

**REDUCTION OF SPECTRAL CORRELATION IN LIBS DATA USING LORENTZIAN FITTING.** Barry. R. Lienert<sup>1</sup>, Shiv K. Sharma<sup>1</sup> and David E. Bates<sup>1</sup>, <sup>1</sup>Hawaii Institute of Geophysics & Planetology, 2525 Correa Rd., Honolulu HI 96822, lienert@soest.hawaii.edu.

**Introduction:** Laser Induced Breakdown Spectroscopy (LIBS) is one of the methods deployed on the Mars Science Lander for determining chemical composition. An important problem in LIBS analysis is removing the correlation resulting from overlapping spectral peaks. Simultaneously fitting theoretical peak shapes, such as Gaussian or Lorentzian, to groups of peaks provides a way of removing this correlation. Such fitting also provides analytic integrals from the fitted peak parameters whose accuracy is better than integrals of the raw data, particularly if it is spectrally undersampled.

**Methods:** LIBS spectral data were collected at a range of 3 m using a 150 mm telescope coupled to an Ocean Optics S2500+ spectrometer. Excitation was provided by 50 mJ Nd:YAG laser pulses at a repetition rate of 20 Hz. The laser beam was expanded to 30 mm diameter then focused to a spot diameter of 100  $\mu\text{m}$  on the target using a commercial beam expander. Five or more repeat measurements were made on each sample. To provide a fresh surface, each sample was rotated a small amount between measurements. Spectral baselines were estimated using a custom-written interactive program that iteratively fits polynomials to adjoining sections after initially removing the largest spectral peaks. This program also identifies the spectral peak positions. An example of one of these baselines fitted to a LIBS spectrum is shown in Fig. 1.

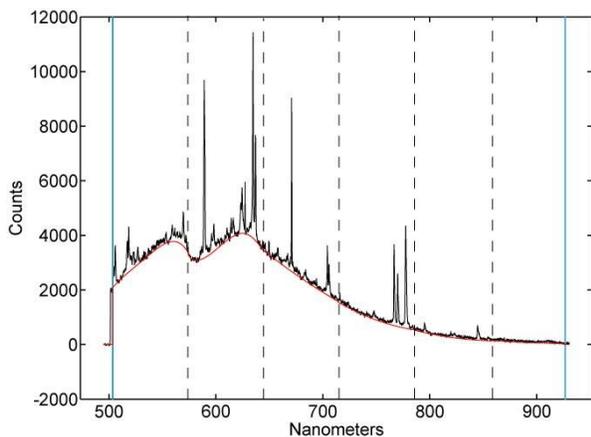


Figure 1. Multiple polynomials (red lines) fitted to a LIBS spectrum (solid black line) in the six equal intervals defined by the dashed lines. The outer blue lines define the fitting limits.

Fitting of both Gaussian and Lorentzian functions to isolated LIBS peaks indicated that a Lorentzian provided a much better fit, particularly at the lowest amplitudes. We therefore used a sum of  $N$  Lorentzian functions having the form

$$L(x) = \sum_{i=1}^N \frac{a_i}{1 + (x - b_i)^2 / c_i^2}$$

where  $x$  is wavelength and  $a_i$ ,  $b_i$  and  $c_i$  are the amplitudes, peak wavelengths and widths, respectively. The integral of the  $i$ th Lorentzian is then  $\pi a_i c_i$ . Solutions for  $a_i$ ,  $b_i$  and  $c_i$  were obtained using a MatLab routine which performs a non-linear inversion of the spectral data containing the peaks. An example of non-linear fitting for a set of LIBS spectral peaks after baseline removal, including four Fe I spectral lines, is shown in Fig. 2.

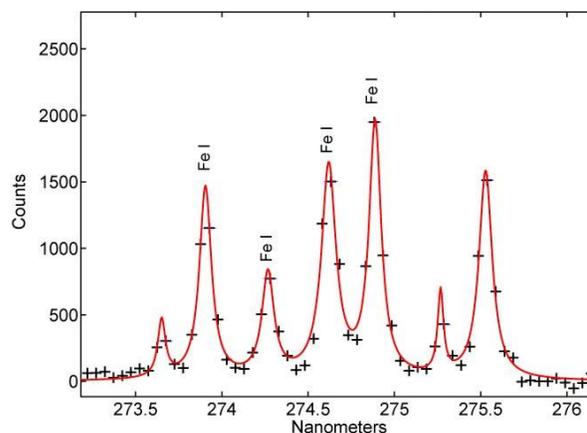


Figure 2. LIBS spectral data (crosses) and sum of 7 Lorentzians (red curve) fitted to them.

The fits in Fig. 2 indicate that taking products of spectral data points directly, as is done in a multiple regression, could underestimate the amplitudes of the spectral peaks, particularly if they are undersampled, which appears to be the case in this data.

The energy added to the sample by the laser pulse is reasonably constant, or it can be measured and normalized. The volume in which the LIBS plasma is generated will be affected by other sample properties such as its specific heat and thermal conductivity. If these are assumed constant for a group of samples, to a first approximation, the weight of the plasma will be constant. Since the LIBS spectral response will be proportional to the number of excited atoms, the number of atoms/g is the elemental concentration needed. We

have therefore used moles/g,  $M'$ , for elemental concentrations. This is calculated from each sample's measured weight fraction of oxide,  $W$ , using  $M' = WFA$ , where  $F$  is the molar fraction of oxide and  $A$  is the element's atomic weight.

**Results:** A set of nine clay samples was used for analysis. Three of these (brick, plastic and flint clays) are NBS reference materials while analyses of the other six are reported in [1]. The calculated moles/g for these samples appear in Table 1.

Sample	Si	Al	Fe	Mg	Ca	Na	K	Ti
NIST97b	5.56	5.60	0.42	0.03	0.01	0.01	0.20	0.68
NIST98b	7.48	3.86	0.59	0.09	0.03	0.03	1.10	0.39
SRM679	6.84	2.97	4.55	0.18	0.07	0.03	0.95	0.28
SWy-2	8.07	3.15	1.70	0.43	0.34	0.25	0.06	0.03
SHCa-1	6.12	0.12	0.13	2.93	4.01	0.23	0.05	0.01
KGa-1b	5.69	5.51	0.14	0.01	0.01	0.01	0.00	0.48
KGa-2	5.71	5.45	0.45	0.01	0.01	0.01	0.01	0.55
PFI-1	7.92	1.59	1.46	1.55	0.54	0.01	0.28	0.14
STx-1b	9.19	2.55	0.47	0.56	0.50	0.05	0.02	0.08

Table 1. Measured moles/g,  $M'$ , of the nine clay samples.

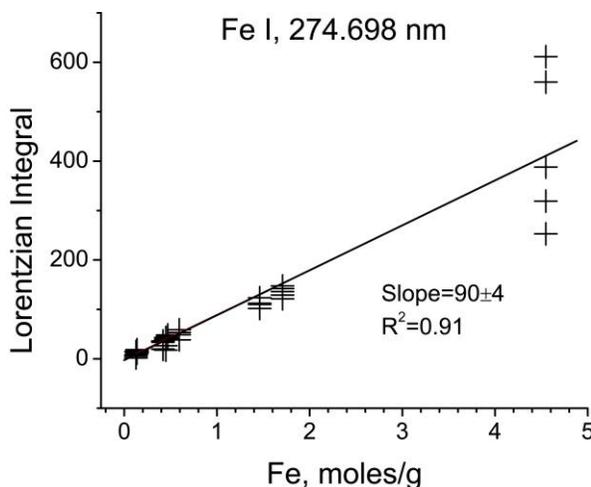


Figure 3. Integrated Lorentzian values fitted to the Fe I peak at 274.698 nm for the 9 clay samples.

Integrals of the Lorentzians fitted to the four Fe spectral lines in Fig. 2 were calculated for the nine sets of five clay spectra (five repeat measurements on each sample). Results for one of these lines (the other three were similar other than having different slopes) are shown in Fig.3. The data in Fig.3 indicate a good linear fit and low scatter in the repeat measurements for all the samples except the one with the highest Fe, the

brick clay. Whether this poor repeatability is related to the large amount of Fe is not clear. Fitting was then repeated on one of the Mg peaks. The results appear in Fig. 4. The data indicate that the variation of spectral amplitude with Mg concentration is not linear, but appears to saturate at about 5 moles/g of Mg. There is also more scatter in the repeat measurements. Similar analyses on peaks for the other elements in Table 1 also showed higher scatter in the repeat measurements.

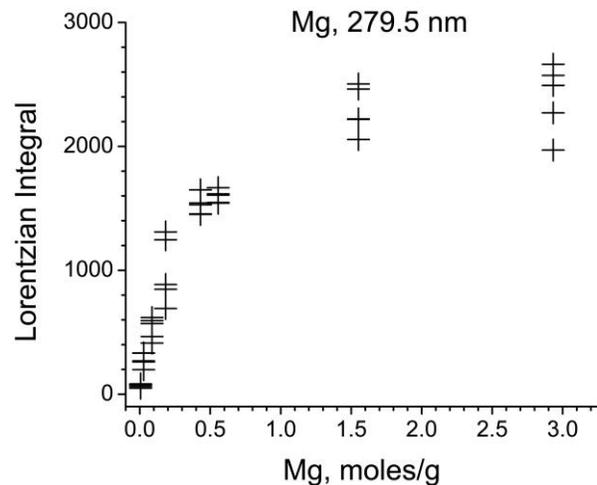


Figure 4. Integrated Lorentzian values fitted to the Mg I peak at 279.5 nm for the 9 clay samples.

**Discussion:** We have demonstrated that baseline removal, followed by fitting of LIBS spectral peaks by multiple Lorentzians results in a linear relationship between integrated spectral amplitude and Fe molar concentration in clay samples. However, the poor repeatability of LIBS spectral amplitudes for elements other than Fe is still a problem.

#### References:

- [1] Ahmet R. Mermut It and Angel Faz Can, Baseline Studies Of The Clay Minerals Society Source Clays: Chemical Analyses Of Major Elements, *Clays and Clay Minerals*, Vol. 49, No. 5, 381-386, 2001.