Pre-flight calibration and initial data processing for the ChemCam laser-induced breakdown spectroscopy instrument on the Mars Science Laboratory rover

R.C. Wiens [a,*], S. Maurice [b], J. Lasue [b], O. Forni [b], R.B. Anderson [c], S. Clegg [a], S. Bender [d], D. Blaney [e], B.L. Barraclough [d], A. Cousin [a,b], L. Deflores [e], D. Delapp [a], M.D. Dyar [f], C. Fabre [g], O. Gasnault [b], N. Lanza [a], J. Mazoyer [h], N. Melikechi [i], P.-Y. Meslin [b], H. Newsom [j], A. Ollila [j], R. Perez [k], R.L. Tokar [d], D. Vaniman [d]

[a] Los Alamos National Laboratory, Los Alamos, NM 87544, USA
[b] Institut de Recherche en Astrophysique et Planetologie, Toulouse, France
[c] United States Geological Survey, Flagstaff, AZ, USA
[d] Planetary Science Institute, Tucson, AZ, USA
[e] Jet Propulsion Laboratory, Pasadena, CA, USA
[f] Mount Holyoke College, South Hadley, MA, USA
[g] Georessources, Nancy, France
[h] LESIA, Observatoire de Paris, Meudon, France
[i] Delaware State University, Dover, DE, USA
[j] University of New Mexico, Albuquerque, NM, USA
[k] Centre Nationale d'Etude Spatiale, Toulouse, France

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ABSTRACT

The ChemCam instrument package on the Mars Science Laboratory rover, Curiosity, is the first planetary science instrument to employ laser-induced breakdown spectroscopy (LIBS) to determine the compositions of geological samples on another planet. Pre-processing of the spectra involves subtracting the ambient light background, removing noise, removing the electron continuum, calibrating for the wavelength, correcting for the variable distance to the target, and applying a wavelength-dependent correction for the instrument response. Further processing of the data uses multivariate and univariate comparisons with a LIBS spectral library developed prior to launch as well as comparisons with several on-board standards post-landing. The level-2 data products include semi-quantitative abundances derived from partial least squares regression.

A LIBS spectral library was developed using 69 rock standards in the form of pressed powder disks, glasses, and ceramics to minimize heterogeneity on the scale of the observation (350–550 μm dia.). The standards covered typical compositional ranges of igneous materials and also included sulfates, carbonates, and phyllosilicates. The provenance and elemental and mineralogical compositions of these standards are described. Spectral characteristics of this data set are presented, including the size distribution and integrated irradiances of the plasmas, and a proxy for plasma temperature as a function of distance from the instrument. Two laboratory-based clones of ChemCam reside in Los Alamos and Toulouse for the purpose of adding new spectra to the database as the need arises. Sensitivity to differences in wavelength correlation to spectral channels and spectral resolution has been investigated, indicating that spectral registration needs to be within half a pixel and resolution needs to match within 1.5 to 2.6 pixels. Absolute errors are tabulated for derived compositions of each major element in each standard using PLS regression. Sources of errors are investigated and discussed, and methods for improving the analytical accuracy of compositions derived from ChemCam spectra are discussed.

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1. Introduction

The ChemCam instrument suite was selected to be the remote sensing composition facility for the Mars Science Laboratory (MSL) rover. ChemCam consists of a remote micro-imager (RMI), capable of ~50 mrad resolution, and the first remote laser-induced breakdown spectrometer (LIBS) to be sent to another planet, capable of determining elemental compositions of rocks and soils within 7 m of the instrument [1,2]. The ChemCam LIBS instrument was selected for its ability to actively remove dust and coatings or weathering rinds from rocks to determine their underlying composition, and also for its ability to analyze potential coatings and rinds themselves. Another advantage of LIBS is its ability to rapidly detect many elements, including the light elements H, Li, Be, B, C, N, and O.

LIBS applications have increased over the last 20 years with the advent of miniaturized fiber-optic spectrometers and lasers (e.g., [3,4]). LIBS involves focusing a pulsed laser beam with an irradiance of at least 10 MW/mm^2 onto a solid, liquid, or gaseous target. The intense photon flux breaks down the target material resulting in a plasma. The excited electronic states in the plasma emit light at characteristic wavelengths, resulting in a strong glow that lasts several microseconds [5]. Collection and spectral dispersion of the light allow detection and calibration of the elemental abundances of the target. On solid targets each laser pulse excavates a small distance into the target. Multiple laser pulses at the same location can be used to depth profile into a sample; in the case of ChemCam, depths of 0.5 mm into rock targets have been achieved with 500 laser shots [1]. LIBS spectral line intensities are affected by the atmosphere in which the plasma is produced. Knight et al. [6] showed that at the reduced pressure corresponding to the Mars atmosphere LIBS spectral line intensities are stronger than at terrestrial surface pressures, and the continuum background, line broadening, and self-absorption are all reduced, facilitating simpler LIBS analyses for Mars conditions. For example, the precise time-gating of the detector that is often used to reduce these features in LIBS spectra under terrestrial conditions is not necessary in the Mars environment.

Quantitative LIBS analyses of complex matrices such as geological samples have been hampered by chemical matrix effects, in which the presence of some element, even a minor or trace element, affects the relationship between concentration and emission line intensity of other elements. Matrix effects can be related to differences in coupling efficiency of the laser to the material, or they can be caused by phenomena in the plasma phase, such as the quenching of electronic states and temperature-affecting phenomena [7]. Several approaches have been taken to reduce this problem. One approach, called calibration-free (CF) LIBS, e.g., [8–10], assumes a local thermodynamic equilibrium in the plasma and attempts to solve the Saha equation for all prominent lines of the elements present. CF LIBS has been studied quite extensively and is relatively successful in that quantitative abundances with relative accuracies averaging ± 15–20% are achieved on some matrices with no calibration standards whatsoever. The CF LIBS method requires that the plasma temperature be accurately determined, which requires that the electron density be closely estimated, and that a large fraction of all emission lines be observed for each element. The ChemCam spectrometer was not designed to be comprehensive in observing all emission lines from enough elements to make this a feasible approach.

Another approach to chemical matrix effects involves using calibration standards covering the possible range of compositions of the samples of interest and relying on multivariate analysis to correct for the matrix effects. Multivariate analyses can utilize all available spectral channels, rather than one or two emission lines, to produce a correlation model fitting the multi-channel data with a number of standards. The correlation model for a given element commonly has both positive and negative correlations. Channels that have significant correlation factors but do not correspond to an emission line of the element in question represent corrections for a chemical matrix effect as well as geochemical affinities in which the abundance of one element trends with that of another. The latter effect can aid in determining the abundance of the element in question, but care must be taken that the model does not over-emphasize the influence of elements with strong geochemical affinities over emission from the element in question, as correlations based on geochemical affinities can be far from exact in unusual samples. Moreover, trace element abundances predicted purely by geochemical affinities based on abundances in terrestrial standards may not be relevant for Mars. A number of studies using partial least squares (PLS) of principal components have shown the success of this method for major and strongly emitting minor and trace elements in geological samples [11–17]. However, less complex methods such as univariate analyses still have their place, particularly in quantifying elements characterized by weak spectral peaks that would be overlooked, and

might have negligible influence relative to the stronger peaks of other elements.

In addition to chemical matrix effects, another factor that must be considered for ChemCam is that of sample-to-instrument distance. As a near-range remote-sensing instrument, the conditions of the laser beam vary, with the focused beam spreading farther at longer distances, leading to differential plasma conditions. Eventually, at great enough distances, the energy density becomes too weak to produce detectable plasma. A significant effort is being made to understand how to produce distance corrections to the signal so that calibrations at one distance will suffice for a sample at a different distance.

This paper provides a comprehensive view of the pre-delivery calibrations undertaken with the ChemCam LIBS instrument and outlines the strategy determining elemental compositions from LIBS spectra. We first give a short description of the instrument and the experimental conditions under which the calibrations were done. A comprehensive description of the standard set is provided. The LIBS plasma size at Mars pressure is presented, along with emission line irradiances and detection limits for emission lines observed by ChemCam under various conditions. Following this, the data treatment methods are described for quantitative calibration using PLS. Finally, the discussion concludes with a short summary of strategies for analyses on Mars and an initial univariate view of the first data taken on Mars of the onboard calibration targets.

An overview of the general multivariate calibration plan is shown in Fig. 1. Standards of known composition were selected during the instrument development time period. LIBS spectra were acquired prior to delivery of the instrument to the rover. These spectra were pre-processed through a number of steps to produce a database from which multivariate training models can be made. Spectra obtained on Mars, indicated in the bottom row, are also pre-processed using exactly the same routines. The team must consider any potential changes to the instrument response on Mars, and must also normalize the spectra to correct for the effects of variable distance. The multivariate training model built on the pre-delivery spectra mentioned above is applied to the Mars spectra to determine their elemental abundances and uncertainties, and to classify the spectra. Classification can also be done purely among Mars samples without referring back to terrestrial standards, and this is useful, for example, in determining differences in regional soil compositions or other changes in Mars samples. Classification can also be done in comparison to terrestrial rock samples for which precise elemental composition is unknown. This can be beneficial in observing the spread in spectral phase space.

A drawback of the model described so far is the limitations of the standards available prior to instrument delivery. It was impossible to accurately anticipate the composition of the Gale Crater samples prior to landing there. For this reason, it is important to have the capability to analyze additional standards using laboratory instruments that are sufficiently similar to ChemCam. This is represented in the middle row of Fig. 1. Before accepting standards from laboratory instruments into the ChemCam multivariate training database, a rigorous comparison must be done between spectra taken by ChemCam on standards that were available prior to delivery, with spectra of the same standards taken with laboratory instruments, to ensure that these new spectra match those from ChemCam in terms of resolution, wavelength, spectral range, and plasma temperature (ratios of peak heights for a given composition). The discussion of data processing will follow the different elements in the figure. The accuracy of the model is quantified by performing leave-one-out analyses on the pre-delivery spectral database.

2. Experimental

2.1. Instrument and experimental layout

The ChemCam instrument is described in detail in two separate papers [1,2]. Briefly, it utilizes a passively-cooled diode-pumped Nd: