STAND-OFF UV LASER INDUCED FLUORESCENCE AND UV ENHANCED RAMAN SPECTROSCOPY FOR MINERAL ANALYSIS.

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Introduction: Identification of minerals and possible organics in planetary and space exploration is of paramount importance in addressing the origin and formation of the Solar system, in searching for evidence of past or present life, in planning in-situ resource utilization activities, and extraterrestrial mining. Up to now, landers and rovers used methods that need close contact with a sample (e.g., X-ray, microscopy analysis). This requires the rover to cover large distances or areas to determine which specimens are of potential interest. This process is time and power consuming. On the other hand, the orbiters rely on visible, near infrared and infrared spectroscopies that generate broad and overlapping mineral spectra that are challenging to interpret. UV laser induced fluorescence has much the same features, but when done on the surface, spatial resolution can be much better and identifiable spectra not as much diluted in too large a surface. INO has measured multiple UV LIF mineral spectra on surfaces of the order of a cm^2 or less from 390 to 640nm using 355nm laser excitation and shown that identification was possible using measurable differences. In contrast, Raman spectra of minerals exhibit narrow and largely non-overlapping features which allow a much more reliable mineral identification. This dual capability enables rapid mineralogical analysis of rocks and outcrops in the vicinity of a lander, rover or hovering probe studying large and small celestial bodies (planets, moons, asteroids, trans-neptunian objects…).

Current INO LIF/Raman standoff sensor: The current INO Raman standoff sensor uses a picosecond pulsed 355nm laser, a very light weight carbon fiber collection telescope with a 20cm diameter optically fast primary mirror, a fiber bundle for coupling a maximum of light between the telescope and the spectrometer and for eventual Raman imaging, a reflective spectrometer and a fast-gating intensified camera.

Although any short pulse (less than 1 nanosecond) laser would probably have worked, the experiments described in this abstract used an 8ps pulsewidth solid state laser. This is an integrated laser that only needs to be powered and commanded. There is no external power supply or controller. The pulse energies at 355nm are of the order of 150µJ at 200Hz repetition rate for an average power of 30mW. This is an example of lasers that could be used for LIF and Raman stand-off detection, based on diode pumped low frequency, medium energy solid state Nd doped lasers.

The receiver telescope structure, as the rest of the structure, is made almost exclusively of lightweight reinforced carbon composite. The primary is a fast (f/2.46) 20cm clear aperture diameter UV enhanced silver coated glass mirror. This is the heaviest component of the telescope. The secondary is a 10cm flat mirror with the same type of coating. The return signal is focused in a plane in which a fiber bundle is placed. The fiber bundle is on a motorized stage for the system to adapt to varying measurement distances while maximizing the collection efficiency.

Reflective spectrometers are readily available for the wavelengths used in this project. They can be lightweight and of relatively high throughput. Every fiber images a different small spot (every independent fiber behaves as a small telescope), thus providing possible enhanced spatial resolution within the laser spot when coupled to the imaging spectrometer.

The key to the successful detection of Raman spectra for this instrument is the fast-gating intensified camera. Commercial ICCDs are used for the INO LIF/Raman standoff sensors. In this particular case, the ICCD has minimum gate duration of 3 ns, with gate rise and fall times of less than 1ns. The ICCD quantum efficiency was also optimized for UV wavelengths.

Experiments: INO visited the Planetary and Space Science Centre at the University of New Brunswick (UNB) in Fredericton, Canada, for a series of measurements on mineral samples from the rock collection there. These are preliminary measurements to investigate the best ways to use stand-off spectroscopic detection in the context of planetary space exploration.

Measurements done at UNB were all for fluorescence monitoring. Time and equipment did not allow for the Raman stand-off measurements. Other measurements, LIF and Raman, were done at INO on other mineral samples. When going from low resolution LIF to higher resolution Raman, the diffraction grating inside the imaging spectrometer was changed. As will be seen in the results, the spectral ranges covered in the two instances are different. It is not necessary to cover more than 60nm in the case of Raman monitoring.

Figure 1 shows spectra for talc and ruby. From these spectra a number of preliminary conclusions can be drawn: 1) All spectra contain violet (~425nm) and blue (~450nm) peaks that dominate the spectrum; 2) There is a shoulder indicating a peak ~410nm; 3) A fourth large peak in the 460nm – 470nm range is also present, as seen by the varying spectral width of the blue region; 4) There is a fifth peak in the green, around 510nm; 5) Two other regions could then be defined, a yellow region between 550 and 590nm and a red region between 590 and 640nm; 6) Defining 7 peaks/regions seems optimum; 7) The ratio of these peaks and regions change from one mineral to another; 8) Fluorescence returns vary wildly in strength, from 1600 counts in hematite to 22 000 counts in halite and talc.

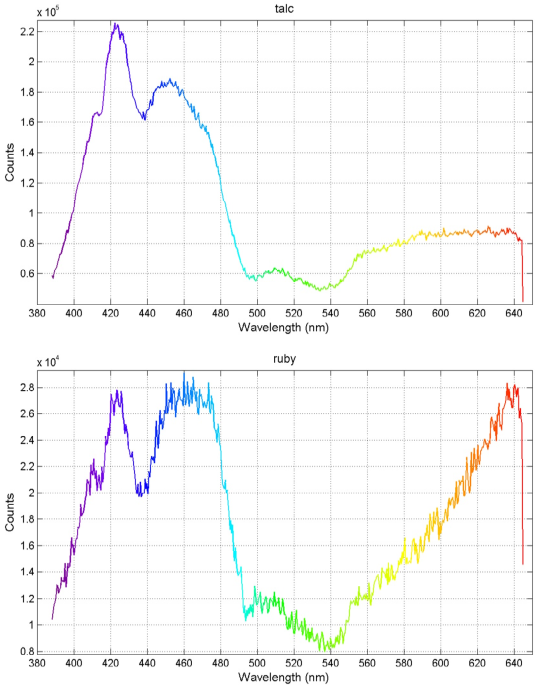

Figure 1. Fluorescence spectra

Using the data collected, we attempted a preliminary run at identification and classification. A principal components analysis (PCA) was done. Since the raw data is substantial, a number of steps were taken to simplify the approach. And as a result, the first two principal components account for 92% of the total variance. The principal components are combinations of the 512 initial variables that minimize the correlations between these new variables, called principal components. The results are plotted in Figure 2.

LIF and Raman experiments with samples of extraterrestrial origin (Moon, Mars, asteroids) are currently being carried out at INO.

Proposal for a space LIF/Raman standoff sensor: For space applications, the instrument would most probably be different. A Raman standoff sensor would make use of all previously mentioned technological choices. The major differences would be in the weight, power consumption, and packaging for low temperatures required. The system would be modular, being composed of two main parts, one sitting on a pan and tilt unit (PTU), the other one directly on a rover, thus reducing the weight on the PTU. On the PTU, the sensor head would include a telescope (4” to 6” diameter) having a fast f/# to reduce its length and weight and used to collect light. A focus mechanism would move the collection fiber bundle in order to optimize light collection from 1.5 m to 10 m. At such short distances and for such a distance span, the image spot in the telescope would be at noticeably different positions inside the telescope. The UV-laser would be installed in the sensor head. A fast-photodiode would be used to detect the outgoing laser pulse and synchronize the gating of the ICCD. Since the gate delay is determined from the laser pulse emission itself, a passively Q-switch laser could be used, reducing the weight and cost of the laser. Beam shaping optics would tailor the emitted beam and adjust its diameter to the eye-safe criterion. Finally, an optical fiber bundle with a limited number of fibers, would be used to collect light in the telescope.

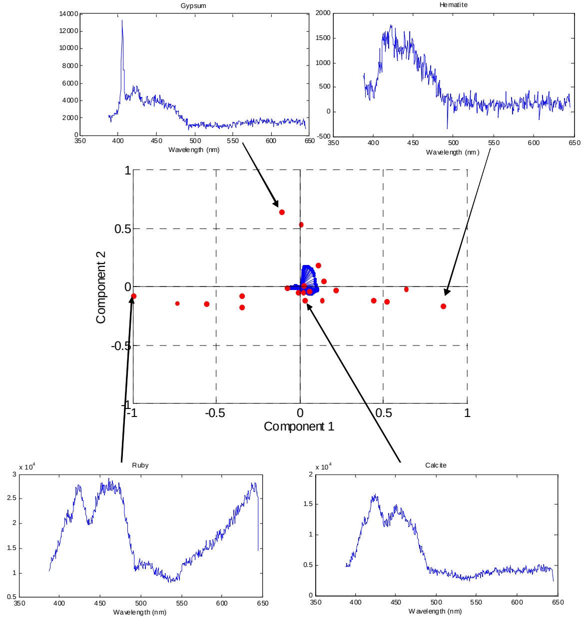

Figure 2. Principal components analysis

Small solid-state microchips lasers where the cavity is formed from a monolithic assembly by applying the mirrors directly on the gain media, would be used. These passively Q-switch lasers provide sub-nanosecond pulses at high repetition. Developing a custom ICCD, the weight of the camera could be reduced by a large factor. Finally, a critical part of the system would be the analysis algorithm. Precise detection of minerals, with or without interferents, will necessitate processing of the acquired data.

We believe that such an instrument would bring significant science returns for Lunar or Mars exploration missions.

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