Laser Induced Breakdown Spectroscopy under Martian conditions: optimization of operating conditions.

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Introduction: The project called MALIS (Mars Analysis by Laser Induced Spectroscopy) aims at performing high accuracy in situ geochemical analyses of Martian soils and rocks toward the end of the decade. This presentation reports on the statistical procedure performed to achieve optimization of Laser Induced Breakdown Spectroscopy (LIBS) under Martian conditions.

In the LIBS technique a pulsed laser beam is focused on the sample surface and creates a plasma that emits spectral lines which are characteristic of elements embedded in the sample. LIBS technique has many advantages, especially a remote capability up to 20 meters and a rapid analysis time (a few minutes).

Due to space requirements in terms of size, weight, available power, and telemetry, it is important to characterize the method for optimum performance [1-4]. To determine optimum operating conditions for accurate and reliable analyses of Mars soils and rocks, we used a Doehlert matrix design for the optimization scheme [5]. Following this, a spectral database for LIBS under Martian conditions is being built in the optimized operating conditions.

Experimental Setup: The experimental setup, made with commercial components, is depicted in [6]. The main compounds are: a Nd:YAG laser (pulse width 5 ns and repetition rate 10 Hz; Quantel, France), a sample cell with CO_2 at Martian pressure range (5-12 mbar), an optical fiber for signal return in the direction of the laser beam and an echelle spectrometer (ESA 3000, LLA, Germany). The spectrometer ranges from 200 to 780 nm with a resolution of 10,000. The signal detection device is an ICCD camera with a measurement gate (temporal resolution). We tuned the laser beam energy to simulate the laser output values expected for a compact device on Mars: energy consumption being strictly limited, for space application we consider as a maximum of 40 mJ at 1064 nm. Therefore, the maximum energy available will be 20 mJ at 532 nm and 10 mJ at 355 nm.. For statistical experimental design achievement, the working distance was fixed at 1 m. Another study [6] deals with varying the distance to the target.

Doehlert matrix design: Signal intensity of the plasma emission depends on many parameters such as laser wavelength, angle of incidence of the incident beam, delay and duration of the measurement gate after the laser pulse, nature and pressure of the surrounding gas, number of laser shots and sample surface characteristics. An optimization procedure based on a statistical design of experiments was chosen to deal with such a number of factors. Indeed a conventional experimental method consisting in varying the parameters one by one i) is really time consuming and ii) does not account properly for interactions between variables. Experimental designs based on statistical methods have already been used in ICP/AES techniques [7-8].

Non-relevant factors: In the first step, we used a screening design in order to eliminate factors with little or no effect. The nature of surrounding gas (CO_2 or air) under Martian pressure showed no influence on LIBS signal. The number of laser shots is determined by the characteristics of the laser to be used on Mars and the measurement gate duration has to remain inferior to the plasma lifetime, previously determined to be less than 3 µs at Martian pressure [2].

Determination of the Doehlert matrix: In the second step, a Doehlert design was built with the remaining four factors: laser energy, gate delay after the laser pulse, angle of incidence and pressure of CO_2.

Much attention was focused on the laser energy used in these experiments. Because the laser energy depends on laser wavelength, we chose to test the 3 wavelengths independently (each of them up to the maximum energy available on Mars): we performed 3 independent sets of Doehlert designs, one for each wavelength. As the angle of incidence cannot be controlled in the case of in-situ analysis, the influence of this factor has to be taken into account [9]. The experimental design with 4 factors was built from the Doehlert matrix previously described in literature [10]. The first sample studied was a glass (33 % Si, 9.9 % Na, 7.4 % Ca, 1.6 % Mg, 1 % Al, 46.3 % O). Each experiment was repeated 5 times. Since 3 wavelengths were independently tested, 315 planned experiments were performed in this second step.

Results: The results, in term of peak height for two spectral lines Mg (II) at 279.553 nm and Ca (I) at 422.673 nm, have been processed using the STATISTICA software [11]. The two selected lines were found without self-absorption in previous works ([1] for Ca line and [12] for Mg line).

A pareto diagram is used to outline the factors with the most important effect on the LIBS signal. The results obtained for each wavelength (for 279.553 nm Mg line) are shown in figure 1: the interaction effects are noted by * and the quadratic effects are mentioned by “quadra”. At 1064 nm, the ANOVA results for Mg II line show that pressure presents no significant interaction with any other factors, in the domain corresponding to Mars atmosphere conditions. The results for Ca I line demonstrate that pressure has no significant linear influence. For the Mg II line, all the factors present significant quadratic effects, while there are no quadratic effect for Ca I line. Therefore, the influence and interactions of parameters are different for an atomic spectroscopic line and an ionic line. The same study, performed on a second sample (a boninite from New Caledonia) showed similar trends.

Conclusions: From these designed experiments and their statistical analysis, we determined the best operating conditions for in situ LIBS analysis on Mars: i) 1064 nm laser wavelength, ii) maximum energy available, iii) gate delay as short as possible taking into account self-absorption effect (200-300 ns), iv) angle of incidence less than 50 °. Analysis for two types of spectroscopic lines, atomic line from Ca and ionic line from Mg, showed different behavior: this effect must be taken into account in the selection of lines for LIBS analysis.

Elaboration of a spectral database: As an example, figure 2 shows two spectral ranges of a boninite spectrum at working distance of 5 m (composition is 28.1 % Si, 9.2 % Mg, 6 % Fe, 5.4 % Al, 2.6 % Ca, 1.5 % Na). From the study above the operating conditions are: 1) wavelength 1064 nm, 2) energy 40 mJ, 3) delay of 200 ns, 4) normal incidence. The CO_2 atmospheric pressure is 7 mb. The recording duration is 2500 ns. The exposure time for the ICCD is 6 sec. Complete database will allow selection the most sensitive spectral lines for the elements of interest, taking into account possible interference and self-absorption.

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Figure 1 - Pareto chart for Mg II peak height (279.553 nm).

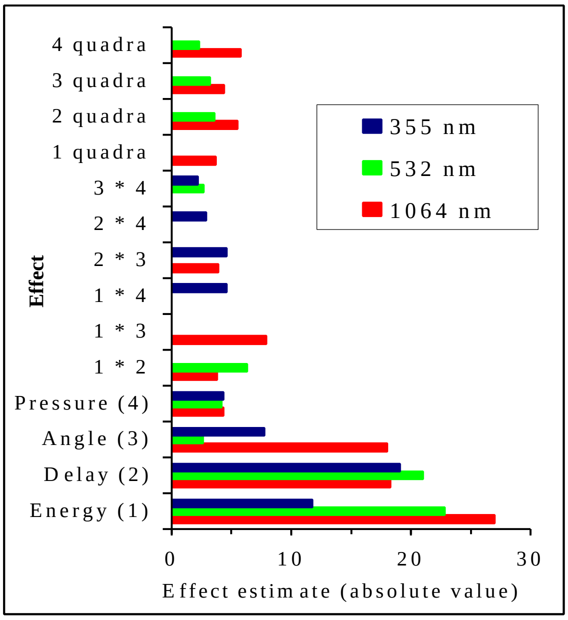
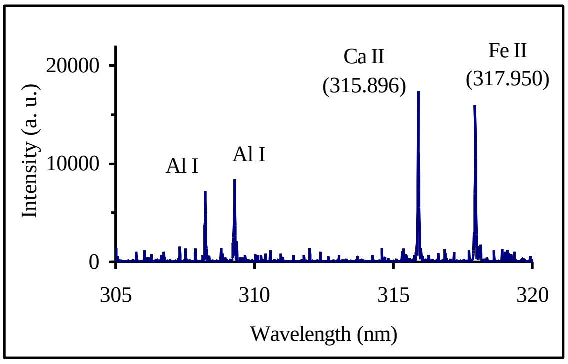


Figure 2 - Spectrum of boninite at 5 meters.

a) range 305 - 320 nm



b) range 278 - 281 nm