

A COMPARISON OF MULTIVARIATE AND PRE-PROCESSING METHODS FOR QUANTITATIVE LASER-INDUCED BREAKDOWN SPECTROSCOPY OF GEOLOGIC SAMPLES R. B. Anderson¹, R.V. Morris², S.M. Clegg³, J.F. Bell III^{1,4}, S. D. Humphries³, R. C. Wiens³, ¹Cornell University, Department of Astronomy, Ithaca, NY 14850 (randerson@astro.cornell.edu), ²NASA Johnson Space Center, 2101 NASA Parkway, Houston, TX 77058, ³Los Alamos National Laboratory, P.O. Box 1663 MS J565, Los Alamos, NM 87545, ⁴ Arizona State University School of Earth and Space Exploration, PO Box 871404 Tempe, AZ 85287

Introduction: The ChemCam instrument selected for the Curiosity rover is capable of remote laser-induced breakdown spectroscopy (LIBS). [1] We used a remote LIBS instrument similar to ChemCam to analyze 197 geologic slab samples and 32 pressed-powder geo-standards. The slab samples are well-characterized and have been used to validate the calibration of previous instruments on Mars missions, including CRISM [2], OMEGA [3], the MER Pancam [4], Mini-TES [5], and Mössbauer [6] instruments and the Phoenix SSI [7].

The resulting dataset was used to compare multivariate methods for quantitative LIBS and to determine the effect of grain size on calculations. Three multivariate methods - partial least squares (PLS), multilayer perceptron artificial neural networks (MLP ANNs) and cascade correlation (CC) ANNs - were used to generate models and extract the quantitative composition of unknown samples. PLS can be used to predict one element (PLS1) or multiple elements (PLS2) at a time, as can the neural network methods. Although MLP and CC ANNs were successful in some cases, PLS generally produced the most accurate and precise results.

Experimental: A 1064 nm Nd:YAG laser, pulsed at 10 Hz and 17±1 mJ per pulse was used to analyze the samples at a distance of 6.92 m in a vacuum chamber filled with 7 Torr CO₂ to simulate martain surface pressure. The LIBS emission was collected with an 89 mm telescope directed to three Ocean Optics spectrometers covering most of the 240 – 800 nm range. A demultiplexer similar to the one on ChemCam was used to simultaneously monitor all three spectral ranges. Each spectrum represented 50 laser shots and at least 5 separate spots were analyzed per sample.

Multivariate Methods: The oxide weight percents were converted to atomic fractions prior to all calculations, since the intensity of emission lines in the LIBS plasma is sensitive to atomic fraction [8]. Observations were converted back to oxide weight percent for ease of interpretation by assigning an appropriate amount of oxygen to each cation and normalizing the total composition to 100 percent, assuming that all Fe is in the form Fe₂O₃ and that the samples contain no P₂O₅, CO₂, SO₃, or H₂O. The low-volatile silicate samples were sorted by SiO₂ content and alternately assigned to a training set and a test set for use with the three calibration methods. A subset of samples was removed from the test set and used as a validation set.

Neural networks have been shown to perform better than PLS on doped soils with significant non-linearities in the signal. [9] A genetic algorithm (GA) was employed to optimize the number of hidden nodes in the MLP network for each prediction. CC ANNs, an alternative type of neural network that determine their own structure as they are trained [10], were also tested, using the FannTool graphical interface to the open-source Fast Artificial Neural Network (FANN) library [11].

In addition to testing the methods using the full LIBS spectrum, an open-source GA [12] was used to perform feature selection on the input spectra. Feature selection identifies variables that are “most informative” for the calibration, which simplifies the model, reduces computation time, and can improve the predictive ability. [13] In most cases, the five GA-selected wavelengths corresponded to strong emission lines for the element of interest. The three multivariate methods were also compared after averaging all spectra in the training set for samples with identical composition. This spectral averaging was applied alone and in conjunction with feature selection.

Results: We demonstrated that PLS2 is successful with natural rock slab samples (Figure 1), with an average relative SiO₂ error of ~4.7% for igneous rock samples when trained with the full training set and ~4.5% when trained only on igneous rocks in the training set. The calculated composition of unusual samples such as banded iron formation and silcrete were less accurate than silicate rocks with an average relative SiO₂ error of ~21% when trained only on igneous rocks. Including additional samples in the training set reduced the RMSE for unusual samples to ~11%.

We calculated the root-mean-squared error (RMSE) of each method (PLS, MLP and CC) for each of the major elements and each combination of averaging and preprocessing (Figure 2). We also calculated an overall RMSE for each method by taking the square root of the sum of the MSEs for each major oxide. We used a Student's-t test to assess the statistical significance of the differences between methods [14]. PLS1 with feature selection and averaging had the lowest RMSE for seven of the ten major elements considered, and PLS2 using the full spectrum had the lowest overall RMSE. However, all of the PLS results, as well as MLP using the full spectrum and CC using feature selection and spectral averaging were statistically equivalent at the

