

Calibration and Quantification of a close-up Mini-LIBS system for planetary in-situ analysis. I. Rauschenbach¹, E. K. Jessberger¹, S. G. Pavlov², S. Schröder² and H.-W. Hübers², 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 [1–4] and other planets and moons, like Jupiter’s moon Europa [5] or the Earth’s moon [6, 7]. Since instruments for space missions are tightly limited in mass, we are developing a lightweight miniaturized close-up LIBS instrument, which will have a total mass of about 1 kg in flight-configuration and to be installed on a lander or rover for the in-situ geochemical analysis of planetary surface rocks and coarse fines [8, 9]. Here we report on a systematic performance study of a LIBS instrument equipped with a miniaturized prototype laser of 216 g total mass and an energy of 1.8 mJ. The LIBS measurements with the prototype laser and comparative measurements with a regular 40 mJ laboratory laser were both performed under Martian atmospheric conditions and we determined the Limits of Detections (LOD) and accuracies for both laser systems.

Experimental setup: To compare the performance of the miniaturized LIBS laser with the established laboratory laser, we performed all measurements with two laser systems, a laboratory Nd:YAG laser, the “lab laser”, and our new miniaturized prototype laser, the “prototype laser”. The lab laser is operated at 1064 nm with an energy of 40 mJ, 10 ns pulse width, 10 Hz repetition rate and a spot diameter of about 300 μm . The prototype laser developed by the Laserzentrum Hannover is also operated at 1064 nm with an energy of 1.8 mJ, 2 ns pulse width, 10 Hz repetition rate and a spot diameter of about 50 μm . The plasma emission was analyzed with an Echelle spectrometer equipped with an ICCD detector without amplification. For measurements with the prototype laser, the spectrometer readout was triggered prior to the laser pulse to capture the plasma emission during its entire lifetime to simulate the conditions during a space mission.

Results: Limits of Detection. We calibrated 14 major and minor elements (Si, Al, Mg, Ca, Na, K, Fe, Ti, Mn, Ba, Li, Sr, Cr and Rb) by analyzing 18 certified rock, soil and stream sediment samples. The Limits of Detection (LODs) were calculated from the achieved calibration curves by $\text{LOD} = 3\sigma_B/m$ 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. A detailed description of the applied calibration procedure and the resulting calibration curves are given in [10]. Table 1 lists the LODs together with the Relative Standard Deviations (RSDs). With the lab laser, the LODs are in the range of 10–550 ppm for major elements and above 5 ppm for minor elements with RSD values mostly below 10%. The LODs obtained with the prototype laser range from 0.15 wt.% to 2.5 wt.% for major elements and are ≥ 400 ppm for minor elements with RSDs typically below 13%. Some rare elements (Cr, Li, Rb) could not be determined with the prototype laser because the ablated sample mass is low, $< 2 \mu\text{g}$.

	Lab laser 40 mJ, 300 μm spot $\approx 20 \mu\text{g}$ sample		Prototype laser 1.8 mJ, 50 μm spot $\leq 2 \mu\text{g}$ sample	
	LOD (ppm)	RSD	LOD (ppm)	RSD
K	550	10 %	25500	10 %
Fe	490	10 %	14800	7 %
Al	190	8 %	2900	6 %
Si	160	9 %	7300	8 %
Ca	160	16 %	1570	13 %
Cr	50	7 %	n.d.	n.d.
Mn	50	8 %	1100	5 %
Ti	30	9 %	2200	13 %
Mg	20	8 %	590	6 %
Rb	20	20 %	n.d.	n.d.
Ba	15	8 %	510	9 %
Na	10	11 %	700	20 %
Li	5	8 %	n.d.	n.d.
Sr	5	8 %	410	28 %

Table 1: LIBS Limits of Detection and 1σ Relative Standard Deviations determined with two lasers of different energy.

Accuracy. To determine the accuracy of element contents measured with LIBS, we analysed with LIBS two certified standard materials which had not been used for the calibration procedure. The resulting LIBS element contents in the standard materials, andesite (GBW 07104) and basalt (GBW 07105), are shown in Fig. 1 for both LIBS laser systems in comparison to

the certified values. Altogether, the LIBS results are very close to the certified values, but there are also some deviations. For andesite, using the lab laser, there are significant deviations for Mg and Ti, and using the prototype laser, for Ca and Na. For basalt, using the lab laser, deviations are significant for Na and K, but they are moderate with the prototype laser. Up until now we have no explanation for the different behavior, aside from the speculation that despite the samples were ground to less than 90 μm grain size there are chemical heterogeneities present.

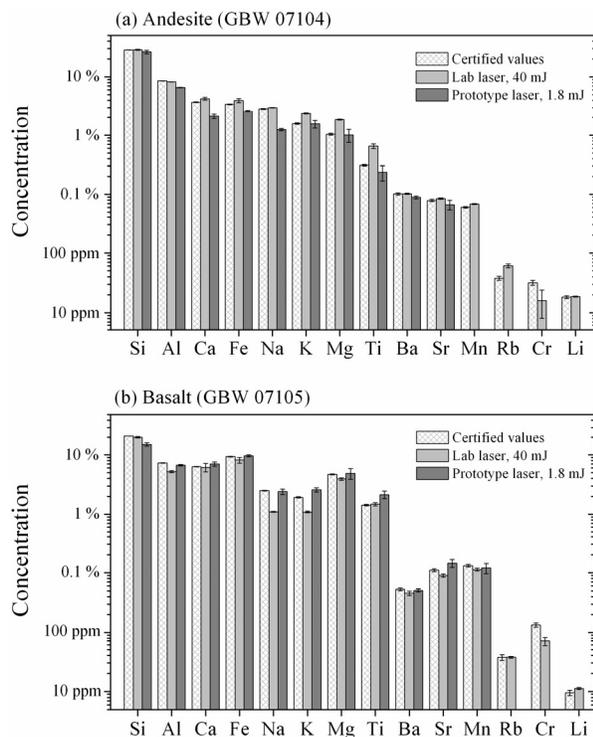


Fig. 1: Elemental concentration in andesite and basalt samples determined by LIBS with two laser systems compared to the respective certified values.

Fig. 2 shows the overall correlation between the certified values of the andesite and basalt standard samples and the element concentrations measured with both, the laboratory laser and the miniaturized prototype laser. With the laboratory laser quantitative element concentrations can be obtained over the wide range from 10 ppm to 30 wt.%, while with the prototype laser the range is from 500 ppm to 30 wt.%.

Conclusions: We calibrated 14 major and minor elements by analyzing 18 natural standard samples. The achieved detection limits are > 5 ppm for the lab laser and > 400 ppm for the prototype laser, reflecting the different analyzed sample masses of ≈ 20 μg and ≤ 2 μg , respectively. To determine the accuracy, we

compared the sample compositions of two standard samples measured with both LIBS lasers to the certified values and found agreement typically within 10–20%. This result prompts us to equate LIBS with Laser Induced Breakdown Spectrometry. In addition we verified that any dust coverage is effectively removed from rock surfaces by the laser blast [10].

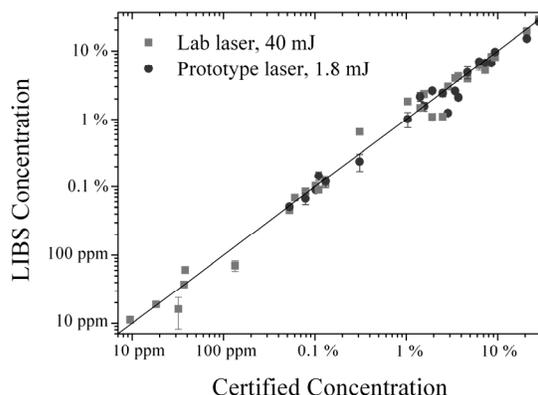


Figure 2: Element concentrations in andesite and basalt samples determined with two LIBS lasers compared to the respective certified values. 1σ error bars not shown are within the symbols.

Our study proves that significant quantitative information on the element abundances can be obtained with satisfying accuracy and sensitivity with the lightweight prototype laser that fulfils the mass requirements for space instrumentation. Our study clearly demonstrates that a miniaturized close-up LIBS instrument (spot size ≈ 50 μm) will decisively enhance the scientific output of planetary lander missions by providing a very large number of microscopic elemental analyses – each within a minute.

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