

LIBS AND PIXL PREDICTION ACCURACIES FOR NI, MN, S, AND MAJOR ELEMENTS: A COMPARATIVE STUDY USING THE SAME STANDARDS. C. R. Ytsma¹, J. Harowitz², and M. D. Dyar¹

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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 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-Kwiatk 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

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Power and Energy Richard Kong, 2015-05-06 Power and Energy contains 86 selected papers from the International Conference on Power and Energy CPE 2014 Shanghai China 29 30 November 2014 and presents a wide range of topics Energy management planning and policy making Energy technologies and environment Energy prospects Conventional and renewable power generation Power system man

Recent Advances in Intelligent Information Hiding and Multimedia Signal Processing Jeng-Shyang Pan, Akinori Ito, Pei-Wei Tsai, Lakshmi C. Jain, 2018-11-10 This book features papers presented at IIH MSP 2018 the 14th International Conference on Intelligent Information Hiding and Multimedia Signal Processing The scope of IIH MSP included information hiding and security multimedia signal processing and networking and bio inspired multimedia technologies and systems The book discusses subjects related to massive image video compression and transmission for emerging networks advances in speech and language processing recent advances in information hiding and signal processing for audio and speech signals intelligent distribution systems and applications recent advances in security and privacy for multimodal network environments multimedia signal processing and machine learning Presenting the latest research outcomes and findings it is suitable for

researchers and students who are interested in the corresponding fields IHH MSP 2018 was held in Sendai Japan on 26-28 November 2018. It was hosted by Tohoku University and was co-sponsored by the Fujian University of Technology in China, the Taiwan Association for Web Intelligence Consortium in Taiwan and the Swinburne University of Technology in Australia, as well as the Fujian Provincial Key Laboratory of Big Data Mining and Applications, Fujian University of Technology and the Harbin Institute of Technology Shenzhen Graduate School in China.

Progress in Pattern Recognition, Image Analysis, Computer Vision, and Applications Eduardo Bayro-Corrochano, Edwin Hancock, 2014-10-23. This book constitutes the refereed proceedings of the 19th Iberoamerican Congress on Pattern Recognition CIARP 2014 held in Puerto Vallarta, Jalisco, Mexico in November 2014. The 115 papers presented were carefully reviewed and selected from 160 submissions. The papers are organized in topical sections on: image coding, processing and analysis; segmentation; analysis of shape and texture; analysis of signal, speech and language; document processing and recognition; feature extraction; clustering and classification; pattern recognition and machine learning; neural networks for pattern recognition; computer vision and robot vision; video segmentation and tracking.

Advances in Neural Networks - ISNN 2014 Zhigang Zeng, Yangmin Li, Irwin King, 2014-11-28. The volume LNCS 8866 constitutes the refereed proceedings of the 11th International Symposium on Neural Networks ISNN 2014 held in Hong Kong and Macao, China, on November-December 2014. The 71 revised full papers presented were carefully reviewed and selected from 119 submissions. These papers cover all major topics of the theoretical research, empirical study and applications of neural networks research as follows. The focus is on the following topics such as: analysis, modeling and applications.

Advanced Machine Learning Technologies and Applications Aboul Ella Hassanien, Mohamed Tolba, Ahmad Taher Azar, 2014-11-04. This book constitutes the refereed proceedings of the Second International Conference on Advanced Machine Learning Technologies and Applications AMLTA 2014 held in Cairo, Egypt, in November 2014. The 49 full papers presented were carefully reviewed and selected from 101 initial submissions. The papers are organized in topical sections on: machine learning in Arabic text recognition and assistive technology; recommendation systems for cloud services; machine learning in watermarking; authentication and virtual machines; features extraction and classification; rough fuzzy sets and applications; fuzzy multi-criteria decision making; Web-based application and case-based reasoning; construction social networks and big data sets.

Digital Forensics and Watermarking Hongxia Wang, Xianfeng Zhao, Yunqing Shi, Hyoung Joong Kim, Alessandro Piva, 2020-03-25. The 22 full papers and 12 short papers presented in this volume were carefully reviewed and selected from 70 submissions. The contributions are covering the following topics: deep learning for multimedia security; digital forensics and anti-forensics; digital watermarking; information hiding; steganography and steganalysis; authentication and security.

Cognitive Systems and Signal Processing Fuchun Sun, Huaping Liu, Dewen Hu, 2019-04-27. This two-volume set CCIS 1005 and CCIS 1006 constitutes the refereed proceedings of the 4th International Conference on Cognitive Systems and Signal Processing ICCSIP 2018 held in Beijing, China, in

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