REACTIVITY ANALYZER FOR SOIL, ICES, AND REGOLITH (RASIR). R. C. Quinn[1], A. J. Ricco[2], P. Ehrenfreund[3], F. Grunthaner[4], O. Santos[2], A. Zent[2], J. W. Hines[2], E. Agasid[2], [1]SETI Institute (NASA Ames Research Center, Moffett Field, CA 94035, Richard.C.Quinn@nasa.gov), [2]NASA Ames Research Center, [3]George Washington University, [4]NASA JPL

Introduction: The Reactivity Analyzer for Soil, Ices, and Regolith (RASIR) is an integrated microanalytical system designed to simultaneously measure the organic content and chemical reactivity levels of martain surface samples. Target analytes include organic compounds, potentially toxic inorganic ions, and reactive soil species expected to play a role in the in-situ degradation of organics on Mars. Results from previous Mars missions, including Viking and Phoenix, indicate that reactive and hazardous chemical compounds (e.g., peroxides, superoxides, oxychlorine compounds) are produced in the martian radiation environment. These species and related reactive intermediates likely play a role in the degradation of biomarkers and limit habitability on the surface of Mars. Additionally, these compounds can complicate the detection of organics by traditional methods (e.g., GCMS) [1] and may pose a threat to human health and safety. By targeting the detection of both organics and reactive compounds, RASIR directly addresses the Mars exploration challenge area 1: *Instrument and Investigation Approaches* by detecting trace-level organic matter in soil and dust without extensive in-situ sample processing, in combination with simultaneous analysis of sample reactivity and potential toxicity pertinent to human health risk reduction.

Technological and Scientific Lineage: RASIR represents the next-generation development of the Space Environment Viability of Organics (SEVO) payload that was developed for the Organism/Organic Exposure to Orbital Stresses (O/OREOS) nanosatellite, the first technology demonstration project of the NASA Astrobiology Small-Payloads Program. Developed and flight qualified at a cost of < $1 M, at NASA Ames Research Center, SEVO was launched and deployed in low earth orbit in the fall of 2010. SEVO utilizes UV-Vis-NIR spectroscopy to measure in-situ physical and chemical changes induced in thin-film organic samples by their exposure to solar and cosmic radiation. The SEVO payload (Figure 1) is housed in a 10-cm cube, weighs 1.1 kg and contains a microprocessor-controlled 24-sample-cell carousel, a UV-Vis-NIR spectrometer that occupies 1/3 of the cube, and fiber optics to transmit light from the sample cell collection optics to the spectrometer [2]. SEVO, as part of the O/OREOS nanosatellite, has functioned nominally for over 18 months in orbit and attained full mission success 6 months after launch.

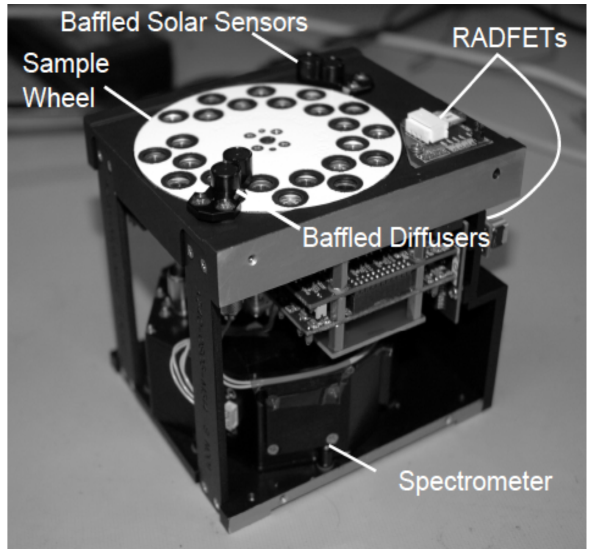

Figure 1. The SEVO fight unit (10x10x10 cm) weighs 1.1 kg and holds 24 sample cells on a microprocessor-controlled carousel. Fiber optics transmit light to a UV-Vis-NIR spectrometer that occupies the lower third of the cube.

In the RASIR implementation of the SEVO payload, direct chemical analysis of martian samples is performed by using chemically sensitive thin-film probe molecules in combination with fluorescence detection. While the hardware platform for RASIR is derived from the TRL-9 SEVO payload, the measurement approach is derived from the Mars Oxidant Instrument (MOI) which was developed to TRL-5 through substantial NASA investment provided by the PIDDP, ASTID, ASTEP, and SBIR funding [3]. By leveraging TRL-9 SEVO hardware, RASIR provides a cost-effective way to achieve MOI measurement objectives with a light-weight 10-cm cube platform.

RASIR Measurement Approach: Commonality between SEVO and RASIR measurement approaches allows the direct adaptation the SEVO hardware for the analysis of the martain surface environment. SEVO was designed to measure spectroscopic changes in organic molecules for the study of organic chemistry in space environments. The SEVO organic samples are deposited as thin films onto an optically transparent window that forms the bottom of a sample reaction cell. After film deposition, the reaction cell is hermetically sealed under a controlled atmosphere creating a "microenvironment" designed to expose the organic sample to a set of chemical and physical parameters relevant to interplanetary and planetary conditions [2].

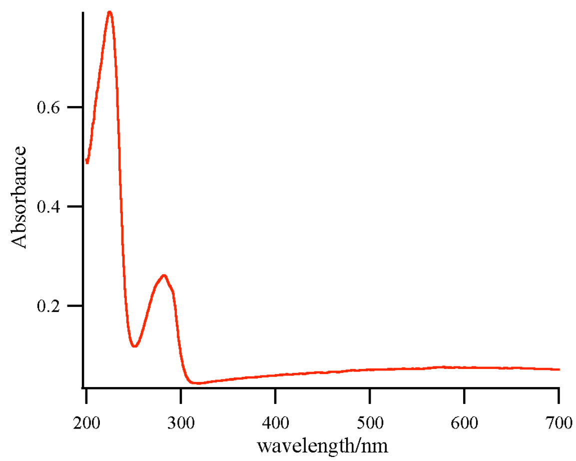

Figure 2. SEVO spectrum of a tryptophan in a controlled relative humidity (2%) sample cell.

Figure 2 shows the UV-Vis spectrum of a SEVO flight cell that contains a thin-film tryptophan sample in a controlled at ~2% relative humidity atmosphere.

In the RASIR implementation, the thin-film organic is prepared, as for O/OREOS-SEVO, by vacuum sublimation. However, RASIR thin films are used as sensors, or probe molecules, to directly analyze martian samples (regolith, soil, or ice) or passively collected dust. This implementation provides direct lineage from previously developed technologies that use thin-film chemistry to characterize sample organic chemistry and redox activity, including the introduction of alternative reaction pathways for less reactive species.

The RASIR instrument package contains 24 sample cells carried in a supporting carousel (Figure 3). The sample carousel is rotated with a stepper motor to bringing the sample cell into position for optical measurements. Processor and memory to control the entire RASIR system, store its spectral and sensor data, and interface to a lander or spacecraft bus, are integrated in the 10-cm-cube package. Two fluorescence excitation sources (solid-state/diode lasers) are directed at 45° incidence onto a chemical sensing film supported on the inside of a transparent window at the bottom of each cell. A UV-Vis-NIR spectrometer (200-1000 nm) is used to record the reflectance, fluorescence, or luminescence spectrum from samples and from each sensing film as a function of time.

The RASIR chemical sensors are commercially available chemical indicators (fluorescent, chemiluminescent, and colorimetric) for the targeted detection of organic and inorganic compounds. Target organics include: amino acids, carboxylic acids and PAHs. Target inorganics include: reactive oxygen and oxychlorine species. The response of the thin-film indicators are measured in combination with reflectance, fluorescence, and chemiluminescence detection. Because entire spectra is recorded, subtle changes that might be difficult to reliably detect by single-wavelength emission intensity changes can be discerned.

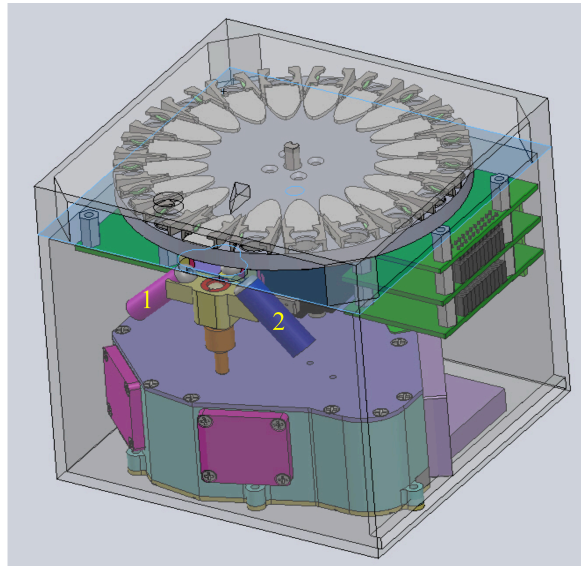

Figure 3. RASIR instrument package. After soil or dust collection, sample cells are individually sealed using a spring-loaded lid compression mechanism. Two fluorescence excitation sources are directed at 45° off-normal incidence (1&2).

Complex samples can contain multiple species with different reactivities and solubilities that can dictate probe molecule response and measurement lifetime for target species. Accordingly, the RASIR measurement approach includes control of temperature and water activity to establish and modify the sample environment and reaction conditions. Relative humidity (i.e., water activity) is increased (to saturation) in a controlled manner with heating to trigger the reaction of target analytes with the probe molecules; each sample cell includes a thermally activated water-release material, as demonstrated with the SEVO flight payload.

RASIR is designed to accept martian samples (regolith/soil) directly from an external sampling system without in situ sample processing. In the absence of a lander/rover sample handing system, RASIR can be operated in a passive dust-capture mode using the spectrometer to characterize dust loading prior to closing the sample cells. RASIR also includes sensors to measure local solar illumination and ionizing radiation dose (Figure 1) to correlate the martain sample chemistry with local environmental parameters and hazards.

References: [1] Boynton et al., Science 325, 61, 2009. [2] Bramall et al., Planetary and Space Science, 2012 doi:10.1016/j.pss.2011.06.014 [3] Quinn et al., Planetary Space Sci., 53, 1376-1388, 2005.