# An Implementation of Calibration-Free-LIBS for the Analysis of Spectra from Planetary Exploration

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LIBS has been proven very useful for in-situ geochemical analysis on the Martian surface [1]. It has also been proposed for future missions to explore other bodies of the Solar System [e.g. 2]. For this reason, it has become more important to understand the capabilities and challenges of LIBS under atmospheric conditions that are different from Earth. There is also a high interest in calibration-free LIBS (CF-LIBS) due to highly versatile measuring conditions in planetary exploration.

In this study, we have developed a method to assist the analysis of LIBS spectra acquired under different atmospheric conditions corresponding to different extraterrestrial mission scenarios. The method is developed from first principles and without resorting to measurements on calibration standards similar to CF-LIBS [3]. Our approach follows from the same theory and assumptions as the standard approaches of CF-LIBS, such as the construction of Boltzmann plots, but many labor intensive steps are automated.

Assuming an optically thin plasma in local thermal equilibrium (LTE) with radial distributions of electron density and temperature, a linear relationship exists between the intensities of the electron transitions and elemental concentrations. Our approach is to set up a system of linear equations between the extracted integrated peak intensities, of a given spectrum, and the theoretically predicted peak-intensities.
From this system of equations, the concentrations are solved semi-analytically by minimizing the residuals between the peak-intensities. The minimization is repeated using different sets of electron densities and temperatures.

Data from time-resolved plasma imaging [4] will give further insight into the spatially and temporally varying temperature and density distributions of the LIBS plasma in different extraterrestrial environments and will give input to this approach.

We evaluate the applicability and limits of the method on data from different sample-matrices, atmospheric conditions and also realistic mission data such as data with a reduced wavelength range and low resolution.

[1] Maurice et.al., Mars. J. Anal. At. Spectrom. (2016).

[2] Arp et.al., Spectrochimica Acta Part B: Atomic Spectroscopy. (2004).

[3] Tognoni et.al., Spectrochimica Acta Part B: Atomic Spectroscopy. (2009).

[4] Vogt et al., this conference, (2018).