



Correcting for variable laser-target distances of laser-induced breakdown spectroscopy measurements with ChemCam using emission lines of Martian dust spectra [☆]



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ABSTRACT

As part of the Mars Science Laboratory, the ChemCam instrument acquires remote laser induced breakdown spectra at distances that vary between 1.56 m and 7 m. This variation in distance affects the intensities of the measured LIBS emission lines in non-trivial ways. To determine the behavior of a LIBS emission line with distance, it is necessary to separate the effects of many parameters such as laser energy, laser spot size, target homogeneity, and optical collection efficiency. These parameters may be controlled in a laboratory on Earth but for field applications or in space this is a challenge. In this paper, we show that carefully selected ChemCam LIBS emission lines acquired from the Martian dust can be used to build an internal proxy spectroscopic standard. This in turn, allows for a direct measurement of the effects of the distance of various LIBS emission lines and hence can be used to correct ChemCam LIBS spectra for distance variations. When tested on pre-launch LIBS calibration data acquired under Martian-like conditions and with controlled and well-calibrated targets, this approach yields much improved agreement between targets observed at various distances. This work lays the foundation for future implementation of automated routines to correct ChemCam spectra for differences caused by variable distance.

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1. Introduction

Since its inception more than five decades ago, interest has grown steadily in the application of laser-induced breakdown spectroscopy (LIBS) for the detection and characterization of various materials [1,2]. This technique is based on the use of laser pulses intense enough to

break down the chemical bonds of the constituents of a sample and ablate a few nanograms per pulse generating a short-lived plasma. Light emitted by this plasma during cooling is collected, typically by a bundle of optical fibers or a lens, and transmitted to a spectrometer for analysis [2]. Spectral lines of the emission spectra yield information on both the chemical composition and the relative abundance of the elements present in the plasma.

LIBS has been used in a number of Earth-based applications [3,4] thanks to its versatility, speed in generating elemental compositions, and the fact that it is complementary to other types of analytical techniques such as Raman spectroscopy and fluorescence spectroscopy. The successful landing of the Mars Science Laboratory (MSL) on the

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red planet on August 6th, 2012 with the Chemistry Camera (ChemCam) instrument on board opened a new chapter for this analytical technique and constitutes the first use of LIBS for planetary science exploration [5]. In addition to the advantages noted above, the ChemCam LIBS instrument offers one key feature that will be exploited in this work: It can *remotely* remove and *yield spectroscopic information on the dust* that may be present on Martian rocks. Typically, ChemCam collects 30–50 individual spectra at each surface location on rocks and soils that may be located at distances up to 7 m from the instrument [6].

Quantitative analysis of LIBS spectra depends critically on our ability to control the analytical conditions. Ideally, these should be such that the generated plasma is reproducible and is an accurate representation of the interrogated sample. The plasma should not be affected by matrix effects, sampling geometry, or small changes in parameters such as its environment. Researchers have reported that parameters including optical collection and sampling geometry and the temporal and spatial characteristics of the laser pulses and the samples to be interrogated are critical [7,8]. Although these parameters can be controlled in a laboratory, this is not always possible for field-based LIBS measurements: for extraterrestrial applications, this is a real challenge that requires novel approaches. Experimental conditions are particularly important when quantitative information and/or identification and classification of various samples are sought. Despite these challenges LIBS has been used for the measurements of relative element concentrations [9], for the quantitative determination of absolute concentrations [10], and for the characterization of large bio-macromolecules [11]. In its *remote* form, LIBS has been used to detect energetic materials [11], biological materials [12] and more recently to identify, quantify, and classify extraterrestrial rocks and soils [13,14].

To optimize reproducibility of the ChemCam LIBS measurements, great care was taken to calibrate the instrument and the spectra as described in Wiens et al. [15]. These include: wavelength calibration to account and correct for potential wavelength drifts in the spectrometer, continuum removal to correct for the effects of bremsstrahlung radiation, instrument response calibration to correct for possible variations in the optical collection efficiency of the detector across the wavelength range of interest, and the development of a data base of calibration standards and multivariate analysis to overcome matrix effects [10,16–20]. In addition to these existing corrections, it is necessary to account for the fact that LIBS spectra are collected at target-to-instrument distances (which will be referred to as distance in the rest of the paper) that vary from 1.56 m to 7 m [7]. Two effects must be addressed in order to evaluate targets located at different distances. First, the spatial characteristics of the laser beam at the target may not be reproducible from one target to the next. Small changes in the spatial profiles of the ablating laser have been shown to yield large changes in the intensities of the measured emission lines [5,7]. Second, the light emitted by the plasma generated at one target travels to the detector following a slightly different optical path than that originating at another target. Therefore, light emitted at different distances may be collected under different optical path conditions. This second effect is partially taken into account in the current data pipeline through a simple solid angle correction included in the instrument response.

In this paper, we show that carefully selected LIBS emission lines acquired on Mars can be used to build a *spectroscopic proxy standard* that in turn can be applied to generate distance calibration curves for individual emission lines. This set of emission lines is derived from the first LIBS spectrum acquired from a subset of the 135 samples analyzed during the first 100 sols of the MSL landed mission. Thus, the spectroscopic proxy standard used for this work is a set of LIBS spectra of the uncontaminated Martian dust. To test this approach, we apply it to LIBS spectra obtained from measurements performed on laboratory-calibrated targets and where the distances are varied by known amounts. This is achieved by calculating the impact of the distance correction on the classification and the quantification of the laboratory-calibrated targets.

2. Development of an internal LIBS spectroscopic proxy standard for distance calibration

During its first 100 sols on the surface of Mars, the ChemCam LIBS instrument fired 30–50 laser pulses at each interrogation point on 63 targets at 1.6 m to 7 m distances from the instrument. The ChemCam LIBS instrument emits laser pulses with an energy ranging from 6.5 mJ to 14 mJ, a pulse duration of 4.5 ns and operating at 1067 nm with a repetition rate of 3 Hz. The plasma light is collected by a 110 mm diameter telescope and is transmitted by a ~6 m optical fiber to three spectrometers in the body of the rover. The spectrometers cover the ultraviolet (UV), violet-blue (VIS), and the remaining visible and near infrared (VNIR) spectral ranges, collectively from 240 to 905 nm. This instrument is designed such that the spectrum generated by a single laser pulse is recorded and can be analyzed independently of the rest. This feature has provided one key result: the elemental composition generated with the first several laser pulses, often up to the first 5, is similar to that of the global Martian fine dust [21–23]. This composition has been studied extensively by scientists on previous rover and remote sensing missions [24,25], and is found to be uniform on a global scale. As it is shown in greater detail below, using a subset of the LIBS spectra of this fine dust, we generate curves of the variation of specific emission lines with distance. These distance calibration curves, based on the behavior of the spectral emission lines with distance, are used to correct for the effects of distance variations on the identification and classification of the various targets interrogated by the ChemCam instrument. This approach is useful because the material used to generate the distance calibration curves is likely to be present everywhere on the surface of the planet and hence constitute an internal standard for ChemCam. Moreover, the emission lines used for calibration are obtained with the same instrument as the rest of the spectra are collected, so that instrumental characteristics remain constant.

Table 1
Signals considered for distance calibration and fit error associated.

Signal (nm)	Error	Signal	Error
Fe I 260.0	10.29%	Al I 396.2	9.05%
Mg II 279.1	37.46%	Ca II 396.8	4.68%
Mg II 279.6	2.72%	Mg I 517.3	32.05%
Mg II 279.8	14.17%	Na I 589.0	35.95%
		Na I 589.6	
Mg II 280.3	46.12%	Si II 634.7	41.95%
Si I 288.2	22.06%	K I 766.5	14.61%
Ca II 393.4	18.83%	Na I 818.3	33.31%
Al I 394.4	4.43%	Na I 819.5	13.20%

Table 2
Median ratios used to identify composition and discriminate outliers for first shot spectra. One standard deviation associated with the calculated value of the median ratio. Ratios are indicated by the elements and the wavelengths in nm of the emission lines. Delta E gives the difference in eV of the upper transition wavelength for the two emission lines in each ratio.

Ratio of signals (nm)	Standard value	One standard deviation	Delta E (eV)
Mg279.6/Si288	5	0.22	0.65
Fe260/Si288	2.58	0.24	0.60
Na589/Ca393	12.01	0.41	1.05
Al396/Si288	2.57	0.24	1.94
Mg279.6/Fe260	1.97	0.11	1.25
Ca393/Al396	0.7	0.21	0.01
Ca393/K766	0.31	0.24	1.53
Na589/K766	3.68	0.39	0.49
Ca393/Si288	1.8	0.29	1.93
K766/Si288	5.62	0.26	3.47
(Fe260 + Mg280.3)/Si288	3.12	0.22	4.17 & 0.66

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