

VUV-LIBS for Volatile Detection in Space Exploration

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) has been used successfully on the Martian surface by the ChemCam instrument aboard NASA's Mars Science Laboratory (MSL) since 2012 [1]. In 2020, two more LIBS instruments will be sent to Mars to study the surface geochemistry [2, 3]. While many major and minor rock-forming elements are reliably detected down to trace level concentrations, the sensitivity for some of the lighter elements like phosphorous and sulphur is low in the commonly employed UV to NIR spectral range [4]. Their strongest emission lines lie in the vacuum ultraviolet (VUV) range. Accordingly, a much higher sensitivity to these elements is expected in this range. Under terrestrial and Martian conditions this spectral range is, however, masked by strong atmospheric absorption. The lack of atmosphere on the Moon and many other celestial bodies such as asteroids might allow for a LIBS instrument targeted towards volatile detection with comparably modest instrumental efforts.

We test different experimental parameters, such as the laser pulse energy required for a stable plasma, and investigate the limits of identification and quantification of in particular sulphur using the LIBS technique in the VUV range in a lunar context.

2. Laser-induced breakdown spectroscopy

LIBS is a form of atomic emission spectroscopy. For this method a pulsed laser is tightly focused onto the sample surface, achieving irradiances of several GW/cm^2 . The uppermost layer of the sample is thereby ablated, heated, and dissociates into its elemental components. The excessive amount of energy results in a plasma plume consisting of ions, electrons and mostly excited atoms. During the decay back to the electronic ground state the ions and atoms emit light of characteristic photon energies allowing

for qualitative and quantitative analysis of elements contained in the sample [5].

3. Vacuum-UV LIBS

VUV denotes the spectral range from 100 nm to 200 nm, which is usually not accessible for detection due to atmospheric absorption from mainly O_2 and CO_2 . Hence, the whole light path from the sample to the detector needs to be evacuated or purged with a non-absorbing gas. As mentioned before, on celestial bodies without atmosphere this would not be an issue and VUV-LIBS instruments might turn out to be very powerful and practical tools.

One challenge for VUV-LIBS is the influence of pressure on the plasma emission: In a terrestrial environment the particles in the plasma are confined to a small volume leading to a high collision rate and thereby collisional re-excitation and a long lifetime. The thin (approx. 700 Pa) atmosphere on Mars is close to ideal for LIBS, allowing some expansion of the plasma and a lower optical density but at the same time still featuring particle collisions and multiple excitation de-excitation cycles. In high vacuum the mean free path length is long enough for the particles to escape with a limited number of collisions, which results in a dim plasma with a short lifetime and therefore less signal available for analysis [6].

Former studies about LIBS in the VUV spectral range mainly focused on sulphur and phosphorous impurity detection in steel and plastics. They often use laser pulse energies above 100 mJ [7, 8] that are not feasible for an instrument on a lander, or work in a gas flow environment with argon or nitrogen [7, 9] to avoid the pressure related loss in intensity. Radziemski et al. investigated the applicability of VUV-LIBS for Martian conditions with experimental parameters realistic for a space instrument [10]. They noted strong absorption due to the CO_2 atmosphere but, on the other hand, benefit from a pressure favourable for LIBS.

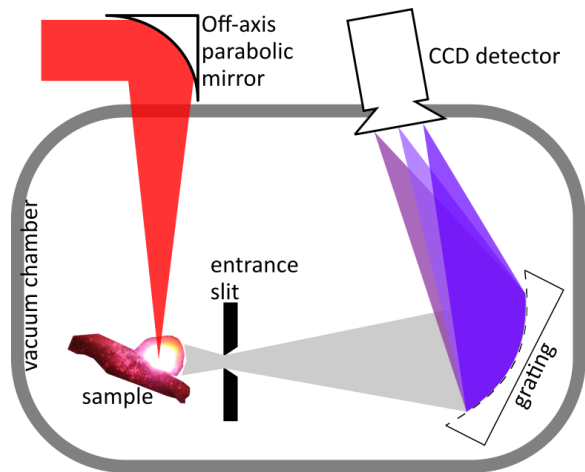


Figure 1: Schematic drawing of the experimental setup.

4. Experimental

We use a Litron Nano S Nd:YAG laser emitting pulses of 6 ns duration with an energy of 15–40 mJ at 1064 nm. The laser light is focused through a window into the sample chamber using a 150 mm focal length off-axis parabolic mirror. Plasma emission is then analysed with a 200 mm Seya-Namioka type spectrometer from H+P Spectroscopy with a 1200 lines/mm grating and detected with an open front Andor CCD camera as depicted in Fig. 1. The combined sample chamber and spectrometer vacuum system is evacuated to a residual air pressure of <0.1 Pa.

5. Results

With conventional LIBS, ionic emission at 542.9, 543.3 and 545.4 nm is often used for sulphur detection [11, 12]. These spectral lines are fairly detectable under ambient pressure, but can be disguised by superimposed Fe and Ti emission. Figure 2 shows Na_2SO_4 spectra taken in the visible (top) and in the VUV (bottom) spectral range, both under vacuum conditions. While the VUV spectrum was taken with the instrumentation shown above, the VIS spectrum was acquired with an Echelle spectrometer and ICCD further described in [12]. A zero delay and a gate width of 100 μs were used for the VIS spectrum to achieve a similarly time-integrated result for both measurements. Though the contribution of the intensifier to both sensitivity and instrumental noise is unknown, comparison of the two spectra clearly demonstrates a higher signal strength for the VUV emission.

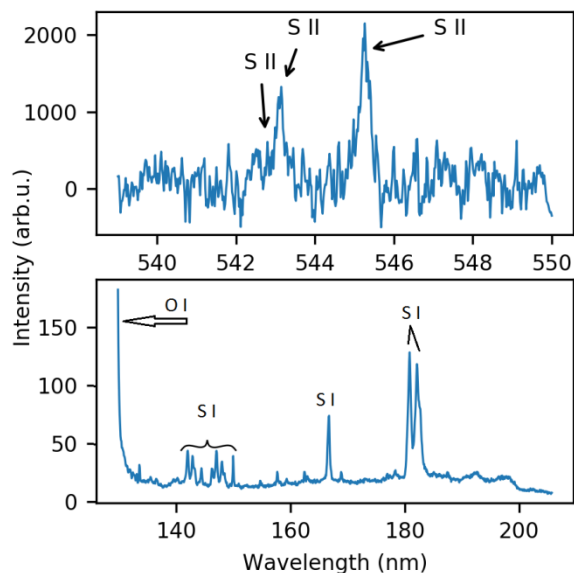


Figure 2: Spectrum of Na_2SO_4 taken in the visible (top) and in the vacuum ultraviolet spectral range (bottom) at a pressure below 1 Pa. For both measurements 50 spectra have been accumulated.

6. Summary and Conclusions

Sulphur in pure sulphate samples is well detectable even under low pressure conditions when using LIBS in the vacuum ultraviolet range. Further, less ambiguity in geological samples often containing iron or titanium is expected due to low transition probabilities for the VUV emission lines of these elements.

We test different experimental parameters such as required laser pulse energy, and investigate the sulphur emission in different matrix materials to estimate limits of detection and calibration, thereby evaluating the suitability of VUV-LIBS instruments for in-situ volatile detection on planetary bodies without atmosphere.

References

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