

QUANTIFICATION OF SALT ANIONS USING LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS). D. E. Anderson¹, B. L. Ehlmann^{1,2}, and S. Clegg³, ¹Division of Geological & Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA (deanders@caltech.edu), ²Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA, ³Los Alamos National Laboratory, NM, USA.

Introduction: Curiosity continues to sample the surface of Mars using its onboard laser-induced breakdown spectroscopy (LIBS) instrument, ChemCam. The instrument ablates the target surface with a laser pulse resulting in the generation of a plume of plasma. Emission produced from the cooling plasma contains continuum, atomic, ionic, and, potentially, as atoms begin to recombine, molecular spectra that together reveal the elemental composition of the sample. Since ionization is required for detection, the LIBS technique is less sensitive to elements with higher ionization energies. Therefore, whereas many cations can be readily identified, distinguishing salts through the measurement of elements such as C, S, and Cl can be challenging. Quantification of these elements in Martian samples requires thorough laboratory work in order to develop appropriate calibration methods, which are often dependent on the LIBS experimental conditions.

In our laboratory study, we aim to identify elemental emission peaks that are capable of providing reliable quantitative information about salt anions such as carbonates, sulfates, and chlorides. Expanding upon previous work by members of the ChemCam team on the emission features of pure elements and compounds [e.g. 1, 2], we elected to analyze mixtures of salt and basalt powders to elucidate the consequences of matrix effects and to create calibration curves using mixtures containing different salt concentrations. In the future, we intend to apply the knowledge gained from our results to a quantitative analysis of salt anions in the ChemCam dataset.

Method: A selection of rock samples and reagents chosen for their relevance to the Martian surface, including carbonates, sulfates, and chlorides (listed in Table 1) in addition to two basalt samples (K1919 and GBW07105, the latter being higher in alkali elements), were processed into powders by crushing and shatter-boxing. The salt and basalt powders were physically mixed at concentrations of 5, 10, 30, 50, 70, and 100 wt % salt to enable the production of calibration curves. For the second sample-set a very low concentration of 0.5 wt % salt was also tested.

LIBS analysis of the mixtures was performed under Mars conditions using the ChemCam-analogue instrument at Los Alamos National Laboratory. The powder samples were pressed into pellets and each pellet was shot with 50 laser pulses in 5 locations on the sample surface. Emission collected spans wavelengths from

240–900 nm. An independent elemental analysis was performed by Activation Laboratories Ltd. on a subset of the mixture samples to verify their compositions.

Table 1: Mixtures, each salt paired with one of two basaltic backgrounds, used in this work

Basalts		Chlorides	Carbonates	Sulfates
K1919	+	CaCl ₂	CaCO ₃	CaSO ₄ ·2H ₂ O
		NaCl	MgCO ₃	Fe ₂ (SO ₄) ₃
				MgSO ₄
				Na ₂ SO ₄
GBW07105	+	NaCl		CaSO ₄ ·2H ₂ O

Data Analysis. Pre-processing of the data included a background spectrum subtraction, denoising, global continuum removal, and the application of an instrument response function [3]. We are not currently applying any normalization to our spectra. Further analysis was performed on elemental emission lines of C, S, and Cl from the NIST [4] and Martian databases [1]. Emission lines were fit with a combination of Lorentzian functions with an underlying linear local continuum using the nonlinear least squares Levenberg-Marquardt algorithm. Using these fits to the mean spectra of all 250 laser pulses, the emission line areas were computed.

Calibration curves of average emission line area vs. mole fraction of element were created. An example is shown in Figure 1 for the 837.8-nm Cl I peak. Using these curves in addition to the LIBS spectra for the three chloride mixtures, a selection of lines were identified for their ability to provide quantitative information about chlorine in the sample. These lines were chosen based on the following criteria: (1) the emission line was successfully modeled with a Lorentzian function, (2) the area of the emission line increased for increasing concentrations of chloride salt as indicated visually by the spectra and quantitatively by a positive slope in the calibration curve, (3) the calibration curve exhibited predictable behavior (currently taken to mean linearity with an R² value greater than 0.9), and (4) the emission line behavior was not influenced by direct overlap with an emission line from the corresponding salt cation or the basaltic matrix.

Results: Chlorine emission lines that satisfied the above criteria are listed in Table 2. The columns of the table provide a comparison between the three chloride

mixtures from this study, revealing differences in matrix effects between salts with different cations (e.g., Na vs. Ca, see Figure 2) and between different basaltic backgrounds (NaCl in K1919 vs. GBW07105). The final two columns show chlorine lines that were identified in the literature as being most useful for further LIBS analysis [1, 2]. The selected lines vary depending on the composition of the laboratory samples analyzed. The more robust chlorine lines, which are identified in multiple samples despite the various interference effects due to different sample compositions, will be the most effective for the detection of chlorine in materials of unknown composition on Mars.

Table 2: Chlorine emission lines identified as being most useful for further LIBS analysis using mixtures from this work in comparison to previous studies [1, 2]. Green shaded lines may be most important in analysis of the Mars dataset.

λ (nm)	CaCl ₂ (K1919)	NaCl (K1919)	NaCl (GBW)	Cousin et al.	Schröder et al.
268.9	✓				
310.5				✓	
385.2		✓			✓
386.1					✓
426.6				✓	
479.5					✓
481.0					✓
481.9					✓
489.7					✓
507.9				✓	
510.1	✓				
521.9		✓		✓	✓
539.4	✓	✓	✓		✓
542.5	✓	✓	✓		✓
544.5	✓	✓			✓
545.9	✓	✓			✓
725.9	✓	✓			✓
754.9	✓	✓	✓		
771.9				✓	
792.7	✓				
809.1	✓				
822.4	✓				
833.6		✓			✓
837.8	✓	✓	✓	✓	✓
842.8					✓
858.8	✓	✓			
904.1		✓			

Ongoing & Future Work: Further testing of how the data processing steps and the line selection criteria affect the results will be performed. Similar analyses will also be completed on the carbonate and sulfate mixtures listed in Table 1. These results will be compared to previous work by members of the ChemCam

team on carbon [5] and sulfur [6] lines to identify the most reliable lines for quantitative analysis of these elements. Collectively, the results of the analysis of these mixtures will build upon previous work on the C, S, and Cl elemental lines to reveal a selection of lines that are best suited for detection and quantitative analysis of carbonates, sulfates, and chlorides in Martian samples using ChemCam.

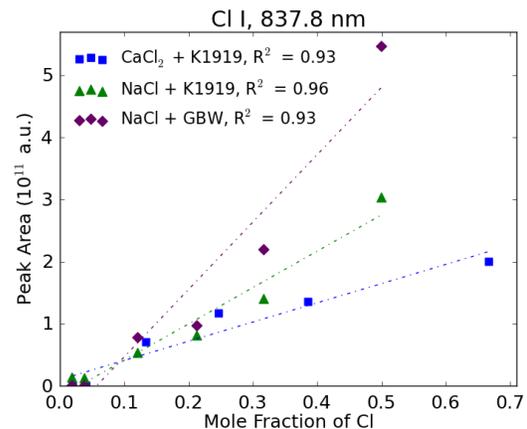


Figure 1: Calibration curves for Cl I emission line at 837.8 nm in the three chloride mixtures analyzed in this work

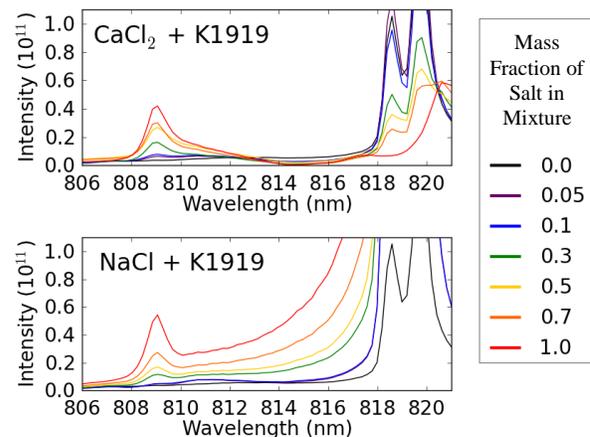


Figure 2: Chlorine peak due to a set of Cl I emission lines at 808-809 nm in mixtures of CaCl₂ or NaCl with K1919. In the NaCl & K1919 case, the nearby Na I emission lines at 818.6 & 819.7 nm contribute to the 809-nm Cl peak, altering its shape in comparison to that in the CaCl₂ & K1919 mixture.

Acknowledgements: Thanks to Rhonda McInroy for running of samples at LANL and to the ChemCam team for advice on data processing.

References: [1] Cousin, A. et al. (2011) *Spectrochim. Acta B*, 66, 805–814. [2] Schröder, S. et al. (2013) *Icarus*, 223, 61–73. [3] Wiens, R. C. et al. (2013) *Spectrochim. Acta B*, 82, 1–27. [4] Ralchenko, Y. et al. (2011) *NIST Atomic Spectra Database* (v.4.1.0), <http://physics.nist.gov/asd> [5] Ollila, A. M. (2011) *LPS XLII*, 2395. [6] Dyar, M. D. et al. (2011) *Spectrochim. Acta B*, 66, 39–56.