

LIBS-BASED DETECTION OF As, Br, C, Cl, P, AND S IN THE VUV SPECTRAL REGION IN A MARS ATMOSPHERE. L.J. Radziemski¹, D.A. Cremers², K. Benelli³, C. Khoo³, and R.D. Harris⁴; ¹Research Corp., 4703 E. Camp Lowell, Suite 201, Tucson, AZ 85712 USA (ljr@rescorp.org), ²SDN Research, 1111 Piedra Rondo, Santa Fe, NM 87501 (Daividsantafe@aol.com), ³Group C-ADI, Los Alamos National Laboratory, Los Alamos, NM 87545, ⁴Group EES-2, Los Alamos National Laboratory, Los Alamos, NM 87545.

Introduction: Several elements important to planetary geology (e.g. Br, C, Cl, P, S) and the human exploration of Mars (e.g. toxic elements such as As) have strong emission lines in the purge and vacuum ultraviolet (VUV) spectral region (100 to 200 nm). This spectral region has not been extensively studied using geological samples. Prior LIBS work by others examined sulfide mineral identification and Cl/C and Br/C ratio determinations in organic materials [1,2]. We studied emissions from the LIBS plasma in this region using a sample chamber filled with 7 torr (930 Pa) of CO₂ to simulate the Martian atmosphere. Lower pressures were also used to evaluate the effect of residual CO₂ on the spectra. The effects of time delay and laser energy on LIBS detection at reduced pressure were examined. The effect of ambient CO₂ on the detection of C in soil was also evaluated. Lines useful for the spectrochemical analysis of As, Br, C, Cl, P, and S were determined, calibration curves prepared, and limits of detection determined for these elements. The experiments reported here were aimed at in-situ (close-up) analysis rather than stand-off detection at many meters [3-5].

Experimental: Laser pulses of 7 ns duration with a Gaussian-like spatial profile, were generated using a Q-switched Nd:YAG laser operating at 1064 nm. The laser pulses were focused vertically downward onto the samples by a 20-cm focal length glass lens, with the plasma formed about 2 cm from the spectrometer entrance slit. Spectra were recorded using a 0.3-m vacuum spectrometer fitted with an intensified CCD camera. The laser pulse repetition rate was 5 or 10 Hz. Pulse energies of 40 mJ were used to simulate the energy achievable by a compact LIBS module currently under development for a future rover mission [6]. A sealed acrylic chamber was mounted over the spectrograph entrance slit to house the samples. The chamber was evacuated using an oil-free pump and then backfilled with CO₂ gas to the desired pressure. The spectrometer and chamber were pumped from the chamber side to avoid ablated debris accumulating on the slit because of gas flow through the slit. Pressures used were 7 and 0.26 torr of CO₂, the latter to determine the effects of CO₂ absorption on the spectra.

The chamber contained a rotatable stage upon which up to eight samples were positioned for sequential analysis without opening the chamber. The samples were tilted toward the slit so the groove ablated into the samples would not block light from the base of the plasma from reaching the spectrometer slit. A lens was not used to focus the plasma light onto the entrance slit. Although light collection in his configuration would be less than that achieved with lens imaging of the plasma light onto the entrance slit, this geometry was chosen for its simplicity and as a configuration that may be deployed in an actual compact in-situ LIBS analyzer.

Samples. For survey spectra, used to identify element emission lines, samples containing elements of interest at high concentrations were used. These included Al metal, graphite, NaCl, NaCl in soil, Los Alamos soil, elemental S in soil and phosphate samples. A series of samples containing the elements of



Fig. 1. Appearance of the LIBS plasma at 7 torr formed on basalt rock. Width of the image is about 4 cm.

interest at known concentrations were used to prepare calibration curves. A synthetic silicate soil stimulant (Brammer Standard Company, GBW07710) was also used to map out strong VUV emission lines of major elements normally found in geological samples. This sample had major elements (SiO₂:72%; Al₂O₃:15%; Fe₂O₃:4%; CaMg(CO₃)₂ (pure dolomite):4%; Na₂SO₄: 2.5%; K₂SO₄: 2.5%). For a few samples, a surrogate matrix was devised by mixing sea sand (SiO₂) with the clay bentonite (e.g. SiO₂ 49.9-55.19%; TiO₂ 0.96-1.52%; Al₂O₃ 15.51-19.6%; Fe₂O₃ 6.50-10.20%; MgO 1.34-2.72%; CaO 0.11-5.57%; Na₂O 0.43-3.65%; K₂O 0.61-2.06%).

All powdered samples (3-4 grams) were pressed into pellets (32 mm diam. X 4 mm thick) prior to analysis.

Results. Figure 1 shows the appearance of the LIBS plasma at 7 torr. This photo was obtained using an ICCD camera imaging system with a delay of 2 μ s and an 80 ms gate width. At 7 torr, the plasma appears as a large luminous ball due to expansion of the plasma at pressures below atmospheric pressure. At lower pressures, however, the luminous ball decreases in volume significantly, appearing only near the surface, because of fewer collisions between species in the plasma with the surrounding atmosphere. The ablated material expands away from the surface into the low pressure region above the surface. Species are readily ejected at high velocity away from the laser-target interaction zone on the surface. This small plasma, however, still provides useful, but reduced, analytical capabilities compared to the plasma formed at higher pressures [7].

Figure 2 shows the LIBS spectrum of the synthetic silicate soil simulant at 0.02 torr of air in the VUV region examined here. The major emission lines are identified. Below a wavelength of 175 nm and extending to about 125 nm, absorption from residual CO₂ becomes significant even at 7 torr. Within this region some of the stronger emission lines of elements are detectable but weaker lines and

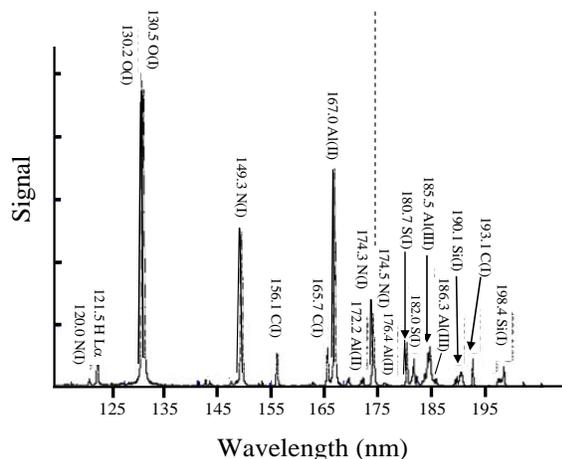


Fig. 2. LIBS spectrum of soil simulant in 0.02 torr of air. Below about 175 nm (dashed line) absorption by CO₂ becomes prominent even at 7 torr.

strong analyte lines at the peak of CO₂ absorption, 130-150 nm, will not be useful. At lower pressures, e.g. below 0.02 torr, these lines will become useful.

Figure 3 shows calibration curves for C in soil for ambient CO₂ pressures of 7 and 0.26 torr. Clearly, the CO₂ atmosphere affects the C calibration curve, reducing sensitivity. This will complicate the detection of C in geological samples.

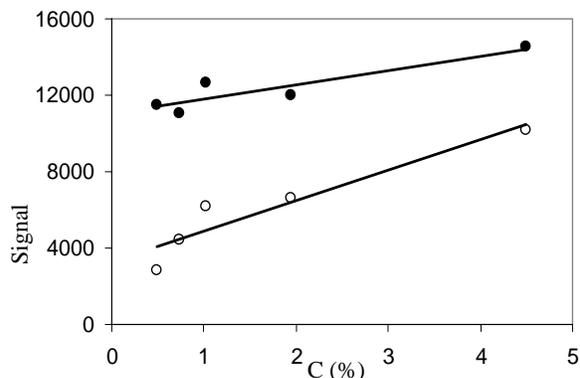


Fig. 3. Calibration curves for C in soil in CO₂ at 7 torr (upper) and 0.26 torr (lower). C(I) at 193.1 nm was monitored.

Calibration curves for the elements As, Br, Cl, C, P, and S were made using lines in the VUV region. One curve for As is shown in Fig. 4.

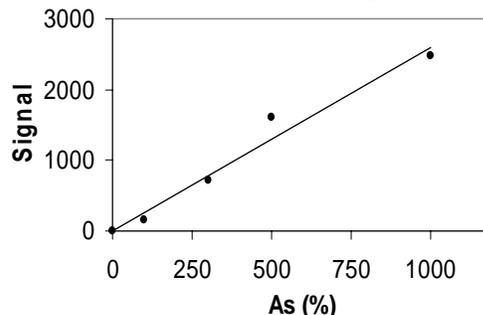


Fig. 4. Calibration curve for As in soil (189.04 nm line).

Using the calibration curves, detection limits (DL) were determined for the elements examined here using different lines and analysis conditions. Some of the results are listed in Table 1.

Table 1. LIBS detection limits for VUV region.

Element	Line (nm)	CO ₂ press. (torr)	DL (wt%)
As	189.0	7	0.044
Br	163.3	0.25	5.6
C	193.1	7	0.32
Cl	133.6	0.25	7.5
P	178.3	7	0.028
S	180.7	7	1.03

References: [1] Kaski S. et al. (2003) Miner. Eng. 16, 1239-11243. [2] Kaski S. et al. (2004) J. Anal. At. Spectrom. 19, 474-478. [3] Knight A.K. et al. (2000) Appl. Spectrosc. 54, 331-340. [4] Colao F. et al. (2004) Planet. Space Sci. 52, 117-123. [5] Salle B. et al. (2004) Spectrochim. Acta 59B, 1413-1422. [6] Maurice S. et al. (2005) this volume. [7] Harris R.D. et al. (2005) this volume.