

SPECTRAL DATA PROCESSING FOR LIBS QUANTITATIVE ELEMENTAL ANALYSIS OF GEOLOGICAL SAMPLES. P. Sobron, Alian Wang. Dept. Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington University, St. Louis, MO, 63130 USA (psobron@levee.wustl.edu).

Introduction: Laser-induced breakdown spectroscopy (LIBS) has been recognized as a powerful tool for stand-off geochemistry investigations during landed missions on planetary bodies including Mars[1], the Moon[2], and Venus[3,4], with potential contributions to mineralogy and petrology. A LIBS spectrometer is part of the ChemCam instrument, included in the scientific payload of NASA's 2011 Mars Science Laboratory (MSL) rover[5]. The LIBS instrument will determine the chemical composition of rocks and regolith at distances ranging from 1 to 7 meters.

We have built a Planetary Environment and Analysis Chamber (PEACH) that includes a LIBS front optics. Our experimental setup simulates the environmental conditions under which ChemCam will collect LIBS spectra on Mars[6]. In this abstract we describe a methodology for fast LIBS spectral data processing and a calibration methodology for quantitative characterization of sulfates under Mars surface conditions simulated inside the PEACH. Currently, we concentrate our effort on sulfates, because they provide one of the best means of identifying potentially habitable environments on Mars, mainly due to their association with ancient aqueous environments in which life might have thrived. In all, the combination of our instrumental setup, the spectral processing, and the calibration methodologies presented here have the potential to help extracting geochemical information from the LIBS spectra obtained by ChemCam.

LIBS data processing methodologies: Most common approaches use calibration procedures to generate calibration curves for one or several elements from the spectra of standard samples. The concentrations of the elements in unknown samples are determined from the calibration curves by measuring spectral features in their spectra. In order to compensate for matrix effects and fluctuations in the experimental conditions, normalization procedures are employed [1,7]. Multivariate analysis (MVA) is widely used and seem to be preferred for the identification and classification of materials relevant to Mars exploration [8,9]. The use of artificial neural networks (ANN) has also been suggested as a powerful identification and classification approach [10-12].

Our approach uses the standard calibration curve (SCC) technique in combination with normalization, noise reduction, and peak deconvolution methods to obtain LIBS calibration functions and fast quantification of the concentrations of major and minor elements in sulfate matrixes. Our motivation in exploring SCC

methods as a means of retrieving LIBS quantitative information is to provide a tactical advantage in rover operation by means of an effective fast evaluation of LIBS spectra. The tools we have developed can help the decision-making efforts in a mission scenario, e.g., MSL rover operations. Although the SCC approach is in general less accurate and precise than MVA and ANN [11], these later two methods involve resource consuming algorithms (i.e., high memory capacity and calculation time) to provide detailed quantitative information. Such resources (especially, time) are often limited during daily tactical rover operation. MER operation has demonstrated that between the data downlink and next sol's instructions uplink, only a few hours, at the most, are allocated for data processing and decision making. Seven series of LIBS spectra (each series comprising up to 75 spectra) can be expected from a single day of ChemCam measurements[13]. It is our opinion that a tool for fast geochem evaluation of such high-volume LIBS data packages would be very useful.

The routines we have developed are able to process 25 LIBS spectra collected at the same spot of a target and to yield quantitative information of the analyzed sample in less than 900 ms when using an Intel® Core™2 Duo E6550 CPU running Microsoft Windows XP. The processing includes filtering, normalization and averaging of the 25 spectra, search-match against a database of 100+ atomic spectral lines, computation of band areas and wavelengths, and the atomic fractions of up to eight elements in the interrogated spot.

LIBS set-up and calibration set: Our LIBS set-up has been described in previous abstracts[14]. Most of the sulfate samples used for calibration are commercial-grade chemicals, although certified natural samples were also used. Samples were powdered and pressed into pellets. A manual pellet press was used to apply ~4 tons of pressure to the powdered samples, which were placed in compressible aluminum cups (Chemplex Industries, Inc. PelletCups®) to form solid briquettes with flat surface for LIBS analyses. The samples were analyzed by XRF to determine precise atomic fractions of the relevant elements.

Data pre-processing: Spectral data must be pre-processed to minimize the influence of variable experimental conditions and matrix effects. Our LIBS set-up stores single-pulse (individual) spectra, hence allowing manipulating each of the spectra within a spectral series collected from a sampling spot. The pulse-

to-pulse analysis we have developed for the pre-processing of the LIBS spectra is divided in 4 steps:

(1) Baseline removal: In this work we have used the baseline removal routines reported by Sobron et al. [15] to generate a baseline by linear interpolation from a certain number of spectral points, which is then subtracted point by point from the spectrum.

(2) Normalization of the spectra: Each of the collected spectra is normalized to the total emission intensity to correct for pulse-to-pulse variations in the laser energy, spot size, plasma geometry and brightness, collection geometry, and matrix effects.

(3) Outlier discarding: After the normalization process, the differences in the spectral features among spectra in the same series are relatively minimal, yet noticeable, resulting in so-called outlier spectra within a series. Our pre-processing methods include a routine to remove such outliers based on the Chauvenet criterion. When an outlier spectrum is found, it is discarded from the series. The routine is iteratively applied to the remaining spectra in the series until: (i) no outliers are found, or (ii) the number of remaining spectra in the series is less than 40% of the original total number of spectra.

(4) Spectra averaging: Once the outlier spectra are removed from the spectral series from a sampling spot, the remaining spectra are averaged.

Quantification of LIBS peaks:

Spectral peak selection: The pre-processed spectrum is compared to a database of emission lines built upon the NIST Atomic Spectra Database and our own spectral libraries to identify the elements in the analyzed sampling spot. Our routines operate on a search-match principle [15] against a database (DB). Our DB has been constructed in such a way that the emission lines for a given element show minimal or no overlap with the emission lines of other elements. This is very difficult to achieve as most geological samples have complex compositions that give raise LIBS spectra populated with many peaks, most of which overlap with each other. Another constrain we have imposed to our DB is that it includes lines within the spectral range of ChemCam (225-320, 381-471, and 497-528 nm) [13], so that our methods can provide the necessary support to the upcoming MSL mission.

Peak area quantification: The spectral peaks related to the elements identified in the spectrum after comparing to the DB are then fitted to Voight functions using a Fourier-based self-resolution and self-deconvolution along with a non-linear least-squares optimization algorithm. The fitted peaks are characterized in terms of wavelength, intensity and area.

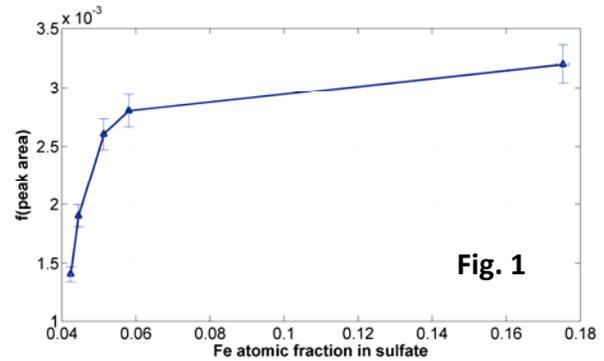


Fig. 1

Calibration: The area(s) of the atomic emission peak(s) from a recorded spectrum that is(are) assigned to a particular element is(are) used to estimate the concentration (atomic fraction) of that element in the sample. This is done in our software by using a calibration function for each of the relevant elements derived from a series of independent measurements on the XRF-characterized reference samples. The calibration function is generated by multiple regression of the area(s) of the peak(s) associated to a particular element. By way of an example, Figure 1 shows the calibration curve for Fe under martian atmosphere.

Summary: We have developed a set of routines aimed to characterize geological samples through dedicated processing of their LIBS spectra. Elements are identified by their fingerprint spectra and their atomic fraction is calculated by using calibration functions constructed upon analysis of reference materials under relevant atmospheric conditions (Earth and Mars). The mathematical basis of our software, and our database and calibration curves for K, Na, Mg, Ca, Al, Fe, S, H in sulfates will be reported at the conference.

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