

Improvement in Qualitative and Quantitative LIBS Analysis of Elemental Compositions of Basalts.

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Introduction: Laser Induced Breakdown Spectroscopy (LIBS) has been advanced as a tool for quantitative analysis of elemental compositions of rocks for the Mars Science Laboratory (MSL) [1-5]; in an effort to increase the precision and accuracy of such predictions, we present for the first time the effect of various experimental parameters on qualitative and quantitative analyses with LIBS. In particular, the effect of the bremsstrahlung background and the calibration of spectral response of the system are reviewed.

The effect of instrument calibration as well as the bremsstrahlung background on quantitative predictions of elemental compositions of rocks using LIBS, such as will be conducted by the MSL [1], was studied. Predictions were made using multivariate regression [6, 7], and the effect of the background and net system spectral response on the LIBS data was analyzed. This technique may be useful for analyzing Mars Science Lab's ChemCam data. In general, proper background removal reduces the number of principal components necessary to explain an equivalent amount of the variance as well as increasing the relative distance between probability clusters as measured by the Euclidian distance between principal component vectors. Careful removal of the background and compensation for the spectral response of the system are shown to increase the accuracy of composition prediction of unknown samples provided a standard set of calibration samples is available.

Methods of Analysis: Two methods were considered of most interest: qualitative grouping of samples using the Euclidian distance between principal component vectors (PCA), and quantitative elemental analysis by partial least squares (PLS) regression. Decreased spacing of the principal component vectors between measurements of the same sample (increased "clustering") and increasing spacing between vectors of different samples is desired for optimal qualitative analysis. A reduced number of principal components and increased correlation coefficient (R^2) are needed for quantitative analysis by PLS, to get a more precise prediction.

Experiment Design: LIBS spectra were taken of six Brammers geological standards (two andesites: JA-1 and AGV-2; and three basalts: BCR-2, GUWBM and VS2116-81; one synthetic limestone with trace elements (GBW-72117), and one α -quartz (α -SiO₂) sand sample. The samples were compressed into 1 inch diameter pellets at 20 kpsi. The samples were placed onto a rotary stage in a simulated Martian envi-

ronment composed of 6.9 to 7.1 Torr CO₂. The samples were interrogated with a 1064 nm Nd:YAG Continuum Surelite II laser at 90 mJ per pulse at 20 Hz with an integration time of 5 seconds; in the far field, the laser spot diameter was 600 microns. The net optical path length between the sample and the receiver was 5 m. The resultant radiation was fiber coupled to three Ocean Optics LIBS 2500+ spectrometers and digitally recorded. These spectrometers recorded the emission in three spectral regions: 225-325 nm ("UV unit") and 384-469 nm ("VIS unit"), and 500-930 nm ("VNIR unit").

A calibrated tungsten filament thermal source was used to determine the spectral response of the collection system and detector, such that the total optical system transfer function and detector gain were characterized and removed from the spectra in the Fourier domain.

Characteristics and Analysis of Samples:

Sample compositions are reported in oxide weight % and were converted to atomic fractions as described by Clegg et al. [6]. Spectra were normalized so that the integral intensity over the wavelength of the individual spectral regions was 1; and the total intensity of the entire normalized spectrum was 3. A multivariate partial least squares analysis (PLS2) was then performed with the data using Unscrambler software as in [6]. The resulting Principal Components Analysis plots of PC1 and PC2 are shown in Fig. 1(a) for the raw LIBS data and in Fig. 1(b) for base-line corrected LIBS data. Note an increased spacing between clusters of different samples in the base-line corrected data. Removal

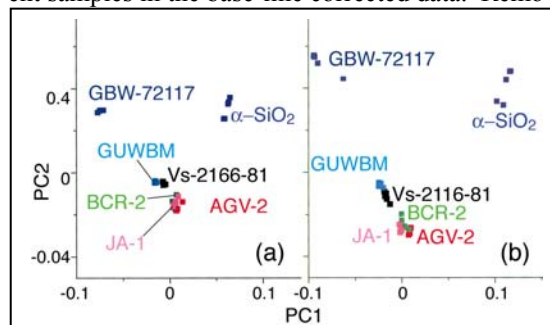


Fig. 1. PCA plots of LIBS data showing discrimination between various samples (a) uncorrected LIBS data; (b) base-line corrected LIBS data.

of the background improves discrimination between different geological classifications and improves the accuracy of qualitative analysis.

The validation plots for the different elements, with the amount of explained variance and the number of principal components required for analysis are shown in Figs. 2-5. Again, note in some cases the reduced number of principal components to explain similar amounts of the variance, e.g., Fig. 2 for Si.

Discussion: The broad bremsstrahlung baseline was shown to induce correlations between elements it increased the number of principal components required to analyze an equivalent amount of the sample variance and reduced the spacing between groups of data

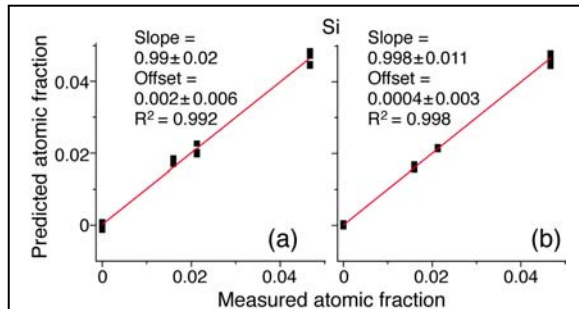


Fig. 2. Predicted atomic fraction (black squares) vs. measured atomic fraction of Si. The red line is the model validation line (a) derived from uncorrected data with three PCs and (b) from baseline corrected data with two PCs.

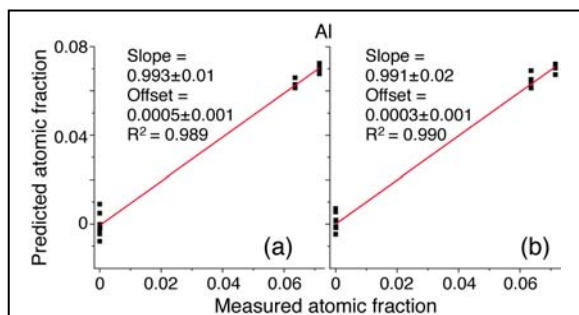


Fig. 3. Predicted atomic fraction (black squares) vs. measured atomic fraction of Al. The red line is the model validation line with three PCs (a) derived from uncorrected data and (b) from baseline corrected data.

taken from the same sample, reducing qualitative discrimination as seen in Fig. 1 and quantitative precision as seen in Figs. 2-5. Calibration of the LIBS system was found to increase the precision of the quantitative PLS2 predictions much more than the effect on qualitative Principal Components grouping. Removal of the background increased the number of PCs that might be included before over fitting the data, as shown in Fig. 4 for Ca. This is a clear indication that the background was de facto “noise” for prediction of atomic fraction. This was clear from the residual variance plots (not shown in the Fig. 4).

The background increased the number of principal components necessary to explain the same amount of

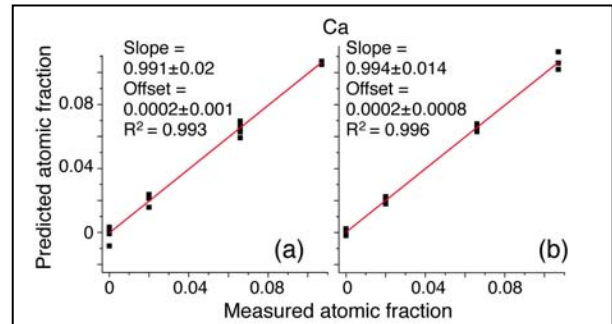


Fig. 4. Predicted atomic fraction (black squares) vs. measured atomic fraction of Ca. The red line is the model validation line (a) derived from uncorrected data with three PCs and (b) from baseline corrected data with four PCs. Removal of the background allowed for more PCs to be included in the model before over fitting.

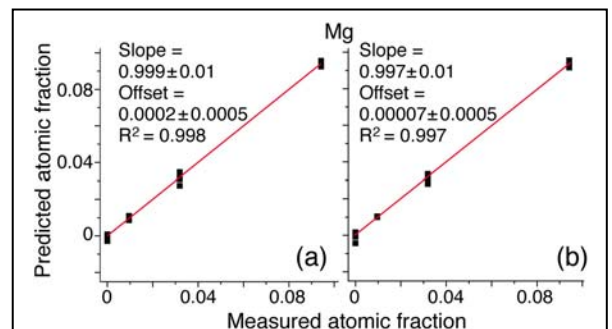


Fig. 5. Predicted atomic fraction (black squares) vs. measured atomic fraction of Mg. The red line is the model validation line with three PCs (a) derived from uncorrected data and (b) from baseline corrected data.

variance; nominally, this increase was one principal component. This somewhat impacted both the qualitative and quantitative analyses; the maximum improvement was ten percent, demonstrating the robustness of both the PCA and PLS2 analysis techniques. In conclusion, careful consideration of relevant data sources, and removal of data that does not contain information about the elemental emission lines related to the predictions of interest, will improve the analysis of the elemental compositions of rocks with LIBS data.

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