

PRELIMINARY COMPARISON OF HANDHELD XRF SPECTROMETERS FOR GEOLOGICAL UNIVARIATE CALIBRATIONS. J. L. King^{1,2}, J. C. Watts^{1,2}, M. D. Dyar¹, J. Bleacher³, A. McAdam³, J. Hurowitz⁴, K. Young⁵. ¹Dept. of Astronomy, Mount Holyoke College, South Hadley, MA, 01075, ²Harvey Mudd College, Claremont, CA, 91711 (pking@g.hmc.edu), ³Goddard Space Flight Center, Greenbelt, MD 20771, ⁴Dept. of Geosciences, Stony Brook University, Stony Brook, NY 11794-2100, ⁵Johnson Space Center, ARES Astromaterials Group, Houston, TX, 77058.

Introduction: X-ray fluorescence (XRF) spectroscopy is one of the “gold standard” analytical techniques for geochemical analysis of bulk samples. Miniaturized, portable versions of XRF spectrometers have recently become commercially available, providing rapid, *in situ* analyses for mining and industrial applications. These handheld XRF (hXRF) instruments have great potential for use in planetary science exploration, both on Earth and by astronauts, but current technology and calibrations are not well-suited for geological analyses. Few calibration curves exist for geologically relevant elements and matrices. There is a need to expand the diversity of geological standards for hXRF, with appropriate calibration curves to relate spectral intensity to element concentration.

This project compares different methods of creating calibration curves by using peak intensity and area, summed manually and with two different mathematical models, and by analyzing available K- α , L- α , and M- α peaks. Results are used to compare the Bruker Tracer III-SD and Olympus Innov-X Delta Premium hXRF units with varying settings to determine the best calibration for major and trace elements.

Instruments: The Bruker Tracer III-SD comes with four filters and easily adjustable current and voltage settings [1-3]. Seven different settings for analysis of Na, Mg, Al, Si, K, Ca, Sc, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Sn, Cs, Ba, La, Ce, and Pb were evaluated, as described in [3]. Based on this work, two different settings were used for this comparison: no filter for light elements, and yellow filter for heavier elements. The Olympus DELTA Premium does not come with filters, but instead fires two different beams each time it is run: beam 1 for analysis of heavier elements, and beam 2 for light elements. This configuration is far more convenient for users, because there is no need to manually change filters (as is needed on the Tracer).

Samples and Methods: Samples used for this study were a subset of the >3000 standards in the Mount Holyoke College Mineral Spectroscopy Lab collection, pressed into powder pellets as described in [4]. Of these, roughly 600 samples of different geological rock types (basalt, rhyolite, sea sand, etc.) were doped with up to 10 wt% of the element of interest (e.g., [5-7]). A combined total of 3566 spectra

were collected on the two hXRF instruments. The lab website nemo.cs.umass.edu:54321 [8] was used to process the data. Individual peaks at the x-ray lines for each element were fit using three different algorithms: Gaussian and Lorentzian line-shapes and a “Summed Area,” routine that simply sums the total counts under each peak. Each algorithm calculates both the intensity of the peak and the area under the peak, yielding an intensity and area value for each of the three techniques, or a total of six possibilities. Four different settings were used: Tracer Yellow Filter (TY), Tracer No Filter (TN), Olympus Beam 1 (O1), and Olympus Beam 2 (O2). Calibrations were created for each combination of settings up to three polynomial degrees, giving 72 calibrations for each element.

PolyReg-CV, another web interface, was used to create calibrations and calculate cross-validated leave one out root mean square errors (LOO RMSE-CV), which allowed for direct comparison among calibrations (<http://bregman.cs.umass.edu:5693>).

Univariate Calibrations: **Table 1** shows analyzed elements arranged by atomic number. Major elements (Mg, Al, Si, K, Ca, Ti and Fe) are highlighted in grey, while the rest are trace elements. The key to color coding and abbreviations in **Table 1** is provided in **Table 2**. Both LOO RMSE-CV (prediction error on each element for unseen data) and the average concentration of that element are provided to facilitate comparison of calibration accuracy among elements.

Values of RMSE were tested for significance using ANOVA (analysis of variance) with $\alpha = 0.05$, to examine each variable (filter, algorithm, and area vs. intensity). Statistically significant settings are given in blue font in **Table 1**. In some cases, there were two superior settings, and the second best setting is displayed in parentheses.

Peak Area vs. Peak Intensity and Algorithms. Use of peak areas to predict concentration rather than peak intensity was expected to yield lower RMSEs, but this was not the case. Calibrations created with peak area were not significantly different than those created using intensity. Typically, algorithm type had no statistically significant effect on RMSE, but when it did, the Summed Area technique was consistently best.

Differences in Filter with Atomic Number. The most important factor in creating a calibration with a low RMSE was the choice of filter. O2 and TN were expected to be most successful with light elements, while O1 and TY should be better at detecting heavier elements. However, O1 was the best filter for many

Table 1. Optimal Settings for Peak Analyses

Element, α Line	Z	LOO RMSE- CV*	Avg. Conc.	Lowest RMSE Filter	Algorithm/ Intensity or Area
MgO	12	±1.42	4.99%	O2	G/I
Al ₂ O ₃	13	±3.03	12.46%	O2	S/A
SiO ₂	14	±3.89	60.61%	O2	S/A
K ₂ O	19	±0.57	2.35%	O1 (TN)	S/I
CaO	20	±1.08	5.26%	O2 (O1)	S/I
Sc	21	±302	599 ppm	O2	S/I
TiO ₂	22	±0.22	1.09%	TN/O1	S/I
Cr	24	±1527	1086 ppm	TY	S/I
Mn	25	±549	1783 ppm	O1	S/A
Fe ₂ O ₃	26	±1.57	7.25%	O1	L/A
Co	27	±525	1621 ppm	O1	S/A
Ni	28	±235	1392 ppm	O1	S/A
Cu	29	±154	971 ppm	O1	G/I (S/I)
Zn	30	±260	1156 ppm	O1 (TY)	S/A
Ga	31	±229	837 ppm	TY (O1)	L/I
Se	34	±190	1906 ppm	O1	L/I
Rb	37	±267	475 ppm	O1	L/I
Sr	38	±237	872 ppm	TY (O1)	G/I
Y	39	±168	598 ppm	O1 (TY)	S/A
Zr	40	±261	749 ppm	TY (O1)	S/A
Nb (L)	41	±767	836 ppm	O1	S/A
Nb	41	±211	836 ppm	TY (O1)	L/I
Mo (L)	42	±1183	1169 ppm	O1	S/A
Mo	42	±292	1169 ppm	O1	G/I
Sn (L)	50	±940	1192 ppm	O1	S/A
Sn	50	±164	1192 ppm	O1	S/A
Cs (L)	55	±299	1088 ppm	TY	L/I
Cs	55	±234	1088 ppm	O1	S/A
Ba (L)	56	±251	333 ppm	O2	G/I
La (L)	57	±871	764 ppm	TN	S/I
Ce (L)	58	±286	747 ppm	TN	S/A
Pb (M)	82	±716	756 ppm	O1	S/A
Pb (L)	82	±152	756 ppm	O1	L/I

*Oxides given in wt.%, trace elements in ppm. K- α lines were analyzed, unless otherwise specified in element column. Z = atomic number, S = summed area of peak, G = Gaussian, L = Lorentzian; I = Maximum Intensity or A = Area for parameter used. Statistically significant settings are given in blue font.

low-energy peaks. The success of O1 was statistically significant in the case of K due to an Ar instrument detector peak in every O2 spectra that interferes with the K peak.

For high-energy peaks, O1 and TY tended to yield the most accurate calibrations, as predicted. O1 and TY were the best filters six times, while O1 alone was the significantly best filter four times. TY was never the single best filter, which suggests that O1 is the superior filter for creating accurate calibrations for high-energy peaks. Similarly, O2 was more successful than TN for low-energy peak analysis. These results

suggest that the Olympus Innov-X DELTA Premium produces better univariate geological calibrations than the Bruker Tracer III-SD without the need for filter changes, making this instrument easier to use in field applications.

Table 2. Color coding for Table 1.

Key	Description
TN	Tracer III-SD; No filter; 15 keV; 35 μ A; Vacuum ON
TY	Tracer III-SD; Yellow filter; 40 keV; 10 μ A; Vacuum OFF
O1	Olympus Innov-X Delta Premium; Beam 1
O2	Olympus Innov-X Delta Premium; Beam 2
Blue	Significantly lower RMSE than other settings
Grey	Major elements (RMSE and avg. conc. given in wt. %)
White	Trace elements (RMSE and avg. conc. given in ppm)

Conclusions and Future Work: The goal of this study was to suggest methods to predict element concentrations more accurately in geological samples. Although many standards remain to be run, existing calibration models for all elements are available from the authors upon request. Many of the limitations in calibration accuracies for these portable units are likely inherent to the size, safety, and portability of handheld devices. Because many geological applications require accuracies of <1% relative, it is clear from **Table 1** that hXRF is currently only a semi-quantitative field tool. There may be many applications where its predictions are sufficient to answer questions in the field. These results should assist hXRF users in understanding the limits and characteristics of these two popular hXRF spectrometers.

Further research is needed to improve hXRF technology so that it can become a quantitative field tool for geochemical analyses. A more thorough comparison of all possible adjustable parameters on both instruments would be useful. Comparisons of these spectra to those from conventional, laboratory-based XRF units would be desirable to help understand the sources of errors. Samples used in this study include doped pellets with concentrations ≤ 10 wt%; a future study should reexamine calibration curves for naturally-occurring concentrations <1 wt%. Finally, multivariate analysis should be tested to improve prediction accuracy.

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