Peaking Your Interest:
an introductory explanation of how to interpret XRF data

X-ray fluorescence spectroscopy (XRF) is a widely used analytical technique for the identification of the elemental composition of a sample. It works by producing a beam of X-rays which interact with the sample causing the elements present to characteristically fluoresce/emit X-rays. This fluorescence is collected and displayed in a spectrum indicating the elements present and, with proper calibration, their abundance. The technique is non-invasive and non-destructive making it an ideal analytical method for conservation. With advancement in technology, XRF has evolved from a larger stand alone unit to a handheld device which gives a conservator or scientist the ability to visit the art object for analysis rather than having the object brought to the lab. This has prompted many museums and cultural centers to invest in handheld XRF for general analytical purposes.

When initially used, a handheld XRF appears to be an easy and foolproof instrument, but this is certainly not the case. Probably the most important aspect of XRF analysis is looking critically at and interpreting the spectrum. Think of Thomas Alva Edison's saying "success is 10% inspiration and 90% perspiration." Successful XRF analysis is 10% collection and 90% inspection.

The instrument is designed in a smaller handheld package but is no simpler than a "stand alone" XRF unit. X-ray safety is of utmost importance. If you do not handle the unit properly, you run a higher risk of X-ray exposure using handheld XRFs than with their stand alone counterparts. All users should have dosimetery badges to monitor their X-ray exposure.

Like other complex analytical techniques, consultation with, or acquiring the aid of a scientist familiar with the technique will ensure that the methodology and scientific framework of the project are viable and will produce profitable results. In addition, maintaining good communication with the manufacturer to ask detailed questions about the machine and to get advice on the best ways to work towards achieving your goals for a project is crucial to success. The use of handheld XRF has increased significantly in the field of art conservation over the last few years with almost 100 units now being used in institutions related to the field around the United States alone.

This powerful analytical technique has opened new doors for conservators exploring various objects and materials that include metals, ceramics, pigments, papers, photographs, and ethnographic artifacts. Initially these machines were developed for the identification of scrap metal and soil analysis. They have been further developed to deal with diverse conservation applications but the extent of development varies amongst manufacturers. There are many variables which can influence XRF results, but discussion about several key points is especially relevant in improving analytical techniques and subsequent interpretations.

With Edison's quote in mind, I will briefly mention some important aspects concerning the collection of spectra and then focus attention on the interpretation of spectra and related issues.

Before beginning any project that uses XRF, a good understanding of the material being investigated is crucial. For example, what elements do you expect to find and what potential problems do you expect to encounter? These answers will help you determine the ideal machine settings to ensure the best results.

Excitation energy and accelerating voltage should be set according to the material you are analyzing so that 'deadtime' is kept below 40% (ideally between 20-30%).
• Whenever possible, the correct voltage, current, and filter should be set according to the region of the spectrum you are most interested in.
• A set of standardized collection conditions should be considered whenever comparing data between a group of similar objects.
• Sample preparation, including orientation to the beam, is an important consideration to reduce effects of contamination (both within and outside the sample). Without a little time spent to set-up properly, analyses and results can be severely skewed, resulting in misinterpretation. A tripod should be considered when gentle contact is not possible and long collection times are required so as to avoid arm fatigue and slight shifting of beam location.

Although the beam can penetrate quite deep into or even through many objects (depending upon their density/absorption properties, an issue of concern for X-ray safety), the majority of return signal derives from near the surface of the object, particularly for dense materials like metals. This effect was clearly seen in an analysis of Roman silver coins (Tyrian shekels) that were poorly cleaned (Notis *et al* 2008). High levels of iron (over 3 wt%) were detected from surface dirt. After cleaning, the iron levels virtually disappeared. In addition, high zinc values found on these same coins were identified as resulting from a remnant adhesive of early labeling. If you do not have a proper understanding of the material prior to analysis, X-ray physics and the resulting data could easily cause improper results – leading to false data in publications – due to questionable scientific methods.

Once a spectrum is collected it is important, nay, imperative to recognize that there are many factors which affect it during analysis. Each element in the periodic table has characteristic fluoresced X-ray photon emission energies relating to their periodic number, as designated by Bohr's model of the atom. These energies are unique to each element and are the key feature allowing identification of the elemental composition. For example, Cu has two main characteristic emission energies from the K shell, Cu Kα and Cu Kβ at 8,047.78 and 8,905.29 electron volts (eV) respectively. It is the presence of both these emission energies that signifies the presence of copper in an object. However, in some cases there can be spectral emission line overlap where the emission lines from one element can overlap another element creating some difficulty in interpreting the spectrum.

These spectral emission line overlaps cause the majority of problems for accurate qualitative interpretation. An excellent guide discussing all aspects of X-ray theory is

published by Lawrence Berkeley National Laboratory. The booklet has two key tables which provide the emission energies for each element (downloadable in PDF format from X-ray Data Booklet at xdb.lbl.gov/). These tables are an invaluable tool for identifying element peaks and potential alternative or interference peaks within a spectrum. There are also several other on-line tables and programs for checking X-ray emission energies and potential interferences (e.g. Spectral Emission Line Overlap Checker at ucl.ac.uk/archmat/tools/emission.php).

An excellent example of the potential difficulties in interpreting spectra with spectral emission line overlap can be seen in a small section of a relatively complicated spectrum of an ethnographic artifact treated with heavy metal pesticides (figure 1). Note that the Pb Lα (10.55 KeV) and the As Kα (10.54 KeV) emission lines overlap. Are both elements present in this sample? Pb Lβ (12.61 KeV) is a fairly isolated emission line, indicating the presence of lead in this sample. What about arsenic? At the As Kβ line (11.72 KeV) there is an emission line overlap with two additional elements, Hg Lβ (11.82 KeV) and BrKα (11.92 KeV). Both slightly overlap As Kβ, confusing the situation considerably. The Lα peak for Hg (9.99 KeV) and the Kβ peak for Br (13.29 KeV) are both isolated and indicate their presence in the sample, leaving the question as to whether or not arsenic is present. The answer can be found through more complicated XRF theory and comparing peak height ratios, which is beyond the scope of this paper. A very basic explanation is that α peaks tend to have a higher intensity than β peaks at a known ratio (approximately 5:1). If we measure these peak height ratios, it becomes clearer that arsenic is present in the sample.

There are additional spectral interferences that create peaks in the spectrum which are not associated with the elemental composition of the analyzed sample. These include Rayleigh scattering, Compton scattering, sum peaks, and escape peaks.

Rayleigh scattering is the scattering of electromagnetic radiation and is an elastic effect. Simply put, the emitted X-rays from the XRF tube source anode (can be from various

sources but typically W, Rh, Mo, Ag, and Re) enter the sample and elastically bounce off the atoms within that sample with no loss of energy, and are detected as the characteristic energy from the source anode. This results in spectral peaks at the characteristic emission energies originating from the tube source.

Compton scattering results when X-rays from the XRF tube lose some energy in their interaction with the atoms in the sample through photon scattering. This produces a slightly wider peak than the Rayleigh peak with slightly reduced emission energies. The type of anode source in the tube of a particular unit may produce Raleigh and Compton peaks that can interfere with the specific elements that are of interest.

Sum peaks are the result of two characteristic X-ray photons arriving at the detector at the same time. The detector perceives this event as only one photon of twice the energy of the two incident photons. The result is a peak on the spectrum which appears at twice the characteristic elemental energy. For example Pb Lβ has emission energy of 12.61 KeV, so the sum peak would occur at 25.22 KeV which coincidently directly overlaps Sn Kα emission energy. This phenomenon is also known as a double photon counting event.

Escape peaks are caused by the creation of fluorescent Si x-rays from the detector's surface during collection of X-ray emissions from the object of interest. The result is the generation of an escape peakoccurring at 1.74 keV (the energy of the Si Kα x-ray) below each 'true' measured peak. These escape peaks are small and generally less than 1% of the parent peak height. They can be confusing for users to identify when higher concentration elements are present in the sample.

Spectral interferences can be confusing enough but things can get even more complicated when there are several elements in the sample. Matrix effects, both absorption and enhancement can occur and will alter the resulting spectrum and subsequent results. The X-ray source produces a beam that will interact with the sample and cause primary florescence of all elements present. However, when the characteristic X-rays of a higher energy element, for example Fe, are trying to escape the sample, their high energy may be enough to interact and excite lower energy elements like Ca. The result is a false enhancement affect for Ca and a false absorption affect for Fe in the spectrum. This is called secondary florescence. Following the same line of thinking, tertiary florescence can occur as well (see "Basic funamental parameters in x-ray fluorescence" for more details.)
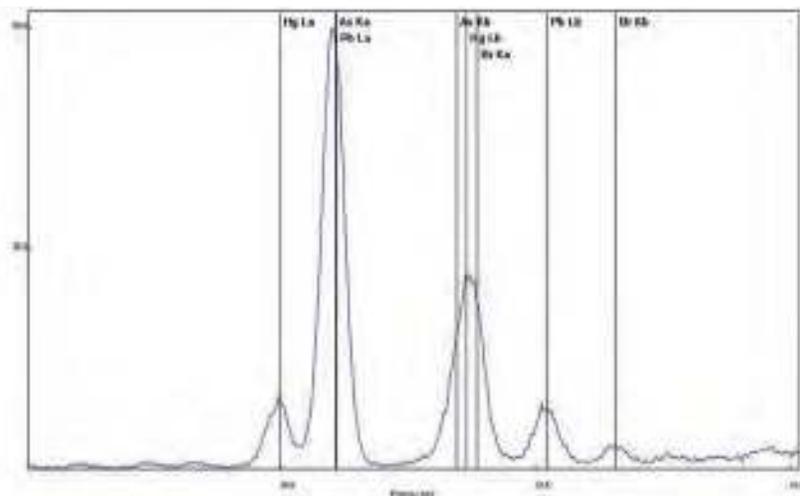

Figure 1: Part of a spectrum from an ethnographic artifact which had been treated with heavy metal pesticides showing spectral emission line overlaps of Pb, As, Br, and Hg (courtesy of the Buffalo Museum of Science).

How little can we detect and how can we quantify it?

Some commonly asked questions asked concerning XRF results include "how little can I detect in my sample?" and "can I quantify my results?" These seemingly similar ideas are actually two very different concepts. The limit of detection (LOD) is the lowest concentration level at which the XRF can detect whether an element is present in a sample. The LOD is typically reported to be as low as 10ppm for many elements by the manufacturers. A common misconception is that the manufacturer's reported LOD is the value at which conservators will be able to identify elements in their samples.

This is not the case. In fact, the manufacturer's reported LOD value is based on analysis of laboratory reference standards and should not be expected to apply with the varied compositions, densities, and thicknesses of the materials examined in conservation projects. In addition, the LOD does not equal the limit of quantification (LOQ) which is a statistically accepted value of 10 standard deviations above a blank background value (see "Limits of detection in spectroscopy" for more details on LOD and LOQ). The values for LOD and LOQ will vary by instrument and with different materials and compositions so you cannot rely on the manufacturer's suggested LOD values or their pre-calculated LOQ. These values must be verified for each instrument you are using for each material you intent to analyze.

Achieving quantification of results for individual elements is a crucial issue for conservators. There are two standard methods which manufacturers use to calibrate the machines for quantification which are pre-programmed into your instrument: Fundamental parameters and Compton peak normalization. Fundamental parameters (FP) is based on the theoretical conversion of measured X-ray peak intensities to the concentrations of elements in the sample. This is typically done using a calibration step and the resulting algorithm will provide fairly reliable results. The Compton peak normalization method uses the analysis of a single standard and the subsequent normalization for the Compton peak. The Compton peak intensity and shape is altered by materials of different matrices which can cause problems with FP calibrations. Normalizing to the Compton peak can reduce problems associated with matrix effect and is the technique that is most commonly used by handheld XRF manufacturers. Both are valid techniques but they are mainly useful for traditional modern material analysis. Applying these pre-conditioned calibrations to samples like the pesticide treated object featured in Figure 1 will result in mis-quantification and poor, if not outright wrong results.

Manufacturers do provide an option for self-calibrating machines to accommodate these different matrices and materials. This calibration option allows the user to add additional reference materials, or standards to the software so that it can better quantify specific spectra. This re-calibration must be done for each unique material conservators wish to study. For heavy metal pesticides there is now a large collaborative program to solve quantification problems for pesticide analysis. The Smithsonian's Museum Conservation Institute (MCI), National Museum of the American Indian (NMAI), National Museum of Natural History (NMNH)), the National Institute for Standards and Technology (NIST), the Canadian Conservation Institute (CCI), and the Environmental Pro-

tection Agency (EPA) have all begun to produce reference materials for calibrating handheld XRF units, specifically for quantification of heavy metal pesticides in museum collections.

The pesticide 'reference material' project was initiated by MCI with the intent to create reference materials specifically designed for calibrating handheld XRFs to accurately quantify heavy metal pesticides on ethnographic artifacts, particularly objects designated for repatriation. This collaborative approach is drawing on the expertise of conservation scientists, conservators, analytical scientists, medical toxicologists, and tribe members. Several roundtable meetings have been held over the last few years to help direct this research (see Sirois *et al* 2008 for more information about these events and working towards finding a solution for pesticide contamination in museum artifacts). In the near future, these reference materials will be made available to XRF users to better calibrate their machines. In any case, for whatever material you are investigating, it is now possible to search several reference material producers and to purchase any required samples to ensure you are calibrating your machine to the best of your ability (start with NIST standard reference materials web pageat ts.nist.gov/measurementservices/referencematerials/index.cfm).

I hope this brief overview has excited an interest in the potential for the handheld XRF in future conservation work. Although there seem to be many obstacles to overcome to obtain valid results from this powerful analytical technique, proper consultation, planning, and collaborating with a museum scientist can help in dealing with most of these issues. The benefits of handheld XRF (its portability, non-destructive analysis, and relative ease of use) ensure that their use will continue to peak interest as a major analytical tool within the conservation community. Remember! As previously stated, successful use of XRF is 90% interpretation, and this may require assistance from manufacturers, conservation scientists, or X-ray spectroscopists. In practicing good XRF analysis, you not only advance the understanding of your own object, you help to advance the development of new equipment that serves a broader spectrum of our community needs.

References

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