

DEVELOPMENT OF A PROTOTYPE LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS) INSTRUMENT WITH STAND-OFF RAMAN CAPABILITIES AS PART OF THE MARS INSTRUMENT DEVELOPMENT PROGRAM. R. C. Wiens¹, D. A. Cremers¹, M. Ferris¹, J. E. Nordholt¹, J. D. Blacic¹, P. Lucey², and S. K. Sharma² ¹Los Alamos National Laboratory (MS D466, Los Alamos, NM 87545; rwiens@lanl.gov), ²Hawaii Inst. of Geophys. & Planetology, University of Hawaii (2525 Correa Road, Honolulu, HI 96822).

Introduction: Laser-Induced Breakdown Spectroscopy (LIBS) is under development as part of the Mars Instrument Development Program (MIDP). LIBS can determine elemental compositions at stand-off distances up to several tens of meters. Major, minor, and trace elements at concentrations in the tens to hundreds of ppm range can be monitored. LIBS can profile through dust layers or weathering rinds to access the pristine rock. A prototype instrument is scheduled for initial field testing in May, 2000. Preliminary work indicates that the LIBS instrument will also have some capability for determining mineralogical compositions via Raman spectroscopy at typical LIBS stand-off distances. Here we summarize recent developments, give the status of the prototype LIBS instrument, and discuss possibilities for using the instrument to also obtain Raman spectra.

The LIBS Concept: In the LIBS method [1], powerful laser pulses are focused on the target sample to form a laser spark or plasma. Material within the spark is the result of vaporization/atomization of a small amount of target material. The spark light contains the emission spectra of the elements within the plasma. Collection of the plasma light, followed by spectral dispersion and detection, permit identification of the elements via their unique spectral signatures. When calibrated, concentrations can be determined. Advantages of the method compared to more conventional elemental analysis methods include: (1) rapid analysis (one measurement/pulse); (2) simultaneous multi-element detection; (3) ability to detect all elements (high and low z); (4) ability to clean dust or weathering layers off of sample surfaces; and (5) stand-off analysis capability [2]. Stand-off analysis is possible because the laser pulses can be focused at a distance to generate the laser sparks on a solid. The distance that can be achieved depends on characteristics of the laser and the optics used to focus the pulses on the target.

Recent LIBS Results: We have recently shown [3,4] that a) semi-quantitative results (e.g., 10-20% accuracy) can be obtained for nearly all elements at stand-off distances of up to 20 m. using a compact laser and detector, b) detection limits for nearly all elements at these distances are in the range of 10 to several hundred ppm, c) LIBS works well at all atmospheric pressures from 1 bar to vacuum, with a maximum efficiency between 10 and 100 Torr, and d) the target mass ablated per laser pulse increases with decreasing atmospheric pressure.

The capability to remove surface material from a sample is important, as all Mars rock observations to date appear to be contaminated with dust [5]. In one recent test, layers of sea sand 1, 2, and 3 mm thick overlying a rock sample were removed in 4, 14, and 28 laser pulses, respectively, under Martian conditions (5 Torr CO₂ atmosphere) [3]. Typical excavation rates for the ~1 mm dia laser-produced craters in basalt are much lower, at ~1 $\mu\text{m}/\text{shot}$, but still sufficient to remove weathering layers with repeated pulses. Analysis spots on samples coated with a Mn-rich desert varnish show the decrease of this element with repeated laser pulses (Fig. 1).

Raman Spectroscopy at Stand-off Distances With the LIBS Instrument: Raman spectroscopy and LIBS are very complementary techniques, the former yielding mineralogical data while the latter gives elemental compositions. Raman spectroscopy has recently been shown to work at stand-off distances similar to those used for LIBS [6]. Because LIBS and Raman spectroscopy use essentially the same instrumental components, we have tested our laboratory LIBS set-up for Raman capabilities. The primary additional component required is a filter to block the reflected laser light. Additionally, the laser power density must be reduced for Raman measurements because a plasma is undesirable. Power density can be reduced by either lowering the laser power or by defocusing the laser beam. The latter allows analysis of a larger area.

We are exploring several design and operational trade-offs for a combined instrument, subject to available funding. These include: 1) Raman capabilities with the pulsed laser used for LIBS vs. a continuous wave laser dedicated to Raman analysis. Preliminary results with the pulsed laser look quite promising, but spectra from more realistic samples, including samples in the field, need to be studied. As a demonstration of current work with the pulsed laser, Fig. 2 shows a sharp line at 564.6 nm corresponding to the symmetric stretch mode of the carbonate ion in calcite. This Raman line is Stokes shifted by 1085 cm^{-1} from the laser exciting line at 532 nm [e.g., 7]. A second line is also visible. Lines below 300 cm^{-1} were obscured by the relatively broadband filter used to block the laser reflected light. 2) A second general trade-off study is to determine the optimum sample area for Raman spectroscopy. The LIBS analysis is confined to a spot ~1 mm diameter due to the high power density required to produce a plasma. Raman analysis spots can, however, cover larger areas. The question is whether there

might be significant advantages to Raman analyses of the exact same spot diameter analyzed by LIBS. The LIBS spot can in principle give the mineralogy of the pristine rock due to excavation by multiple laser shots, whereas Raman analysis over a larger area in a Mars environment might primarily show the mineralogy of adhering dust. However, the effect on Raman spectra of laser modification in the LIBS laser crater needs to be investigated.

LIBS Prototype Development: We are presently building a field prototype instrument for use on K9, the Ames version of the FIDO rover testbed, as well as for stand-alone field tests. The instrument is scheduled to participate in the May, 2000, field exercises at Lunar Lake. A library of calibration standards is also being developed. The sensor head, designed for mounting on the rover masthead, consists of a range-finder, laser, and a beam expander with a focussing stage. A fiber optic cable carries the returned plasma light to a spectrograph and detector mounted in the body of the rover. The current spectrograph has a scanning range which captures a portion of the desired spectrum from each laser shot. Trade-offs between fixed or scanning gratings will be studied for an eventual flight instrument. The prototype presently has a working range of 2-10 meters, which could be extended significantly in either direction by modifying the beam expander. The prototype is being built from off-the-shelf subsystems, and weighs approximately 3.5 kg. A future flight instrument could be much more compact and lightweight, at around 500 cm³ for the sensor head and a total weight of ~1.4 kg. Power should be < 2.5 W with a laser firing duty cycle of 5 sec.

References: [1] Cremers D.A. and Radziemski L.J. (1986) In *Laser Spectroscopy and Its Applications* (L.J. Radziemski, et al., eds.), Chapter 5, Marcel Dekker, New York. [2] Cremers D.A. (1987) Analysis of Metals at a Distance Using Laser-Induced Breakdown Spectroscopy, *Appl. Spectrosc* 41, 1042. [3] Knight A.K. et al. (March, 2000) Characterization of laser-induced breakdown spectroscopy (LIBS) for application to space exploration, *Applied Spectroscopy*, in press. [4] Knight A.K. et al. (1999) *LPS XXX*, 1018-1019. [5] McSween H.Y. Jr., et al. (1999) *JGR 104*, 8679-8715. [6] Lucey P.G. et al. (1998) *LPS XXIX*, 1354-1355. [7] Sharma S.K. (1989) *Vibrational Spectra and Structure 17B*, 513-568.

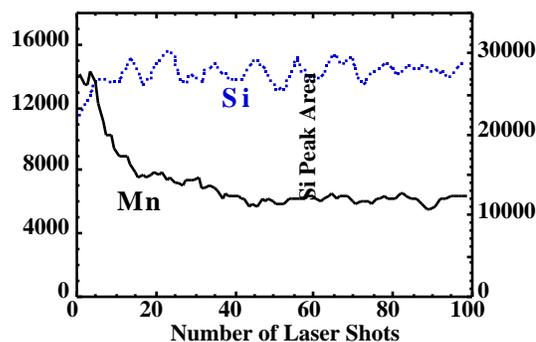


Fig. 1. LIBS Depth profile through a Mn-rich desert varnish on the "Valentine" sample collected during the 1999 Ames Marsokhod rover exercise. Each laser shot corresponds to a depth penetration of approximately 1 μm . Profiling through dust layers is considerably faster, as discussed in the text.

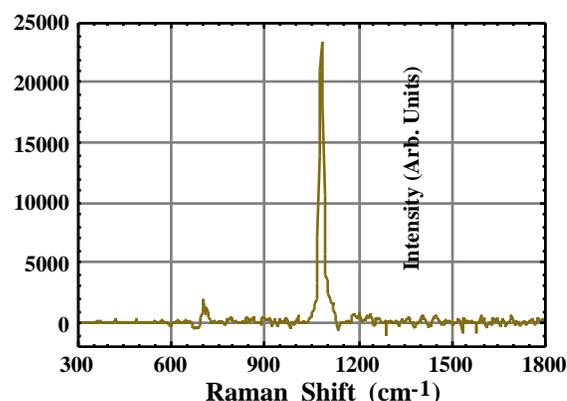


Fig. 2. Laser Raman spectrum of calcite taken using the current table-top LIBS set-up at a stand-off distance of 3 m. This spectrum was obtained using 5-10 mJ pulse energy at 532 nm with a relatively broadband laser-blocking filter.