

**DEVELOPMENT OF LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS) FOR ANALYSIS OF GEOLOGICAL SAMPLES ON PLANETARY MISSIONS.** D.A. Cremers<sup>1</sup>, R.C. Wiens<sup>2</sup>, M.J. Ferris<sup>1</sup>, J.D. Blacic<sup>3</sup>, R. Brennetot<sup>4</sup>, S. Maurice<sup>5</sup>, <sup>1</sup>Chemical and Advanced Diagnostics, Los Alamos National Laboratory (MS J565, Los Alamos, NM 87545 USA; cremers\_david@lanl.gov), <sup>2</sup>Space and Atmospheric Sciences, Los Alamos National Laboratory (MS D466, Los Alamos, NM 87545 USA; rwiens@lanl.gov), <sup>3</sup>Earth and Environmental Sciences, Los Alamos National Laboratory, <sup>4</sup>Centre de Recherche Atomique, Laboratoire d'Analyse par Laser et d'Etude des Surfaces (91191 Gif sur Yvette, France, rivoallan@carnac.cea.fr), <sup>5</sup>Observatoire Midi Pyrennees, Laboratoire d'astrophysique de Toulouse (Observatoire midi pyrennees, 14 avenue Edouard Belin, 31400 toulouse, France; maurice@obs-mip.fr)

**Introduction:** For the past several years, Los Alamos National Laboratory has been investigating LIBS as an elemental analyzer for use on spacecraft. This work has concentrated on rovers and landers to the Martian surface. Currently, LIBS is a semi-quantitative technique for rapidly obtaining elemental compositions of soils and rock samples at distances of several meters from the instrument. The method uses high-powered laser pulses focused on the target at stand-off distances to obtain composition information. Under NASA's MIDP (Mars Instrument Development Program) we have constructed and field-tested two versions of a LIBS instrument. The results of the first test (2000, Nevada Desert) have been reported previously [1]. Recently we conducted a second field test (2001, Mojave Desert) using improved instrumentation and have carried out additional laboratory tests to develop criteria needed for instrument design. Some of these results are reported here.

**The LIBS Technique:** In LIBS [2], powerful laser pulses are focused on the sample to form a laser spark or plasma. Material in the spark is vaporized and the resulting atoms excited to emit light. 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 conventional elemental analysis methods include: (1) rapid analysis (one measurement/pulse); (2) simultaneous multi-element detection; (3) ability to detect high and low z elements; (4) ability to clean dust or weathering layers off of sample surfaces; and (5) stand-off analysis capability [3]. Stand-off analysis is possible because the laser pulses can be focused at a distance to generate the laser sparks on a solid.

Using a laboratory instrument, we have shown [4,5] 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 a 4" objective lens to collect the light, (b) detection limits for nearly elements examined at these distances are in the range of 10 to several hundred ppm and (c) that LIBS works well at pressures from 1 bar to vacuum, with a maximum efficiency between 10 and 100 Torr, (Mars atmospheric pressure is 5-7 Torr). The capability to remove surface material from a sample [2] is important, as all Mars rock observations to date appear to be contaminated with dust [6].

**Field Test, Mojave Desert:** The prototype instrument used for the second field test consisted of two sections: (1) the sensor head, housing the laser, variable focus beam expander with a 2" diameter objective lens, separate light collection optics (4" diameter), and a fiber optic cable for receiving the return signal; (2) the analysis unit consisting of the spectrograph and detector, and the laser power supply. Commercial off-the-shelf components were used for the main components, so weight, instrument volume, power consumption, etc. were not optimized. A compact echelle spectrograph (Catalina Scientific SE2000) was used to spectrally disperse the collected light. The advantage of this spectrograph over that used in the first prototype built by us is the ability to collect the total useful LIBS spectrum (200-1000 nm) on each laser firing. This increased the speed of data acquisition and can potentially reduce noise in the measurements through simultaneous recording of the emission lines of the elements of interest and other lines used for ratioing.

For this field test the LIBS sensor head was mounted on a fixed tripod as the FIDO rover at the test site was fully committed to experiments with other instruments. The analysis unit was connected to the sensor head through fiber optic and electrical cables. Pulses were then directed at selected samples located on adjacent rock formations several meters away.

**Initial Field Test Results:** A typical echelle spectrum obtained during the field test is shown in Fig. 1.

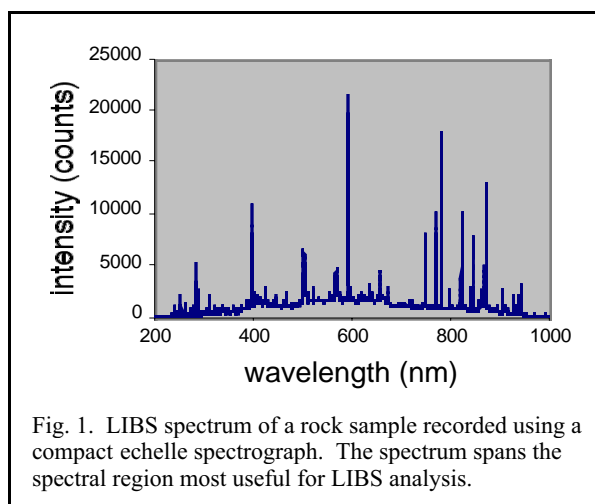


Fig. 1. LIBS spectrum of a rock sample recorded using a compact echelle spectrograph. The spectrum spans the spectral region most useful for LIBS analysis.

The resolution was about  $(\Delta\lambda/\lambda) = 2500$ . During the field test, about 20 samples were analyzed in addition to a set of calibration standards. The samples were collected and returned to the laboratory. Prior to the field test, calibration curves were prepared in the laboratory to calibrate the measurements taken in the field. Software was developed to analyze the spectra automatically. Elements monitored were H, Li, C, O, Na, Mg, Al, Si, P, K, Cl, Ca, Ti, Cr, Mn, Fe, Sr, and Ba. Review of the spectra reveals that emissions from Cl and P were not observed but that emissions from all other elements were recorded.

**Laboratory Results:** As noted above, previous laboratory results have shown that useful analytical data (accuracy, precision) can be obtained in the laboratory under Mars atmospheric conditions at stand-off distances. Using the prototype instrument, some of these measurements were repeated by averaging the spectrum from only 20 laser plasmas. The samples were well-characterized (certified) soils and stream sediments. These highly homogeneous samples (pressed into pellets) were used to determine the best analytical results possible for samples of uniform composition. Some results are summarized in Table 1. Here it is clear that even with compact instrumentation and using few laser shots, useful analytical data can be obtained. Accuracy was determined by constructing a calibration curve for an element using a selected set of the certified samples and then using other certified samples as unknowns and analyzing them. The calibration curves were used to predict the element concentrations in the unknowns. Precision was determined in the usual way by replicate analysis.

Although previous work has shown that under Martian atmospheric conditions, excitation characteristics of the laser plasma are actually enhanced compared to earth conditions [4], other aspects may complicate LIBS analysis on Mars. One problem is dust coatings on optics. In one experiment, we coated the objective lens of the beam expander focusing the laser pulses on the sample (Fig. 2) with different amounts of fine particles to simulate a coating on Mars. The transmission of light through the coated optic was measured ( $T=1$ , no dust) and the laser fired to generate a spark on the target at 3 meters. The spectrum from the spark was recorded using the echelle spectrograph and the intensity of Al at 394.4 nm recorded. The results for different dust coatings are shown in Fig. 3. The results show that even with a high level of dust coating, useful LIBS spectra were obtained.

**References:** [1] Wiens R.C., et al. (2001) Combined remote mineralogical and elemental measurements from rovers: Field and laboratory tests using

reflectance and laser induced breakdown spectroscopy. Subm. Accepted for publication: *JGR-Planets*. [2] 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. [3] Cremers D.A. (1987) *Appl. Spectrosc.* 41, 1042. [4] Knight A.K. et al. (2000) *Appl. Spectrosc.* 54, 331. [5] Knight A.K. et al. (1999) *Lunar Planet. Sci.* XXX, 1018-1019. [6] McSween H.Y. Jr., et al. (1999) *JGR* 104, 8679-8715.

Table 1. Accuracy and precision in the determination of elements in a set of 14 certified soil and stream sediment samples using the prototype LIBS instrument.

element	accuracy	precision
Al	4.4%	5.1%
Cr	7.7	5.6
Mg	3.2	5.2
Mn	4.2	3.8
Si	4.7	3.7
Sr	6.3	6.5



Fig. 2. Photo of main focusing optic of prototype LIBS instrument coated with dust. Even at this apparent high level of dust coating the optic, useful LIBS spectra were obtained at 3 meters.

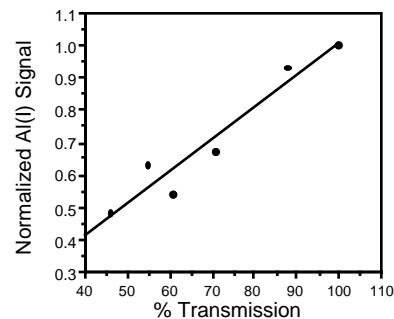


Fig. 3. Intensity of Al emission from a LIBS plasma as a function of transmission through the lens.