UPDATED HYDROGEN, LITHIUM, BORON, CARBON, AND SULFUR PREDICTION ACCURACIES WITH LIBS UNDER VACUUM, EARTH, AND MARTIAN ATMOSPHERES. C. R. Ytsma and M. D. Dyar, Dept. of Astronomy, Mount Holyoke College, South Hadley, MA 01075, ytsma22c@mtholyoke.edu.

Introduction: Laser-induced breakdown spectroscopy (LIBS) is used for elemental detection and quantification in many fields [1-3]. Reliability of LIBS spectra in predicting elemental concentrations varies depending on the amount of each species present (major vs. trace), intensity of measurable spectral lines relative to noise, and matrix effects caused by interactions among elements in the plasma. Most LIBS studies have focused on quantifying elements with $Z \geq 11$, where those elements are ≥1 wt.%. Lighter elements (with $Z \leq 10$) have smaller and fewer peaks in the visible and NIR wavelength ranges, and are thus more difficult to analyze, especially when the element is low in abundance.

To improve predictions of H, Li, B, C, and S, this study uses private and publicly available reference standards with wide ranges of concentrations doped in geological matrices corresponding to common rocks types on planetary surfaces [4]. Additionally, this study compares LIBS spectra collected under Mars atmospheric conditions to Earth (air) and vacuum (pseudo-lunar) environments to compare efficacies of light element prediction in the three environments.

Standards and Spectra: Three powdered rock matrices (two basalts and one rhyolitic glass) were individually combined with C-, B-, Li-, and S-containing chemicals to make powdered mixtures with light element concentrations of 10 wt% (100,000 ppm), 1 wt% (10,000 ppm), 0.5 wt% (5,000 ppm), 1,000 ppm, 500 ppm, 250 ppm, 100 ppm, 50 ppm, and 10 ppm [4]. Because H cannot be artificially added to rock standards, natural standards with known values for structural water were powdered and selected for H quantification.

These powders were shatterboxed to ensure homgeneity and pressed into uniform pellets for analysis using the Mount Holyoke College (MHC) ChemLIBS instrument consisting of a 1064 nm Nd:YAG laser and three spectrometers collecting light in the UV (220-330 nm), VIS (380-470 nm), and VNIR (490-930 nm) wavelength regions. Pressures in the chamber were 3.68 Torr CO_2 (comparable to the Mars mean radius surface pressure of 4.77 Torr) [5], ambient pressure of the laboratory air (Earth), and ~100 mTorr (vacuum) to make a preliminary comparison to the vastly lower lunar surface pressures of 2.0×10^{-12} Torr [6].

Sample Suites: *Initial Training:* Doped samples with concentrations typical of naturally occurring rocks and minerals were used as the training set, as represented in the Dyar lab standard suite [4]. The upper limit of this range was defined as the mean value of each element plus 1.5× the inner quartile range of the natural standards. The lower limit was the 5% confidence interval, unless the limit of detection was higher than this value. The doped samples were chosen becaue they fell within these ranges: 8 samples doped with C, 9 with B, 12 with Li, and 15 with S. A random selection of 29 H-containing standards was chosen for the initial suite.

Test: All undoped natural standards with known values for C (38 samples), Li (160 samples), B (114 samples), and S (60 samples) within the range defined above were included in the test suite. H standards (171 samples) not used in initial training were used for testing.

Final Training: Training standards were combined with test standards, creating a suite of standards that enable the most robust prediction models available.

Univariate Analysis: The 10, 1, and 0.5 wt% standards were doped with a single element to avoid matrix effects. Lower concentration standards were a combination of all four elements. The doped samples' spectra were used to identify strongly correlated peaks for each doped element using the value of the R^2 correlation between channel intensity and concentration. The NIST LIBS database (**Table 1**) [7] was used to confirm that each chosen line arose from the element of interest.

Table 1. Correlated peaks chosen for univariate analysis.

Element	Peak	Transition
H	656.2 nm	$2p - 3d$
C	247.9 nm	C I $2s^22p^2 - 2s^22p3s$
	657.9 nm	C I $2s^22p3p - 2s^22p6d$
Li	610.3 nm	Li I $1s^22p - 1s^23d$
	670.6 nm	Li I $1s^22s - 1s^22p$
B	249.8 nm	B I $2s^22p - 2s^23s$
S	no visible peaks	

Peak areas were fit with OriginPro software using single and multiple Voigt lineshapes. These areas and their sample concentrations were used to make linear models, which were tested for accuracy with leave-one out cross validation (LOO-CV) to obtain root-mean-squared errors (RMSEs). LOO-RMSE-CVs are similar to simple calibration errors, except one sample is removed from the training set, a model is made from the remaining *n*-1 samples, and the prediction error for the withheld sample is found. This process is done iteratively over all samples to make *n* 'folds'. Because of time restrictions, only one spectrum normalization technique was used for univariate analyses – normalization to each spectrometer's total intensity ("norm3").

Multivariate Analysis: Six normalization techniques were applied to sample spectra before multivariate analyses were undertaken: 1) division by the total intensity of each spectrometer individually, "norm3"; 2) division by the total intensity of the entire wavelength range, "L1"; 3) division by the sum of squares, "L2"; 4) division by the maximum intensity, "max"; 5) division by the minimum intensity, "min"; and 6) cumulative sum scaling, "cumulative" [8].

Partial least squares regression (PLS) and the least absolute shrinkage and selection operator (lasso) created predictive models from the entire wavelength range using a web tool that utilizes the SciKit-learn library [9]. PLS was developed for use in situations where highly collinear explanatory (p) variables significantly outnumber observations (N), such that $p >> N$ [10]. Lasso is a penalized shrunken regression method that selects the specific channels for each element that explain the most variance in the concentration of that element [11].

Results: *Initial Training & Test:* All initial training models gave LOO-CV errors below the value of the samples' average concentration, with most below 75% of that value. However, when the best-performing models were used to create predictions on the "unknown" natural test standards' spectra, almost all the errors were higher than training predictions' (**Figure 1**).

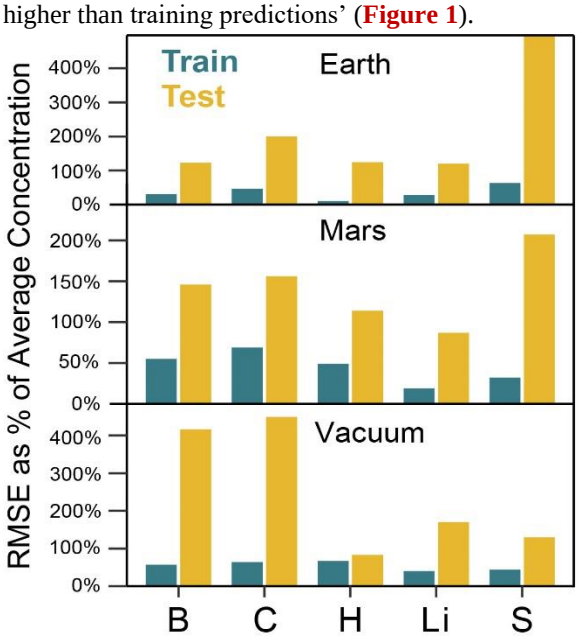

Figure 1. Normalized prediction errors of training and test spectra from the same model. RMSE values for combined final models using training plus test data are given in Table 2.

Final Models: The lowest errors for each element and atmosphere using all available standards are shown in **Table 2**. It is important to contextualize these results in terms of the samples used to make the models, rather than their strict numerical values. So the far righthand column in Table 2 reports errors as a percentage of the average concentration for that training set.

Lines with low transition probabilities are less likely to be seen in vacuum or Mars environments because there is less overbearing pressure to force surface-'atmopshere' interactions. Those elements are thus best analyzed in air, where those same weak lines are enhanced due to the increase in interactions. Alternatively, lines with high transition probabilities are vulnerable to self-absorption effects; these samples have the most interpretable spectra under vacuum. Overall, sulfur results were consistently poor due to a lack of correlated peaks and their low transition probabilities [12].

Table 2. Lowest errors from models using all samples.

Element	Atmosphere	LOO-CV-RMSE	Error as % of Average
H_2O	Mars	± 0.92 wt%	64%
	Earth	± 0.14 wt%	9%
	Vacuum	± 0.99 wt%	65%
CO_2	Mars	± 1.17 wt%	85%
	Earth	± 1.25 wt%	91%
	Vacuum	± 1.13 wt%	82%
Li	Mars	± 16 ppm	43%
	Earth	± 16 ppm	43%
	Vacuum	± 13 ppm	35%
B	Mars	± 39 ppm	70%
	Earth	± 38 ppm	68%
	Vacuum	± 33 ppm	59%
S	Mars	± 412 ppm	106%
	Earth	± 415 ppm	103%
	Vacuum	± 473 ppm	118%

Ongoing Work: LOO-RMSE-CVs will be calculated for univariate models normalized by the remaining five normalization methods and for multivariate models made from limited regions of the spectrum centered on the peaks chosen for univariate analysis (Table 1). All models will then have a new set of RMSEs calculated with a more rigorous method of cross validation where the number of folds is equal to $\sqrt{n}$ instead of n, as used by LOO-CV.

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