

Miniaturized Laser-induced Breakdown Spectroscopy for planetary surface analysis. I. Rauschenbach¹, E. K. Jessberger¹, H. W. Hübers² and S. G. Pavlov², ¹Institut fuer Planetologie, Wilhelm-Klemm-Strasse 10, 48149 Münster, irausch@uni-muenster.de, ²DLR-Institute of Planetary Research, Rutherfordstrasse 2, 12489 Berlin.

Introduction: Laser-induced Breakdown spectroscopy (LIBS) is currently under development for future lander missions to Mars [1–10] and other planets and moons, like Venus or Europa [11, 12]. LIBS spectroscopically determines the visible atomic emission from a plasma that is generated by pulsed laser light focused on a sample surface. The intensities of the many characteristic spectral lines of the elements are direct measures of their concentration in the sample. For Martian environmental conditions it was convincingly demonstrated that quantitative results can be obtained applying suitable calibration methods [2–4].

LIBS serves a tool for rapid elemental analyses and has some advantages compared to established methods in space exploration:

- Rapid analysis ($\ll 1$ minute)
- High lateral resolution ($\geq 50 \mu\text{m}$)
- Needs neither sample preparation nor pumps
- Detects simultaneously and quantitatively major, minor and trace elements
- Removes dust layers and "drills" through weathered rock surfaces.
- Allows depth profiling
- Synergetic integration with Raman spectroscopy [5,6] or microscopy easily feasible
- Profitable in combination with Mössbauer or APXS instruments

Furthermore, we have demonstrated [7,8] that LIBS directly detects ice and liquid pore or adsorption water inside rocks and on rock/soil surfaces. The stringent space mission requirements (weight, size, power consumption) call for the development of a lightweight LIBS instrument which we currently are pursuing in the framework of the GENTNER project for surface missions to Mars or other planets and moons [9,10]. Here we report on our study of different instrument parameters that are of importance for LIBS specifically in the Martian environment.

Experimental: For our studies we utilized a chamber with "Martian" atmosphere (95.55% CO₂, 2.7% N₂, 1.6% Ar, 0.15% O₂) at 7 mbar. We used a miniaturized prototype Nd:YAG laser operated at 1064 nm, with a pulse width of 2 ns and normal incidence onto the sample surface. As the laser mass directly correlates with the laser energy, we first determined with our experimental set up the minimum energy required for LIBS quantitative analyses. To this end, the laser energy was varied from 0.1 to 2.8 mJ

and the repetition rate from 1 to 50 Hz. To ensure a sufficiently high irradiance, the laser prototype had a spot diameter of $\sim 50 \mu\text{m}$. The plasma emission was collected parallel to the incident laser beam and detected with an Echelle spectrometer equipped with an ICCD detector. The latter was used without amplification and temporal resolution to best simulate a probably compact and "simple" flight-spectrometer.

Results: *Optimization of instrumental parameters.*

In order to analyze the influence of the instrumental parameters of the miniaturized LIBS laser, laser wavelength, spot diameter, pulse duration and ICCD settings were kept constant. We found that the best results for this fixed configuration are achieved with

- Laser energy: ≥ 1.2 mJ
- Laser frequency: 10 Hz
- Pulse number: 20–50 for soils, ≥ 50 for rocks
- Normal laser incidence and detection angle
- Focal plane slightly below sample surface

A short section of a basalt LIBS spectrum (laser energy 1.8 mJ, 50 pulses, other settings from above) is shown in Fig. 1. In addition to major element lines also the ionic emission of the minor element Sr is visible.

Note that a full spectrum (250–900 nm) contains hundreds of useful neutral and ionic element lines – a highly over-determined system.

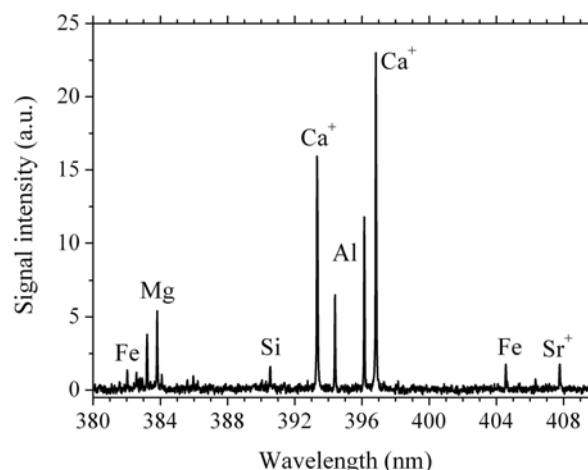


Fig. 1: Excerpt of LIBS spectrum from a basalt sample obtained with optimized instrument settings.

Quantitative analyses. With the optimized instrumental parameters, we performed calibration measurements using a series of various certified standard materials from natural rocks like andesites or basalts

and different certified soils and stream sediment samples. As example Fig. 2 shows calibration curves for Al and Sr. Each data point is the mean value of 5 replicate measurements. The error bars correspond to 97.5% confidence inducing a Student t factor of 2.776. The calibration graph of Al shows a curvature at high concentrations, which results from self-absorption in the plasma. This behaviour was also detected for Mg, Si, Ca and Na. All other studied elements behave like Ba.

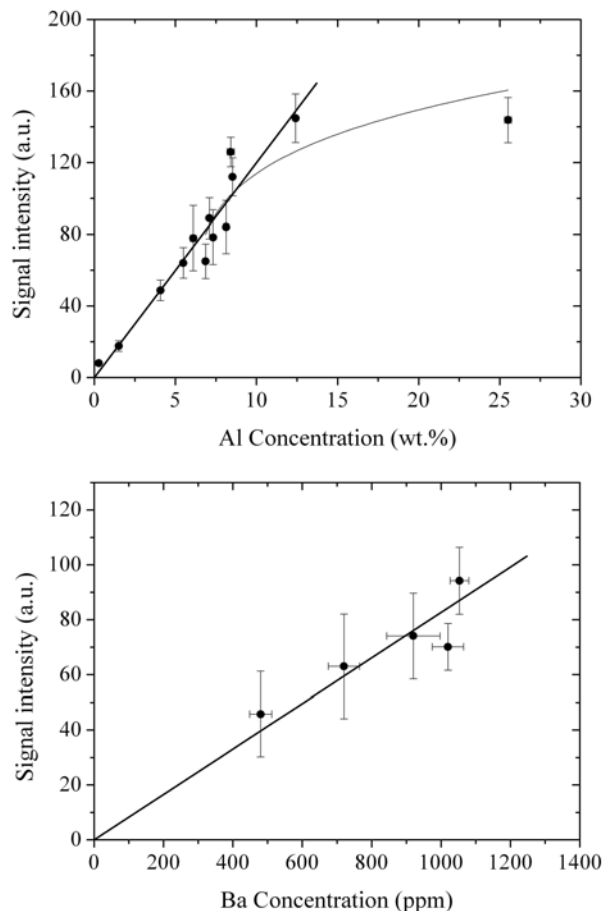


Fig. 2: Calibration curves for Al (309.2 nm) and Ba (455.4 nm) in rock, soil and stream sediment samples.

The limits of detection (LOD) obtained with the miniaturized laser were calculated according to the 3σ IUPAC criterion: $\text{LOD} = 3\sigma_B/m$ [13] with σ_B the standard deviation of the continuum background (noise) determined from the sample of lowest analyte concentration, and m the linear slope of the calibration curve. Table 1 lists selected LODs together with expected standard deviation RSD.

Conclusions: The preliminary results of our LIBS study with a miniaturized laser clearly demonstrate that the application of a light-weight LIBS instrument

for Martian surface analysis and other space applications is highly promising. Useful calibration curves were obtained with a series of certified rocks, soils and stream sediments. The resulting detection limits (a few 100 ppm) have a precision of 5–20% for most studied elements. For the further development of a miniaturized LIBS instrument applicable for space missions we next will employ a compact and light-weight spectrometer.

	LOD (ppm)	RSD (%)
Al	2 900	6 %
Ca	1 600	13 %
Mg	590	6 %
Na	700	20 %
Ti	2 200	13 %
Ba	510	9 %
Mn	1 100	5 %
Sr	410	28 %

Table 1: LIBS detection limits for selected elements obtained with the miniaturized laser prototype.

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