

LIBS studies of ferric salts in frozen solutions under Martian conditions. S.

Schröder¹, S. Pavlov¹, H.-W. Hübers^{1,2} and E. K. Jessberger³, ¹Institut für Planetenforschung, Deutsches Zentrum für Luft- und Raumfahrt (DLR), Berlin, ²Institut für Optik und Atomare Physik, Technische Universität Berlin, ³Institut für Planetologie, Westfälische Wilhelms-Universität Münster

Introduction: Laser-induced breakdown spectroscopy (LIBS) is a promising analytical tool for the geochemical investigation of surfaces and soil in particular for extraterrestrial exploration. With the ChemCam instrument on the NASA Mars Science Laboratory (MSL), which will arrive on Mars in summer 2012, the LIBS technique will be applied for in-situ analysis on a planetary mission for the first time. Additionally other missions with LIBS are proposed for instance for Venus or the Moon, e.g. [1, 2]. To optimize the scientific return with LIBS, i.e. to most precisely obtain the elemental composition of rock, soil and possibly frozen samples with LIBS, qualitative and quantitative methods for data analysis have been developed and improved by a number of studies. One valuable 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. [3]. This study investigates the potential of LIBS for identifying ferric salts (FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$) when pressed into pellets and in frozen salt solutions utilizing partial least squares discriminant analysis (PLS-DA). Ferric salts are considered in the context of possibly existing liquid brines on Mars and are moreover of particular interest for (astro-) biology in view of possible extraterrestrial life since iron is an essential component of life as we know it. Ferric sulfates have been found on Mars at various locations such as jarosite in Meridiani Planum [4] and in soils in Gusev Crater [5, 6]. Chloride bearing salts were also identified in deposits on the southern hemisphere [7]. On Mars these salts could also appear in form of frozen salt solutions [8] which can be investigated using the LIBS technique as shown previously [9, 10].

Experimental and Samples: LIBS is an emission spectroscopy technique and permits rapid multi-elemental analysis with little or no sample preparation in distances of up to several meters. It relies on ablating material from the target by focusing radiation from a pulsed laser onto the sample's surface. Sufficient laser energy enables the production of a small luminous plasma of atoms, excited ions, and simple molecules. Information about the elemental composition is obtained due to specific atomic or ionic transitions and the appropriate emanating photons resulting in characteristic spectral lines. An infrared Nd:YAG laser (1064 nm wavelength, up to

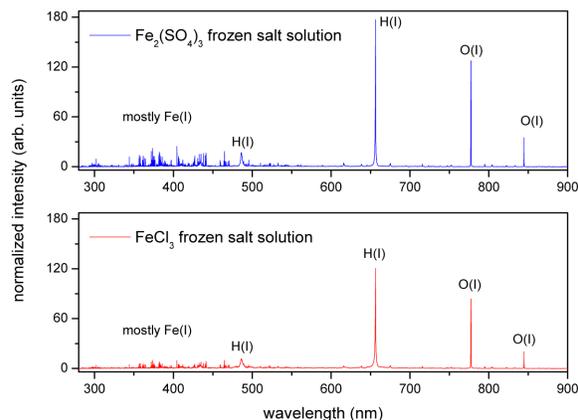


Figure 1: LIBS spectra of a frozen $\text{Fe}_2(\text{SO}_4)_3$ (top) and FeCl_3 (bottom) water solution taken under Martian atmospheric conditions.

220 mJ, 8 ns pulse duration, 10 Hz repetition rate) generated the plasma at distances < 1 m. The plasma emission was detected equipped 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 Martian atmospheric conditions with an appropriate gas mixture composed of 95.55 % Vol. CO_2 at a pressure of 7 mbar. The ferric salts $\text{Fe}_2(\text{SO}_4)_3$ and FeCl_3 were investigated, both, as a pure pressed pellet and in a frozen salt solution. The pressed salt samples with a diameter of 14 mm consisted of 1 g of the pure salt each and were pressed at 5 tons. The ice samples were prepared with the appropriate salt in a solution with salt concentrations of circa 2 wt %. To prevent little 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 ices differed slightly in consistency due to dissimilar eutectic properties and featured small variations in color and opacity. The laser energy was attenuated to 35 mJ by a grey filter and the laser beam spot with a diameter of about $300 \mu\text{m}$ was focused at a new position for each measurement. For each spectrum the emission of 20 laser-induced plasmas was accumulated and 20 spots per sample were probed.

Data Analysis and Results: The LIBS spectra of the pressed salts are very similar and even the strongest lines of chlorine and sulfur are weak in comparison to the strong iron lines in this spectral range, making a distinction of the chloride from the sulfate difficult but not impossible. The most intense lines of both elements were identified using the spectra of the pressed salts. For both ice samples spectra like those shown in Fig. 1 were obtained. Typical features are the intense hydrogen, oxygen and iron lines, whereas chlorine and sulfur are hardly detectable.

The LIBS data was then analyzed using the MVA method PLS-DA. This technique is supervised and focuses on class separation, where the class membership of a sample is known in advance. Latent variables (LVs) replace a bigger number of correlated variables in the data and are derived taking into account both, spectral variance and information about class affiliation. A model was calculated with half of the spectra of each frozen salt solution, the remaining half was used as test set, comprising the "unknown samples". All spectra were rebinned before analysis, reducing the number of initial variables entering the analysis by a factor of five. It was found that this rebinnig has no effect on the PLS model but reduces computing time. Fig. 2 shows the data used for building the model with the projected test set superimposed in the space defined by the first two LVs, where each point represents one LIBS spectrum. Spectra of $\text{Fe}_2(\text{SO}_4)_3$ are widely spread, indicating a more heterogeneous sample in comparison to the FeCl_3 ice. The first LV is correlated mainly with hydrogen and oxygen, for the second LV many iron lines are of importance. It was found that in order to distinguish between both ferric salts a detection of the weak sulfur and chlorine lines is not necessarily required. To a greater degree the essential information is given by the oxygen and hydrogen lines, their amplitudes but moreover their shape as well (modified e.g. by broadening mechanisms), thus comprising additional information about the sample such as consistency and transparency. With the PLS-DA model the test set was then interpreted with regard to class affiliation, the results allowing for the first four LVs are shown in Fig. 3. A value of 1 corresponds to class affiliation to $\text{Fe}_2(\text{SO}_4)_3$ while 0 corresponds to FeCl_3 , good discrimination is obtained when the errors are not overlapping. As can be seen a distinction between both ferric salts can be obtained for almost all spectra.

Conclusion: LIBS is capable of investigating pure salts and frozen salt solutions. Although lines of sulfur and chlorine are hardly detectable in the LIBS spectra of

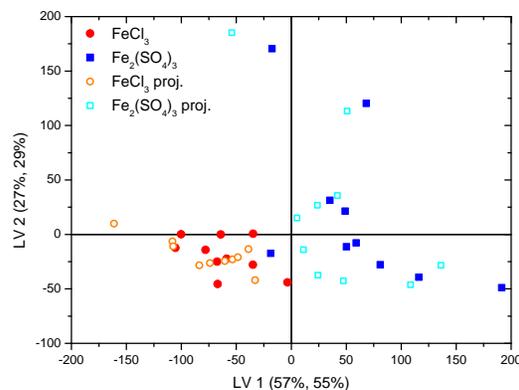


Figure 2: PLS-DA scatter plots with projected "unknown samples" in the space defined by the first two latent variables (LVs).

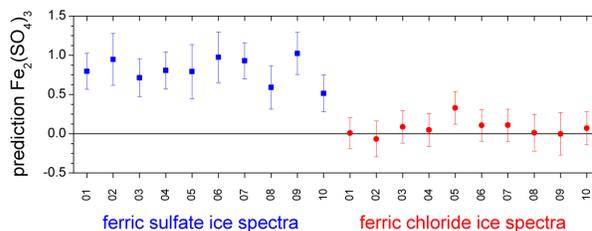


Figure 3: Prediction from PLS-DA model for both ferric salts using four latent variables.

the ices, the ferric chloride can be distinguished from the ferric sulfate on the basis of other lines such as hydrogen and oxygen by applying MVA methods.

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