

IAF SPACE EXPLORATION SYMPOSIUM (A3)
Mars Exploration – Science, Instruments and Technologies (3B)

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A COMBINED RAMAN, LIF, AND MICRO-LIBS SYSTEM WITH TIME-RESOLVED
FLUORESCENCE CAPABILITIES FOR PLANETARY EXPLORATION APPLICATIONS**Abstract**

A team at York University, in partnership with the Institut nationale d'optique/National Optics Institute (INO) and MDA, have combined micro-laser-induced breakdown spectroscopy (micro-LIBS) with two similar analytical techniques, Raman spectroscopy and laser-induced fluorescence spectroscopy, to develop the highly-integrated LIBS/Raman sensor (LIRS). Micro-LIBS is a relatively new subset of LIBS that utilizes μJ laser pulse energies for excitation of plasma emission, carrying out analysis of materials with spatial resolutions approaching micron scales. With a decrease in pulse energy comes the need for tighter focusing to surpass the threshold needed for ablation; the smaller sample areas achieved allow the probing of much smaller features. Knowing both elemental and molecular information, from micro-LIBS and Raman spectroscopy respectively, rocks and minerals can be definitively identified, and fluorescence signatures can aid in identifying organics. Since these three techniques utilize similar equipment such as a laser, spectrograph, and a camera, the combination of LIBS, Raman, and fluorescence spectroscopy into one unit is attractive for planetary exploration missions where mass, volume, and power are greatly restricted. Although some combined systems exist, the best concept for combining Raman, LIF, and LIBS technologies in a way that maximizes flight potential is uncertain.

There are four major differences between the LIBS/Raman sensor (LIRS) instrument and others which make this instrument a novel concept:

- LIRS utilizes 266 nm laser excitation for both Raman and LIF modes,
- a high repetition rate laser with μJ pulse energy for LIBS measurements (i.e., micro-LIBS),
- a single high-resolution echelle spectrograph,
- a single intensified CCD (ICCD) to measure time-resolved fluorescence with a small temporal resolution (1 ns), and,
- measurements are taken at a very high spatial resolution (60 m) but still in a standoff configuration (20–50 cm).

The science team at York University was responsible for characterizing the advantages and disadvantages of the system. This includes, most importantly, the limits of detection (LOD) of each individual technique, and the novelty of combining micro-LIBS, Raman, and LIF into the same instrument. Typical spectra for each mode of the system and LODs for select elements and organic materials, including Si, Ca, Ti, Fe, Al, Mg, Mn, Na, and K, alanine, octacosane, serine, and others, will be presented. Also, a new method for performing chemometric predictions of elemental concentrations will be outlined. Lastly, lessons learned from the characterization of the LIRS breadboard and the implications of this study for a future combined LIBS/Raman/LIF sensor are given.