Sulfur and Chlorine Detection in a Lunar Context Using VUV-LIBS
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1 Introduction
Laser-induced breakdown spectroscopy (LIBS) is an elemental analysis technique, in which a pulsed laser is tightly focused onto the sample. The intense light pulse ablates material and excites a plasma radiating a continuum as well as atomic and ionic line emission, which allows for species identification.

With SuperCam \textsuperscript{1} as a follow-up for ChemCam, and MarsCoDe \textsuperscript{2}, two more LIBS instruments were launched to Mars this summer. The Moon has also been targeted in a recent mission comprising a LIBS instrument \textsuperscript{3}, which unfortunately failed.

While the near-vacuum conditions on celestial bodies without an atmosphere, lead to a dim and short-living plasma emitting only weak LIBS signals, they enable to detect in the vacuum-U (VUV) spectral range without suffering atmospheric absorption. This improves the detectability of elements that are challenging to detect with LIBS in the UV to NIR range, such as C, Cl, P, and S.

In the context of space exploration, only Radziemski et al. \textsuperscript{4} studied the potential of VUV-LIBS using the example of a mission to Mars. They found limits of detection (LOD) of 1.0 at% for S (at 180.7 nm) and 7.5 at% for Cl (at 133.6 nm). The signal enhancement due to simulated Martian atmosphere in their studies should be noted.

We investigated the detection of S and Cl in lunar analogue samples with LIBS in near-vacuum conditions using the same emission lines. The results suggest linear calibration curves and LODs of approx. 1.0 at% for S and Cl.

2 Experimental set-up
The setup is based on a commercial VUV spectrometer, see Fig. 1. The integrated vacuum system features windowless detection of the LIBS signal. The sampling distance is approx. 25 cm.

- Spectrometer: 100-300 nm, 1200/mm curve grating, 80 nm spectral window
- Laser: Nd:YAG, 1064 nm, ≤40 mJ, 6 ns, 5 Hz
- Atmosphere: <1 mPa residual air

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Fig. 1: Schematic drawing of the setup. The vacuum system is evacuated by two turbomolecular pumps (TMP) to <1 mPa.

3 Sulfur detection
Samples: varying amounts of S, K$_2$SO$_4$ and Na$_2$SO$_4$ in Lunar Highlands simulator (Exolith LHS-1), and Na$_2$SO$_4$ in Lunar Mare simulator (Exolith LMS-1)

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Figure 2: Average spectra of the Na$_2$SO$_4$ in LHS-1 samples with 5 concentrations of 0.5, 1.0, 1.5, 2.0, and 2.5 at%. Besides the 0.5 at% trial at 130 nm, the plasma shows mainly emission from ionized Al and Si. The Si lines of interest are located around 180 nm.

Example spectra of Na$_2$SO$_4$ in LMS-1 in Fig. 2 show mainly emission from ionized Al and Si. S I emission is observed around 180 nm and gains intensity for higher S concentrations.

A close-up of the S I emission is shown in Fig. 3. Underlying emission from Al II, Si II and Ti III is accounted for in a fit to the data. The area of the most intense S I line at 180.7 nm (shaded in grey) is used for analysis.

Calibration curves for the S-bearing samples, Fig. 4, show a mostly linear increase of the S I emission intensity with the S abundance. The large variations between measurements on the same sample (see error bars in Fig. 4) have been attributed to the sample heterogeneity. The LOD according to the definition recommended by IUPAC is in the order 1.0 at%, but S I emission has been observed as well in most spectra of the samples with 0.5 at% S.

Figure 3: Example fit for Na$_2$SO$_4$ in LHS-1 at 1.0 at% S. A model of 6 lines is fitted to the data to account for metal ions. The grey area represents the S I intensity measurement for calibration curves.

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4 Chlorine detection
To evaluate the suitability of VUV-LIBS for Cl detection, NaCl has been mixed into LMS-1 at different ratios. A spectrum is shown in Fig. 5.

Figure 5: Average spectrum of the NaCl in LMS-1 sample with 1.9 at% Cl. Four Cl emission lines are located around 125 nm. Continuum emission and Stark broadening due to the high electron density in the plasma centre are suppressed with an aperture placed close to the sample. This increases the resolution in comparison to Fig. 2.

Example spectra of NaCl in LMS-1. Sample with 1.9 at% Cl. Four Cl emission lines are located around 125 nm. The continuum emission and Stark broadening due to the high electron density in the plasma centre are suppressed with an aperture placed close to the sample.

Fig. 6 shows a close-up of the four Cl I emission lines. Interfering Si II and Si III emission lines predicted by the NIST data base are not observed with a significant intensity. With the total area below the four emission lines as an intensity measure for the chlorine signal, a calibration curve has been established, see Fig. 7. The upper panel shows the raw data as extracted from the fit. Due to an observed change of sensitivity through-out the measurement session, the data has additionally been normalized with the close-by O I triplet at 130 nm, see lower panel in Fig. 7. After normalization, a linear regression through the mean intensities results in R$^2$ = 0.96. The signal scatter is again due to sample heterogeneities. The lowest investigated and detected Cl concentration is 1.0 at%.

Figure 6: Example fit for NaCl in LMS-1. The vertical markers indicate the Cl emission lines at 133.5, 134.8, 135.2 and 136.6 nm. The total area of all four peaks is used as Cl intensity.

Reference:

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