



## Sulfur and Chlorine Detection in a Lunar Context Using VUV-LIBS

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### 1 Introduction

The increasing interest in Laser-induced breakdown spectroscopy (LIBS) for space-exploration is confirmed by two more LIBS instruments, SuperCam aboard NASA's Mars 2020 mission and MarsCoDe as part of China's Tianwen 1 mission, being launched towards Mars this summer [1, 2]. SuperCam will be the follow-up of the ChemCam instrument, which has been successfully analysing the Martian surface since its landing in 2012 [3]. In 2019, another LIBS instrument has been launched heading for the Moon [4], but did unfortunately not accomplish a soft landing.

LIBS is a fast and versatile elemental analysis technique. It is based on laser ablation and needs only optical access to the target. For LIBS, a laser pulse is tightly focused onto the sample, where a small portion of material is ablated and excited into a plasma of neutral atoms, ions and electrons. The plasma emits continuum radiation from bremsstrahlung and electron-ion recombination, together with discrete emission lines from the species in the plasma. The latter allow for identification of the chemical elements contained in the plasma, and therefore in the sample.

### 2 Challenging elements in LIBS

In general, all elements of the periodic table are detectable with LIBS. Some of them, however, have their strongest emission lines outside of the typically observed spectral range from approx. 240 to 800 nm. As the emission intensity of a spectral line strongly depends on, amongst other factors, the population density of the transition's upper level, transitions between lower energy levels are typically strong. For neutral S, the fundamental ground state transition is located at 180.7 nm, while Cl atoms have their strong ground state transitions between 133 and 138 nm. Both elements are therefore expected to be well detectable in the vacuum-UV (VUV) range below 200 nm.

### 3 VUV-LIBS

VUV-LIBS means the emission of the plasma is detected in the VUV spectral range. In terrestrial environment, this range is obscured due to absorption by O<sub>2</sub> and H<sub>2</sub>O vapour from the atmosphere. VUV absorption in CO<sub>2</sub> and CH<sub>4</sub> further reduces the applicability of VUV-LIBS on e.g. Mars or Titan. For celestial bodies without a significant atmosphere, however, the predicted high emission intensities in the VUV range for otherwise challenging elements like S and Cl could be exploited to increase the sensitivity for these elements.

One drawback of LIBS in a very low pressure environment is the short life time of the plasma and its relatively low intensity. While the reduced atmospheric pressure on Mars in the order of 1 kPa is beneficial for LIBS and produces a large and bright plasma, the low confinement and therefore low probability for collisions of the plasma species at below 10 Pa leads to a short-living and dim plasma [5]. Thus, the sensitivity of LIBS in vacuum is naturally lower, and it could be even more crucial for mission instruments on bodies without atmosphere to make use of the stronger VUV emission lines.

VUV-LIBS is readily used in industrial applications, e.g. for S detection in steel [6]. There, laser pulse energies of several hundreds of millijoules, multi-pulse configurations, and purge gas atmospheres are used to compensate for atmospheric absorption and the reduced emissivity of vacuum plasmas, thereby yielding limits of detection in the order of 10-100 ppm. For space exploration, VUV-LIBS has not yet been extensively studied. Radziemski et al. investigated the applicability of VUV-LIBS for use on Mars, using components realistic for a mass-, size- and power-constrained space instrument [7]. They noted significant suppression of the strongest Cl lines in the 130-140 nm range due to the CO<sub>2</sub> atmosphere, while at the same time benefiting from the LIBS-favourable pressure.

#### 4 Experimental Details

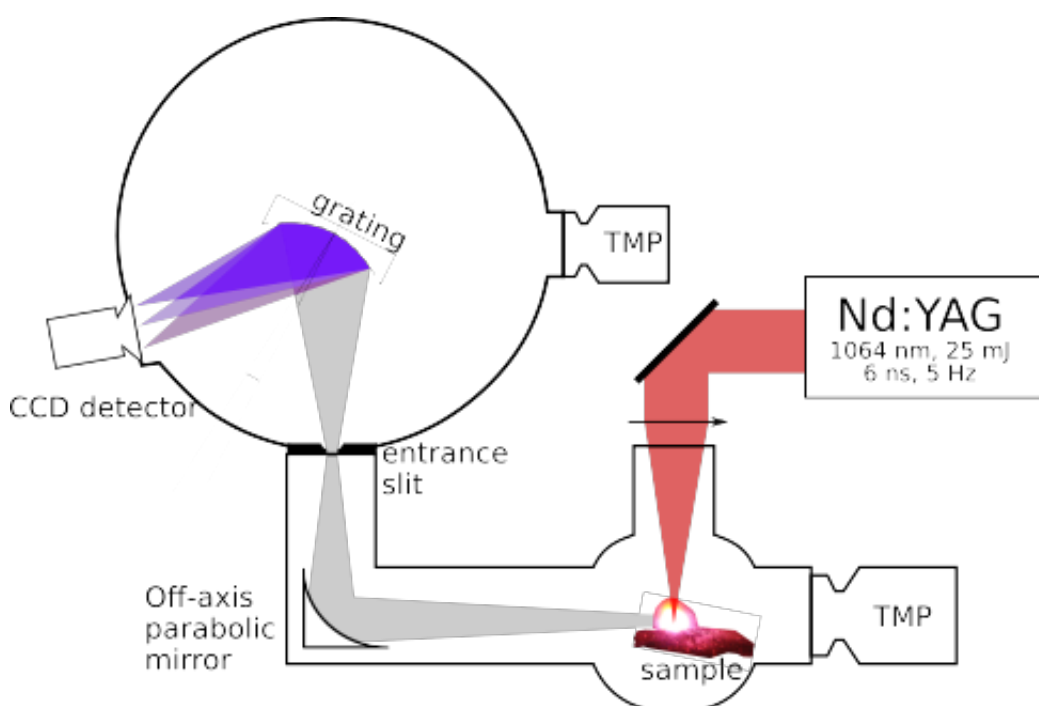


Figure 1: Schematic drawing of the set-up. The vacuum chamber hosting the sample is flanged directly to the spectrometer. The whole system is evacuated by two turbomolecular pumps (TMP) to 1 mPa.

Our set-up is built around a H+P vacuum spectrometer covering the range of 100-300 nm, see Figure 1. The plasma is excited with a pulsed Nd:YAG laser (1064 nm, up to 40 mJ, 6 ns), which is focused vertically onto the sample. The sample is contained in a vacuum chamber, directly flanged to the spectrometer. The radiation emitted by the plasma is coupled into the spectrometer using an off-axis parabolic mirror. The mirror currently limits the spectral range to >120 nm. The whole system is operated at a pressure of  $\leq 1$  mPa.

The samples analysed in this study are lunar simulants (Exolith LHS-1 and LMS-1 [8]) mixed with different amounts of pure sulfur, different sulfates, or sodium chloride. They have been prepared in-house using mortar and pestle, and a hydraulic press. The resulting atomic fractions of S and Cl range from 0.5 to 4.0 %.

## 5 Results

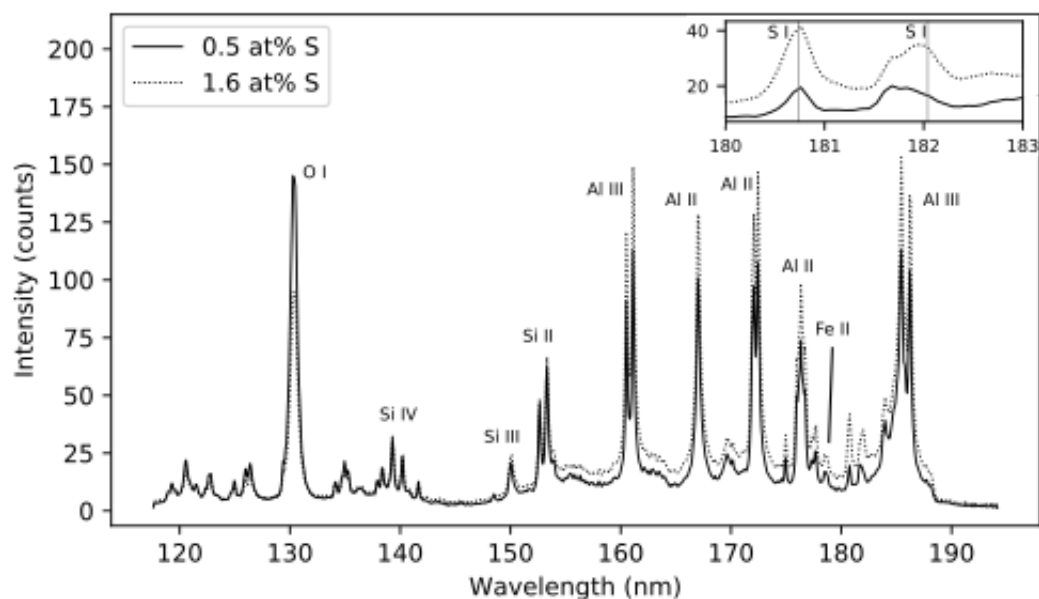


Figure 2: Example spectra of  $\text{Na}_2\text{SO}_4$  mixed in LHS-1 resulting in atomic fractions of 0.5 and 1.6 % S. Despite these low concentrations, the S I line at 180.7 nm is clearly visible.

We successfully detected S in lunar simulant matrices, using the S I emission line at 180.7 nm. Example spectra for  $\text{Na}_2\text{SO}_4$  in LHS-1 at 0.5 and 1.6 at% S are shown in Figure 2. Besides Al, Si and O emission lines from the matrix material, the S I emission line is clearly visible already at those low concentrations. Univariate calibration curves suggest a linear relationship between S concentration and emission intensity for low concentrations.

The Cl I emission lines around 135 nm spectrally overlap with Si II emission, but a change in their intensity upon changes in the Cl concentration is still recognizable.

## 6 Summary and Conclusion

S and Cl have been detected in lunar simulant matrices at atomic fraction levels in the order of 1 %. For low concentrations of S, we found a linear relationship between S concentration and LIBS signal with a univariate approach. These results are promising for improved detectability of volatiles in space exploration, which are usually hard to detect with conventional LIBS in the spectral range of 240-800 nm. Besides S and Cl, emission lines of Al, Fe, Si and O have been identified.

## References

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