

DEVELOPMENT OF A PROTOTYPE INSTRUMENT FOR STAND-OFF ELEMENTAL ANALYSIS

FOR USE ON A MARS ROVER. A. K. Knight¹, D. A. Cremers¹, M. J. Ferris¹, N. L. Scherbarth¹, R. C. Wiens², J. D. Blacic³, W. M. Calvin⁴, and J. E. Nordholt², ¹CST-1, ²NIS-1, ³EES-4, Los Alamos National Laboratory, Los Alamos, NM 87545, ⁴U.S. Geological Survey, 2255 N. Gemini Dr., Flagstaff, AZ 86001.

Introduction: One of the most fundamental pieces of information about any planetary body is the elemental composition of its surface materials. Most space probes to date have acquired such fundamental geochemical data by passive remote sensing at orbital or fly-by ranges of hundreds of kilometers, resulting in relatively low resolution coverage on a partial-to-complete global scale. Future advances in solar system exploration will require much higher spatial resolutions based on observations and analyses at much closer ranges.

On the other hand, the Viking landers employed an XRF (x-ray fluorescence) unit and the Mars Pathfinder mission used an APXS (alpha-proton x-ray spectrometer) unit on board a rover to supply elemental composition information for soils and rocks to which direct contact was possible. Although providing high resolution analysis in relation to orbital or fly-by measurements, these in-situ analyses require that the craft or rover be immediately adjacent to the target sample.

Intermediate between remote and in-situ are measurements that may be termed stand-off analyses. In this case, measurements can be carried out at some distance from the instrument while preserving a high degree of spatial discrimination. The main advantage of such types of analyses is obvious: the sensing element does not need be in contact or even adjacent to the target sample. This opens up new sensing capabilities. For example, targets which cannot be reached by a rover due to impassable terrain or targets positioned on a cliff face can now be accessed using stand-off analysis. In addition, the duty cycle of stand-off analysis can be much greater than that provided by in-situ measurements by eliminating the need for the rover to actually move to the target. This can be seen by considering the small number of analyses described in the mission model proposed by Arvidson et al. [1] for the 2001 Mars Rover/Athena payload using the APXS instrument.

Stand-Off LIBS. As part of the Mars Instrument Development Program we are developing an instrument for stand-off elemental analysis based on laser-induced breakdown spectroscopy (LIBS), which is a form of atomic emission spectroscopy.

The LIBS method has been studied for many years but has only recently been applied to practical applications [2]. In the LIBS method, 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 remove dust or weathered layers from a sample with repeated laser pulses; (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. The distance that can be achieved depends on characteristics of the laser and the optics used to focus the pulses on the target. The use of LIBS for space applications has been discussed previously but detailed studies for this application have not been reported [4].

Experimental Apparatus. Using a laboratory "breadboard" LIBS system, a number of experiments have been carried out demonstrating the capabilities of LIBS for stand-off analysis. The breadboard system consists of an Nd:YAG laser (10 ns pulsewidth, <100 mJ/pulse, 1064 nm wavelength), a beam expander (x10 or x20) to expand and focus the pulses on the sample, a target chamber that can be adjusted to simulate the composition of the Martian atmosphere (5-8 Torr CO₂), a lens to collect the spark light and a spectrograph and optical array detector to process the spectra. In the current configuration, stand-off distances up to 19 meters between the target and the instrument can be achieved.

Results. A number of measurements have been carried out to validate the stand-off capabilities of LIBS. Analytical parameters of interest that have been investigated include (1) detection limits for major and minor elements in certified soils and synthetic soil samples, (2) measurement precision and accuracy, and (3) the "best" analytical emission lines to use for selected elements. Several operational parameters have been studied including (1) the effect of laser pulse power density and energy on element signals, (2) the effective Rayleigh length over which useful

spectra can be obtained, and (3) the size of light collecting lens needed to obtain useful signals. In addition, ranging of the laser pulse (i.e. the time difference between the outgoing and reflected laser pulse) has been shown to be useful to set the focusing distance on the optical system.

Selected detection limits for some minor elements are presented in Table 1 for samples at a distance of 19 meters in an atmosphere of 5 Torr CO₂ and for a laser energy of 100 mJ/pulse. These limits were determined by constructing a calibration curve for each element using synthetic silicate soil samples and then plotting the element signal versus concentration as shown in Figure 1 for Cr. Also listed in Table 1 is the average precision of the measurements designated as the %RSD (% relative standard deviation).

Table 2 presents data relating to the measurement accuracy and precision for the detection of some major elements in certified soil samples. The Ave. % Diff. is the average of the absolute value of the difference between the predicted concentration and the certified concentration of the element. The average was determined from 30 individual measurements for each element listed. The %RSD is also the average precision determined from 30 distinct measurements for each element in Table 2.

Table 1. Detection limits (C_L) for elements in synthetic soils at 19 meters.

element	C _L (ppm)	%RSD
Ba	21	5.5
Cr	39	8.2
Cu	43	10
Hg	647	27
Li	20	8.8
Ni	224	14
Pb	95	13
Sn	84	14
Sr	1.9	6.3

Table 2. Accuracy and precision for the detection of some major elements in soils.

element	Ave. % Diff.	%RSD
Al	11	6.4
Ca	11	5.2
Fe	12	7.7
Mg	11	7.0
Si	12	5.6

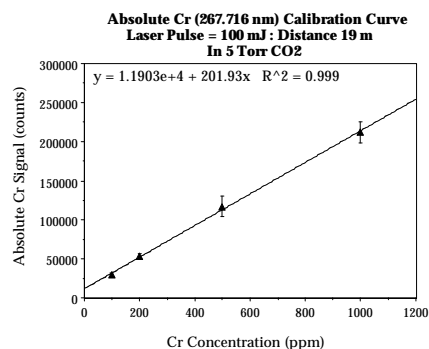
Prototype Development. Although this work is currently in the initial phase aimed at characterizing LIBS for stand-off measurements, we have shown in one experiment that a compact Nd:YAG laser

(25x25x150 mm, 6 ns, 35 mJ) can generate useful spectra from soil (and rock) at distances of 19 meters thereby validating scaling of a LIBS system to small size. Experiments are currently in progress for testing the efficiency of removing dust layers and/or weathering rinds by repeated laser sampling of the same spot. This capability may also aid pristine analyses by other stand-off instruments.

Construction of a prototype instrument for use on a rover testbed will begin in late 1999. Suggested flight instrument mass is under 2 kg. The power requirement is <3 W based on a modest laser repetition rate of 0.3 Hz. Such an instrument could prove useful, not only to the Mars program, but to lunar, asteroidal, or other missions where surface measurements are desired.

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Figure 1. Calibration curve for Cr in soil.



References: [1] Arvidson R.E., C.S. Niebur, and J. Bowman (1998) A mission model for the 2001 Mars Rover/Athena payload, *Mars Surveyor 2001 Landing Site Workshop Program*, NASA Ames Research Center, January 26-27. [2] Cremers D.A. and Radziemski L.J. (1986) Laser Plasmas for Chemical Analysis, in *Laser Spectroscopy and Its Applications* (L.J. Radziemski, R.W. Solarz, and J.A. Paisner, eds.), Chapter 5, Marcel Dekker, New York. [3] Cremers D.A. (1987) Analysis of Metals at a Distance Using Laser-Induced Breakdown Spectroscopy, *Appl. Spectrosc* 41, 1042. [4] Blacic, J.D., Petit, D.R. Cremers D.A., and Roessler N. (1992) Laser-Induced Breakdown Spectroscopy for Remote Elemental Analysis of Planetary Surfaces, *Proc. Intl. Symp. on Spectral Sensing Res.*, 302-312, Maui, HI.