

FILTER SELECTION FOR ANALYSIS OF GEOLOGICAL SAMPLES WITH HANDHELD BRUKER TRACER XRF. J. C. Watts^{1,2}, J. L. King^{1,2}, M. D. Dyar¹, C. Ytsma³, J. Bleacher⁴, A. McAdam⁴, J. Hurowitz⁵, K. Young⁶. ¹Dept. of Astronomy, Mount Holyoke College, Mineral Spectroscopy Lab, South Hadley, MA, 01075, ²Harvey Mudd College, Claremont, CA, 91711 (jwatts@g.hmc.edu), ³Dept. of Chemistry, Smith College, Northampton, MA 01063, ⁴Goddard Space Flight Center, Greenbelt, MD 20771, ⁵Dept. of Geosciences, Stony Brook University, Stony Brook, NY 11794-2100, ⁶Johnson Space Center, ARES Astromaterials Group, Houston, TX, 77058.

Introduction: X-Ray Fluorescence (XRF) spectroscopy is an analytical method used widely in the geological field that has been touted for its benefits of low cost and ease of use. In recent years, miniaturized, portable versions of XRF spectrometers have become commercially available, providing rapid, *in situ* compositional analysis in field settings. However, handheld XRF (hXRF) technology has been tailored for mining and industrial applications rather than for geological and planetary science. There is a need to expand the diversity of geological standards for hXRF, with appropriate calibration curves to relate spectral intensity to element concentration.

Any hXRF-based calibration depends on optimization of instrument settings. This study focuses on the Bruker Tracer III-SD hXRF, which allows the user to control the voltage, current, and vacuum, and provides a choice of four filters; few recommendations for settings have been published [2-4]. This work aims to provide a data-supported guide for selecting optimal settings on the Tracer when detecting various major and trace elements.

Samples: Columbia River basalt, rhyolitic Mexican obsidian, pure augite from Harcourt, Ontario [5], and a basalt from Holyoke, MA (MIX205) were used for analysis of major elements. Tests for Na and Mg required two additional samples, albite A131705 and ultramafic MIX67. Geological standards for the analysis of trace elements were created using the standard protocol for creation of XRF standards. A ~9:1 mixture of matrix:dopant was shatterboxed to create a homogenous powder. This 10 wt.% powder was then weighed into



Figure 1. Lab benchtop setup for Tracer III-SD with vacuum at right.

successively greater amounts of matrix to create mixtures with concentrations of 5, 1, 0.5, and 0.1 wt.% and 500, 250, 100, 50, and 10 ppm of dopant depending on its molecular weight. Each mixture was then re-shatterboxed to homogenize and reduce the grain size to <15 μm . Aliquots of each mixture were analyzed by lab-based XRF at U Mass Amherst [6,7] and by XRF and ICP-MS for trace elements at the Bureau Veritas Mineral (Vancouver BC, Canada), for comparison with the as-weighed concentrations. Matrix rocks consisted of a granite, sea sand, two rhyolites, three basalts, and a 50:50 mixture of diopside and olivine (~ultramafic rock). Doped elements included Ba, Ce, Co, Cr, Cs, Cu, Ga, La, Li, Mn, Mo, Nb, Ni, Pb, Rb, S, Sc, Se, Sn, Sr, Th, U, Y, Zn, and Zr. These standards are analogous those described in [8-10].

Methods: Using guidelines for filter, voltage, and current selection in the Tracer III-SD standard operating procedure published by the MIT Center for Materials Science and Engineering [2], seven different setting combinations were tested (**Table 1**). The MIT standard operating procedure also served as a guide for using the instrument. With the Tracer III-SD arranged in a benchtop setup (**Figure 1**), data were acquired under all seven settings using Bruker's S1PXRF software. After each timed run, counts at the K- α peaks for each element of interest were recorded. Each peak count was normalized to the total accumulated counts to calculate a count ratio. By comparing various count ratios for the same sample, the setting that yielded the most pronounced peak for each specific element was identified.

Results and Discussion: Overall, the general trends of filter performance as observed from the collected data align with the recommendations in the MIT guide. For example, setting 2C (shown in light gray, **Figure 2**) becomes less effective as atomic number (Z) increases,

Table 1. Setting Combinations [2]

#	Filter	V	C	Vac	MIT Suggested Elements
1	Yellow	40	10	Off	Metals (Ti to Ag, W to Bi)
2A	None	40	5	On	General analysis (metallic)
2B	None	40	20-25	On	General analysis (non metallic, except S and Cl)
2C	None	15	35-55	On	Light elements (Cu and below, except S and Cl)
3	Red	40	15	Off	Heavy metals (Hg, Pb, As)
4	Green	40	15	Off	Heavy elements in ceramics
5	Blue	15	55	On	Light elements (Fe and below, except for Ti and Sc)

= setting; V = voltage (kV); C = current (μA); Vac = vacuum

Table 2. Optimized Settings Per Element

Elements (Atomic #)	Setting Yielding Highest Count Ratio	Next Highest Settings
Na, Mg (11, 12)	not detectable	(2C)
Al, Si, K, Ca, Sc, Ti (13,14,19,20,21,22)	2C	2A, 2B
Cr, Mn (24, 25)	2C	2A, 2B, 5
Fe (26)	2C, 5	2A, 2B
Co, Ni, Cu (27,28,29)	5	1
Zn, Ga, Se (30,31,34)	1	3
Rb, Sr, Y, Zr, Nb, Mo (37-42)	3	1,4
Sn, Cs (50,55)	4	3
Ba, La, Ce (56,57,58)	2C	2A, 2B
Pb (82)	1	3

consistent with the conclusions in the MIT guide. Although the trends generally match with the guide, there are a few inconsistencies that are discussed below (**Tables 1, 2**).

Major Elements. Na, Mg, Al, Si, K, Ca, Ti, and Fe were analyzed using 60 second timed runs. Results are summarized in **Table 2**. In the doped standards, Na and Mg were difficult to detect due to low abundances, so additional samples A131705 and MIX67, with 8.49 wt.% Na₂O and 18.02 wt% MgO, respectively, were added to the sample set. Because Mg has a low Z, its peaks were extremely weak; however, small peaks were observed for settings 2A-C and 5, with the highest count ratio observed using setting 2C. There were no Na peaks, likely due to its low atomic number. Although setting 2C consistently yielded a slightly better count ratio for the light elements, these analyses always had a Cl peak at 2.62 keV which overlapped with S and Ar peaks. Therefore, Cl, S, and Ar must be analyzed with setting 5. In summary, settings 2C and 5 are generally optimal for light element analysis.

Trace Elements. Spectra were collected on pressed powder pellets doped with 10% by weight of a series of trace elements (Sc, Cr, Mn, Co, Ni, Cu, Zn, Ga, Se, Rb, Sr, Y, Zr, Nb, Mo, Sn, Cs, Ba, La, Ce, and Pb) using all seven settings during 45 second timed runs (**Table 2**). Because these dopants are heavier elements, K- α , L- α , and M- α peaks were analyzed. To obtain the total count

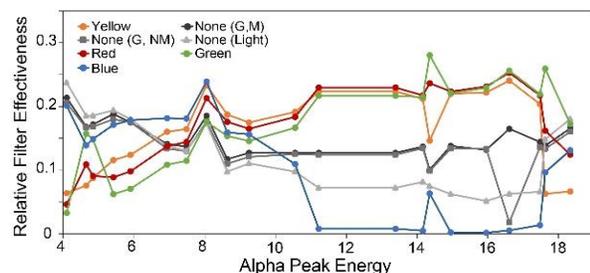


Figure 2. Relative count ratios for different filters plotted as a function of dominant α peak energy.

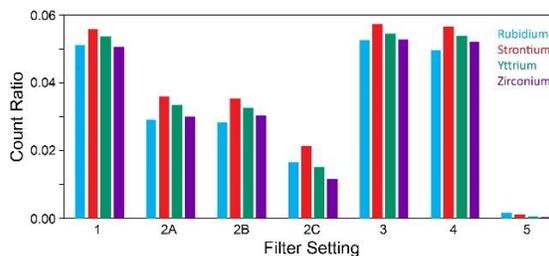


Figure 3. Bar graph showing comparison of count rates for trace elements (left to right) Rb, Sr, Y, Zr for each setting.

ratio, counts from each measured α peak were normalized to the total accumulated counts.

Elements with adjacent atomic numbers had remarkably similar behavior with each filter (**Figure 3**). Surprisingly, La and Ce, both relatively heavy elements, yielded the highest count ratios with setting 2C, which is meant for light elements. The energy values for the most prominent K- α peaks for La and Ce (33-35 keV) fall at the edge of the detection range of the instrument, resulting in low counts at those peaks. However, the lower energy L- α peaks for La and Ce (4-5 keV) have a similar energy as the K- α peaks of Cr and Mn (5-8 keV), which were easily detected using light element settings. Therefore, due to instrumental limitations, the most prominent peaks for La and Ce were L- α , explaining why some heavy elements were best detected with filters optimized for light elements.

Future Work: This paper establishes standard analytical techniques for rock and mineral analysis using hXRF. Trends observed should help other users with Tracer filter selection, even if their elements of interest were not specifically analyzed in this work. Further ongoing work with these settings, such as using prediction accuracy as a comparison method among filters [11], could improve our recommendations.

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References: [1] Young K. E. et al. (2016) *Appl. Geochem.*, 72, 77-87. [2] Speakman S. A. (undated) *Using the Bruker Tracer III-SD Handheld X-Ray Fluorescence Spectrometer using PC Software for Data Collection*, <http://prism.mit.edu/xray/odite/Bruker%20XRF%20SOP.pdf>. [3] Bloch L. (2015) *Use of Handheld XRF Bruker Tracer III-SD*, <http://archaeology.sites.unc.edu/files/2017/03/UNC-Handheld-XRF-Manual.pdf>. [4] *User Guide: Tracer Series*, http://arf.berkeley.edu/webfm_send/278. [5] Byrne S. A. (2015) *LPS XLVI*, Abstract #1499. [6] Rhodes J. M. (1996) *JGR-Solid Earth*, 101, 11729-11746. [7] Rhodes, J. M. and Vollinger M. J. (2004) *Geochem. Geophys. Geosyst.*, 5, Q03G13. [8] Breves E. A. et al. (2015) *LPS XLVI*, Abstract #2338. [9] Lepore K. et al. (2017) *LPS XLVIII*, Abstract #1293 [10] Mackie J. et al. (2017) *LPS XLVIII*, Abstract #1292. [11] King J. L. et al. (2018) *LPS XLIX*, this volume.