

Identifying perchlorates under Mars conditions in soil samples and in frozen solutions using LIBS.

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Introduction: For the investigation of geological surfaces in particular for extraterrestrial exploration laser-induced breakdown spectroscopy (LIBS) has been suggested as a powerful analytical tool. With the ChemCam instrument on the Mars Science Laboratory (MSL) [1] to be launched in 2011 the LIBS technique will be applied for the first time for in-situ analysis on a planetary mission. Other missions with LIBS instruments are suggested [2, 3, 4]. To obtain the chemical composition of rock, soil and maybe frozen samples with LIBS on Mars qualitative and quantitative analytical methods have been developed and improved by a number of studies. One attempt to compensate for matrix effects and other factors that influence the plasma's composition and properties and therefore the LIBS spectra are multivariate analysis (MVA) methods, see e.g. [5]. In this study the focus was on the question whether with LIBS and principal component analysis (PCA) perchlorates can be distinguished from chlorides with metal atoms of the same kind, here sodium and magnesium. Perchlorates and chlorides as well as the cations Mg^{2+} and Na^+ have been found in Martian soil at the Phoenix lander site [6]. Furthermore, they appear in form of frozen salt solutions [7]. These can also be investigated using the LIBS technique as shown previously [8, 9].

Experimental and Samples: LIBS permits rapid multi-elemental analysis and relies on ablating material from the sample by focusing a pulsed laser onto its surface. This produces an expanding plasma of atoms, ions, and electrons. The emitted photons, which feature characteristic wavelengths of the elements composing the sample, are collected and analyzed spectroscopically.

In this laboratory study an infrared Nd:YAG laser was used to generate the plasma at short stand-off distances ($< 1m$): 1064 nm wavelength, up to 220 mJ pulse energy, 8 ns pulse duration, 10 Hz repetition rate. The plasma emission was detected with an echelle spectrometer with a time-gated intensified CCD enabling a continuous coverage from 280 nm to 900 nm. The samples were placed in a dedicated simulation chamber, wherein pressure and temperature range are variable. Measurements were performed simulating a Martian environment with an appropriate gas mixture com-

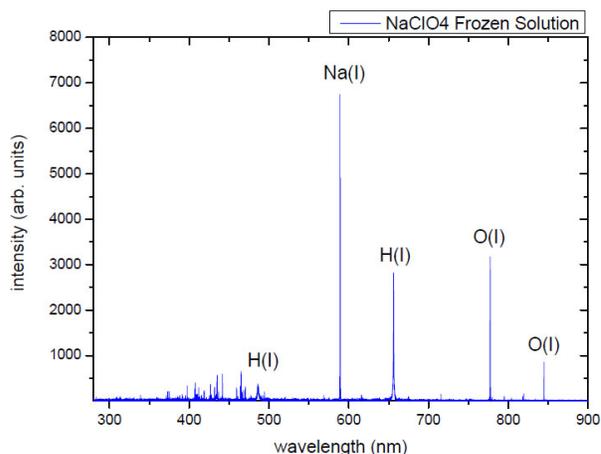


Figure 1: LIBS spectrum of frozen NaClO₄ water solution taken under Martian conditions.

posed of 95.55% Vol. CO₂, 2.7% Vol. N₂, 1.6% Vol. Ar, and 0.15% Vol. O₂ at 6 mbar.

Two sample sets with magnesium perchlorate Mg(ClO₄)₂ and sodium perchlorate NaClO₄ were prepared as follows. In a first test series the perchlorate salts were mixed with JSC Mars-1A Martian Regolith Simulant (MRS) and compressed into pellets containing about 2 wt% of the pure salt. 1 g of the soil mixture was pressed at 5 tons to pellets with a diameter of 14 mm. Moreover, pellets were prepared with the same amount of MgCl₂ and NaCl salt, each, as well as a pellet consisting of pure MRS. A second test series was done with the perchlorates and chlorides in frozen water solutions with salt concentrations of approx. 2 wt%. To minimize inclusions of air, the solutions were degassed before freezing. The ices were cooled to a temperature of 200 K by feeding liquid nitrogen into the mounting; this temperature was kept constant throughout the measurement.

The laser energy was attenuated to 50 mJ by a grey filter. The laser beam spot with a diameter of about 300 μm was focused at a new position for each measurement. 40 spots were probed on the pressed samples and 20 laser shots were accumulated. 20 spots were probed on the frozen salt solutions.

Data Analysis and Results: The LIBS data was analyzed qualitatively using the MVA method PCA, where

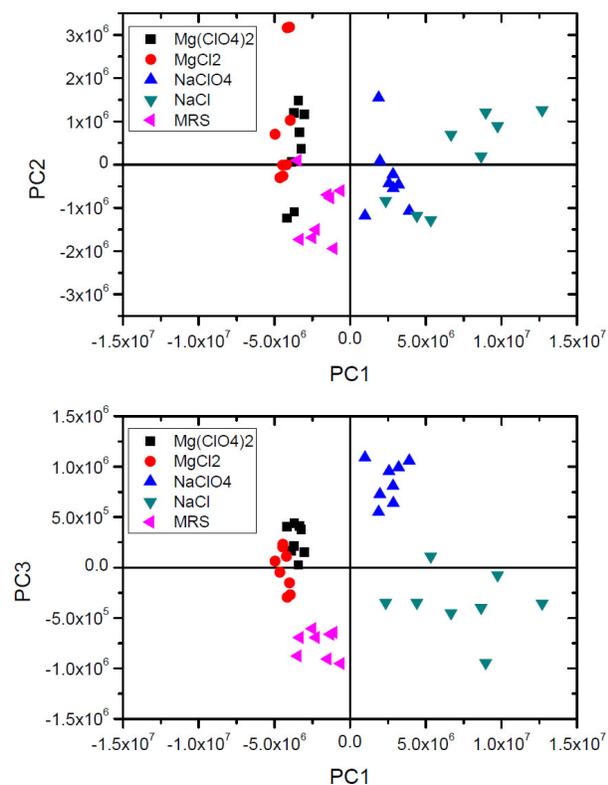


Figure 2: Principal component analysis plots of LIBS data of $\text{Mg}(\text{ClO}_4)_2$, MgCl_2 , NaClO_4 and NaCl mixed and pressed with Mars JSC 1A analogue material and a pure sample (MRS). Shown are the plots of the first with the second PC (top) and first with third PC (bottom).

the spectra are sorted due to their similarities and variabilities. Uncorrelated variables called principal components (PCs) replace a bigger number of correlated variables in the data and similar spectra cluster in the space defined by the PCs. All spectra were rebinned before analysis, reducing a total of more than 32000 bins to about 6500, which is the number of initial variables entering the analysis. It was found that this rebinning has no effect on the quality of the PCA but reduced computing time. Moreover, the average of five spectra was used in case of the pressed samples, while four spectra were averaged in case of the frozen salt solutions. For the PCA of the pressed samples as well as for the frozen solutions a much better clustering of spectra of the same kind was found when variables were preselected i.e. only certain elemental lines of the spectra were used. The spectra of the pellets, which mainly consist of the the Martian analogue material MRS, are dominated by the known spectral lines such as Ca, Al and Fe. However, to distinguish

between the salts and in particular to distinguish perchlorates from chlorides Na, Mg, H and O lines were found to be most important. The first two principal components PC1 and PC2 separated spectra of samples with sodium salts from those with magnesium, spectra of MRS without additional salt appeared closer to the latter. Considering PC3 a good separation and clustering at least for the case of the sodium salts can be found in the PCA plots (Fig. 2). Also in case of the frozen solutions a pre-selection of variables improved the PCA outcome (Fig. 3). Spectra of the same salt solution cluster when PC1 is plotted against PC2. The strongest chlorine line, which is at 837.6 nm concerning this laboratory set-up, was not strong enough to influence the PCA, neither in case of the pressed samples nor for the frozen solutions.

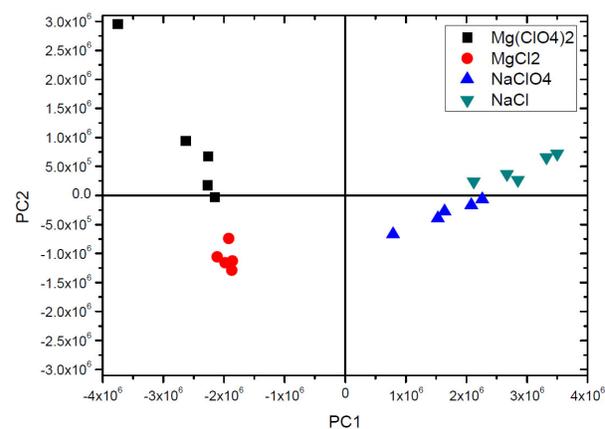


Figure 3: PCA graph of LIBS data of frozen chloride and perchlorate water solutions.

Conclusion: Although this is an initial study the results show that it is feasible with LIBS to analyze and classify samples of similar salts in pellets of Martian regolith simulant and even in frozen water solutions. Further experiments will be done varying the compositions of the samples and having salts of different kind in the same samples.

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