

LIBS AND PIXL PREDICTION ACCURACIES FOR NI, MN, S, AND MAJOR ELEMENTS: A COMPARATIVE STUDY USING THE SAME STANDARDS.

C. R. Ytsma¹, J. Hurowitz², and M. D. Dyar¹
¹Dept. of Astronomy, Mount Holyoke College, 50 College St., South Hadley, MA 01075, ytsma22c@mtholyoke.edu, ²Dept. of Geology, Stony Brook University, 100 Nicolls Rd, Stony Brook, NY 11794.

Introduction: Calibration models for detection and accurate quantification of elements on Mars are necessary to understand the composition of its surface. *Mars 2020* will carry Planetary Instrument for X-ray Lithochemistry (PIXL), an x-ray fluorescence (XRF) instrument, and a laser-induced breakdown spectroscopy (LIBS) instrument as part of the SuperCam instrument for geochemical analyses. No comparison of prediction accuracies between these two techniques using identical standards has been undertaken to date, making it difficult to compare results from the two methods.

Another issue with Mars geochemical accuracies is that most calibration models are made using terrestrial geologic standards with concentrations that may be significantly lower than those of, especially, Ni, Mn, and S in Martian soils [1], where these elements may be enriched by contributions from meteorites and volcanic gasses. Accordingly, this study uses standards created from several different rock types doped with up to 1 wt% (10,000 ppm) of these elements to create appropriate calibration models.

Background: With XRF, samples are bombarded with high-energy X-rays, resulting in ejection of inner shell electrons. The resultant holes in the inner-shell orbitals are filled by electrons from outer shells, in the process ejecting a photon with energy diagnostic of each individual element. In contrast, LIBS uses energy from a laser pulse to excite electrons into higher energy orbitals. When electrons return to their ground state, they release photons detected by spectrometers from the UV to the NIR. These transitions occur at longer wavelengths and lower energies than those measured in XRF, due to differences in the energy of the two excitation sources (plasma heat and x-rays, respectively). So these two techniques are highly complementary, and each has its strengths and weaknesses.

Methods: Doped samples consisted of 7 matrices with different bulk compositions, including three basalts, one granite, one rhyolitic volcanic glass, sea sand, and a 50:50 mixture of diopside and forsteritic olivine. Standard preparation and analyses are described in [2]. These powders were pressed into pellets and a subset of the 84 samples was analyzed under Mars conditions with the Mount Holyoke College ChemLIBS-analog instrument as well as with the Stony Brook University PIXL-analog instrument in air.

Spectral Preprocessing: XRF spectra from three pellet locations were summed over a total dwell time of one or two hours using data from two spectrometers.

X-axis resampling and baseline calculations for later removal were performed by PIQUANT, a software created specifically to analyze PIXL spectra [3-4]. To remedy temporal count differences, the spectra were normalized by the emission counts at 2.697 keV, which derive from Rh-anode L-emission lines in the PIXL X-ray tube.

LIBS spectra were averages of 36 individual shots taken on 6 locations across the pellets' surfaces. Spectra were preprocessed using the same method as the ChemLIBS *Curiosity* team and normalized by the total intensity of each of the three spectrometers [5]. The baselines were removed using the Kajfosz-Kwiatkiewicz method (bottom width of 50 and top width of zero) [6].

Modeling and Analysis: Both datasets were uploaded to a web tool that utilizes the SciKit-learn library and allows for convenient multivariate analysis with partial-least squares (PLS) and the least absolute shrinkage and selection operator (lasso) regression methods [7]. Calibration models for the dopants (Ni, Mn, S) and the major oxides (SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MgO, CaO, Na₂O, K₂O, P₂O₅) were made using both the entire available spectral range (0-40 keV for PIXL and ~240-850 nm for ChemLIBS) as well as limited regions of the spectra that contain emission peaks specific to the element of interest (**Table 1**). XRF regions used each element's k- α fluorescence peak, while LIBS focused on regions with the most intense peaks or clusters of peaks found with the NIST LIBS spectral database [8]. PIXL calibrations for Na and Mg were not possible because their XRF emissions are not measurable in air.

Table 1. Limited ranges used by calibration models.

Element	XRF (keV)	LIBS (nm)
Ni	7.25–7.70	298–315
Mn	5.72–6.07	255–265, 290–300
S	2.2–2.42	no peaks
Si	1.64–1.86	245–300
Ti	4.3–4.7	245–460
Al	1.35–1.65	245–400
Fe	6.2–6.6	245–450
Mg	no peak	275–285
Ca	3.5–3.87	310–400
Na	no peak	325–335, 560–600, 815–825
K	3.1–3.5	760–775
P	no visible peak	245–260

Root mean squared errors from cross-validation of the models (RMSECVs) were calculated with two methods: leave-one-out (LOO), which is similar to a simple calibration RMSE, and a more rigorous cross

Table 2. Lowest RMSECVs of XRF and LIBS models.

Element/Oxide	XRF	LIBS
Ni	± 786 ppm	± 953 ppm
Mn	± 1297 ppm	± 913 ppm
S	± 939 ppm	± 2041 ppm
SiO ₂	± 7.78 wt%	± 5.37 wt%
TiO ₂	± 0.57 wt%	± 0.53 wt%
Al ₂ O ₃	± 2.54 wt%	± 1.87 wt%
Fe ₂ O ₃	± 2.72 wt%	± 2.12 wt%
MgO	ND	± 3.20 wt%
CaO	± 1.75 wt%	± 1.13 wt%
Na ₂ O	ND	± 0.46 wt%
K ₂ O	± 0.60 wt%	± 0.56 wt%
P ₂ O ₅	± 0.15 wt%	± 0.15 wt%

validation where the number of folds equaled the square-root of the total number of samples (84 total samples giving approximately 9 folds).

Results: RMSECV results from the best performing model for each element and instrument are shown in **Table 2**, and were very similar to the LOO-RMSECV results. It is important to contextualize these results in terms of the concentration ranges used to make the models, rather than their strict numerical values. So **Figure 1** shows these same errors from Table 2 divided by the average value per element of the 84 calibration standards.

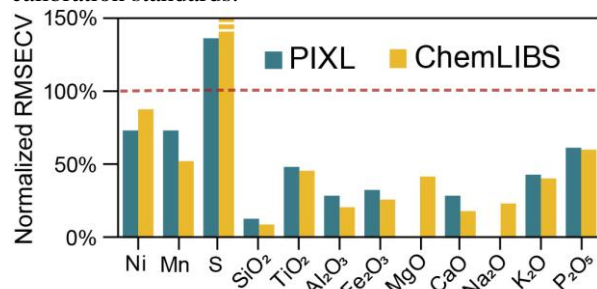


Figure 1. Best RMSECVs normalized to the standards' average concentrations. ChemLIBS' S RMSECV is 295%.

The best major element models for PIXL spectra utilized PLS regression on the full spectral range rather than energies corresponding only to specific peaks. The only exception to this was for TiO₂, which had better results when the model input was centered only on the energy range containing its fluorescence peak. Ni, Mn, and S best models were evenly split between using full or limited range inputs. Nearly all the LIBS models performed best using PLS or lasso on the entire wavelength range.

Discussion: Figure 1 shows that Ni, Mn and major oxides were predicted by PIXL and ChemLIBS models with comparable accuracies, though LIBS error bars are consistently slightly smaller than those for XRF. The exception to this rule is the S predictions from LIBS, which are known to be poor in accuracy due to the low transition probabilities of S that result in weak LIBS lines [9]. LIBS has an advantage with PLS anal-

yses because there are so many emission peaks, whereas XRF uses only x-ray lines that are more sparse. This implies that linear calibrations based on a single peak (XRF) or even several peaks (LIBS) will probably have higher uncertainties than calibrations using multivariate methods that take advantage of a range of features, like PLS.

Use of PLS or multivariate analysis in general for XRF applications is untested because that community more generally uses linear methods combined with theoretical models [3]. However, all the methods must somehow account for matrix effects. The presence of many interacting components in a material affects LIBS emission lines non-linearly and is also an effect for XRF. For this reason, the PLS models are popular with LIBS applications and deserve further testing for XRF and PIXL data in particular. Our results show agreement between the two contrasting techniques, and provide confidence in PLS prediction accuracies for Mars geochemical applications.

Future Work: An obvious next step in this project is to compare PLS predictions for PIXL to those from the PIQUANT software that is planned to be used on *Mars 2020*. PIXL team members are currently preparing a major upgrade to the PIQUANT instrument calibration that is specifically tailored to the Stony Brook unit. Once that is in hand, PIQUANT performance for data reduction of PIXL data can be directly compared to these multivariate analysis results. We also plan to undertake additional comparative analyses of geochemical standards on the new MHC SuperLIBS (a higher-sensitivity LIBS instrument with increased sensitivity and 2D CCD detectors identical to those fabricated for SuperCam), which will then provide direct comparisons of accuracies relevant to the *Mars 2020* mission. Comparing and contrasting precision and accuracy of instruments and software methodologies will ensure that PIXL and LIBS analyses enhance science return from the mission, leveraging complementary capabilities of both methods.

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