

**LIMITS OF DETECTION FOR MINOR AND TRACE ELEMENTS USING SCIAPS Z-300 PORTABLE LIBS.** Danielle D. Michaud<sup>1,2</sup>, Lindsey M. Rolloson<sup>1,2</sup>, Cai R. Ytsma<sup>2</sup>, and M. Darby Dyar<sup>2</sup>, <sup>1</sup>Harvey Mudd College, 301 Platt Blvd., Claremont, CA 91711(dmichaud@hmc.edu), <sup>2</sup>Dept. of Astronomy, Mount Holyoke College, 50 College St., South Hadley, MA 01075.

**Introduction:** Laser-induced breakdown spectroscopy (LIBS) has become an increasingly popular analytical method because of its wide range of detectable elements, including light elements. Portable LIBS instruments (pLIBS) that are now commercially available are capable of outputting geochemical predictions seconds after analysis. Such instruments show great potential not only for terrestrial geological field work, but also for astronaut sorties on remote surfaces, informing sample selection for subsequent analyses. We are testing the capabilities of one such instrument, the SciAps Z-300 for field exploration [1,2]. Here, we compare its reported limits of detection (LODs) for select elements with those determined on a much larger standard suite housed in the Mineral Spectroscopy Laboratory at Mount Holyoke College (MHC).

**Sample Selection:** Samples used in this study are a subset of rock powders doped with elements of interest to LIBS [3]. All are available as loose powders or as standards that have been hydraulically pressed into aluminum cups to form pellets with flat surfaces. Standards chosen for univariate analyses have compositions with dopant abundances that are found naturally within rocks. The number of available spectra used for each element is given in **Table 1**.

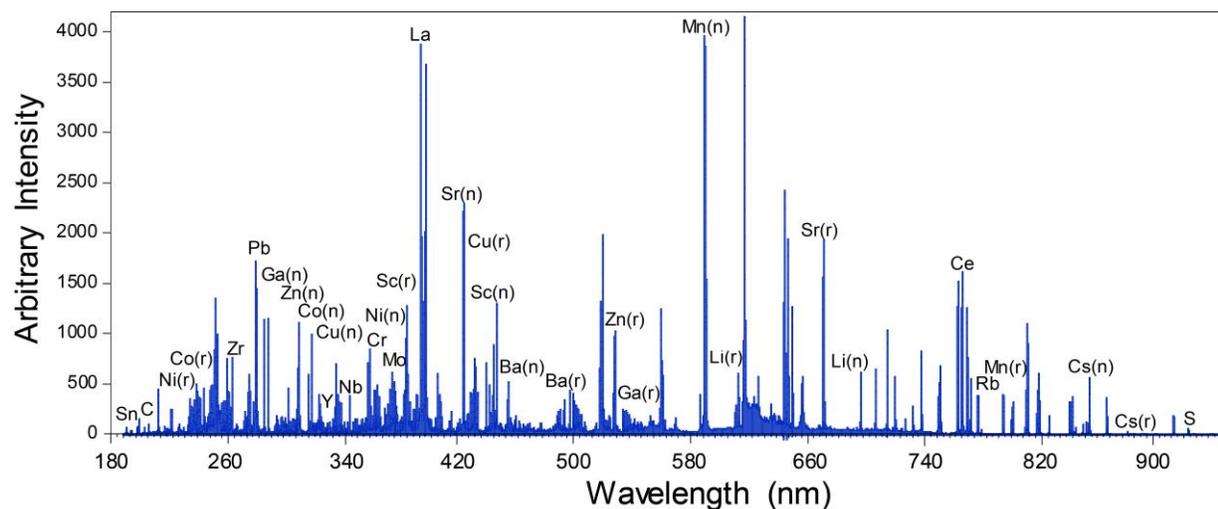
**Spectral Acquisition:** The SciAps Z-300 pLIBS firing window was held flush to each pellet and 4×3 plasma arrays were taken at three random locations on the samples' surface. Spectra from the plasma ar-

**Table 1.** Near-zero concentration ranges ("Limit", ppm) and the wavelengths (nm) that gave the lowest LODs.

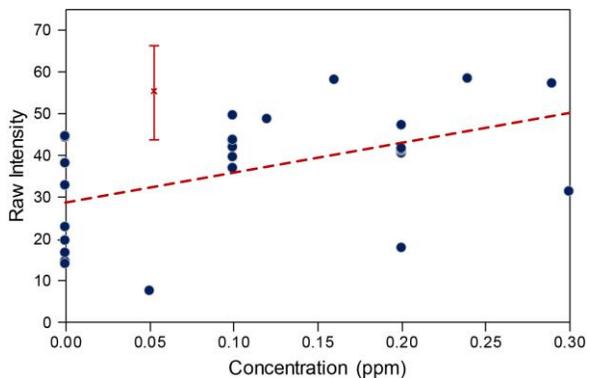
Element	Z	Limit	N	rLOD $\lambda$	nLOD $\lambda$
Li	3	2.5	69	610.37	670.97
C	6	655	53	193.07	193.07
S	16	27	246	922.30	922.30
Sc	21	1.1	169	363.03	437.57
Cr	24	10	591	360.57	360.57
Mn	25	22	37	794.63	585.57
Co	27	1.6	68	231.17	284.33
Ni	28	2.7	494	221.66	378.46
Cu	29	2.0	93	398.97	324.77
Zn	30	1.7	51	532.93	300.13
Ga	31	0.2	41	553.63	294.37
Rb	37	2.7	366	780.00	780.00
Sr	38	5	93	661.80	421.57
Y	39	0.6	10	339.20	339.20
Zr	40	2.9	11	264.40	264.40
Nb	41	0.3	29	340.53	340.53
Mo	42	0.1	4	379.83	379.83
Sn	50	0.3	40	190.00	190.00
Cs	55	0.3	131	895.37	852.10
Ba	56	12	103	493.40	455.40
La	57	0.7	71	394.20	394.20
Ce	58	2.0	42	769.63	769.63
Pb	82	0.1	45	280.23	280.23

rLODs = raw spectra, nLOD = normalized spectra, N = number of samples with near-zero concentrations

rays were averaged and the resulting three output spectra were exported and averaged to generate one spectrum per sample, for a total of 10,092 spectra. These spectra were then normalized by dividing the



**Figure 1.** pLIBS spectrum of pure Holyoke basalt matrix labelled with the peak channels at which the LODs for each element were calculated.



**Figure 2.** Near-zero Nb concentrations plotted against raw intensities at 340.53 nm. Red error bar represents the  $S_o$ .

intensity of each channel by the sum of intensities over the entire spectrum. LODs were calculated using both raw and normalized spectra. **Figure 1** shows a typical LIBS spectrum with labelled peaks chosen for LOD calculations.

**Calculations:** A subset of the 2,900 available standards was used to gather spectra of samples with ‘near zero’ concentrations for each element, here defined as the lower tail of a 95% confidence interval of the concentrations of all samples in the set. Before this interval was calculated, the samples were sorted by greatest concentration and outliers were removed. Samples at the top of the range that had unnaturally high concentrations due to doping were removed, while natural samples were included. Other outliers were removed by calculating the interquartile range (IQR) and eliminating those that had concentrations greater than 1.5IQR plus the mean value.

$R^2$  correlation was used to evaluate the symmetry between normalized intensity at a certain wavelength and the samples’ composition to find regions of the spectrum most influenced by the presence of each element. Intensities at wavelengths most highly correlated to elemental abundances and those that had the strongest NIST emission peaks were chosen to calculate LODs for each element.

LODs were calculated using  $3\sigma_o/S_o$ , where  $\sigma_o$  is the slope of the intensity vs. concentration regression line at ‘near zero’ concentration and  $S_o$  is the standard error of the regression-predicted versus true values (**Figure 2**).  $S_o$  was calculated by the ‘STEYX’ Excel function, defined as:

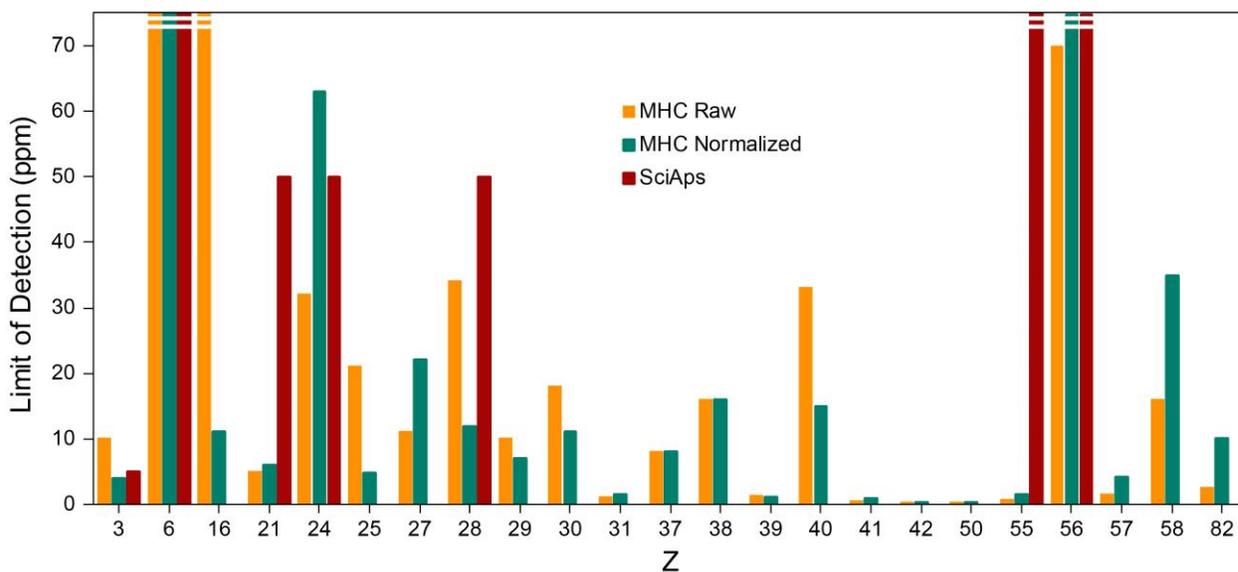
$$\sqrt{\frac{1}{(n-2)} \left[ \sum (y-\bar{y})^2 - \frac{[\sum (x-\bar{x})(y-\bar{y})]^2}{\sum (x-\bar{x})^2} \right]}$$

where  $x$  is concentration and  $y$  is intensity.

**Results:** **Figure 3** compares MHC-calculated values for raw and normalized spectra to SciAps-reported LODs. Because the LODs determined by SciAps used a much smaller suite of standards, it is to be expected that they differ from the values derived here. Overall, the performance of the portable LIBS was surprisingly good, suggesting a bright future for this technology in portable implementations for field work, both on Earth and other terrestrial bodies.

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**References:** [1] Ytsma C. R. et al. (2019) this conference. [2] Rollosso L. M. et al. (2019) this conference. [3] Dyar M. D. et al. (2019) this conference.



**Figure 3.** LODs determined using raw (yellow) and normalized (green) spectra from the SciAps Z-300, with instrument-reported LODs in red. Dashed lines indicate LODs that reach beyond the maximum table value, with some over 2,000 ppm.