Simple modelling of Plasma Parameters to Assist the Analysis of LIBS Spectra for Planetary Exploration

Peder B. Hansen (1), David S. Vogt (1), Kristin Rammelkamp (1), Simon Kubitza (1), Susanne Schröder (1), Sven Frohmann (1), Heinz-Wilhelm Hübers (1,2)

(1) German Aerospace Center (DLR), Institute of Optical Sensor Systems, Berlin, Germany, (2) Humboldt-Universität zu Berlin, Department of Physics, Berlin, Germany (PederBagge.Hansen@dlr.de)

1. Background

Laser-Induced Breakdown Spectroscopy (LIBS) is a method of atomic emission spectroscopy used for elemental analysis. A measurement is done by inducing a luminous plasma of sample material and capturing the emitted light through a spectrometer.

LIBS allows for multi elemental analysis of remote targets without any sample preparation and optical access only. This, and the possibility for a compact instrument design, e.g. [1], makes LIBS well-suited for planetary in-situ investigations. The Curiosity rover, which is exploring Mars since 2012, is carrying the first LIBS instrument for planetary exploration [2]. LIBS instruments have also been proposed for future missions to explore other bodies of the Solar System, e.g. [3].

In this study, we developed a method to assist the analysis of LIBS spectra acquired under different atmospheric conditions corresponding to different extraterrestrial mission scenarios. Plasma parameters, the plasma temperature and electron density, and concentrations estimates are obtained from LIBS data with labour-intensive steps automated and instead of manually identifying and choosing emission lines for the analysis, all lines in a spectrum are used and without the need for prior identification.

2. Method

In the case of negligible self absorption the total observed intensity from an electronic transition inside an atom is [4]:

$$I_{ul,e,s} = F \cdot A_{ul} \cdot c_e \cdot n_s \cdot n_u \quad (1)$$

F is an experimental parameter and is equal for all transitions in a spectrum, A_{ul} the Einstein coefficient for spontaneous emission, c_e the concentration of element e, n_s the population fraction of the ionic state s and n_u the population fraction of the upper electronic state. The value of F is linked to the units of measuring and to the fraction of the emitted light that is captured. Its value might be unknown, but by considering relative concentrations it is divided out.

Assuming a local thermal equilibrium [4] and introducing the plasma temperature, T, and electron density, n_e, the ionic- and electronic state distributions are approximated by the Saha- and Boltzmann equations, respectively. By manually selecting and identifying intensities of different emission lines in a spectrum the elemental concentrations can be estimated by constructing Saha-Boltzmann plots using eq. (1) [4]. This is the general approach.

2.1. Our Approach

Our approach is to set up a system of linear equations between expected line intensities from eq. (1) and the extracted intensities from a spectrum. The inputs are tabulated reference lines from a database [5] and extracted intensities from a spectrum. The outputs are estimates of plasma temperature, electron density and elemental concentrations.

Eq. (1) is linear in the element concentrations. The intensity at a concentration equal to one will be referred to as the "transition amplitude" and is denoted with a hat:

$$\hat{I}_{ul,e,s} \equiv I_{ul,e,s}(c_e = 1) \quad (2)$$

Intensities at arbitrary concentrations can therefore be found by multiplication with the transition amplitude. Assuming that the temperature and electron density are known, transition amplitudes can be calculated from eq. (1). This allows us to set up linear equations between the expected line intensities, from the transition amplitudes, and the extracted intensities:

$$c_1 \cdot \hat{I}_{1,1} + c_2 \cdot \hat{I}_{2,1} + \cdots + c_n \cdot \hat{I}_{n,1} = P_1$$
$$\vdots \qquad\qquad (3)$$
$$c_1 \cdot \hat{I}_{1,m} + c_2 \cdot \hat{I}_{2,m} + \cdots + c_n \cdot \hat{I}_{n,m} = P_m$$

where $\hat{I}_{n,m}$ is the sum of transition amplitudes of element n with tabulated wavelengths inside peak m and P_m is the intensity of peak m, as extracted from the

spectrum. For each peak an equation appears which requires no line identification. All the reference lines from the database with wavelengths close to a specific peak are in the corresponding equation. The concentrations are solved semi-analytically by the method of linear least squares and the relevance of each transitions for the model is obtained from the derived concentrations.

In a fit routine are the transition amplitudes modelled using different sets of plasma parameters, temperatures and electron densities, and the residuals are minimized each time fitting the plasma parameters and concentrations so that they best match the extracted intensities.

3. Results

We have applied our approach to the spectra of a Martian regolith simulant recorded from 760 ns to 1260 ns after laser ignition in an experimentally simulated Martian atmospheric environment. Fig. 1 overviews the residuals for different sets of constant values of temperatures and electron densities. The best set of plasma parameters were found to be $n_e = 4.7e24$ m^{-3} and $T = 18276$ K. The corresponding concentration estimates are visualized in Fig. 2. Here large deviations are seen and they will be discussed.

We are further discussing the insights obtained from our model with comparison to LIBS data taken in different environments and at different times after laser ignition. Also, we are discussing the limits of the model that so far uses only constant plasma parameters and the assumption of negligible self-absorption.
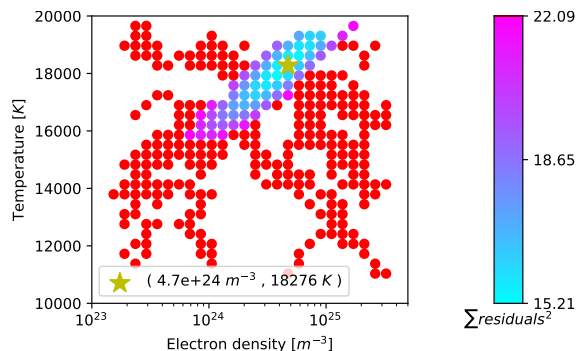

Fig. 1: Color plot showing the minimized residuals using transition amplitudes modelled from different sets of plasma parameters. Red dots corresponds to residuals above 22.09. The set of plasma parameters giving the minimum residuals is marked with the star.
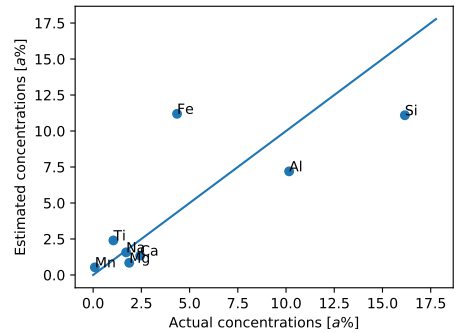

Fig. 2: Estimated concentrations from the best set of plasma parameters plotted against actual concentrations of the sample. The concentrations are normalized for better comparison since only relative concentrations are estimated.

4. Outlook

Inputs from time resolved plasma imaging [6] will allow us to include gradients of the plasma parameters in the modelling to better account for the transient and spatially varying nature of the plasma. We are furthermore working on corrections for self absorption that particular affect the intensities of the intense emission lines.

References

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