EVALUATION OF A COMPACT SPECTROGRAPH/DETECTION SYSTEM FOR A LIBS INSTRUMENT FOR IN-SITU AND STAND-OFF DETECTION.

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Introduction: Laser-induced breakdown spectroscopy (LIBS) is a method of determining the elemental composition of a material at in-situ or stand-off distances. The information content of the plasma is high. For this reason, LIBS is being developed for instruments to planet surfaces [1-4]. Each laser plasma generates a light signal containing a high density of information regarding the elemental components of the target material. The useful spectral range of the emitted light extends from the vacuum ultraviolet (≈120 nm) out to 850 nm. Within these extremes are strong emission features from all elements useful to identify the element in the target and also to perform quantitative analysis. The detection system (spectrograph and detector) used to process the plasma light determines the quality and quantity of the data gathered.

The processing of the collected plasma light by the spectrograph and detector includes (1) spectral dispersion of the light, (2) recording the spectrally resolved light signal and (3) converting the photonic information to digital form. The characteristics of these two components are crucial to the performance of a LIBS instrument.

Spectrographs and detection systems being considered by us for a LIBS flight instrument include a very compact grating type spectrograph integrated in a single package with a CCD detector. An example is the commercially-available Ocean Optics HR2000 spectrograph. This system provides spectral coverage over a fixed limited range with a certain spectral resolution. For such a system, the trade off is between spectral coverage and resolution. Additional units may be used, however, to monitor simultaneously other spectral ranges. A second type of detection system under consideration is an echelle spectrograph with a 2-dimensional array detector [5]. Inherently, this system provides complete spectral coverage with the resolution being determined by the size of the spectrograph and pixel spacing of the detector array. Both systems are being evaluated. Here we present an evaluation of the HR2000 system.

Overview of the HR2000: General characteristics of the HR2000 spectrograph are listed in Table 1 and the unit is shown in Fig. 1. The unit is a czerny-turner design including a 2048 element linear CCD array detector. This detector is not gated as are the more sophisticated gated-intensifier CCD arrays typically used for LIBS. The small size of the entrance slit (typically 10-20 microns) limits the light that can be directed into the unit.

Fig. 1. HR2000 compact spectrograph/detector system.

Table 1. Specifications of the commercial HR2000

Dimensions	148.6x104.8x45.1 mm
Mass	570 gm
Power draw	90 mA at 5 VDC
Optical	F/4, 101 mm focal length
Data transfer	13 msec/full scan readout
Pixels (size)	2048 (14 x 200 μm)

Table 2. Specifications of evaluated units

Serial number	Wavelength range	Resolution
HR2B224	381-471 nm	0.07 nm
HR2B248	225-320 nm	0.09 nm

Evaluation: Two spectrographs, with spectral ranges and resolutions listed in Table 2, were evaluated using a typical LIBS set up. Repetitive laser pulses were directed onto the samples (100 mm focal length lens) contained in a sealed chamber. The laser pulse parameters were; 35 mJ/pulse, 10 ns duration, 10 Hz rep rate, 1064 nm wavelength. The chamber was evacuated and then back-filled with CO_2 at 7 Torr to simulate the Mars atmosphere. Two configurations were used to collect the plasma light depending on the application. For in-situ analysis, the fiber was pointed at the laser plasma at a distance of about 65 mm without focusing the light on the fiber end. For remote analysis, the light collection lens (50 mm diam.; 20 cm focal length) was located 5.5 meters from the laser plasma. The collected light was focused onto a fiber optic cable (600 μm diam.).

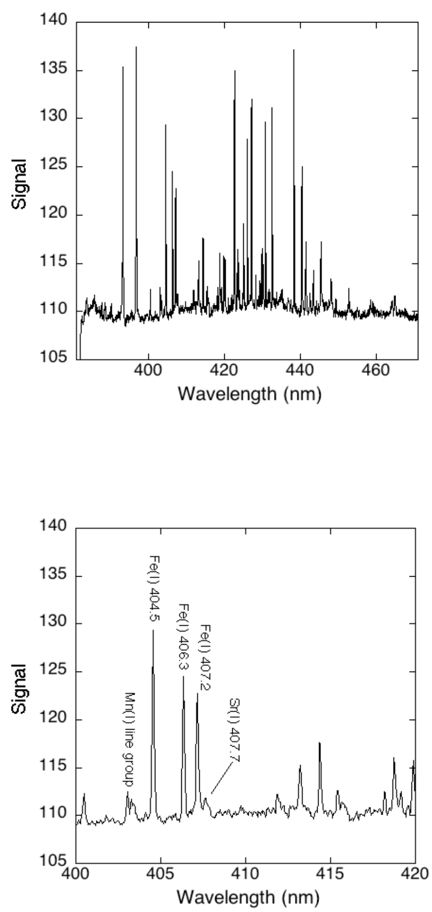

Fig. 2. (top) Spectrum of basalt rock obtained with HR2B224. (bottom) Expanded region showing resolution.

Performance: Initial measurements evaluated the feasibility of using a non-gated detector, such as the type used in the HR2000. At atmospheric pressure there can be strong background continuum from the plasma that interferes with detection of element emissions. At 7 Torr, these emissions were significantly reduced. LIBS spectra of solid basalt rock are shown in Fig. 2. The basalt was maintained in 7 Torr CO_2 and light from 50 plasmas was averaged to produce the spectra. These results and those for soil samples show that analytically useful spectra can be obtained without gating the detection system.

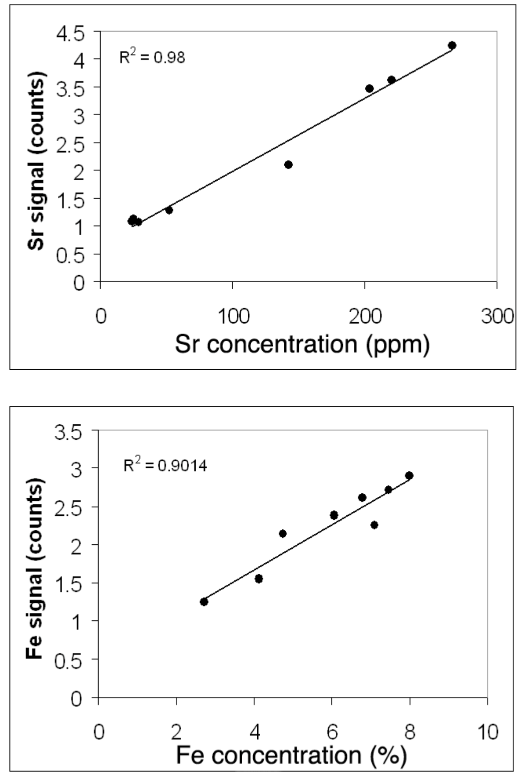

Fig. 3. HR2000 calibration curves for Sr and Fe.

Calibration curves were prepared using a set of certified soil and stream sediment samples. These were interrogated in the chamber under 7 Torr CO_2. Five replicate measurements (50 shots averaged) were obtained using each sample. Calibration results for a minor and a major element are shown in Fig. 3. Curves prepared for other elements (Si, Ba, Ca, Mg, Al) show similar results.

Conclusions: This preliminary work shows the commercial HR2000 unit has the resolution and sensitivity to be useful for in-situ and stand-off LIBS detection. We are presently evaluating (1) light throughput of the units, (2) analytically useful element emission lines (at 7 Torr CO_2), and (3) the spectral range required for a flight instrument to monitor geochemically important elements. We are also working to develop flight-rated HR2000 units.

References: [1] Knight A.K. et al. (2000) *Appl. Spectrosc. 54*, 331-340. [2] Wiens R.C. et al. (2002) *JGR-Planets 107*, 10.1029/2000JE001439. [3] Brennetot R. et al. (2003) *Appl. Spectrosc. 57*, 744-752. [4] Arp Z.A. et al. "Evaluation of Laser-Induced Breakdown Spectroscopy (LIBS) for a Venus Mission," submitted to XXXV LPSC. [5] Lindblom P. (1998) *Anal. Chim. Acta 380*, 353-361.