

Laser Induced Breakdown Spectroscopy (LIBS) Library under Martian Conditions A. Cousin¹, S. Maurice¹, O. Forni¹, O.Gasnault¹, J. Dalmau², M. Saccoccio², R. Wiens³, and the ChemCam team,¹Centre d'Etude Spatiale des Rayonnements, Toulouse (agnes.cousin@cesr.fr), ²Centre National d'Etudes Spatiales, Toulouse, ³Los Alamos National Laboratory, New Mexico.

Introduction: ChemCam is an active remote sensing instrument using the Laser Induced Breakdown Spectroscopy (LIBS) technique and micro-imaging (RMI) to investigate details of the Martian surface geochemistry [1, 2]. It is part of the Mars Science Laboratory (MSL) rover payload, scheduled for launch in fall of 2011.

ChemCam has several parts: the “Mast Unit” (6 kg), located at 2 m height on top of the remote sensing mast, the “Body Unit” (3 kg) in the core of the rover, and an array of calibration targets. The body and mast units are connected by a 6 m long optical fiber. The mast-unit comprises a high power laser, a telescope to focus the laser beam onto a target and to collect the plasma light, a micro-imager to obtain context data, and an electronic box (see figure 1). The body unit consists of a demultiplexer, three spectrometers, front-end analog electronics for the spectrometer CCDs, and a digital unit that operates the whole instrument and interfaces with the rover. ChemCam’s key innovation is to perform LIBS analysis at remote distances, from 1 to 7 meters.



Figure 1: ChemCam Mast-Unit. The qualification unit, used for this work, is identical to the flight unit.

The general purpose of our work is to calibrate the ChemCam experiment, to understand the instrument biases and its idiosyncrasies, to exercise and improve the control-command of the instrument. The specific goals of this study, which will be reported at LPSC, are (1) to acquire remote LIBS spectra under a wide range of pressure conditions, (2) to build a library of LIBS emission lines under Martian conditions, (3) to develop software for autonomous analysis of ChemCam data.

Experimental Setup: For the Mast-unit, we use

the Engineering and Qualification Model (EQM) of ChemCam, which is identical to the flight unit. So far it is used at room temperature, which reduces the laser energy to half its value on Mars. Near-term plans are to cool down the EQM at -10°C where the laser energy is maximal (30 mJ output for 17 mJ on target). Because of this limitation, we could not yet obtain reasonable signal-to-noise beyond 5 meters.

For the Body-unit, we use three commercial-grade spectrometers from Ocean Optics and a single fiber that is alternatively connected to each of them. Hereafter, the spectrographs are denominated UV (239-340 nm), VIS (384-471 nm), and VNIR (494-930 nm). Note that we do not use the demultiplexer of ChemCam, a dichroic-based optical system to trifurcate light to the spectrometers. During a burst of laser shots, we record a single spectrum. The flight unit has the capability to record shot-to-shot for depth profiling. We are currently improving these aspects.

To simulate the Martian environment, part of this work was to develop an apparatus to reproduce the Martian pressure and atmosphere (5-10 mbar, 95.7% CO₂, 1.6% Ar, 2.7% N₂). Other environments, at ambient pressure with Earth or Mars atmospheric composition, or vacuum (10⁻³ mbar) are also possible for comparison studies. The Martian chamber is ~70 l with a carrousel for sample handling and a 1 m long extension to avoid focusing the laser beam on the 200 mm diameter window. To simulate the distance to target, the chamber is mounted on a structure, which moves on a 10 m track (see figure 2).

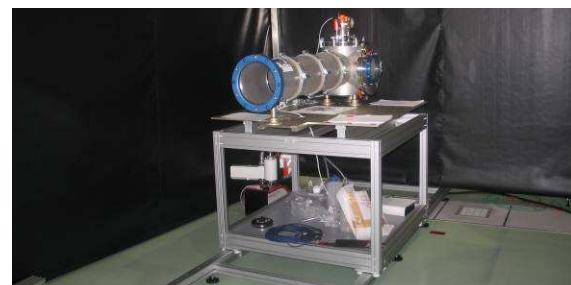


Figure 2: Mars simulation chamber, which can move 10 m along tracks to replicate the distance to target.

Experiments and results: Since we do not try here to analyze the full complexity of natural targets [3,4], we have used pure targets of major elements, as

sheets of aluminum and silicon, coupons of titanium, iron, copper, nickel, lead, etc. When distance is not the issue, targets are at 3.5 m, under vacuum, Martian, or ambient conditions. We usually perform 5 bursts of 10 laser shots at a frequency of 10 Hz for each sample.

Peak fitting: The first step of data processing is peak fitting. We use multiple-fit routines, developed under IDL (see figure 3 for an example). We apply Lorentzian shape to account for the extended wings of the emission. Theoretically, the shape is a Voigt function (convolution of a Lorentzian for the signal and a Gaussian for the response function of the instrument), but the Lorentzian fit is sufficient for our need. When performing such fits, typical FWHM are: 0.4 nm for UV, 0.2 nm for VIS, and 1.5 nm for VNIR.

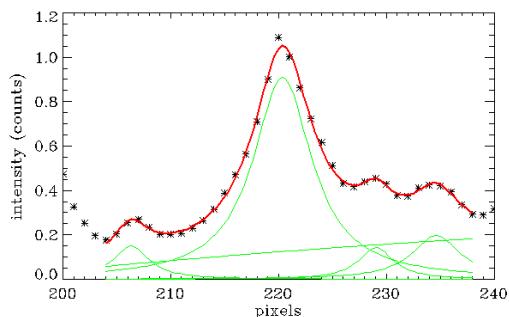


Figure 3. Example of multiple peak fitting on a series of Al and Ti lines.

Wavelength calibration : Once the peak position is obtained to a fraction of a pixel, we perform wavelength calibration of the spectrometers. To benefit from a large number of lines, for the UV and VIS we use a synthetic spectrum, which is the sum of the aluminum, silicon and iron spectra, and for the VNIR we use directly the iron spectrum. The positions of the most preeminent peaks (ten per spectrometer) are compared with those of the NIST data base. A quadratic regression is performed. For the UV and VIS, the accuracy is ~ 0.08 nm, and for the VNIR it is 0.25 nm. The latter is poorer, mostly because of the intrinsic resolution of the spectrometer.

Peak identification: Once the spectrometers are calibrated, all peaks greater than one sigma of the total intensity are compared (position better than ± 0.5 nm) against the NIST [5] (see figure 3 for an example) and CREOSA [6] libraries. The former is the most comprehensive of all databases. Note that we used only the emission lines observed (not those calculated from the atomic energy levels). The latter is an experimental library more specific to LIBS, but the peak identification can be inaccurate (due to He

contamination for instance) and the wavelength calibration not always sufficient for our needs.

Most of the LIBS lines we observe can be found and identified unambiguously in the NIST library – of course, the reverse is not true. Because of the 0.5 nm flexibility we allow for the peak position, often several NIST lines match our detection. There are still a few lines in our spectra which cannot be automatically identified. Among the identified emission lines in the NIST database, a few correspond to higher than single ionization states.

As an example for the emission-rich Ti, we observed 84 lines in the UV, 95% of which could be tracked down in the NIST database. In the VNIR, only 70% were automatically identified. Work is in progress to improve this score, which depends on the spectrometer resolution. The correspondence with the CREOSA database is respectively 55% and 30%. The accuracy of the wavelength calibration of the CREOSA spectra needs to be investigated.

Finally, when comparing with the environmental conditions, we find that reduced pressure enhances the signal-to-noise over the ambient pressure or vacuum [also in 3], but the net signal intensity is not necessarily larger. We find no general influence from the atmospheric composition, which will need to be revisited when we search specifically for C and H detections.

Future work: We have set up an experiment and software tools to build a comprehensive library of LIBS emission (position and relative intensity) under Martian conditions. This library will be an important component of the ChemCam data processing tools.

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References: [1] Wiens et al. (2005), *LPSC 36th*, #1580. [2] Maurice et al. (2005), *LPSC 36th*, #1735. [3] Sallé et al. (2005), *Spectrochimica acta Part B*, 60, 479-490. [4] Sirven et al. (2007), *Journal of Analytical Atomic Spectrometry*, 22, 1437-1568. [5] NIST Atomic Spectral Database (version 3.1.5) National Institute of Standards and Technology, Gaithersburg, MD. Available: <http://physics.nist.gov/asd3>. [6] CREOSA: Center of research and Education in Optical Sciences and Applications. <http://www.creosa.desu.edu/LIBS.html>