FLUORESCENCE MITIGATION USING THE COMPACT INTEGRATED RAMAN SPECTROMETER (CIRS) FOR IN SUTU ANALYSIS OF MINERALS AND ORGANICS.

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Introduction: Raman spectroscopy offers the capability to detect and identify a wide variety of mineral and organic materials. It utility has demonstrated itself in the numerous extensive Raman spectra databases compiled and used by a variety of scientists, from chemists to mineralogists. Furthermore, Raman spectrometers, specifically our Compact Integrated Raman Spectrometer (CIRS), has demonstrated its high-performance capabilities in environments relevant to planetary exploration [1]. CIRS's continuous wave 532 nm laser is used to acquire Raman spectra while its integrated context imager can acquire focusable images of the sample. Further improvements have been made in the overall capabilities of CIRS, allowing it to address the needs of future lander missions at locations like Europa and Mars.

Fluorescence Mitigation: A main critique of a the simplest and most robust variant of Raman spectroscopy (CW excitation at 532nm) is the potential for background fluorescence to overwhelm the desired Raman signals. However, the scale of this issue is exaggerated since previous studies of extraterrestrial samples have shown that fluorescence from such materials is low-to-non-existence [2, 3].

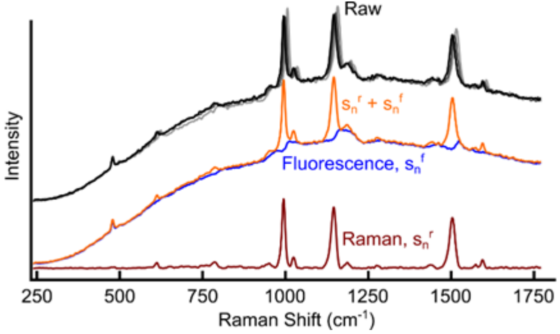

Figure 1. The raw and SSE-extracted Resonant Raman and fluorescence spectrum of *Deinococcus radiodurans.* 532 nm excitation, 8 mW, 5 spectra each with 1 min exposure.

In an effort to address instances where background fluorescence is an issue, we have integrated Serial Shifted Excitation (SSE) [4] into CIRS (TRL 6) as a simple and effective method for extracting Raman signals from strong fluorescence backgrounds without the need for complicating hardware. SSE is performed by collecting spectra at numerous discrete excitation frequencies, spanning a total range of ~15 cm^{-1}, by simply adjusting the temperature of the laser. While fluorescence is immune to small changes in the excitation frequency, Raman signals will experience a shift. As shown in Figure 1, an algorithm can then be used to extract these shifting peaks from the raw spectra, separating static features (fluorescence and background light) from shifting ones (Raman). These "background-free" Raman spectra can then be compared to spectral databases to assign unknown samples.

We have demonstrated this SSE capability with both 532 and 785 nm excitation. Between these two sources, about 92% of all known minerals can be identified [5]. Parts of the remaining 8%, typically unassignable due to fluorescence, can now begin to be addressed with SSE.

Sensitivity: The limit of detection for our CIRS instrument was determined for a variety of analytes highlighted as scientifically important for future missions to the surface of Europa. The signal-to-noise ratio (SNR), as defined by McCreery [6], for the 1065 cm^{-1} peak of CO_3^{2-} in water (10 s, 8.7 mW, 532 nm excitation) was determined at variety of concentrations, giving a LoD (SNR = 3) of 6.90 ± 0.43 parts per thousand (wt/wt), which is 1-2 orders of a magnitude lower than the thresholds specified by the Europa Lander Science Definition Team [7].

With carbonate's well-defined Raman scattering cross-section and LoD as well as our system's laser power and acquisition time, our system's figure of merit, F'_{SNR} [6], was determined to be 5.92e-4 photons$^{-1/2}$ sr$^{1/2}$ cm$^{1/2}$. This figure of merit can then be used to estimate the LoD for any analyte with a known Raman cross-section, allowing us to gauge the sensitivity for numerous analytes of interest including sulfates, nitrates, chlorates, phosphates, and sulfur-containing species, all with LoD below 25 ppt for relatively low laser power (8.7 mW) and acquisition time (10 s).

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ISBN: 0-471-25287-5. [7] *Europa Lander Study 2016 Report* (2016) NASA