Progress on Calibration of the ChemCam LIBS Instrument on the Mars Science Laboratory (MSL) Rover

1. Introduction: ChemCam is being built for NASA’s 2011 Mars Science Laboratory (MSL) rover. ChemCam combines laser-induced breakdown spectroscopy (LIBS) with a remote micro-imager (RMI) that provides images of the target. It provides elemental analysis of spatially resolved solid samples (<0.5 mm diameter) at distances of 1-7 m. ChemCam’s primary objective is to quantitatively determine the chemical composition of rocks and regolith in order to characterize the materials in the vicinity of the rover. ChemCam’s small LIBS spot size enables chemical stratigraphy of fine layers and measurement of small-scale features such as “blueberries.” Since LIBS removes dust and weathering layers using multiple laser shots, contamination from Martian soils does not deter ChemCam results.

2. Instruction Description:

- **Mast Unit**: located on the rover mast, it consists of a Nd:KGW laser capable of 17 ml pulses, a 110 mm Schmidt Cassegrain telescope for both sending and receiving, a Remote Micro-Imager (RMI) camera, and a fiber coupler to send spectra to the body unit. The unit was designed and built by CESR, Toulouse with funding and support from CNES.
- **Body Unit**: located in the rover body, it contains spectrometers covering 240-850 nm with 6144 14-bit channels, and a command and data processing unit. The Body Unit was built at LANL, where the instrument is integrated and tested. IPL is responsible for the thermo electric cooler.
- **Calibration Targets**: Rover-mounted targets of volcanic and synthetic basalt glasses, ceramic mixtures of nontronite and kaolinite, gypsum, and basalts, a graphite target for C identification, and a Ti plate for wavelength calibrations. The assembly mounts on the back of the rover 1.54 m from the Mast Unit.
- **Cables**: The 6 m optical fiber connecting Body and Mast units, as well as electrical cables, are built by JPL and GSFC.

3. Operations: The figure above shows a typical operation sequence. A typical LIBS consists of 5 shots at 3 Hz. The first several shots are used to clean the sample spot. The remaining ~40 spectra are usually averaged together, but can be analyzed separately, e.g., for weathering rind analyses. A single ChemCam analysis requires only ~2 Whr and 6 minutes, including both LIBS and RMI, excluding heater & TEC budgets. Whole rock analyses require multiple analysis spots on the same rock. Remote depth profiling into rocks to 1 mm will be done with ~1000 laser shots.

4. LIBS: Brief, 5 ns laser pulses create light-emitting plasmas. The emission spectra consist of spectrally narrow atomic and ionic emission lines from the elements contained in the sample. Emission lines can be seen for nearly all elements, including H, C, N, O, with most elements displaying multiple emission lines across the spectrum. Sensitivity to alkali and alkali earth elements is very high, with detection limits ~100 ppm for Li, Sr, and Ba. The image shows a LIBS plasma on a rock in our Mars chamber.

5. Imaging at 3 m: The Remote Micro-Imager provides high resolution (100 µm) images over a 20 mRad field of view. Its primary purpose is to provide close-up context images of the LIBS analysis spots, but it can operate at any distance from 1.2 m to infinity. Along with one of the two MastCams it will be the highest resolution long-range camera on Mars.

6. Current Status: Several issues have been resolved over the past year. The biggest were installation of a thermo electric cooler (JPL) for the detectors to allow the instrument to operate longer hours of the day, and replacement of the detectors due to non-linearity at low count rates. Because of this change, LIBS calibrations are being re-done. Below is the spectrum of the BT-2 standard in air at 2.67 m, taken with the new detectors. The spectrum is averaged from 50 plasmas and background subtracted. The instrument response has not yet been corrected.

7. Initial ChemCam LIBS Calibrations: We assembled 65 certified rock powder standards for the initial calibrations in late 2008, including basalts, andesites, rhyolites, granite, dolomites, limestones, gypsum, and marine and river sediments. The results were background subtracted and corrected for system transmission. The data are then processed by multivariate classification techniques, such as principal or independent component analysis (PCA / ICA), and by quantitative fitting such as partial least squares (PLS). For PLS it is clear that limiting the range of standards to those close in rock type to the actual sample significantly improves accuracies. A best-case example of PLS results is shown in the table at right for median errors for a group limited to 22 basalts, andesites, and rhyolites analyzed at 3.5 m. Of these the rhyolites had by far the most error. It is not clear why elements which have the largest number of emission lines (calcium and iron), had the largest median error. The mean errors were significantly higher than the medians due to much larger errors on standards with lower abundances of the elements.

8. Preparations for Final Calibrations: Additional sulfate and clay standards were added to the original group. Plots showing the compositional ranges of the standards for individual elements are shown to the right. In addition, standards are plotted on a TAS diagram below. Some of the philosophy and issues regarding the ChemCam LIBS calibrations are listed below.

- **Types of rock**: Given the uncertainty in the landing site, the standards are about 50% igneous, 25% sulfates, and 25% sedimentary. There are a number of standards incorporating material from two or three of the above groups.
- **Pure minerals or not?**: We prefer to use mixtures. Pure minerals are easy to spot in a spectrum, due to the fact that only a few elements will be present. Mixtures are much more challenging to calibrate.
- **Minor and trace elements**: LIBS spectra should give Li, Rh, Sr, and Ba abundances (standard ranges shown at right). Note that emission lines for all of these elements are visible in the BT-2 spectrum displayed above.
- **Organic standard**: We plan to include one organic standard. The Green River Shale, SGR-1, has > 3% organic carbon, being very oil rich. This standard’s spectrum may include N peaks and CN and C2 molecular peaks as well as the expected carbon emission lines.
- **Hydrogen calibration**: Represents a serious challenge because a) we don’t trust most H abundances listed for standards in the literature, and b) some standards such as gypsum are very likely to de-volatilize in the Mars chamber. Work on H calibration will be ongoing.

9. Aspects Requiring Additional Work: A significant issue is how to apply calibration standards at one distance to unknown samples at a different distance. Response functions of different emission lines vary with distance based on the energy of the atomic transition (cf. Cho et al., 2015, this meeting). We intend to work on the distance correction algorithms in the near future.

10. ChemCam Cost: The LANL budget for ChemCam is approximately $12.5M for Phases A-D. This is one of the least expensive of the MSL instruments for NASA, thanks in part to the contribution of the Mast Unit by CNES.

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