

NORMALIZATION AND BASELINE REMOVAL EFFECTS ON UNIVARIATE AND MULTIVARIATE HYDROGEN PREDICTION ACCURACY USING LASER-INDUCED BREAKDOWN SPECTROSCOPY.

C. R. Ytsma¹, M. D. Dyar², K. H. Lepore², C. M. Wagoner², and A. E. Hanlon². ¹Department of Chemistry, Smith College, 1 Chapin Way, Northampton, MA 01063 (cytsma@smith.edu), ²Department of Astronomy, Mount Holyoke College, 50 College Street, South Hadley, MA 01075.

Introduction: Laser-induced breakdown spectroscopy (LIBS) is used by the *Curiosity* rover's ChemCam instrument for remote quantification of rock and soil compositions. To develop calibrations for elements of interest, geologic standards with known compositions are analyzed with LIBS in the laboratory using parameters similar to those found on Mars. Hydrogen is a particularly important element because hydrous minerals indicate the presence of water on Mars at the time the sample was formed.

LIBS is a useful method for detecting H because strong H emission lines occur in the visible region. Unfortunately, reported chemical analyses on most geological standards are given as LOI (loss on ignition) results that lump all volatiles (e.g., H₂O, CO₂ etc.) together, and thus are too imprecise to be used to calibrate H. We have identified only 16 existing commercially-available standards for which H has been directly and specifically measured.

Fortunately, our laboratory collections include many H standards characterized by the uranium extraction technique for previous studies (e.g. [1-3]) of structural/ internal H. The materials cover a range of minerals, rocks, and glasses. To develop a LIBS calibration for H, we have collected 203 standards that are used here to test uni- and multivariate comparisons. We use these standards to evaluate an array of normalization techniques suggested by other workers to improve prediction accuracy for H analyses by LIBS [4-6].

Methods: All 203 geologic standards were available as powders which were then pressed into discs for analysis with the Mount Holyoke College (MHC) LIBS. It differs from the flight instrument in that it has more limited sensitivity (by factors of 8 in the UV, 4 in the visible region, and 6 in the visible/near infrared region) because its spectrometers utilize 1D CCD detectors rather than the 2D detectors used on the ChemCam flight instrument. The MHC instrument is also limited by detector readout noise, making it necessary to integrate over multiple plasmas. However, the standards suites are physically located at MHC and the current MHC instrument is typical of (or better than) most commercially available LIBS units. It also has the capability of adjustable laser power, allowing spectral power to be matched to what is observed on Mars in terms of plasma temperature [e.g., 6]. Comparisons between these two instruments allow some of the variables affecting quantitative analysis of hydrogen and other elements to be better understood.

Data collected at MHC are compared with laboratory data on some of the same standards collected on the ChemCam engineering model at Los Alamos National Laboratory (LANL). These data are publicly available on the ChemCam Planetary Data System website. This study thus compares three sample sets: (i) 16 standards run at LANL for which H analyses were available, (ii) the same 16 samples run at MHC at 5% laser power, and (iii) all 203 MHC standards (16 commercially available standards and 187 from lab collections), also run at 5% laser power.

Analyses: Univariate analyses were undertaken by regressing the intensity at the centroid of the H-alpha Balmer emission line at ~656.5 nm in the samples, as used by [4], against known H concentration expressed as wt% H₂O. This was repeated for nine variations to massage spectral intensity, normalizing to (1) total intensity over the energy range of each of the three spectrometers individually: "norm3"; and (2) collectively: "cumulative"; (3) the intensity of the highest peak in the entire spectral range: "max", (4) the sum of absolute values: "L1"; (5) the sum of squared values: "L2"; (6-9) and the area under the peaks for H at 656.6 nm, C at 247.8 nm [5] and 657.7 nm, and O at 777.5 nm. The normalized 656.6 nm intensity was then compared to known weight percent of structural water in the sample. In some cases, the peaks were slightly offset but visual inspection was used to select the correct peak (e.g., **Figure 1**). The results for each sample set were plotted and the R² value of each normalization method was entered into **Table 1**.

The least absolute shrinkage operator (lasso) was also used to predict H concentration [e.g., 8]. These multivariate analyses use a range of wavelengths that extends beyond the intense 656 nm peak, capturing possible predictive information from other features.

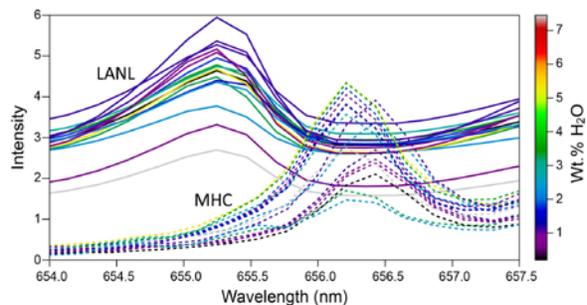


Figure 1. Spectra of the same 16 hydrogen containing samples for LANL and MHC, displaying intensity $\times 1e^9$ and $1e^9$, respectively.

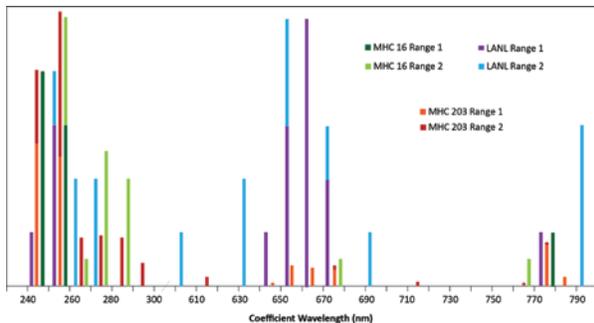


Figure 2. Histogram of occurrences of peaks in wavelength ranges used by different methods shown in Table 2.

Seven multivariate lasso models were tested over different wavelength ranges (**Table 2**): 243-253 nm, 650-675 nm, 773-783 nm, all three together, 240-300 nm, 600-800 nm, and both 200-300 and 600-800 nm. These tests were performed on unnormalized data. The effect of baseline removal was also tested.

Results: LANL results for univariate analyses were only slightly more accurate than MHC's on average, as seen in Table 1. This implies that detector sensitivity matters somewhat but is not a limiting factor. Baseline removal is shown to only slightly increase the value of R^2 in each sample set. Normalization methods greatly improve the prediction accuracy of raw data, but the R^2 values on the univariate regressions are much too low to use for definitive H quantification. The univariate methods are likely poor performers because of chemical matrix effects that change the 656.6 nm peak's intensity. This problem is evidenced by the weak correlation between intensity and H in both LANL and MHC spectra seen in **Figure 1**.

For multivariate comparisons, H quantification accuracy increases dramatically for data from both

Table 1. R^2 values of 656.6 nm intensity vs. H_2O wt%.

Normalization Method	LANL 16 H Samples		MHC 16 Samples 5%		MHC 203 H Samples 5%	
	no BLR	BLR	no BLR	BLR	no BLR	BLR
Cumulative	0.22	0.27	0.08	0.08	0.04	0.07
Norm3	0.00	0.08	0.10	0.10	0.01	0.01
Max	0.04	0.18	0.08	0.08	0.25	0.25
L1	0.34	0.26	0.09	0.10	0.08	0.08
L2	0.28	0.22	0.08	0.09	0.14	0.14
H 656.6 peak area	0.04	0.04	0.00	0.00	0.25	0.27
C 657.7 peak area	0.04	0.01	0.03	0.02	0.32	0.20
C 247.8 peak area	no peak	0.28	0.23	0.08	0.02	0.02
O 777.5 peak area	no peak	no peak	0.73	0.28	0.34	0.04

Table 2. RMSE values of lasso results for predicting H_2O wt%.

Ranges (nm)	LANL 16 H Samples		MHC 16 Samples 5%		MHC 203 H Samples 5%	
	no BLR	BLR	no BLR	BLR	no BLR	BLR
243-253	0.00	0.22	0.00	0.00	1.39	1.42
650-675	0.01	0.01	0.00	0.00	1.45	1.45
773-783	1.25	0.76	0.00	0.00	2.74	2.87
all 3	0.00	0.00	0.00	0.00	1.51	0.50
240-300	0.02	0.00	0.00	0.00	0.13	0.15
600-800	0.00	0.01	0.00	0.00	0.20	0.25
both	0.00	0.00	0.00	0.00	0.25	0.25

instruments studied and across multiple scenarios. **Table 2** shows that less sensitive 1D detectors (MHC) perform better with wider wavelength ranges while the 2D detectors on ChemCam perform better with tighter wavelength ranges. With all sample sets, PLS baseline removal is shown to have negligible effects on the prediction accuracy, which is expressed as root mean square error (RMSE) in units of wt.% H_2O .

Figure 2 illustrates the distribution of channels chosen by the multivariate methods to predict H. Range 1 covers 243-253, 650-675, and 773-783 nm. Range 2 covers 200-300 and 600-800 nm. Raw data were used for both plots. Wavelengths chosen by the lasso methods were indexed against the NIST atomic emission database. Interestingly, most of the lines chosen for H predictions from the larger MHC data set used Fe II emission lines.

Summary: Multivariate lasso analysis is shown to be a dependable method of H prediction for the range of LIBS instrument sensitivities tested. Univariate analysis is slightly more dependent on specific instrument characteristics.

Acknowledgments: Research supported by NASA grants NNX14AG56G and NNX15AC82G and NSF grants IIS-1564083, CHE-1306133 and CHE-1307179.

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