

Portable X-ray Fluorescence Spectrometry (pXRF): The Good, the Bad, and the Ugly

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Archaeologists are champions at using technology invented and used by other disciplines. For the last thirty years, X-ray fluorescence spectrometry (XRF), adopted mainly from geological applications, has been used particularly for the analysis of volcanic rocks (Shackley 2005, 2011). In nearly every case of interdisciplinary borrowing, the results have given our field tremendous leaps in method and allowed for shifts in theory, as well; yes, methods do sometimes drive or hopefully intertwine with theory (see Joyce 2011). In the last decade—indeed, the last five years—archaeologists worldwide, and particularly in North America, have been experimenting and employing portable X-ray fluorescence spectrometry (pXRF) for a host of applications—volcanic rocks, all other stone, ceramics, and soils. This, as I have written elsewhere, is good, can be bad, and sometimes is ugly (Shackley 2010, 2011). I want to say from the very beginning that I own and use pXRF in the field, museum settings, and the laboratory, and I have worked closely with Bruker in developing methods and calibrations particularly for obsidian provenance. I have used both Niton and Bruker pXRF instruments.

What is good about XRF is also mainly applicable to pXRF: analyses are rapid, easy to use (and train students to use), cost effective (compared to other instrumentation), and, most importantly, nondestructive, whereas neutron activation analysis (NAA) and inductively coupled plasma mass spectrometry (ICP-MS) are not. But there are other aspects of analysis that XRF, and particularly pXRF, cannot do:

- Sample size limits: Samples >10 mm in smallest dimension and >2 mm thick are optimal for XRF analyses, although smaller samples can be analyzed with decreasing level of accuracy (see Davis et al. 2011; Lundblad et al. 2008). With pXRF instruments now, samples down to about 2mm can be analyzed, but again, the level of accuracy correspondingly decreases (Jeff Ferguson, personal communication, 2012).
- Restricted elemental acquisition: Nondestructive pXRF is restricted generally to the elements from titanium (Ti) to niobium (Nb), but this region contains excellent elements for volcanic rocks (Shackley 2005). While some rare earth elements and those with low atomic numbers, or with very low concentrations, can be useful in discriminating sources, in most cases pXRF cannot solve that problem. Furthermore, only recently have some pXRF instruments been able to generate the energy to go beyond tin (Sn) on the periodic table, essentially eliminating heavier elements that

are useful in discriminating some sources (Shackley 2011). This is discussed in detail in Glascock's recent comparison between XRF and NAA (Glascock 2011). This is not the case with the majority of modern laboratory XRF instruments, where most elements between sodium (Na) and uranium (U) can be measured with a predictable level of precision.

- XRF cannot characterize small components: XRF, like NAA, is a mass analysis—every component in the irradiated substance is included in the analysis. It is possible to adjust the instrument to focus on small components, such as various minerals, but environmental scanning electron microscopy (ESEM), electron microprobe, or laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) are much better suited to this kind of analysis.

So, there are good uses for pXRF, and bad—or at least poor—uses of pXRF. The same can be said of laboratory XRF, but there are analytical and practical differences that bring me to the next issue with pXRF and archaeological “culture.”

Recently, in print and in the discipline in general, applications of pXRF that have no real foundation in science have appeared—mainly “just shoot a substance, and report the results.” I recently reviewed a pXRF submission to a major archaeological science journal that stated, rather emphatically, that it did not matter that the results did not match any others that could be acquired at any other lab, “that internally consistent results, were adequate to address the provenance.” However, if you cannot evaluate an analysis, it throws out a basic tenet of scientific inquiry—reliability and validity. Now, I am not saying that this is rampant in North American archaeology, but I have heard it a number of times from pXRF users. Indeed, one of the commenters on the above paper said that he or she did not care about the issues of reliability or validity. Whatever the analyst said was fine by them!

This “practice” is the ugly side of pXRF applications in archaeology, but it does not have to be that way. As noted above, some pXRF manufacturers care about reliability and validity. Below is a table of results from a recent in-press paper to the *Journal of Archaeological Science* (Speakman and Shackley 2012):

Table 2. Replicate analyses of USGS RGM-1 and comparison to published values.

| | Mn | Fe | Zn | Th | Rb | Sr | Y | Zr | Nb |
|----------------------------|--------|-----------|------|--------|-------|--------|------|--------|---------|
| Bruker Tracer (n=5) | 321±28 | 13075±69 | 40±2 | 16±1 | 157±3 | 104±1 | 26±1 | 223±3 | 10±1 |
| USGS Recommended | 279±50 | 13010±210 | 32 | 15±1.3 | 150±8 | 110±10 | 25 | 220±20 | 8.9±0.6 |
| Shackley (2012) | 302±14 | 13116±308 | n.r. | 16±3 | 151±3 | 106±3 | 25±2 | 219±5 | 9±2 |
| Skinner (1996) | 291±47 | 13480±745 | 37±7 | n.r. | 152±3 | 107±9 | 24±3 | 217±8 | 11±1 |
| Hughes (2007) | 278±10 | 13079±140 | n.r. | n.r. | 143±4 | 105±3 | 23±3 | 214±4 | 8±3 |

n.r.—not reported

The first row is an analysis of the USGS RGM-1 obsidian standard by the Bruker Tracer pXRF at the University of Georgia, and the next line is the USGS recommended values based on thousands of analyses by XRF, INAA, and ICP-MS. The Shackley (2012) line is 34 analyses of RGM-1 by the Berkeley lab XRF; Skinner (1996) is the analyses of RGM-1 on a different lab XRF by Craig Skinner; and the Hughes (2007) is analyses of RGM-1 by yet another lab XRF by Richard Hughes. While there are statistical differences between these laboratories, most of the measurements are within 1% including the Bruker Tracer pXRF measurements—and, most importantly, Craig Skinner, Richard Hughes, and I have been using each other's data to assign obsidian to source for twenty years, because we calibrate to international standards and strive for reliability and validity. There is no reason that pXRF instruments cannot do the same, as shown by the Bruker calibration.

Portable XRF instrumentation is expanding exponentially in American archaeology. We know now that these instruments, at least for volcanic rocks, can be an essential part of the archaeologist's toolkit. We just need to learn to use them properly and make the manufacturers produce instruments that can be calibrated such that we can all share and understand data on a level scientific playing field—all to the good.

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