INVESTIGATION OF NORMALIZATION METHODS USING PLASMA PARAMETERS FOR LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS) UNDER SIMULATED MARTIAN CONDITIONS

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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 NASAs Mars Science Laboratory mission and is analyzing Martian targets with LIBS since 2012. Also the follow-up instrument SuperCam on Mars2020 will use LIBS in combination with other spectroscopic methods. Despite its many advantages, LIBS suffers from shot-to-shot variations, mainly due to small-scale inhomogeneities and matrix effects as well as varying experimental parameters. This affects both univariate and multivariate data analysis and calibration and requires a suitable normalization method. This is especially important for LIBS aplications 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. Several normalization methods have been proposed in previous studies, such as using the total emission intensity [2], the emission intensity with continuous emission removed [3], the C(I) 247 nm peak [4] or the plasmas continuous emission [5]. It was shown that these approaches can work well under specific conditions, but do not provide a general normalization method.

In this work we want to test the suitability of plasma parameters -temperature T and the electron density n_e- for the normalization of LIBS data taken under martian atmospheric conditions. *Panne et al.* [6] have shown that normalization with both parameters reduces the fluctuations of line ratios in terrestrial laboratory LIBS data. Also *Feng et al.* [7] 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.

Plasma Parameters: The LIBS plasma is a complex state and simply measuring the plasmas temperature and electron density is not possible, but they can be derived from the spectral data. The theory for the plasma temperature determination is based on a Boltzmann distributed level occupation. 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. Moreover self absorption has to be avoided, the plasma needs to be optical thin. This can be obtained by chosing a low laser energy and excluding ground state excitations from the evaluation.

In this work we calculated the plasma temperature via Boltzmann Plots and electron densities by using the quadratic Stark effect. Detailed explanations of the theory can be found in [8], [9].

In general the plasma temperature and electron density determined by these methods without any spatial resolution should be understood as temporal and spatial averages and not as real values for the whole plasma.

Samples: As samples we chose Andesite, Basalt and Basaltolivin since these rocks are known to be present on Mars. For our study we took powder and pressed it with a pressure of $5t$ into pellets. The Andesite and Basalt were certified by the "National Analysis Center for Iron and Steel" in Beijing (China). The composition of some major elements are for Andesite (Basalt): SiO_2: 63.1 (44.6); Al_2O_3: 16,1 (13.8); Fe_2O_3: 4.7 (13.4); MgO: 0.8 (7.8) (all in wt%).

Experimental Set-Up: 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 Nd:YAG Laser (1064 nm, 8-10 ns, 10 Hz). The laser energy was reduced to 15 mJ. We chose the delay and gate time both to be 500 ns. The experiments were performed using both available spectral ranges: UV (190-375 nm) and NIR (270-850 nm). All measurements were performed under simulated martian conditions, which means a pressure of 600 Pa and the following atmospheric composition: 95.55 CO_2, 2.7 N_2, 1.6 Ar and 0.15 O_2; all values in Vol.%.

In order to obtain LIBS data with good signal-to-noise ratios we averaged the spectra of at least 5 shots. In the first series of measurement we recorded 60 times a 5 shots integrated measurement on 10 different positions on each sample. For the second series we recorded 10 times a 30 shots integrated spectrum at 10 different positions.

Data Analysis: All peaks were fitted with a Voigt profile and an underlying linear background. For the Boltzmann plots we did a selection of lines with known transition probabilities and uncomplicated fit environments. We chose the Si(I) transitions (all in nm): 212.4; 221.7; 251.4; 251.6; 251.9; 288.2 and the Fe(II) lines: 238.2; 259.8; 261.4; 262.8; 268.5; 269.3; 274.0; 275.6 (Values for the upper level energy and degeneracy g_j and transition probability A_{ij} were taken from [10]). For the electron density calculation the Mg(I) 285.2 nm line was chosen and theoretical values as w the electron-impact width were taken and interpolated from [8].
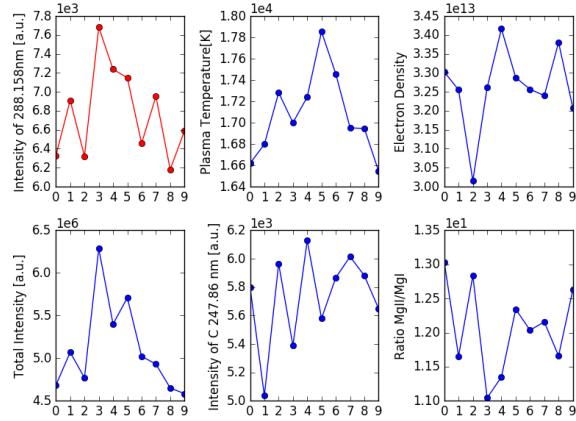
Figure 1: Variation of the 30 shots measurement series of Basalt.

Results: For every sample we determined two temperatures T_{FeII} and T_{SiI} due to the two sets of lines for the Boltzmann Plots. Also, the total intensity, the ratio between intensities of Mg(II) 280.3 nm and Mg(I) 285.2 nm and the intensity of the C(I) 247.9 nm peak were used for normalization. Figure 1 shows the behaviour of these parameters for the 30 shots measurements of Basalt. In Figure 2 the variability of the temperature and the intensity variation of Si(I) 288 nm is shown for the Basalt 5 shots measurement.

As a measure of the quality of the normalization the Relative Standard Deviation (RSD) of the Si(I) 288 nm intensity for every measurement series was calculated. In Table 1 the results are listed. For the 30 shots measurements the RSD is already very small and improvements were only given by the temperature T_{FeII}, the density n_e and the total intensity normalization. The RSD values of the 5 shots measurements do not improve by any normalization.

Discussion: The temperature and density determination are both derived from the spectral data and therefor come with an uncertainty themselves. As soon as
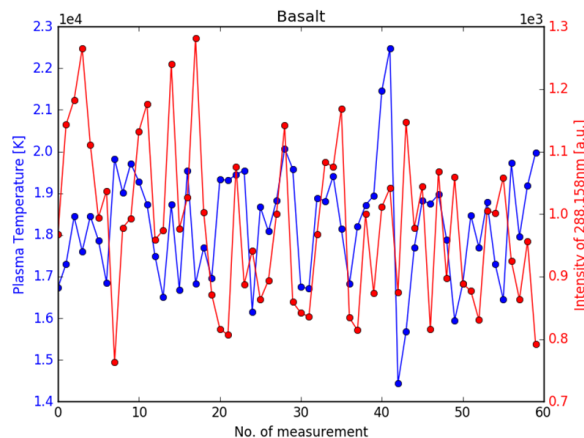

Figure 2: Variation of the Si(I) 288.158 nm intensity and the Plasma Temperature T_{FeII}.

SiI 288.158 nm	RSD 30 shots	RSD 5 shots
Basalt		
original data	0.068	0.128
Temperature (SiI)	0.080	0.151
Temperature (FeII)	0.066	0.150
density n_e	0.067	0.161
total intensity	0.047	0.355
CI 247.856 nm	0.104	0.237
ratio MgII/MgI	0.111	0.205
Andesite		
original data	0.066	0.138
Temperature (SiI)	0.084	0.155
density n_e	0.091	0.231
total intensity	0.186	0.403
Basaltolivin		
original data	0.030	0.140
Temperature (FeII)	0.029	0.153
density n_e	0.045	0.178
total intensity	0.038	0.228

Table 1: Overview of the RSD values for different normalization methods. The RSD 30 shots (5shots) corresponds to 10 (60) measurements, respectively.

self absorption occurs or LTE conditions are not fullfilled, the parameters can become fault-prone. Thus, an upcoming study of the data will test other methods of calculating the plasma parameters, e.g. using other lines or multielement Saha-Boltzmann Plots. Another problem might come with the multi-pulse measurement of at least 5 pulses, because only a single pulse to single pulse analysis ensures a proper evaluation. As mentioned before the parameters are rather averages than real physical properties, even in a single pulse measurement without spatial resolution. An additional error source might be the use of Stark broadening for the density determination. *Gornushkin et al.* [11] showed in a study that for low pressures the Stark broadening might not be the dominant broadening feature. This problem will be overcome by using a Saha-Boltzmann analysis. Following *Feng et al.* [7] we will also test the ratio between the ion and atom number density in combination with the plasma temperature for normalization.

References: [1] Knight et al. (2000), *Society for Appl. Spectroscopy*; [2] Body and Chadwick (2001), *Spectrochim. Acta B*; [3] Wiens et al. (2013), *Spectrochim. Acta B*; [4] Rapin et al. (2016), *Earth and Planetarty Sc. Letters*; [5] Schröder et al. (2015), *Icarus*; [6] Panne et al. (1998), *Spectrochim. Acta B*; [7] Feng et al. (2010), *Spectrochim. Acta B*; [8] Griem (1964), *McGraw-Hill Inc., New York*; [9] Aragón and Aguilera (2008), *Spectrochim. Acta B*; [10] NIST, http://www.nist.gov/physrefdata/asd/lines_form; [11] Gornushkin et al. (1999), *Spectrochim. Acta B*