XRF Standards and Reference Comparison
Correspondence with Dr. David Murray (Geologic Sciences, Brown University)

28 Jul 2008
Dear Dr. Murray,

I have completed some preliminary analysis of the data from the XRF gun. I have compared the results from the tests performed on the two NIST soil standards (2702 and 2781), the Blank SiO2 standard, and my three reference glasses. I have some concerns about the lack of correspondence of the data between tests as well as between the test and the known values. These discrepancies are both quantitative and qualitative. I have attached the excel file which catalogues this data and compares it with the known values (see tabs 2 and 3 for a complete tabulation of the known data). I have color coated the data to draw your attention to my relative assessment of the consistency and accuracy of the data. Below are some of my general observations:

Based on the relative consistency of the data before and after the tearing of the film, I do not think that this had an effect on the results. However, between the four tests of the NIST standards performed over the course of our testing, I found some significant variation. Not only are these inconsistencies in data outside the "+/-" variance reported by the instrument, but they are not consistent to a particular element or test. Therefore, I would recommend in the future that multiple readings be performed on each spot so that these anomalies can be identified and the data adjusted accordingly. Since I only took one reading of the reference glasses, I am even more dubious about these results.

The instrument very consistently took a reading of "<LOD" for all elements on the Blank SiO2 sample. However, there was one reading of 81ppm of antimony – which further demonstrates the inconsistency between tests (even for this relatively accurate reading).

Comparing the average reading of the instrument on the NIST standards, with the values reported in the literature you supplied, I have only identified those elements which DID agree. Cr, Zn and Pb measurements for both standards agreed well. K, Mn, Co, Cu, As, Se, Rb, Sr, and Mo measurements only agreed well for one of the standards. The values for Fe were relatively accurate for both samples (for NIST 2702 the reading was 10% greater than the known value, while for NIST 2781 it was 20% greater). However, the other elements (P, Ca, Ti, Ni, Zr, Cd, Sv, Ba, and Hg) showed poor correlation with the known values for both standards.

In the case of the reference glasses, I would like to reiterate that I only have one reading with which to compare the known values (a fact which I believe makes the data very unreliable to begin with). Comparing these values to the known values, I find that all the readings for the Reference Glass C show very poor correspondence. However, the measurements of K, Co, and Sr for Reference Glass B and D are surprisingly accurate, as are the values for Ca, Mn, CO, Cu, and Sn for Reference Glass B, which suggests that the instrument is likely capable of measuring these element levels accurately, but leads me to wonder why the rest of the data is so inconsistent. Perhaps you may have some ideas?

When the quantitative values were off, I also tried comparing the relative, qualitative relationships between the known values (in the case of the corning references, they were purposely designed to have compositions whose elemental contributions have geometric relationships – i.e. 2, 5, or 10 times one another). However, as in the case of the Ba and Pb content, the instrument was only able to distinguish the specimen with the highest concentrations (Reference C), but inaccurately reported the relative (qualitative) amounts of these elements in the other two samples (Reference B and D). Once again, these discrepancies do not seem limited to only one or two elements, and thus leave me questioning which data to trust…

I am wondering what sorts of calibrations you had made prior to our use of the instrument (and since?). I hope that my analysis will be helpful in tuning the instrument. Also, I am wondering if there is a particular reason why you chose these two standards (NIST 2702 and 2781). Can the instrument be adjusted to only look for a particular group of elements? Would this improve its accuracy? I am also wondering what you make of the inconsistency between readings of the same sample. Please let me know if you require further explanation of my analysis, or if there is further quantitative analysis which you would like me to perform. I look forward to trying to improve on these results and retesting our specimens at your earliest convenience. We are hoping to make some more measurements before the end of this week (our reports are due the end of next week). Thanks for your help and consideration.

Regards,
Andrew

7/29/2008

Andrew-

What you've done in terms of standard evaluation is exactly the process needed to determine which elements are reliable and which are suspect. At this point we have not done any evaluation of other standards but plan to in the future. We are relying on the factory prescribed calibrations to concert the intensities to concentration. The two standards came with the instrument so that's why we used them. You are only the second group to have used the instrument so we have limited data to evaluate accuracy for the full suite of elements that the unit "spits out". Also I expect some elements to be close within a certain concentration range but would deviate at other concentrations and as the matrix/sample composition varies. There are also element interferences such as As and Pb. Arsenic is unreliable in the presence of elevated levels of Pb.

Our plan it to prepare and measure a set of 10 or more certified standards (mostly sediments) with a range of elemental concentrations and use these data as you have to evaluate the reliability of the measurements over a specific concentration range. We may be able to get to this next week. However the matrix of these will not be the same as your glass samples so that may not solve your issues of those types of samples. We have a wavelength dispersive XRF but samples need to be powdered and mixed with a binder before analysis. Based on a set of 10 sediment standards, the following elements are considered reliable:

Si Al Fe Na Mg K Ca Ti Mn
Cr Cu Ni Pb Sr V Zn

I realize that the info I've given you do not solve your issues of what data to believe and what not to believe. At this point, I hope you have some info that can identify some different trends in the data (hi vs. low) for certain elements that you've deemed reliable. For your glass samples, electron microprobe would likely give you more accurate data for certain elements, but would likely take some time and cost some money.

I will be around on Wednesday and can work with your group to make more measurements.

Dave Murray