months through the year 2014. Such programs include missions already in progress, such as Mars Pathfinder landed on July 4, 1997, Mars Global Surveyor which will arrive on Mars in September, 1997 and follow-on Mars orbiter and lander missions (1998). Missions in the planning stages include a series of Mars Surveyor missions which will have landers with rovers in 2001, 2003 for sample selection and sample return in 2005, All of the lander missions will require scientific payloads of small, light weight and low power in-situ instruments to probe properties of the surface, near surface, and subsurface environments, including analyses of elemental, chemical and mineralogical compositions. From the Viking missions in 1976, the first phase of information was obtained through analytical instruments such as X-Ray Fluorescence Spectrometer (X RFS) and Gas Chromatography/Mass Spectrometry (GC/MS). They obtained elemental analysis, as well as the presence of active oxygen species inferred through biology labclled release and gas exchange experiments. Other instruments already developed or in the development stages are: Neutron Activation y-ray Spectrometer for the measurement of elemental composition of the Martian surface and the atmosphere, Differential Scanning Calorimeter - Gas Chromatography for the characterization of physical states of water in the soil, and Mars Oxidant Experiment (MOx) which will measure the level of oxidation activity of the Martian soil as it comes in contact with thin metallic and organic coatings of the sensor probes. The recent Mars Pathfinder Missions deployed an Alpha Proton X-ray (APX) spectrometer for elemental compositions of surface materials. The

logical step for the next Mars exploration should involve efforts to understand the chemical aspects of the Martian soil in molecular detail, such as the structure of active oxygen species, the presence of water in the soil, carbonates, clay mineralogy, to name a few. For the purpose, we have been developing miniature Magnetic Resonance Spectrometers (MRS), namely, Nuclear Magnetic Resonance (NMR) and Electron Paramagnetic Resonance (EPR) spectrometers, to obtain much needed Martian surface chemical information.

The magnetic resonance method has inherent advantages over most other analytical techniques because it allows investigation of samples under near-ambient conditions with little disruption of surface structures or chemical equilibria and requires little sample preparation. Studies of minerals or clays can be performed under environmentally realistic conditions. For example, there is no need for surface preparation, and it is not confounded by the sample matrix regardless of its chemical complexity, as long as it is diamagnetic. Therefore all diamagnetic materials with paramagnetic centers are accessible to study. The analyses can be carried out with gram- to milligram-size Martian surface or subsurface samples with minimum or no extra sample preparation. We have developed the miniature MRS in two configurations, one for conventional internal detection mode with samples placed inside the MRS, the other for external detection mode by placing the MRS over a sample surface. The latter is best suited for selection of samples by a rover mounted MRS for sample return missions.

PRINCIPLE OF OPERATION

Magnetic resonance spectrometers can be used to study atoms or molecules with nuclear spin(s) (NMR) or electron spin(s) (EPR). The spins act like tiny magnets and when placed in a magnetic field, they align themselves like needles in directional compasses, some of them parallel or others antiparallel (due to thermal fluctuation) to the field. One can obtain magnetic resonance spectra by irradiation of radio frequency (RF, NMR) or microwave (EPR) electromagnetic wave to such samples with nuclear or electron spins, in a laboratory magnetic field. When the RF or microwave is scanned through, and the energy

difference between the parallel and antiparallel spins match with the electromagnetic wave quantum, resonance occurs, and the sample will absorb RF or microwave power. By detecting the frequency and applied magnetic field where the resonance occurred, one can characterize the nucleus or electron and its surroundings, thus molecualr environment of the spin(s).
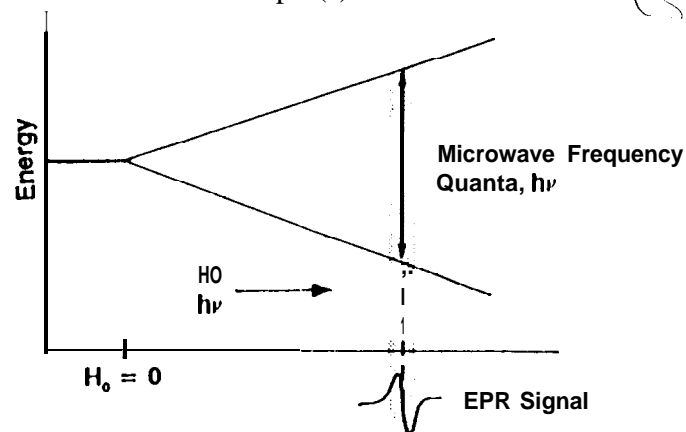

Figure 1. Energy level as a function of magnetic field. Resonance are observed when the energy difference between the levels matches the electromagnetic wave quanta, hν.

In order to obtain resonance conditions, and observe spectra, one can either scan the electromagnetic wave as a function of frequency under a fixed external magnetic field (e.g., with a permanent magnet), or scan the magnetic field (electromagnet) under a fixed frequency electromagnetic wave. For the miniature MRS, we have chosen the former approach, for a compact, low power, light weight miniature instrument.

PROTON-NMR

Science Objective   According to NASA, the prime objective of Martian exploration will be focused on the detection, and estimation of distribution and quantity of water in the planet, since it provides a common thread to answer the most important questions such as evidence of past or present life forms, weathering processes and climate history; and also provides information on resources for utilization during future human exploration, possibley in 2013. According to the models based on volatile inventory of Mars, it is possible and even likely that orders of magnitude

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more of H_2O and CO_2 arc adsorbed on Martian regolith than arc present in the atmosphere-plus-caps system[2,3]. For the detection of water, several instruments have been under development, e.g., infrared spectrometers, thermal gas analyzers such as subsurface sampling and water detection experiment for Mars 98 mission (DS 2). However, the proton-NMR offers a specific, and non-invasive approach, the detection is unique and not confounded by surface features. There can be many forms of water in the Martian soil, for example, surface adsorbed H_2O on soil or crushed rocks, interlayer water in smectite, or chemically bound water as oxyhydroxides. Such different forms of water can be characterized and quantified by the proton NMR spectroscopy, since they display different spectral lineshapes, particular in linewidths, Av, e.g., free or adsorbed water Av= - 4 kHz, and chemically bound water at $\Delta\nu > 40$ kHz.

NMR Instrumentation

<u>Internal Dection Mode</u> A conventional continuous wave (CW) marginal oscillator circuit is used for the detection (see Fig. 3). A JFET marginal oscillator whose frequency is electronically adjustable for frequency sweep and FM modulation drives the NMR coil. Power absorbed by the sample duc to the magnetic resonance effect is detected through
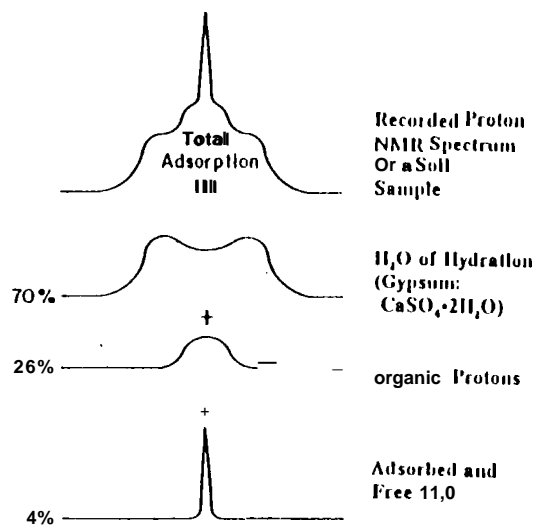

Figure 2. Differences in spectral lineshape (shown in absorption spectrum) can be used to quantitatively measure adsorbed or chemically bound water from a complex NMR spectrum.

the power drawn by the oscillator. A microprocessor generates frequency sweep and FM modulation signals, samples the detected power absorption using synchronous detection, measures the oscillator frequency, and sends the data to the host computer (lap-top PC) for processing. A permanent magnet (Halbach array, Fig. 4) was used
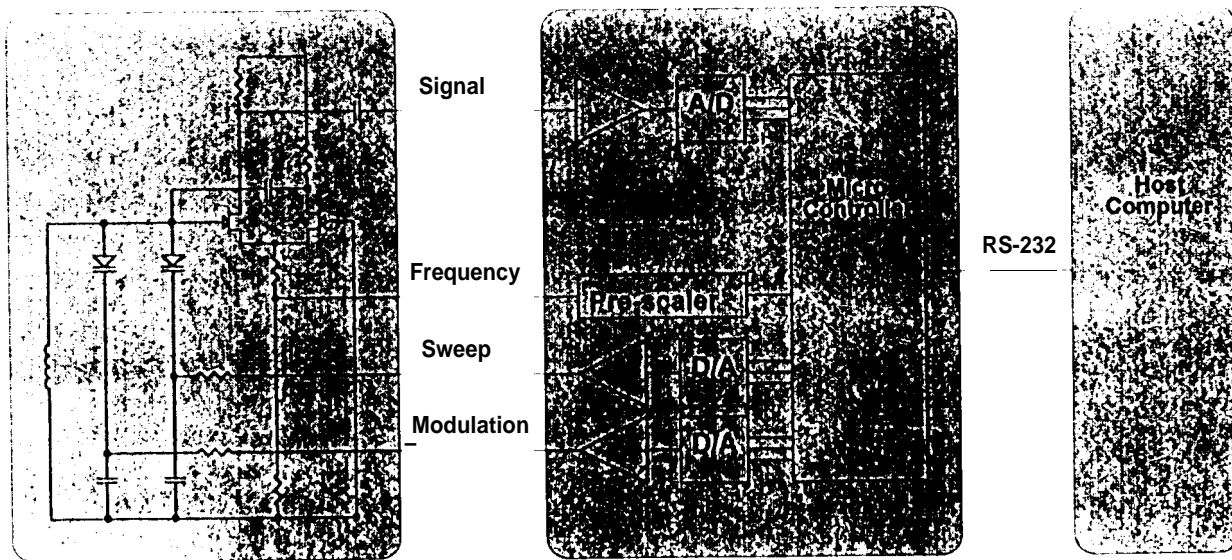

Figure 3. CW-NMR marginal oscillator circuit.

for the prototype miniature NMR, shown in Fig. 5. The NMR is operated by a lap-top PC, through an RS 232 connector.

Figure 4. Permanent magnet (Halbach array, 300 g, 3 kGauss, inhomogeneity = 1 Gauss/3000 Gauss) used for the miniature NMR shown in Fig. 5.

External Detection Mode It is based on nuclear spin echo technique by transmitting two short RF pulses which rotate the proton nuclear spins in the sample by 90°, then by 180°. This sequence causes the sample to emit a small RF signal (echo) shortly after 180° pulse. This signal is amplified and synchronously detected by multiplying with an RF reference of the same phase and frequency as the original RF pulses. A microprocessor is used to generate the RF pulses and digitize the received signal, The pulsed NMR is built around the NMR coil shown as an inductor in Fig. 6. A network of capacitors, inductors, and diode-pairs allows the power amplifier to be coupled to the coil during transmission of the powerful RF pulse while de-coupling it during sampling so that tiny RF signals can be detected and amplified. The amplified signal is multiplied by the Larmor reference frequency which was used to generate the RF pulse; this produces a detected envelope signal which can be sampled at sub-RF rates. A microprocessor generates the Larmor reference frequency using a PLL and also drives the gating circuitry which generates the RF pulse. Following the pulse, the microprocessor samples the envelope signal and sends the results to the host computer (lap-top PC) for processing. a prototype external detection NMR is shown in Fig. 7.
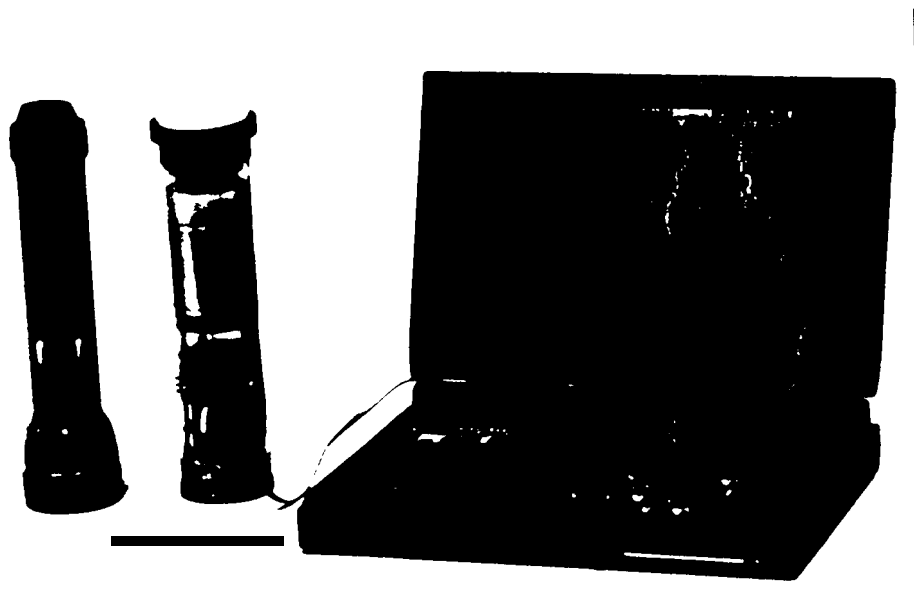

Figure 5. Operational mode of the miniature NMR (900 g, 0.25 W) is shown with a flash light for a size comparison.
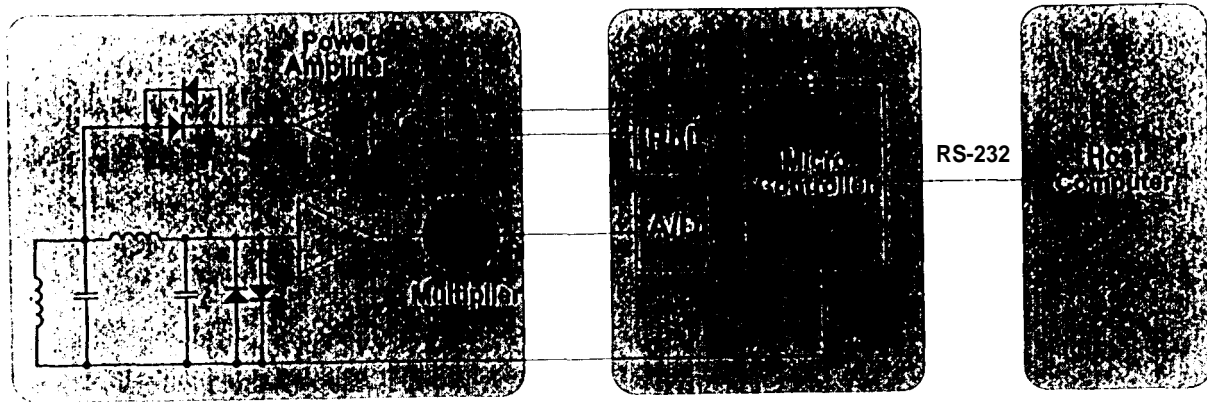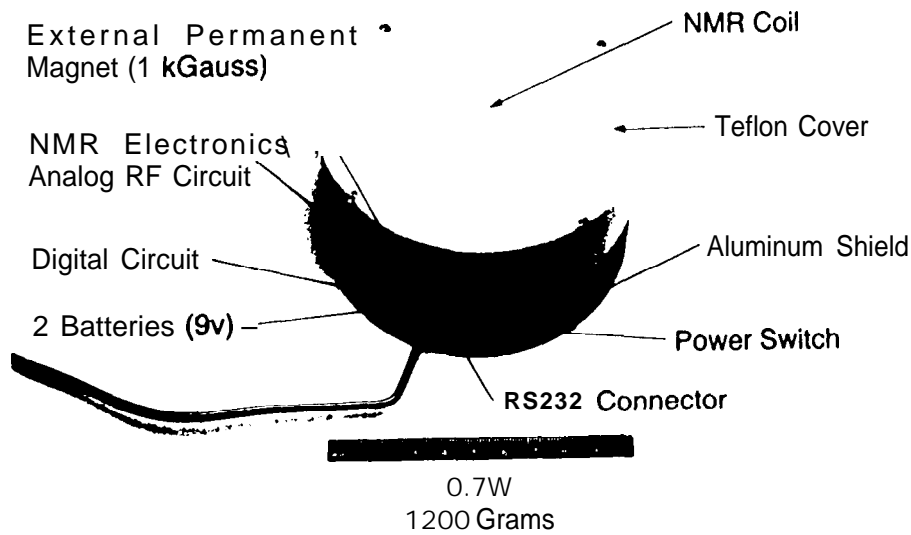
Figure 6. Pulsed-NMR circuit.

External Permanent Magnet (1 kGauss)

NMR Coil

NMR Electronics, Analog RF Circuit

Teflon Cover

Digital Circuit

Aluminum Shield

2 Batteries (9v)

Power Switch

RS232 Connector

0.7W
1200 Grams

Figure 7. External detection miniature NMR.

Iron-NMR (^{57}Fe-NMR)

Science Objective   Iron mineralogy can be used as a probe. for deducing conditions of planetary formation from original iron oxide phases, such as olivine and pyroxenes, as well as evolution of planets from weathering products such as oxyhydroxides through interaction with planetary atmosphere (and water). It is believed that the reddish coloration of Mars is due to the presence of ferric iron oxides or oxyhydroxides. According to the data obtained by the Viking landers, Mars soil is estimated to have - 18 wt% of iron oxides (Fe_2O_3)[1] with 1 - 7 wt% as magnetic phase materials.[2] Magnetic minerals of particle size larger than 10 nm, show unique internal fields (300 -550 kGauss)

due to spontaneous alignment of electron spins of iron atoms. One can conveniently utilize the internal field (without additional applied field) and obtain NMR by scanning RF field (zero-field NMR). By detection of mineral specific internal hyperfine fields through such NMR, one can uniquely characterize mineral phase of the particles. For iron mineralogy, so far Mössbauer spectroscopy has been extensively applied. However, for the characterization of magnetic phases such as ferromagnetic, ferrimagnetic or antiferromagnetic minerals, zero field NMR has advantages, such as higher energy resolution, faster spectral acquisition time, with comparable sensitivity.

In the iron-NMR, we are using the fact that ^{57}Fe

Dual Range
(43-54 MHz,
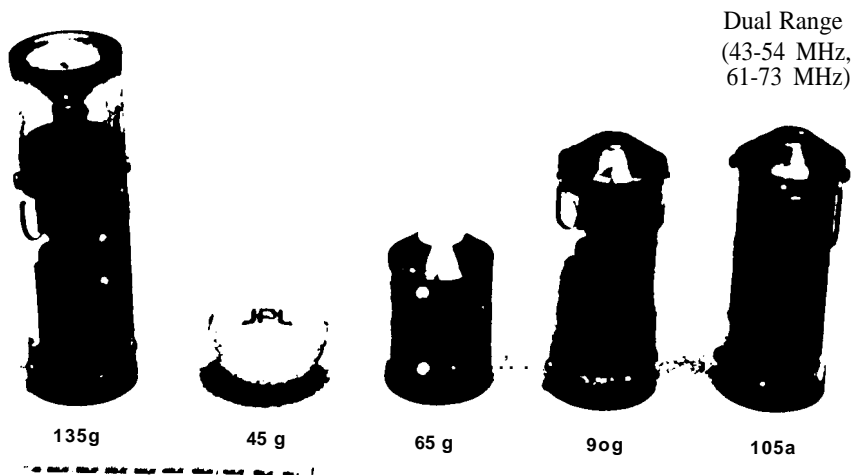61-73 MHz)

135g   45 g   65 g   9og   105a

Figure 8. A suite of miniature iron-NMR spectrometers (0.2 W, 9 V).

(natural abundance 2.19%) has nuclear spin, $I = 1/2$. Since each magnetic mineral phase already has characteristic internal field to split the nuclear spins into two energy states, e.g., hematite (517 kGauss), magnetite (491 kGauss for tetrahedral site, 462 kGauss for octahedral site), maghemite (500 kGauss), goethite (< 382 kGauss), in order to obtain NMR spectra, one need to apply only the RF field without the need for additional laboratory magnetic field, and the ^{57}Fe nucleii will show resonances at distinct frequencies depending on the mineral phases, e.g., 71.1 MHz (hematite), 67.6 MHz (magnetite, tetrahedral site), 63.5 MHz (magnetite, octahedral site), goethite (<52.6 MHz), respectively. The NMR characterization is absolute, there is no ambiguities, i.e., the iron nucleii in the magnetic phase minerals act like 'FM radio stations.'

Instrumentation Since there is no need for a permanent magnet to provide DC magnetic field to the sample, the iron-NMR spectrometers we produced are light weight (- 100 g) and low power (0.2 W) as shown in Fig. 8. The ^{57}Fe-NMR scan ranges are 43 - 73 MHz, and it can cover for most of the iron phase minerals known to exist. We have developed two configurations, one for internal detection mode by placing small magnetic particles inside a sample chamber, the other for external detection mode by placing the NMR on sample surfaces, as shown in Fig. 9.
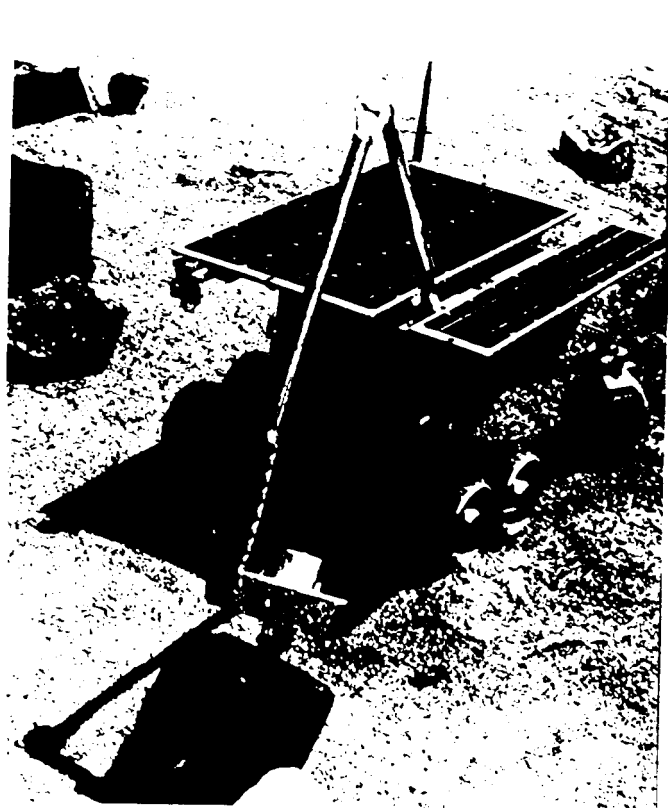

Figure 9. The Iron-NMR spectrometer deployed by a rover (Rocky-7) for a field demonstration.

EPR Spectrometers

<u>Science Objectives</u>   EPR spectroscopy can be used to answer the following specific questions.
(a) Nature of oxidant in Martian soil: Through the Viking Biology Experiments, it is speculated that there is about > 1 ppm of a thermally labile oxidant such as H_2O_2 and about 10 ppm of a thermally stable oxidant in the Martian soil[1]. Many of the thermally stable yet highly reactive oxygen species arc paramagnetic in nature and they can bc readily detected in native form by the EPR method. Compared with the sensor, "Mars Oxidant Experiment (MOX)", the EPR will be able to characterize the electronic state and molecular structure of the oxidant with specificity and higher sensitivity. (b) Oxidation states of paramagnetic ions: The oxidation states of paramagnetic ions (e.g., Fe, Mn, Ti), including those produced photochemically in the soil can be characterized. (c) Chemical characterization of volatiles through detection of color centers: The Martian surface receives a continuous flux of solar wind particles and galactic cosmic rays (GCR) which will create radicals and color centers in the solid and icy matrices. Such radicals or color centers (RCC) can be characterized with high sensitivity by EPR spectroscopy and used as probes to obtain chemical information of the matrices. For example, the presence of adsorbed CO_2 on the regolith in the form of carbonates can be studied from the frozen soil particles by the detection of carbonate radical, CO_3^-, formed by ionizing radiations (cosmic ray, γ-ray and solar wind proton) by the use of EPR spectroscopy. (d) Detection of possible organics from subsoil: The general consensus formed on the basis of the Viking results is that there is now no life on Mars. However, this conclusion has to bc reconsidered in view of the later suggestions[6-8]: ()) That a wetter climate once prevailed and life may have evolved and flourished on Mars in the past; (2) Endolithic life forms can theoretically survive on Mars, protected from the harsh ionizing radiation and highly oxidizing chemical environment. Therefore, it has been suggested[8] that major objectives of a Mars lander missions should include: (1) Search for evidence of fossil life forms; and (2) Study of the chemical environment in the subsoil and within rocks. Since EPR is a specific, non-destructive analytical tool for the characterization of

paramagnetic species having unpaired electrons, it can also detect organic compounds in the form of free radicals preserved in Martian subsoils or in organic fossils such as kerogen-like materials which are difficult to detect by the Viking type pyrolysis-GC/MS experiments. Carbonaceous chondrites which contain a substantial amount of organic free radicals have been shown to give rise to detectable EPR signals characteristic of kerogen-like materials present[9,10].

EPR Instrumentation

The frequency scan mode at a fixed magnetic field has been utilized for commercial CW NMR spectrometers in RF frequency ranges, but not for EPR in the microwave ranges due to technical reasons, one of which is the narrowband nature of sample cavities (Q - 5000) employed. Under the constraints of a miniature spectrometer, one way to achieve broader scan ranges, and thus obtain applications for wide ranges of paramagnetic species is to usc a microwave scan mode (2 GHz - 6 GHz) at a fixed magnetic field (e.g., @ 1.3 kGauss). Limited examples of the frequency scan mode of wideband EPR have been reported in the literature, such as "microcoil"[55] or a helical resonator.[sb] We have deve.loped two resonators for the frequency scan EPR, based on Loop-Gap Resonator (LGR) for the internal detection mode, and a microstrip resonator for the external detection mode.

<u>Internal Detection EPR</u>
Since 1977, a range of RF-microwave resonators with high microwave magnetic field, H_1, high filling factor, η, and reasonable quality factor, Q -500, have been reported by several authors. [5,''] [61] They arc variously designated as slotted tube resonator, split-ring resonator, folded half-wave resonator or loop-gap resonator (LGR). Electrically, the LGR can bc viewed approximately as a series tuned resonancc circuit whose resonance frequency, ν, depends on the inductance, L, of the conductive cylinder (the loop) and the capacitance, C, of the gap (see Fig. 10):

$$\nu = \frac{1}{2\pi\sqrt{LC}} \qquad (1)$$

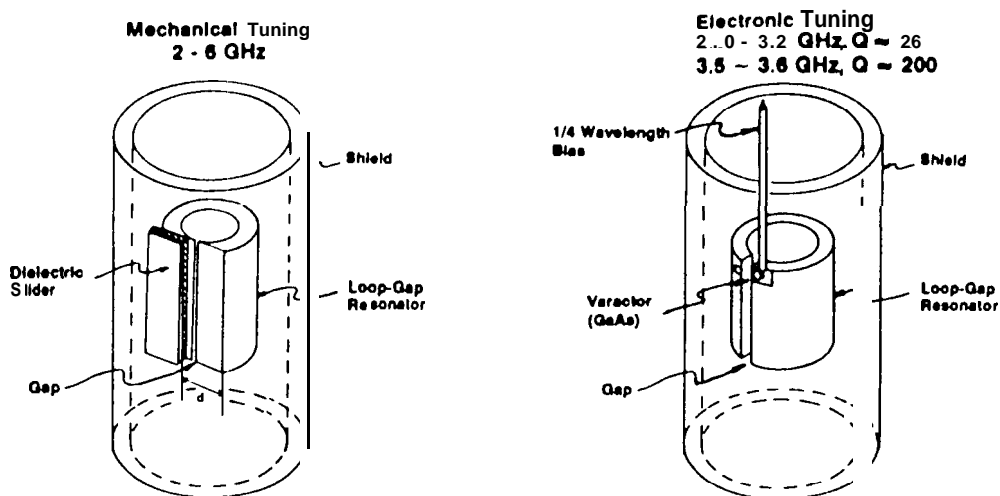We arc in the process of developing a frequency

Figure 10. Schematic drawing of mechanical and electronic tuning LGR.

scan EPR (2 -6 GHz) employing both mechanical (coarse tune) and electronic tunable (fine tune) LGR, as shown in Fig. 11. The mechanical tuning is achieved by mechanically sliding a dielectric material ($\epsilon_R = 38$) over the gap. The mechanical tuning arrangement yielded a tuning range of 2-6 GHz, quality factor, Q = 50 - 100. A voltage tunable LGR with a tuning range of 2 -3.2 GHz, and a quality factor, $Q \approx 25$, was fabricated with

GaAs varactor diode (Q – 50) through a strong coupling to the resonator (by a large coupling capacitor, — 10 pF) as shown in Fig. 11. This yielded the moderate tuning range, but resulted in a resonator of low Q due to the low Q of the varactor used. This resonator gave an EPR signal with low signal to noise ratio. Another resonator, a narrow band/high sensitivity voltage tunable LGR with tuning range of 3.5 -3.6 GHz, and a $Q \approx 200$
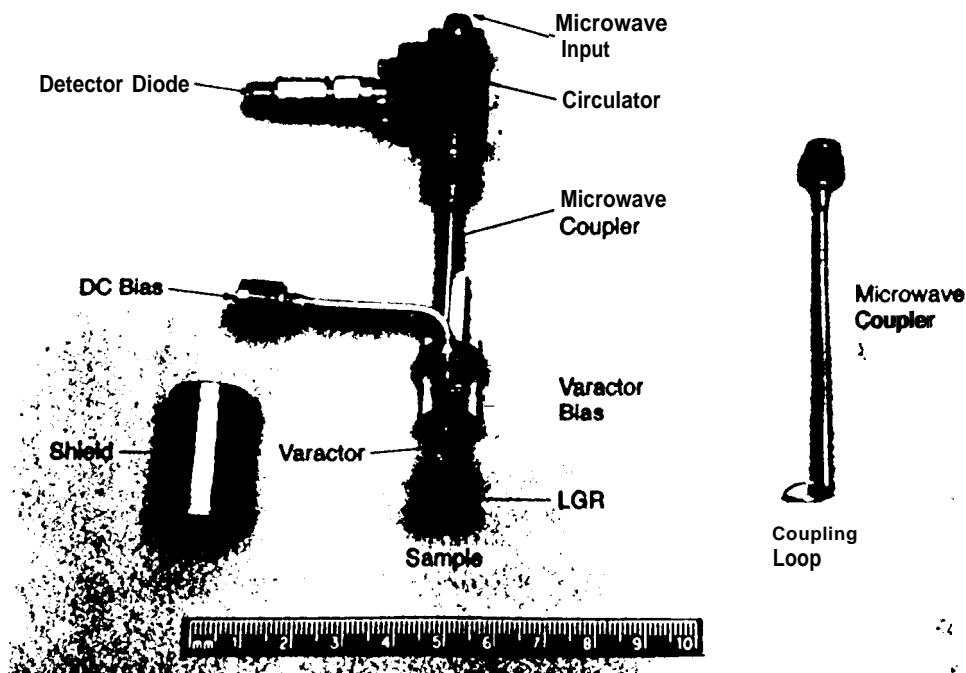

Figure 11. A narrowband (3.53 - 3.63 GHz) electronic tunable LGR assembly (reflection mode).

was fabricated with the GaAs varactor diode weakly coupled to the resonator (by a small capacitor, - 0.2 pF) yielding higher Q, but with smaller tuning range (scc Fig. 11). This configuration was also tested with laboratory magnet and yielded an easily detectable DPPH EPR signal. Several different detection configurations, including; transmission, absorption and reflection mode were tested. For broadband applications, transmission or absorption mode are judged to be preferable because they do not require microwave circulators, but arc inherently less sensitive. In the narrowband prototype, the reflection mode will be used because it is twice as sensitive as the other configurations, and good quality narrowband circulators are commercially available. As a proof of concept for frequency scan EPR, we obtained EPR spectra with DPPH (diphenyl picrylhydrazil, stable radical) at a fixed magnetic field (1 kGauss) provided by a laboratory electromagnet.

External Detection EPR

Various microstrip resonators are tested as sensors for this application. The basic eonfiguration of a half-wave ($n = 1$) microstrip resonator, as shown in Fig. 12, is a conductor suspended above a ground plane by a sheet of dielectric material ($\epsilon_R = 2.2$). The microwave energy is coupled into the resonator capacitively. In order to achieve voltage tuning, high Q GaAs varactors ($\gamma = 0.5$, $Q = 80$ @ 2.5 GHz) are placed at the end of the microstrip resonator. The degree of coupling between the resonator and the varcators can be varied by the location of the varactors on the strip, e.g., to have lcss coupling, the. varactor diodes can be shifted toward the center of the resonator strip. This will raise the Q, but narrow the tuning ranges. This type of trade-off is inherent in varactor controlled resonator design. The microwave magnetic field associated with microstrip resonators are spatially complex, but arc approximately normal to the axis of the microstrip upper conductor. They arc also symmetrical to and maximum at the center of the resonator. The voltage wave is minimum at the center of the resonator, so the DC bias to the varactor is supplied at the center to minimize the field perturbation as well as degradation of Q. Several resonators have been tested, with average $Q \approx 70$, and tuning range of 10%. The overall tuning range could be increased by over moding ($n > 1$) the resonator.
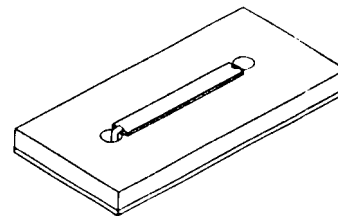

Figure 12. A microstrip resonator used for external detection EPR.

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