

DETECTION OF SUBSURFACE ORGANICS USING DEEP UV RAMAN AND FLUORESCENCE SPECTROSCOPY: IMPLICATIONS FOR SHERLOC ON MARS 2020. B. L. Carrier*, L. W. Beegle, R. Bhartia, W. J. Abbey, E. K. Hara, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA (*bcarrier@jpl.nasa.gov).

Introduction: The Scanning Habitable Environments with Raman and Luminescence for Organics and Chemicals (SHERLOC) instrument will be part of the Mars 2020 payload. SHERLOC will use a 248.6 nm laser to induce fluorescence emissions and Raman scattering from minerals, organics, and potential organic biosignatures in both natural and abraded surfaces on Mars [1]. Fluorescence is generated from electronic transitions in aromatic organics and Raman scatter is generated from vibrational bonds in both organics and minerals. Understanding how deep into a substrate an analyte can be detected is key to understanding limits of detection for SHERLOC measurements and will help define what a null detection means [2].

Here we report on preliminary results using a SHERLOC-like laser to detect the Raman and fluorescence spectra of aromatic and aliphatic organics under thin layers of MMS basalt (Mojave Mars Simulant) [3], kaolinite, Bishop tuff and gypsum. These thin layers were formed using crushed rock or mineral powder and a mechanical press.

Methods: Pellets analyzed consisted of 2 layers. The bottom layer consisted of the organic of interest. Organics investigated include phenylalanine, phenanthrene, alanine, histidine, lysozyme and adenosine 5'-monophosphate. The top layer was a thin layer (~100-300 μm) of organic free pressed rock or mineral. The thickness of the top layer was measured using a Mitutoyo digital thickness indicator before being applied on top of the organic layer. Each pellet was analyzed at 58 micron spot size over >150 discrete points. Fluorescence spectra were obtained with 25 pulses and Raman spectra with 1200 pulses.

Results and Discussion: Results indicate that aliphatic organics can be detected to depths of at least 100 μm in all substrates investigated, while aromatic compounds could be detected at > 250 μm . Figure 1 shows, for example, the Raman spectrum of alanine obtained under a layer of MMS with a thickness of 99 ± 10 μm (average of spectra taken at 156 points), while the inset shows the spectrum of pure alanine. Peak locations and relative intensities of the subsurface sample correlate well to the spectrum of pure alanine. The relative intensity between subsurface and surface samples of alanine was on the order of ~1.5% in this case.

For each pellet analyzed there was substantial variability from point to point, ranging in some cases from 0 to near 100% signal transmittance. This is likely due to natural heterogeneity in the mineral matrices. Natu-

ral martian rocks will also show significant variability in their compositions and crystal structures, highlighting the benefits of mapping areas of interest rather than taking single point spectra to be representative of the bulk material.

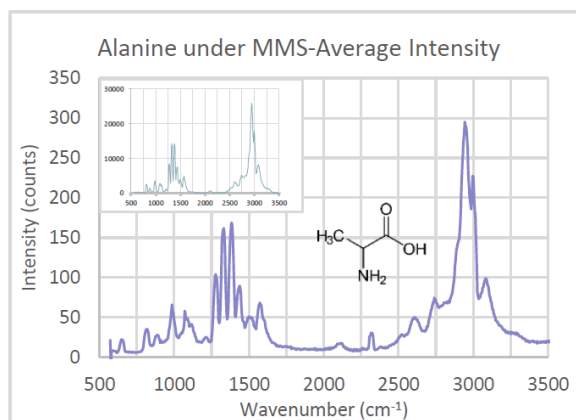


Figure 1. Averaged Raman spectrum of alanine under 99 ± 10 μm MMS. Inset-Raman spectrum of alanine on a surface.

Conclusions: Detection of organics by deep UV Raman and fluorescence spectroscopy can be achieved at depths greater than previously anticipated, potentially allowing for lower limits of detection and larger interrogation volumes for the SHERLOC instrument on Mars. The actual LODs will depend on the mineral matrix as well as the nature of the organic to be detected. The point to point variability in signal strength for each pellet analyzed highlights the advantages of detailed mapping of an area of interest.

Acknowledgements: This work was carried out at the Jet Propulsion Laboratory, The California Institute of Technology under a contract from NASA.

References:

- [1] Beegle et al. (2015) *IEEE*, 90, 1-11. [2] Bhartia, R., W.H. Hug, R. Reid, L. Beegle, (2015) Explosives Detection and Analysis by Fusing Deep UV Native Fluorescence and Resonance Raman Spectroscopy. P.M. Pellegrino, E.L. Holthoff, M.E. Ferrell (Eds.) *Laser-based Optical Detection methods of Explosives*, Boca Raton, FL: Taylor & Francis Group. [3] Peters et al. (2008) *Icarus*, 197(2), 470-479.