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Investigation of plasma parameter determination of LIBS plasmas in martian conditions

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1. Introduction

Laser Induced Breakdown Spectroscopy (LIBS) is a powerful tool for the elemental analysis of rocks and soils, in particular in-situ for planetary explorations [1]. The ChemCam instrument is part of NASA's Mars Science Laboratory mission and is analyzing Martian targets with LIBS since 2012 [2]. Also the follow-up instrument SuperCam on Mars2020 will use LIBS in combination with other spectroscopic methods[3]. Despite its many advantages, LIBS suffers from variations of the plasma emission due to varying experimental conditions, small-scale inhomogenities and physical and chemical matrix effects. This is important in particular for LIBS applications in the field of planetary exploration, as the encountered geological samples show variations on different scales and the measurement parameters are not fixed like in a laboratory. The differences in the LIBS data reduce the precision and accuracy of computed quantities by univariate and multivariate approaches. Since the LIBS plasma is characterized by parameters such as temperature and electron density, which can be calculated from the LIBS spectra, these parameters can be used for normalization and correction of the differences in the total emission or for particular emission lines.

Panne et al. [4] have shown that normalization with both parameters reduces the fluctuations of line ratios in terrestrial laboratory LIBS data. Also Feng et al. [5] observed a smaller signal variation in a pulse-to-pulse analysis by normalizing to temperature and the ratio between densities of neutral and single ionized species.

In this work we investigate the experimental conditions, mainly the timing of the measurement, for an optimized derivation of the plasma parameters from LIBS data taken under martian atmospheric conditions. With the results we will further evaluate their suitability for normalization.

2. Plasma parameters

The LIBS plasma is a complex state and simply measuring the plasmas temperature and electron density is not possible. However, they can be derived from the spectral data. The theory for the plasma temperature determination is based on a Boltzmann distributed level occupation of the electrons. For that a thermal equilibrium or at least a local thermal equilibrium (LTE) is a necessary assumption, which can be favored by short measuring times. Detailed explanations of the theory and calculations can be found in [6] and [7].

In general the plasma temperature and electron density determined from measurements without any spatial resolution and finite measurement times should be understood as temporal and spatial averages and not as real values for the whole plasma.

3. Experimental

Data was taken with the DLR LIBS set-up with a simulation chamber, an Echelle spectrometer (Aryelle Butterfly, LTB Berlin) with a time-gated intensified CCD and a pulsed Nd:YAG Laser (1064 nm, 8 ns, 10 Hz). The laser energy was reduced to 15 mJ and measurements were performed under simulated martian conditions(pressure 7 mbar, appropriate gas mixture).

The ICCD allows for time gated measurements but limits the quality of single shot LIBS spectra. The plasma of at least 5 shots have to be accumulated to obtain a spectrum of sufficient intensity. A similar problem occurs for measurements with short (< 300 ns) integration times. As short integration times are required to hold LTE conditions, several measurements were done to determine the best combination of number of accumulated LIBS spectra and the integration time.

A silicon wafer was used as a simple and homogeneous target. The delay time was 150 ns and we measured with two integration times, 50 and 100 ns, respectively, where the number of accumulated spectra was varied.

4. Evaluation

First, the signal-to-noise ratios (SNR) of the Si(I) 288 nm emission line was determined, see Table 1. For further comparison we took previously measured data with longer integration times (500 and 1000 ns). The SNR becomes better with more accumulated LIBS spectra. Note here that we did three measurements and for the data with longer integration times ten.

Plasma temperatures were calculated applying the Boltzmann plot method with Si(III) lines. Figure 1 shows the temperatures for different integration times and number of accumulated shots. For the shorter integration times the variation is larger. Also the temperature itself is in most cases higher for a shorter integration time.

Table 1: Signal-to-Noise ratios of Si(I) at 288 nm.

gate time [ns]	# of acc. shots	SNR
500	30	20
1000	30	41
50	30	5
50	50	16
50	70	23
50	100	23
100	30	12
100	50	12
100	70	16
100	100	52

5. Conclusion and outlook

Although the temperature determination is more stable for longer integration times, we will further investigate the shorter gate times and study their effect on the LTE conditions. Also the electron density will be analyzed. Since this study has the final objective to evaluate the plasma parameters for normalization, we have to bring the best conditions and measuring parameters for their determination in line with the largest gain of information about the analyzed target. Even though short integration times are favored to fulfill LTE conditions, they do not allow for high SNR and the detection of molecular bands for example. The results of this study are interesting for upcoming missions to Mars that will have the possibility for time-resolved LIBS measurements such as SuperCam on Mars2020. With SuperCam, the third wavelength range can be used for time gated measurements.

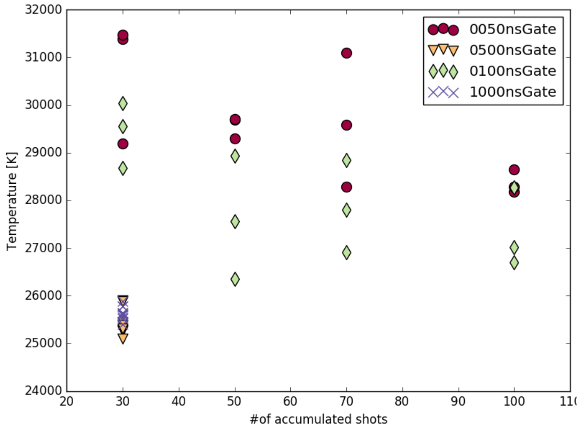

Figure 1: Plasma temperatures calculated from the measurements with the shorter gate (integration) times (50 and 100 ns) and the previous measured data with longer gate (integration) times.

References

[1] Knight et al., *Characterization of Laser-Induced Breakdown Spectroscopy (LIBS) for Application to Space Exploration*, 2000, Society for Appl. Spectroscopy

[2] Maurice et al., *ChemCam activities and discoveries during the nominal mission of the Mars Science Laboratory in Gale crater, Mars*, 2016, Journal of Anal. Atomic Spectrometry

[3] Maurice et al., *Science objectives of the SuperCam instrument for the Mars2020 rover*, 2015, Lunar and Planetary Science Conference

[4] Panne et al., *Analysis of glass and glass melts during the vitrification process of fly and bottom ashes by laser-induced plasma spectroscopy. PartI: Normalization and plasma diagnostics*, 1998, Spectrochim. Acta B

[5] Feng et al., *Study to Reduce Laser-induced Breakdown Spectroscopy Measurement Uncertainty Using Plasma Characteristic Parameters*, 2010, Spectrochim. Acta B

[6] Griem (1964), *Principles of Plasma Spectroscopy*, McGraw-Hill Inc., New York

[7] Aragon and Aguilera, *Characterization of laser induced plasmas by optical emission spectroscopy: A review of experiments and methods*, 2008, Spectrochim. Acta B