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Title:

SINGLE VARIABLE AND MULTIVARIATE ANALYSES OF REMOTE LASER-INDUCED BREAKDOWN SPECTRA FOR PREDICTION OF RB, SR, CR, BA, AND V IN IGNEOUS ROCKS

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SINGLE VARIABLE AND MULTIVARIATE ANALYSES OF REMOTE LASER-INDUCED BREAKDOWN SPECTRA FOR PREDICTION OF RB, SR, CR, BA, AND V IN IGNEOUS ROCKS.

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Introduction: Laser-induced breakdown spectroscopy (LIBS) will be employed by the ChemCam instrument on the Mars Science Laboratory rover *Curiosity* to obtain UV, VIS, and VNIR atomic emission spectra of surface rocks and soils. LIBS quantitative analysis is complicated by chemical matrix effects related to abundances of neutral and ionized species in the resultant plasma, collisional interactions within plasma, laser-to-sample coupling efficiency, and self-absorption [1]. Atmospheric composition and pressure also influence the intensity of LIBS plasma. These chemical matrix effects influence the ratio of intensity or area of a given emission line to the abundance of the element producing that line [1].

To compensate for these complications, multivariate techniques, specifically partial least-squares regression (PLS), have been utilized to predict major element compositions (>1 wt.% oxide) of rocks [1,2]. PLS methods regress one or multiple response variables (elemental concentrations) against multiple explanatory variables (intensity at each pixel of the spectrometers). Because PLS utilizes all available explanatory variable and eliminates multicollinearity, it generally performs better than univariate methods for prediction of *major* elements [1,2]. However, peaks arising from emissions from *trace* elements may be masked by peaks of higher intensities from major elements. Thus in PLS regression, wherein a correlation coefficient is determined for each elemental concentration at each spectrometer pixel, trace elements may show high correlation with more intense lines resulting from optical emissions of other elements [1]. This could result in error in predictions of trace element concentrations.

Here, results of simple linear regression (SLR) and multivariate PLS-2 regression for determination of trace Rb, Sr, Cr, Ba, and V in igneous rock samples are compared. This study focuses on comparisons using only line intensities rather than peak areas to highlight differences between SLR and PLS.

Methods: A suite of 100 igneous rock samples was analyzed by LIBS at Los Alamos National Laboratory using methods and samples described in [2]. Wavelength calibration was performed for each spectral region, and the wavelength scale was standardized for all spectra. Analyses for each sample were averaged and smoothed before the baseline was modeled and subtracted. An additional step of normalizing intensity at each pixel to total spectral intensity was performed to compensate for fluctuations in laser power between samples.

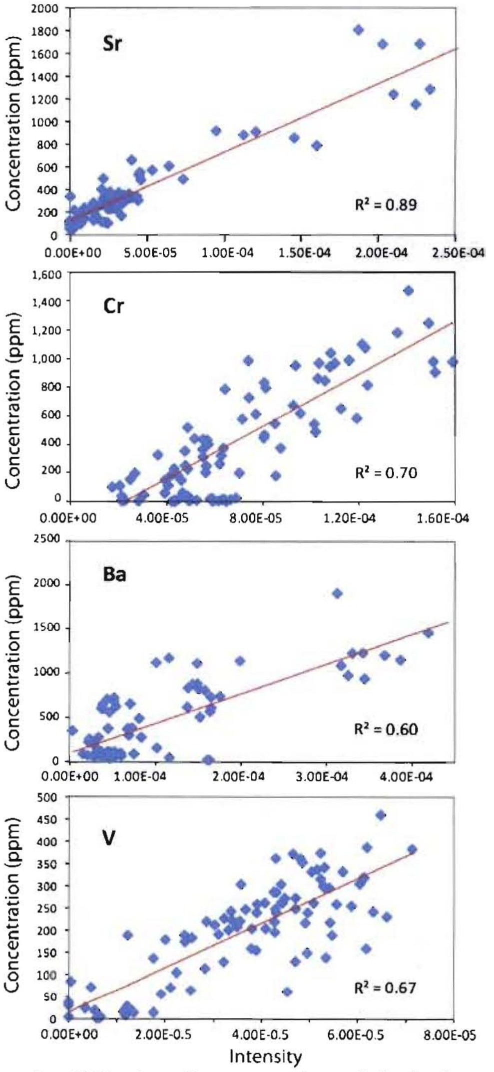

Figure 1. SLR plot of concentration of single lines selected for optimal predictions of Sr, Cr, Ba, and V plotted vs. intensity. This analysis uses only a single channel's intensity; dramatic improvements in prediction sare expected when peaks areas rather than single-pixel magnitudes are used (work in progress), as was shown for S peaks [4], which are similarly weak lines in LIBS spectra.

Simple Linear Regression. For each element, each of 6144 channels was tested for correlation between normalized intensity and elemental concentration. From those with high R^2 values, several candidate lines were considered for each element; the NIST atomic emission database [5] was then queried to ensure that the line chosen was actually an emission from the element of interest. After an optimal lines was chosen for each element, concentrations were predicted using the equation of the calibration curve, as shown in Fig. 1.

PLS-2 Regression. After preprocessing as described above, data were analyzed using software written in GNU R by MLC [6]. This customized software wraps routines from several packages, including hyperSpec, Peaks, and PLS. PLS-2 regresses multiple response variables (elemental concentrations of Rb, Sr, Cr, Ba, and V) against multiple explanatory variables (intensity at each spectrometer pixel) to predict concentration. Internal leave-one-out cross-validation was used. The number of components used in the model was determined individually for each element using the first local minimum value of root-mean-square error predictions (RMSEP).

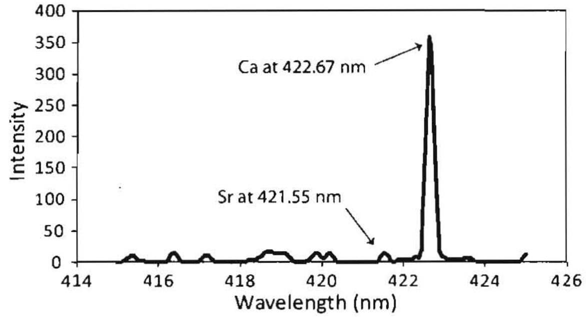

Figure 2. Comparison of the intensity of the Sr line at 421.55 nm (the best line out of 6144 channels for predicting Sr) with that of Ca at 422.67 nm. Not only are the concentrations of these elements vastly different, but their transition probabilities are also distinct: A_{ki} for this Sr II line is 1.27e+08, while A_{ki} for the Ca line is 2.18e+08. These A_{ki} values relate to line strength, S, by the relationship [2]: $1.499 \times 10^{-8} A_{ki} \lambda^2 g_k = 303.8 \lambda^{-1} S$.

Results: *Simple Linear Regression (SLR).* For chosen peaks, R^2 correlation coefficients between normalized intensity and elemental concentrations ranged from 0.59 (Ba) to 0.89 (Rb and Sr), as seen in Fig. 1.

PLS-2 Regression. Examination of the resultant correlation coefficients between elemental concentrations and intensity at each pixel shows that for all elements studied, the first several most highly-correlated pixels correspond to optical emissions of other elements because the peaks corresponding to trace/minor elements are also"minor" and of low intensity (Fig. 2).

Discussion: *Simple Linear Regression.* For Rb, Sr, and V, relative errors from SLR predictions are lower than from PLS-2, and SLR produces very good results (Fig. 1). SLR may perform better for these elements because intensities at only one pixel that is both highly correlated with the element being predicted and known to be an optical emission of the element are used. Predictions of Ba concentration are comparable between SLR and PLS-2. Prediction of Cr concentration is significantly worse using SLR rather than PLS-2. The Cr peak at 427.48 nm occurs on the shoulder of a larger peak, and thus simple regression of peak intensity at 427.48 nm may not suffice for prediction of Cr.

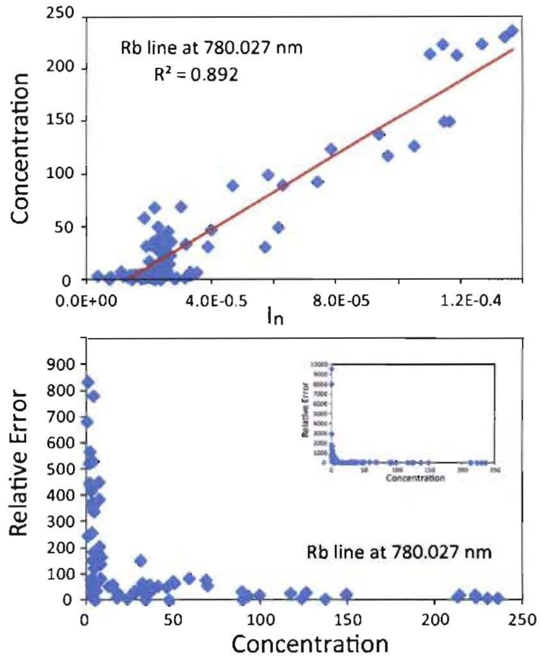

Figure 3. (top) SLR plot of concentration of the Rb line at 780.027 nm vs. intensity, which has an R^2 of 0.892. (bottom) The relative error of Rb predictions based on this line, showing the exponential decrease in relative error in SLR predictions with increasing concentration. Inset shows the full range of concentration.

For the elements studied, relative error in SLR predictions decreased exponentially with increasing concentration (Fig. 3). Some scatter in the SLR calibration curves undoubtedly occurs due to chemical matrix effects and possible overlap from lines attributed to other elements [1]. Because peak intensities of the minor elements are relatively small (Fig. 3), our results will be improved by modeling and subtracting the baseline around the peak of interest rather than for the entire spectrum. Use of peak area rather than intensity may also improve SLR results [4]. These results from PLS-2 and SLR indicate that models that focusing on small regions of the spectra where minor element emission peaks are present may be necessary to optimize predictions of minor and trace elements.

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