

LESSONS LEARNED FROM LIBS CALIBRATION DEVELOPMENT. M. D. Dyar¹, E. A. Breves¹, K. H. Lepore¹, T. Boucher², S. Giguere². ¹Mount Holyoke College, Department of Astronomy, South Hadley, MA, 01075, mdyar@mtholyoke.edu, ²College of Information and Computer Science, University of Massachusetts, Amherst, MA 01003.

Introduction: More than ten years of work in our and others' research groups have been dedicated to development of robust standards, data processing, and calibration tools for laser-induced breakdown spectroscopy (LIBS). Here we summarize major considerations relating to LIBS calibrations as we and others have encountered them, with a focus on our group's work.

Calibration suites. As with most analytical techniques, the number of standards and their elemental compositions must represent the magnitude of variation in the unknowns to be analyzed. This is particularly important for LIBS because matrix effects (largely arising from interactions within the plasma) have a first order effect on peak intensities, especially for light elements. Currently the largest set of LIBS calibration data on rocks comes from a suite of 2883 rock and mineral powders acquired in our laboratory [1], each shot 30 times at >5 locations using 3 different laser powers. Included in this suite are 320 samples consisting of 8 rock matrices doped with Ni, Zn, Cr, Mn, Co, Rb, Sr, Y, Zr, Ce, La, Se and Pb in concentrations ranging from 10 ppm to 10 wt%. Preliminary analyses suggest that a significant improvement in prediction accuracy results from such a broad training set.

Laser Power. Work by [2] used the ratio of intensities of the Si II line at 644.7 nm against that of neutral Si at 288.2 nm to demonstrate that the plasma temperature recorded in Mars ChemCam spectra is variable. This effect can be reproduced in the laboratory as well, where even under ideal conditions, the laser power on target has some variability. Because the population of species and their ionization states is temperature-specific, it is critical for LIBS calibration data to be collected over a range of plasma temperatures that spans those used in the instrument of interest.

Normalization. LIBS data require normalization for comparisons among conditions, data sets, and instruments, but the optimal method for this is still being investigated. The ChemCam team [3,4] and most workers normalize to the total intensity on each of the three spectrometers. Some workers [5] have suggested that other types of normalization, such as to the magnitude of the continuum or to specific spectral lines (e.g., C at 247.9 or 658.0 nm or O ca. 777.2 nm) may be required for analysis of trace elements.

Continuum removal. There is as yet no consensus on the best practice for continuum (baseline) removal in LIBS spectra. We have recently [6] examined the causes, effects, and optimization of continuum removal

in LIBS from geological samples. Nine previously published methods for baseline subtraction generally produce equivalent prediction accuracies for major elements after optimizing their adjustable parameters. Ideally, these parameters should be determined separately for each variable. We proposed a new technique for custom baseline removal (BLR) [7] that significantly improves prediction accuracy over existing methods across varying geological data sets, instruments, and analytical conditions. The current practice of using generalized, one-method-fits-all-spectra baseline removal results in poorer predictive performance for all methods. The extra steps needed to optimize baseline removal for each predicted variable are shown to be well worth the additional computations required.

Angle of incidence. Spectral variability due to changes in collection geometry is typically ignored, despite work [8,9] showing that differences in orientation of continuum and emission lines could complicate the practice of normalization. So we [10] have tested results of varying ablation and collection angles from 0-60° on LIBS spectra of glasses and rocks with compositions from basalt to rhyolite. We varied ablation and collection angle together as well as separately. Summed spectral intensity increases as ablation or collection angle approaches normal to the standard surface. Spectral intensity of the fitted continuum varies more with ablation or collection angle than spectral intensity of the emission lines. Most importantly, results show that an additional analytical uncertainty of >30% is added to LIBS errors if the ablation angle onto the target surface is unconstrained or unknown.

Univariate vs. multivariate analyses. Analysis techniques for LIBS data fall in two categories. Univariate analyses use the intensity of a single peak (or peaks) to determine concentration using a calibration curve relating those two variables, but they suffer greatly from the matrix effects mentioned above. The alternative is multivariate analysis, generally partial least-squares (PLS), which is currently used in tactical activities for ChemCam [3]. We and others [11-16] have worked to find ways to improve upon PLS, either by applying more modern methods or through novel approaches to data preprocessing; 10-30% improvements in prediction accuracy result depending on the element predicted and the training set used.

We have recently [17] investigated the issue of univariate vs. multivariate prediction accuracy using 1356 spectra from 452 geologically-diverse samples,

the largest suite of LIBS rock spectra ever assembled. Univariate predictions are by far the least accurate, regardless of the region of channels/wavelengths chosen and the prominence of the selected emission lines. The best wavelength region choice for any given univariate analysis is an inherent property of each specific training set that cannot be generalized. In comparison, multivariate analysis using PLS almost universally outperforms univariate analysis, producing results that improve in accuracy by 63% for major elements and 3% for minor elements. This difference is likely a reflection of signal to noise ratios, which are better for major elements than for minor elements, and likely limit their prediction accuracy by any technique. Masking out channels to focus on emission lines from a specific element [17] worsens prediction accuracy for major elements but is useful for minor elements with low signals and proportionally much higher noise; use of PLS rather than univariate analysis is still recommended for the elements tested, which included Si, Al, Ti, Fe, Mg, Ca, Na, K, Ni, Mn, Cr, Co, and Zn [17].

Components in PLS Models. A key parameter of models like PLS is the number of components used. In a manner analogous to choosing the polynomial order in a multiple regression model, the fewest possible number of components should provide the most generalizable prediction model. For this reason, the number of components in LIBS PLS models is usually held to be <12 [e.g., 3,4]. Tests using a dataset with 1356 LIBS spectra [18] showed that after increasing the search range to include up to 50 components, prediction accuracy improved in 30.8% of cases, stayed the same in 57.0% of cases, and became worse in 12.2% of cases. This implies that the complex interactions resulting from variation in elemental composition produce a system with an intrinsic dimensionality larger than 12 components, so use of predictive models with a larger numbers of components is justified. The fact that model performance converges on <50 components indicates the compressibility of LIBS data in general.

Calibration Transfer. We have learned that LIBS data are extremely sensitive to instrumental differences as well as all the factors discussed above. Machine learning provides tested techniques for resolving discrepancies among datasets from different instruments, a task known as calibration transfer (CT). For example, CT can be used to correct for differences found between spectra of deployed extraterrestrial instruments, like ChemCam, and Earth-based laboratory facilities.

Using a latent variable CT method, we showed that the predictive accuracy of major elements like CaO can be improved up to 60% [19]. CT can also be used to align and aggregate suites of spectra with a small number of common samples, allowing better models to

be built with combined data sets. With a linking set size >10 samples, models trained on a suite of data sets aligned with piecewise direct-standardization (PDS) were more generalizable with lower prediction error [20] than those of the individual data sets. Unfortunately, PDS requires the differing instruments to share the same sampling wavelength range and frequency and cannot correct for larger differences.

Our group has introduced a novel framework for CT based on recent advances in the field of convex optimization [21]. A customizable CT loss function is constructed using a series of penalty terms that target specific behaviors, spectroscopies, and task types. It is optimized using alternating direction method of multipliers capable of transferring multiple data sets with millions of samples and thousands of channels. We have introduced a framework for CT that does not require any overlapping subset of samples [22]; it aligns disparate data sets by embedding samples in a shared low-dimensional latent-space to preserve their local geometric structures. This is effective when data sets are large but the overlapping subset is small or absent, though overlapping subset CT methods are preferred.

Future Work. Although much has been done to improve accuracy of LIBS as a chemical analysis tool, several issues remain. These include effects of uneven/porous surfaces/grain size, problems relating to prediction of trace and light elements, and experimental factors such as laser stability/power distribution. As these are studied, the usefulness of LIBS in planetary exploration will continue to improve.

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