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Title: CHARACTERISTICS OF STAND-OFF DETECTION OF
GEOLOGICAL SAMPLES AT MARS ATMOSPHERIC
PRESSURE USING LASER-INDUCED BREAKDOWN
SPECTROSCOPY (LIBS)

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CHARACTERISTICS OF STAND-OFF DETECTION OF GEOLOGICAL SAMPLES AT MARS ATMOSPHERE PRESSURE USING LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS). D.A. Cremers¹, Z. Arp¹, A.K. Knight¹, N.L. Scherbarth¹, R.C. Wiens³, and S. Maurice⁴; ¹Chemical and Advanced Diagnostics and Instrumentation, Los Alamos National Laboratory (MS J565, Los Alamos, NM 87545 USA; cremers_david@lanl.gov), ²Pit Disposition Science and Technology, Los Alamos National Laboratory (MS J565, Los Alamos, NM 87545 USA; zaa@lanl.gov), ³Space and Atmospheric Sciences, Los Alamos National Laboratory (MS D466, Los Alamos, NM 87545 USA; rwiens@lanl.gov), ⁴Observatoire Midi Pyrennees, Laboratoire d'astrophysique de Toulouse (Observatoire midi pyrennees, 14 avenue Edouard Belin, 31400 Toulouse, France; maurice@obs-mip.fr),

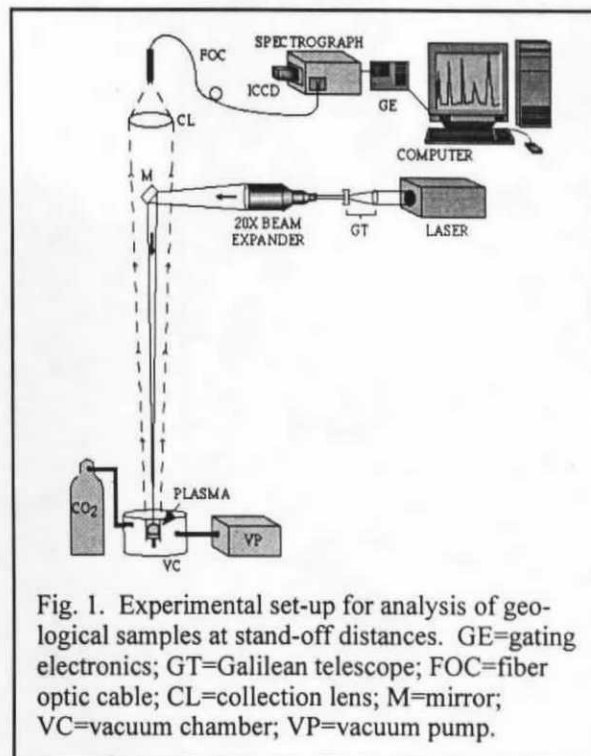
Introduction: LIBS has been proposed as a new method for stand-off detection of geological samples for use on landers and rovers to Mars [1] and studies are on-going to determine capabilities [2-4]. Because of the severe size, weight, ruggedness and power requirements for space instrumentation and the need to maximize scientific return, it is important to benchmark capabilities with parameters representative of compact instrumentation likely to be used in a flight instrument. Some of these issues are addressed here.

Background: Briefly, LIBS is a method of elemental analysis that uses a powerful laser pulse focused on the target sample to generate a hot plasma. Material in the plasma is vaporized/atomized and the resulting atoms are excited to emit light. The plasma light is collected, spectrally resolved and detected to determine elements in the target. At stand-off distances of interest, 2-20 meters, the laser pulse can be used to interrogate solid materials. Our work here has focused on stand-off analysis although in-situ analysis is also applicable

Experimental: One experimental set-up used here is shown in Fig. 1. The samples were maintained in a chamber that was evacuated and then back-filled with 7 Torr CO₂ to simulate the Martian atmosphere. A constant flow of CO₂ gas was maintained through the chamber that was mounted on a movable cart to easily permit changes in the distance between the turning mirror (M) and sample. Distances up to 19 m could be accommodated.

Laser pulses were from a Q-switched Nd:YAG laser (1-10 Hz, 1064 nm). The pulses were expanded (x20) and then focused on the samples through a quartz window on the chamber. The plasma light was collected by a 76 mm-diameter quartz lens and focused on the end of a fiber optic cable. The distal end of the fiber was connected to a spectrograph (Chromex 500IS) and the detector was an intensified CCD (ICCD) camera (Andor InstaSpec IV).

Results: Data obtained included the effect of power density, total laser pulse energy, angle of incidence, spot size, etc. on analyte signals. Additional data were obtained regarding the effect of some of these parameters on detection limits for selected ele-



ments. One set of representative data is shown in Fig. 2. Here the absolute analyte signals (for Sr, Fe) are plotted versus the laser pulse energy. These data, recorded at 19 m, show essentially a linear increase in the signal with pulse energy. This is expected at 7

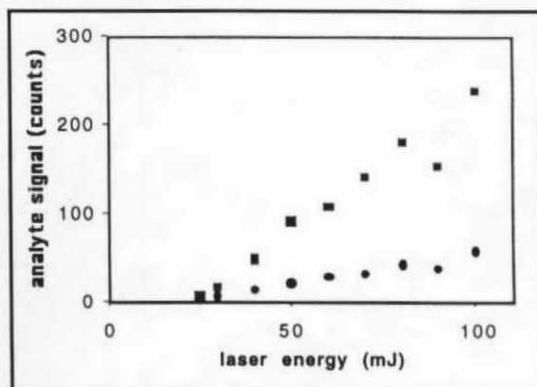


Fig. 2. Dependence of analyte signals on laser pulse energy for Sr (circles) and Fe (boxes). Similar results were obtained for other elements.

Torr because of increased ablation with increased energy in the absence of significant plasma shielding.

In another experiment, the effect of the number of laser pulses averaged on the slope of calibration curves and measurement precision (represented by % relative standard deviation, %RSD) were determined. Some

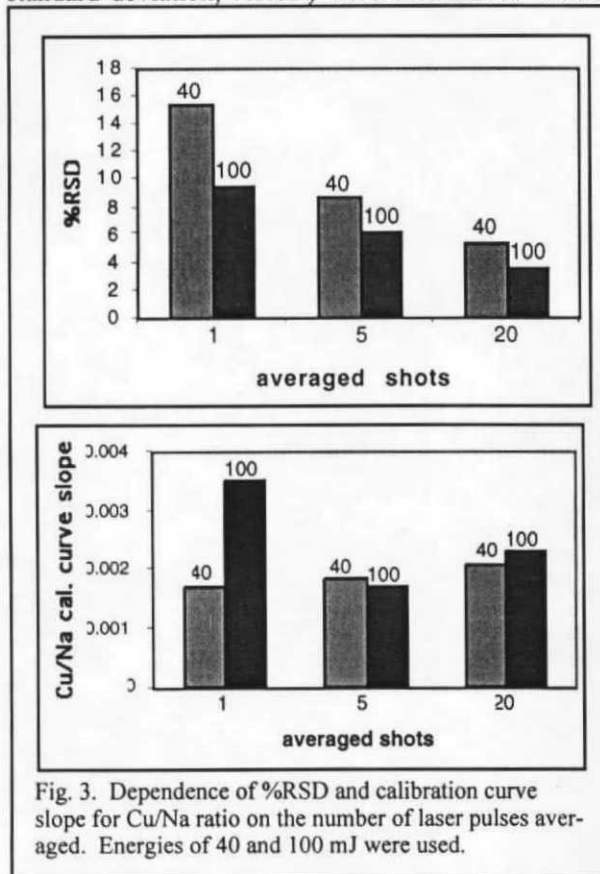


Fig. 3. Dependence of %RSD and calibration curve slope for Cu/Na ratio on the number of laser pulses averaged. Energies of 40 and 100 mJ were used.

results for Cu/Na are presented in Fig. 3 for two pulse energies.

Evaluation of a compact spectrograph/detector.

In another experiment, a pair of commercially available compact spectrographs (Ocean Optics HR2000) were investigated for stand-off detection. These units spanned the wavelength regions of 220-330 nm and 500-850 nm over which a large number of emission lines important to LIBS analysis of rocks and soils are present. The HR2000 units use unintensified CCDs so these measurements will provide information regarding useful stand-off detection ranges that can be achieved with low cost, compact detectors. Spectra were recorded at distances up to 7 m - an example is shown in Fig. 4. A 76 mm diameter collection lens focused the plasma light on the end of a fiber optic connected to the spectrographs. Light from only ten laser plasmas was averaged.

Calibration curves were prepared and measurement accuracy and precision determined using a set of certified soil samples. A preliminary calibration curve for

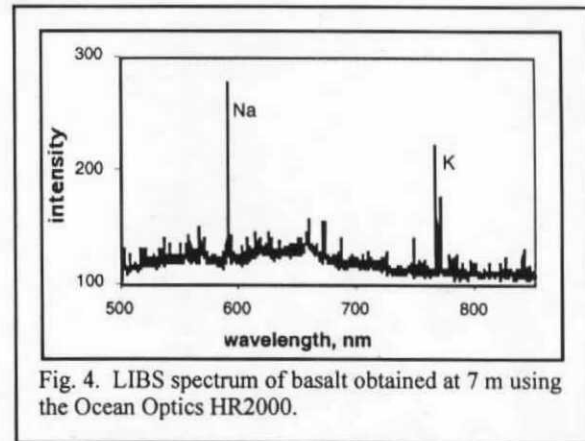


Fig. 4. LIBS spectrum of basalt obtained at 7 m using the Ocean Optics HR2000.

K is shown in Fig. 5. One hundred shots were averaged for each data point.

The CCDs in the HR2000s are not gated so all the plasma light is recorded including the strong continuum light at early time. For the conditions of these measurements, however, non-gated detection proved adequate, suggesting a gated detector (greater size and

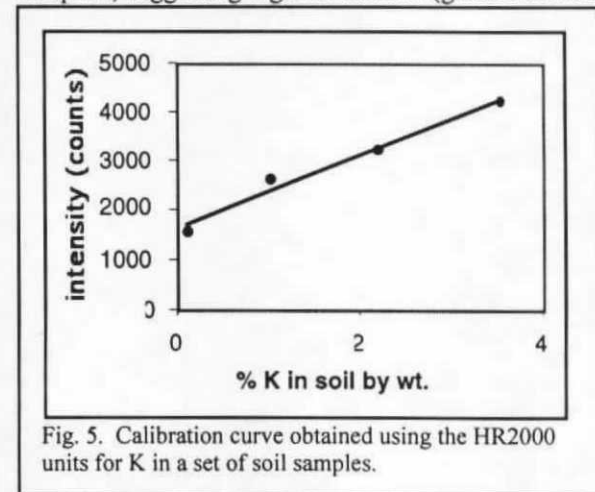


Fig. 5. Calibration curve obtained using the HR2000 units for K in a set of soil samples.

mass) typically used for LIBS studies, may not be needed for a flight instrument.

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