

# Detection of trace organics in Martian soil analogs using fluorescence-free surface enhanced 1064-nm Raman Spectroscopy

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**Abstract:** A significant technology challenge in planetary missions is the *in situ* detection of organics at the sub-part-per-million (ppm) level in soils. This article reports the organic compound detection in Mars-like soils at the sub-ppm level using an ultra-sensitive spectral sensing technique based on fluorescence-free surface-enhanced Raman scattering (SERS), which has a significantly improved sensitivity and reduced fluorescence noise. Raman spectral detection of ppm level organics in Antarctic Dry Valley and Mojave Desert soils have been obtained for the first time, which otherwise are not detected by other Raman spectral techniques.

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**OCIS codes:** (280.4788) Optical sensing and sensors; (160.1435) Biomaterials; (240.6680) Surface plasmons.

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## 1. Introduction

Planetary soils, rocks, and liquids are potential targets for scientists to study the possibility of life elsewhere and the habitability, nature, and evolution of planetary systems [1]. For example, there is great interest in detecting organic biomarkers such as lipids, polycyclic aromatic hydrocarbons, and cyanobacterial pigments in sedimentary rocks which contain fossil remains providing some of the most ancient records of life on Earth [2]. Even though these compounds represent only a minor proportion of the sedimentary organic molecules, their chemical composition and stability provide invaluable information for understanding ancient life and ecosystems. Similar ways of study may be implemented in other planets to investigate their nature, evolution, and life that may be present.

In the context of the search for life on other worlds, Mars is of prominent importance. A key challenge in Mars missions is to detect organics at very low levels in Martian samples. The results from the Viking Gas Chromatograph Mass Spectrometer (GCMS) were first interpreted to indicate that there were no organics in the soil on Mars at the parts-per-billion (ppb) level [3]. Even with an absence of any other (e.g., biological or abiotic) sources, organics are still to be expected on Mars due to the infall of meteorites [4]. Following the discovery of perchlorates by the Phoenix mission [5], it was suggested that perchlorate and soil organics (~ppm levels) in the Viking soils could explain the lack of organics and the presence of chlorinated organics in the mass spectra [6]. It has subsequently been suggested that the organic component needed to react with the perchlorate to make the chlorinated organics could have been produced from carbonate [7]. The overall Viking, Phoenix, and now Curiosity [8] results indicates that there is some indirect indication that there are low levels of organics on Mars but the concentration is very small (sub ppm). Unfortunately, Viking, Phoenix, and Curiosity all relied on heating to volatilize organics in the sample for analysis by a mass spectrometer or a GCMS. It is now realized that this method failed due to the presence of perchlorates in the soil. In the temperature range of 300–400°C, perchlorates decompose and releases reactive O and Cl atoms which react with organics in the sample. Most organics are oxidized to CO<sub>2</sub> but some minor fraction is chlorinated. These chlorinated organics appear to have been detected by Viking 1 (chloromethane) and Viking 2 (dichloromethane) [3] and Curiosity (chlorobenzene) [8].

The realization that perchlorates are ubiquitous on Mars has lead to a search for alternate methods to detect low levels of organics in Martian samples that do not require heating of the sample. Raman spectroscopy is a good candidate method for detection of organics on Mars in

a way that will not heat the perchlorate or be affected by the presence of 0.5% perchlorate in the sample. In recent years, Raman spectroscopy has emerged as a high-efficiency means to detect and analyze biological, chemical, geochemical, geophysical, and astrobiological materials. Raman spectral sensing has been demonstrated as one of the most reliable methods in laboratories. There are several prototype portable Raman spectrometers under development for space and planetary exploration. While they are based on similar optic design and CCD technology, the laser excitation wavelength typically varies from 532 nm and 785 nm [9–11]. As of the beginning of our research, there has not yet been a constructed dispersive 1064-nm Raman field unit that can achieve spectrum performance with the sensitivity needed to detect organics at the ppm level. This is due to the fact that existing Raman systems are often affected by strong fluorescence interference in organics rich samples, which overwhelms the weak Raman scattering signal, thus reducing the probability of organics detection.

Raman and Fluorescence spectroscopy are two competing events that arise from the light interaction with molecules of materials under investigation. Fluorescence is often several orders of magnitude more intense than Raman scattering. Although the fluorescence background can be removed mathematically, the random noise (shot noise) from fluorescence cannot be removed, obscuring the Raman spectra. It is known that the fluorescence can be eliminated or reduced by selecting longer excitation wavelengths [2]. Our previous research has found that 1064-nm laser excitation yields the best quality information for the mineral samples since fluorescence is avoided [2]. However, conventional Raman spectrometers designed to accommodate 1064-nm excitation are interferometer-based FT-Raman, which is bulky and suffers from a longer acquisition time. To address these issues, we built a 1064-nm fiber-optic dispersive Raman sensor that has a faster response time and higher sensitivity. It should be noted that there is a small drawback of using a longer wavelength for Raman excitation because the Raman signal decreases as is manifested in the  $1/\lambda^4$  rule [12]. The absolute intensity of a Raman peak at  $1000\text{ cm}^{-1}$  measured with the Nd:YAG 1064-nm line is only 30% of that measured with the 785 nm laser line, provided that the power of each laser line is equal. On the other hand, Surface-Enhanced Raman scattering can enhance Raman signal by a factor of  $10^8$ – $10^{11}$  or higher [13–18]. SERS is becoming an important technique for identification of organics as it can provide significantly enhanced signals, leading to improved detection limits and sensitivity.

To search for organic compounds on Mars for future NASA space missions, the Raman signal must be amplified at least a million times. In order to fill this technology gap, we combined two techniques: (a) fluorescence-free 1064-nm excitation with increased signal-to-noise ratio ( $>10^2$ ), and (b) nano-surface enhancement with amplified Raman signals ( $10^8$ – $10^{11}$ ). Another reason to select 1064-nm Raman excitation wavelength is the proven availability of a space rated pulsed laser at the wavelength of 1064 nm [19]. Figure 1 shows the schematic of the fluorescence-free Raman spectral sensor constructed using a SERS fiber-optic probe to detect organics evaporated from a water solution placed on the substrate. The Raman unit consists of four components: (1) a compact fiber-coupled 1064-nm diode laser, (2) a remote fiber-optic Raman probe with SERS capability, (3) a dispersive fiber-optic spectrophotometer, and (4) nanostructured SERS substrate which also acts as the platform on which the solution of soil extract is evaporated.

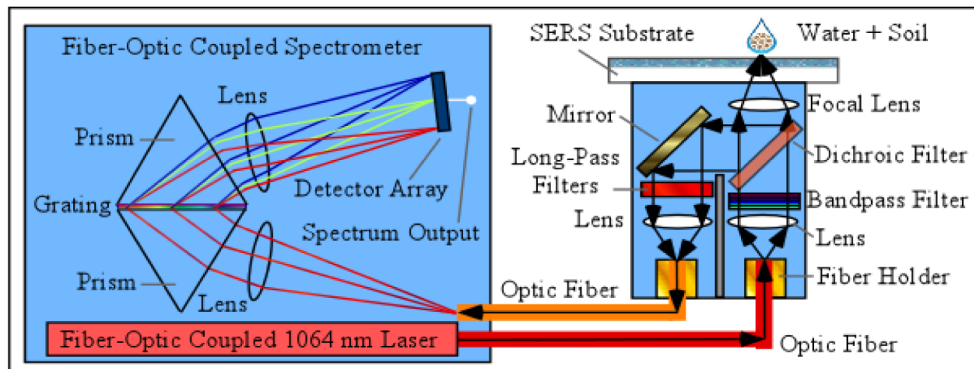


Fig. 1. Schematic of Raman spectral sensor using fiber-optic SERS probe.

## 2. Experiment

Figure 2 shows the 1064-nm Raman spectral sensor with fiber-optic SERS probe, which consists of (1) a highly efficient 1064-nm fiber-optic coupled diode laser with a narrow linewidth of 0.02 nm and output power of 20 mW at the output end of the Raman probe, (2) infrared 512-element InGaAs detector array with 1 ms response time and cooled to  $-55^{\circ}\text{C}$ , (3) fiber-optic SERS probe, and (4) transmission grating based spectrometer with a spectral range from 1099 nm to 1352 nm and a spectral resolution of 1.24-1.45 nm ( $8\text{-}10\text{ cm}^{-1}$ ). The fiber-optic SERS probe excitation and collection optics contained a dichroic filter, a bandpass filter for the exciting beam, and a long-pass filter for the receiving beam. The SERS substrate was arranged at the output end of the fiber-optic probe, which could be easily replaced for each different sample. The SERS substrate is based on gold nanoparticle (Au NPs) and was prepared by NASA Ames Research Center. These Au nano-particles were fabricated through controlled reduction of chloroauric acid ( $\text{HAuCl}_4$ ) by ascorbic acid in aqueous solution. The inset figure in Fig. 2 shows the photograph of scanning electron microscope of the SERS substrate with Au NPs of diameter in the range from 20 nm to 30 nm.

Two soils with known low organic content from Mars analog sites were used in this work. The sites were Linneaus Terrace in the upper elevations of the Dry Valleys at Antarctica and the arid core region of the Mojave Desert [20]. Linneaus Terrace is located at  $87.598^{\circ}$ ,  $161.001^{\circ}$ , elevation 1722 m and has been the focus of study [20] because of the cryptoendolithic organisms growing in the sandstone, which is warmed by sunlight to temperatures up to  $15^{\circ}\text{C}$  above the air temperature. The mean annual temperature at the site (in 1984) is  $-21.4^{\circ}\text{C}$ , and summer maximum air temperatures is  $+6.2^{\circ}\text{C}$  (in 1984). The weathering of the sandstone provides a source of organic material to the soil. Measurements of the total organic content of Linneaus Terrace indicated 20-30  $\mu\text{g}$  carbon (C) per gram soil, a C/N ratio of 0.9, and mass fragments at 18 (100), 44 (45), 64 (23), 36 (22), 48 (9), 38 (7), 30 (6) [20]. The value in parenthesis is the percent relative abundance of each fragment normalized to the most abundant mass in the temperature range 100–1200 $^{\circ}\text{C}$ ; if more than one mass ion exhibits a similar percent relative abundance, this abundance is given for the lowest mass. Mojave Desert samples were collected from  $35.255^{\circ}$ ,  $115.955^{\circ}$ , elevation 450 m, in the driest region of that desert with average precipitation of about 2.5 cm. Measurements of the total organic content of the sample indicated 145-260  $\mu\text{g}$  C per gram, a C/N ratio of 9.5, and mass fragments at 28 (100), 18 (95), 44 (88), 41 (3), 79 (2), 38, 48 (1), 30 (<1) [20]. A simulation of organic detection based on the Viking (and Phoenix and Curiosity) methods of thermal volatilization (TV) were conducted and found that the detection of organic fragments by TV-mass spectrometry was not correlated with the amount of organic matter present originally in the soil when the soil organic content was at low levels



(<1500 ppm Carbon) [20]. Qualitative and quantitative analysis of these soils represent a challenge for TV–mass spectrometry on Earth.

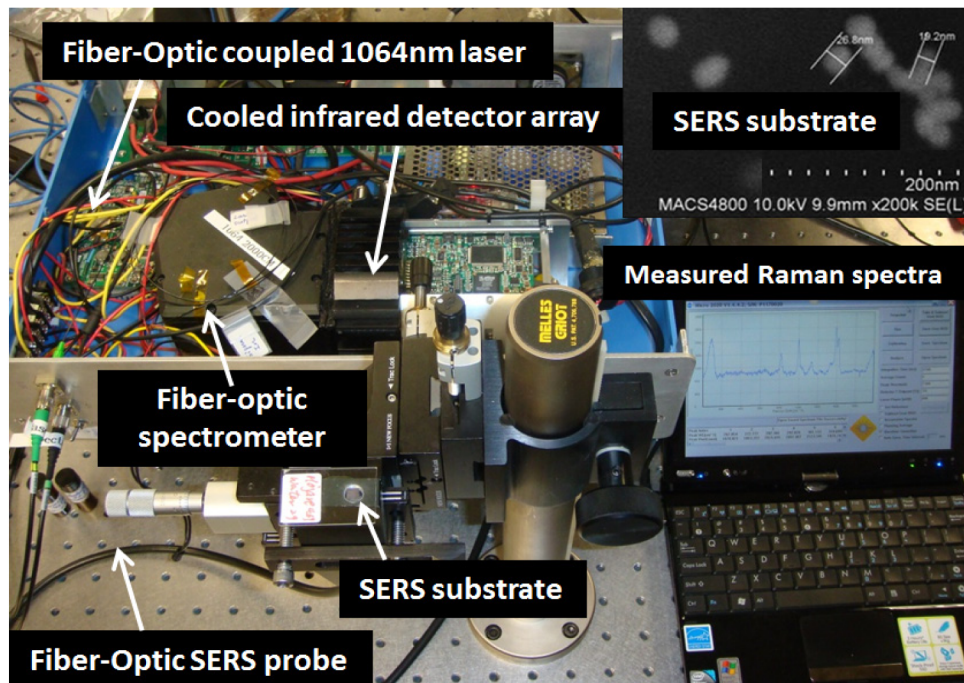


Fig. 2. Photograph of 1064-nm Raman sensor using SERS enhanced fiber-optic probe.

To test the SERS Raman system with Mojave Desert soil, 4.6 grams of the soil was first mixed with 2 grams of water. The solution of soil and water mixture was then dropped onto the SERS substrate for 1064-nm Raman spectral measurement. The measurement was then conducted after the water evaporated leaving behind a residue on the SERS substrate. Figure 3 shows the measured 1064-nm SERS spectrum of Mojave Desert soil extracted by water. The laser excitation power was 20 mW with a laser spot size of approximately 125  $\mu\text{m}$ . The integration time was 20 seconds and the measured data were averaged for 20 times. The Raman peak at 880  $\text{cm}^{-1}$  is associated with the zeolite contained in the soil. The Raman peak at 1333  $\text{cm}^{-1}$  is within the prominent D band of graphite; the peak at 1424  $\text{cm}^{-1}$  is potentially associated with the asymmetric C–C stretching vibration. The organic carbon peak located at 1199  $\text{cm}^{-1}$  corresponds to the defect-related D-band of graphitic carbon and the 1590  $\text{cm}^{-1}$  peak may be from the superposition of the G band of graphite, C = C ring stretching mode at 1590  $\text{cm}^{-1}$ , and D' band at 1620  $\text{cm}^{-1}$ , indicative of disorder in the  $\text{sp}^2$  network. The Raman bands around 1300  $\text{cm}^{-1}$  and 1600  $\text{cm}^{-1}$  could also be due to C = C related C-C, or C-H vibration from aromatic groups in soil components. These observed Raman peaks in Mojave Desert soil are due to the known concentration of organics in this soil which are ultimately of biological origins.

In the experiment with Dry Valley soil from Antarctica, 4.6 grams of the soil was first mixed into 2 grams water. The testing condition was exactly the same as that for the Mojave Desert soil. The measured 1064-nm SERS spectrum of Dry Valleys soil extracted by water is plotted in Fig. 3. The Raman peak at 534  $\text{cm}^{-1}$  is associated with the silicon contained in the soil. The Raman peaks at 1230  $\text{cm}^{-1}$  and 1292  $\text{cm}^{-1}$  are within the prominent D band of graphite. The Raman peak at 1569  $\text{cm}^{-1}$  is within the prominent G band of graphite. The Raman bands around these peaks could also be due to C = C related C-C, or C-H vibration from aromatic groups in soil components. The peak at 1454  $\text{cm}^{-1}$  is potentially associated

with the asymmetric C–C stretching vibration. These Raman spectral peaks observed in Mojave Desert soil and Dry Valleys soil at Antarctica have not been observed by using any other Raman techniques. These Raman peaks indicates the possibility of carbonaceous material of microfossils in these Mars-like soils. For comparison, the direct 1064-nm Raman spectra of Mojave Desert soil and Dry Valleys soil at Antarctica were measured using the same testing setup. As shown in Fig. 3, there are no meaningful peaks in the Raman spectrum of direct measurement for both samples. In the experiment, it is found that the presence of 1% magnesium perchlorate added into the water solution of Mojave Desert soil does not interfere with the SERS detection of Raman peaks associated with organics in Mojave Desert soils.

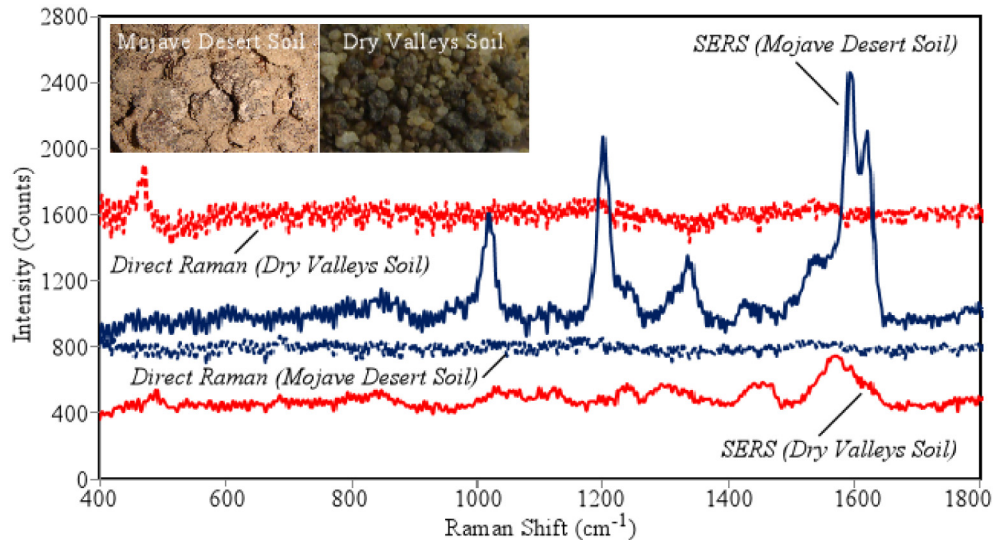


Fig. 3. Measured 1064-nm Raman spectra of Mojave Desert soils and Antarctica Dry Valleys soils extracted by water with SERS enhancement and directly measured 1064-nm Raman spectra of Mojave Desert soils and Antarctica Dry Valleys soils.

### 3. Summary

By combining fluorescence-free 1064-nm excitation and SERS, we have experimentally obtained Raman spectral detection of organics in Mojave Desert soils and Dry Valleys soil for the first time, which otherwise are not detected by other Raman spectral techniques. The SERS spectral sensor using 1064-nm excitation has a clear advantage over the conventional Raman techniques in terms of reduced fluorescence and enhanced sensitivity. Although this research combining both 1064-nm fluorescence-free Raman and SERS was conducted for a very specific goal, it may lead to new discussions in detecting low concentration fluorescence-rich organic samples.

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