A QUALITY INDEX FOR MARTIAN IN-SITU LIBS SPECTRA.

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Introduction: Laser-Induced Breakdown Spectroscopy (LIBS) has been widely implemented in Mars explorations, e.g., ChemCam (CCAM) [1,2], SuperCam (SCAM) [3,4], and MarSCoDe (MSCD) [5], as a versatile technique for in-situ chemical analysis. Compositional calibrations for Martian LIBS are usually carried out with uni/multi-variate models based on laboratory data, which in turn require similarities between ground and Martian data [6]. The violation of this similarity may lead to erratic model behavior, for example, out-of-focus onboard calibration data from MarSCoDe has been found to increase quantification uncertainties [7].

Characterizing such similarity can be reduced to the examination of excitation conditions of the LIBS plasma, providing consistent instrumental response and familiar material types on Mars. One can consider an observation well-excited when the intensity of energy input is generally similar to that in the ground dataset [8]. However, the way to evaluate the intensity of energy input on Mars is limited. The inability to identify insufficient excited data may leave the malfunction of the focus mechanism/laser unattended, or cause unawareness of the compositional inaccuracy of poorly cohesive targets that may be ablated out of the focus [7].

The purpose of this study is to establish an evaluation of Martian LIBS data quality based on the aforementioned requirement of data similarity to laboratory standards so that possible blindness can be prevented in the face of unknown LIBS plasma conditions on Mars.

LIBS Quality Index: The LIBS Quality Index (LQI) to be presented is derived from the intensity and shape of the ionic carbon line at 657.99 nm (abbr., C-658) against standards established from the ground dataset. The emission choice is based on the fact that this emission line is mostly proportional to the intensity of energy input, as shown below.

Mechanism. In a simplified model, which presumes that most of the energy transfer is carried by electrons ($e^-(\varepsilon)$) in the plasma [8], the electrons are first accelerated by the laser photons ($h\nu$) (considering only inverse-bremsstrahlung):

$$e^-(\varepsilon) + \alpha h\nu \rightleftharpoons e^-(\varepsilon + \alpha) \qquad (1).$$

α is the excess kinetic energy. $\mathrm{CO_2}$ molecules in contact with the plasma are subsequently atomized (2), ionized, and excited (3) by these hot electrons:

$$\mathrm{CO_2} + e^-(\varepsilon + \alpha_1) \rightleftharpoons \mathrm{C} + 2\mathrm{O} + e^-(\varepsilon) \qquad (2);$$

$$\mathrm{C} + e^-(\varepsilon + \alpha_2) \rightleftharpoons \mathrm{C}^{+*} + 2e^-(\varepsilon) \qquad (3);$$

$$\mathrm{C}^{+*} \rightleftharpoons \mathrm{C}^{+} + h\nu' \qquad (4).$$

Even though these processes may not be strictly simultaneous, the intensity of ionic emission ($h\nu'$) can still be derived according to the combined reaction

$$\mathrm{CO_2} + (\alpha_1 + \alpha_2)h\nu \rightleftharpoons \mathrm{C}^{+} + 2\mathrm{O} + h\nu' + e^-(\varepsilon) \qquad (5)$$

as

$$I(h\nu') \propto p(\mathrm{CO_2})I(h\nu)^{(\alpha_1+\alpha_2)} \qquad (6).$$

Given a constant atmosphere pressure, the sensitivity is mainly determined by $(\alpha_1 + \alpha_2)$ which is greater for ionic species than in neutral cases, rendering the ionic carbon line (e.g., C-658) an independent and sensitive proxy for received laser intensity at the LIBS target.

Method. The LQI intends to check whether the C-658 is "well-formed" or not, i.e., whether it stands out of the noise and whether its shape is comparable with ground measurements, so that it indirectly qualifies whether the input laser energy is comparable to that of the ground dataset.

This index is built by first fitting the two Voigt profiles between 652 and 663 nm (Fig. 1a) for the hydrogen line at 656.47 nm and C-658:

$$M(\lambda) = A_H \times \mathrm{V}(\lambda; \mu_H, \gamma_H, \sigma_H) + A_C \times \mathrm{V}(\lambda; \mu_C, \gamma_C, \sigma_C) + B \qquad (7)$$

where $A_\mathrm{i}, \mu_i, \gamma_i, \sigma_i\ (i \in \{\mathrm{C}, \mathrm{H}\}), B$ represent the area, center, Lorentzian scale parameter, Gaussian standard deviation, and baseline, respectively.

Certain constraints are added to the fitting: 1) limiting μ_C around 657.99 nm to the local pixel resolution or the uncertainty wavelength calibration; 2) limiting μ_H with $\mu_C/\mu_H = 1.00231$ as a physical constraint; 3) fixing σ_H, σ_C using presumed local instrumental full-width half maximum (FWHM) (see Table 1), as the Doppler broadenings for C and H are generally ignorable [8].

Table 1 Gaussian FWHM for the instruments. Design FWHMs from [3,5,4], respectively. Measured values from either Voigt fittings (ChemCam, MarSCoDe) or employing lamp line FWHM (SuperCam) [4].

FWHM (nm)	ChemCam	MarSCoDe	SuperCam
Design	0.61	0.41	<0.65
Measured Gaussian	0.87	0.36	0.60

The fitting is repeated 10 times, by adding an approximated local noise from the fitted standard deviation of A_C from an initial fitting, to calculate the bootstrapped mean and standard deviation (Δ) for each fitted parameter. Then, two standard-score-like values are introduced: 1) the signal-to-noise ratio of the C-658 area:

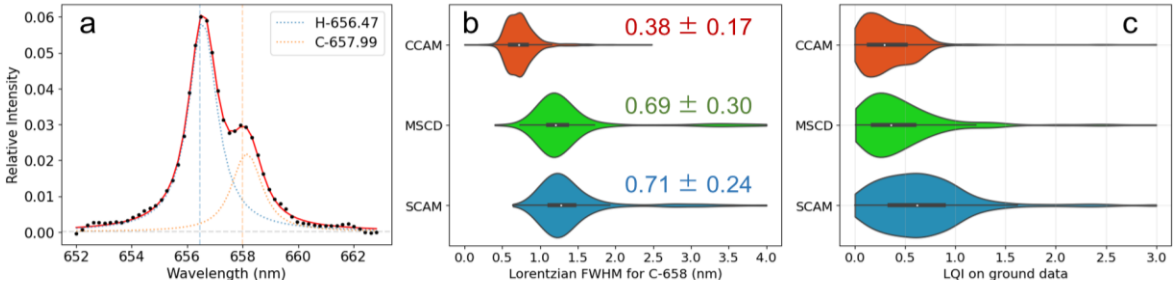

Fig. 1 a) an example of Voigt fitting for C-658 and hydrogen lines. Data from MaSCoDe; b-c) distributions of Lorentzian FWHMs (freely-fitted) and LQIs from ground datasets of the three Martian LIBS instruments [10,7,11].

$$Z_A = \overline{A_C}/\Delta A_c \qquad (8);$$

2) the standard score of the Lorentzian γ_C from the standard distribution of γ_C, i.e., $\Gamma_C \pm \Delta\Gamma_C$:

$$Z_\gamma = |\gamma_C - \Gamma_C|/\Delta\Gamma_C \qquad (9),$$

which quantifies the significance of γ_C's deviation from those in the ground dataset. The $\Gamma_C \pm \Delta\Gamma_C$ values are obtained from the distribution of γ_C on the ground dataset of the given instrument (Fig. 1b) using free Voigt fittings. Lorentzian widths can be standardized here because the electron densities for various targets were found similar for Mars [9] and the resultant Stark broadenings should be at similar scales [8].

Finally, the scores were combined based on their statistical meanings to yield LQI:

$$\mathrm{LQI} = f^{-1}\{1 - f(Z_A) \times [1 - f(Z_\gamma)]\} \qquad (10),$$

where $f(n)$ is the integral of a standard Gaussian distribution between $\pm n$. High LQI values thus imply that the data has a not "well-forming" C-658 emission.

Applications. LQIs were calculated for ground datasets of the three operating Martian LIBS instruments (Fig. 1c) [10,7,11]. Among all spectra, more than 85% were found within LQI<1 and less than 2% were beyond LQI>2. With these distributions, we could practically interpret LQI as a proxy of how much standard data there is that is similar in excitation to the target, which links the LQI values with the data similarity in addition to their statistical meaning (10). We purpose thresholding on LQI values to select data with desired quality, e.g., LQI<1 for sufficiently good spectra and LQI<2 for only removing anomalous data.

The above proposal was validated on ChemCam Mars data from Sol 815-980 which contains many Z-stacks on focus [12] (see Fig. 2 for an example). The task is to identify the steps that exceed 80% of stack-maximum irradiance in visible and near-infrared spectral range. A criterium of LQI<1 for such identification achieved the sensitivity and specificity of 77% and 74%, respectively, i.e., higher accuracy for True Positives, and LQI<2 yielded 70% and 81%, i.e., higher accuracy for True Negatives, which confirmed the proposal.

LQIs were also calculated for MarSCoDe data from Mars. Onboard calibration observations from Sol 92-110 were known out-of-focus [7], where greater averaged LQIs were found (1.3~2.2) except for the dolomite target (0.2), which further validates the index.

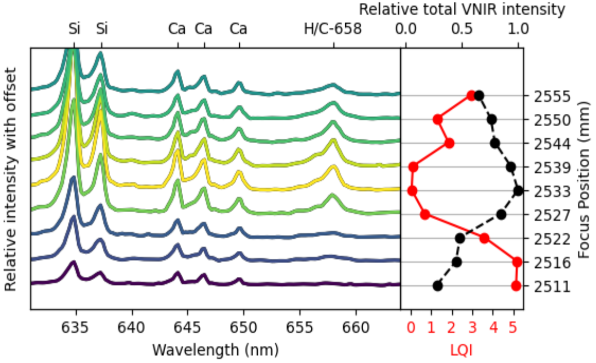

Fig. 2 LQI values along a typical ChemCam Z-stack on Sol 869. The best LQI is achieved at the best focus.

Conclusion and Future Work: The LQI based on C-658 has been demonstrated as a relevant index for Martian LIBS data quality. LQI thresholding can be used to select spectra with sufficiently good excitation (LQI<1) similar to most of the ground datasets, or to filter out anomalous ones (LQI>2). The viability of LQI has been tested on ChemCam and MarSCoDe data.

The merit of independent atmospheric carbon can be further exploited by establishing similar indexes for other carbon lines to provide additional evidence on data quality and to reduce the uncertainty of LQI.

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