

Unique Problems with the Use of the Handheld XRF Spectrometer for Pesticide Surveys of Ethnographic Collections

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Introduction. The handheld X-ray fluorescence (XRF) spectrometer has become increasingly popular as a practical tool for surveying ethnographic collections for the presence of metallic pesticides. Handheld instruments are efficient, easy to use, and do not require destructive sampling in order to obtain good results. But ethnographic collections pose a unique problem for these surveys. Ethnographic objects are often made up of diverse materials. It is not uncommon to have leather, metal, glass beads, vegetal fibers, feathers, fur, pigments, and textiles combined in a single object. Mercury, arsenic, lead, and other metals deriving from these materials may be mistaken for the presence of pesticides. Environmental factors can introduce detectable levels of metallic pollutants into collections. Data from the analyzer itself can be prone to misinterpretation without the proper understanding of its capabilities and limitations.

Nevertheless, the handheld analyzer can provide valuable information about the chemistry, and therefore perhaps, the history, of the objects. It is the intent of this article to provide an overview of some of the complexities associated with the use of the handheld XRF spectrometer in ethnographic collections, and to examine some common sources of non-pesticide metals that one may encounter during an XRF pesticide survey.

Innov-X Systems Portable Handheld XRF Analyzer. The author was recently involved in a survey of a Native American ethnographic collection held by the Charles M. Russell Museum in Great Falls, Montana. The museum is known primarily for its collection of the works of western artist Charles M. Russell and his contemporaries, but it also has a rather large Native American art collection in storage that has never been surveyed. The collection consists mainly of objects from the Plains, Plateau and Southern Plains peoples, as well as a number of Northwestern and Athabaskan items.

The instrument chosen for the pesticide survey was an Innov-X Systems Alpha series Portable Handheld XRF Analyzer. This device uses an X-ray tube rather than a radioisotope X-ray source, making it safe and extremely portable. Embedded software allows the user to add or subtract elements from the scan, calibrate the instrument in the field, and also allows the user to view the actual X-ray spectra in addition to list of elements and concentrations (in ppm). This last feature is essential for proper interpretation of the results, as discussed below. The instrument was set in the soils analysis mode and calibrated by the supplier before being shipped to the museum. The soils analysis mode was chosen in consultation with the Innov-x staff as the best available option for our application¹. Routines for the analysis of arsenic, lead and mercury were included in the software package, as well as various other elements pertinent to soils analysis. The software version was the most current available as of August, 2006.

During the survey, XRF readings were taken directly on the surface of the objects, without removing a sample. Precautions were taken to eliminate false readings from materials beneath the sampled objects. In most cases this was accomplished by using a one to two inch layer of ethafoam or acid free corrugated board underneath the object. When this was not practical, i.e. when an object could not be removed from a permanent installation, background XRF readings of the underlying mounting materials were taken for comparison.

¹ The soils analysis mode assumes a homogenous sample of finely ground soil approximately 1 cm deep. Because the tested ethnographic objects were made of widely varying materials (leather, cloth, feathers, glass, etc.) unlike a soil matrix, the analyzer results could only be considered qualitative in this application, according to the manufacturer. It would be advisable to develop a more precise method of field calibration specifically for different types of ethnographic materials.

The Presence of Lead and Arsenic in Glass Beads. Early in the survey it was noted that the XRF analyzer gave extremely high readings for lead and arsenic when used directly on any object bearing glass beadwork. The average lead reading in or near the beaded areas on these pieces was 19-35%, $\pm\sim 1.1\%$, with levels of arsenic ranging from 7- 10%, $\pm\sim 0.5\%$. Areas of the same object that bore no bead decoration tested negative for both elements in all cases. It was inferred that the high readings were due to the glass beads and not to the presence of pesticides.

The presence of lead and arsenic in glass beads was not surprising, but the high concentrations of arsenic were unexpected. Oxides of lead and arsenic were commonly added to optical glass during the manufacturing process in order to change melting points, hardness, as refining agents to remove bubbles, or to impart color (Kurkjian and Prindle, 1998). Morey (1937) reported levels of As_2O_5 ranging from 0.2- 0.22% in leaded optical glass. An X-ray fluorescence analysis of West African trade beads reported levels of arsenic in leaded glass beads of European manufacture in the 2-4% range. (Davison, et. al, 1971). Typically glass trade beads brought to Africa and the Americas during the 18th and early 19th centuries originated from the same sources in Europe. Arsenic levels in the test results appeared much higher than those examples cited in the literature for glass and glass beads.

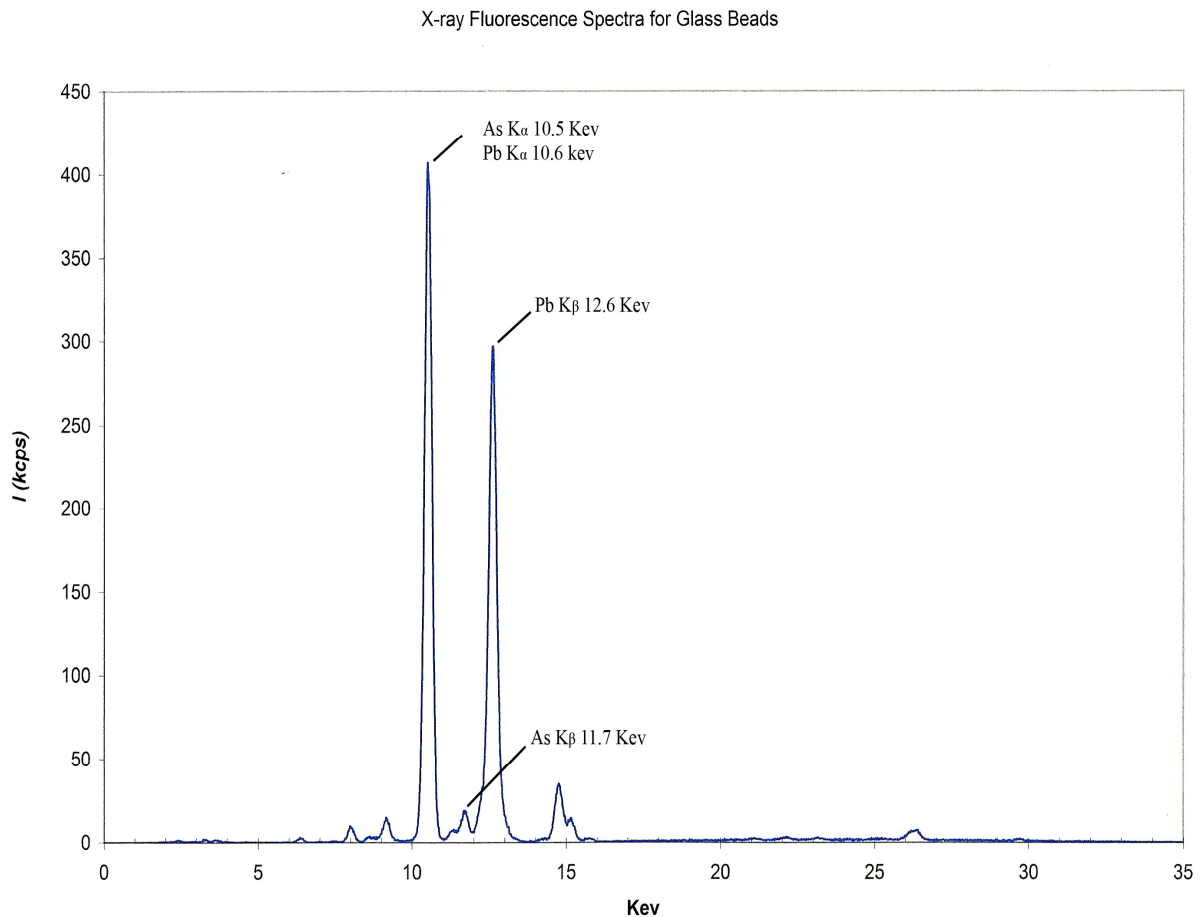


Figure 1. X-Ray Fluorescence Spectra for Glass Beads.

A detailed examination of the chemistry of glass beads is outside the scope of this paper, but it does serve to illustrate a point: at high concentrations of certain elements, the analyzer's interpretation of the data may give unreliable results. It is well known that some elements interfere with others in X-ray fluorescence spectroscopy. Because lead and arsenic have similar emissions spectra in the α (alpha) bands (As: $\text{K}\alpha$ 10.54 KeV, Pb: $\text{L}\alpha$ 10.55 KeV) the only way to tell them apart is by the presence or absence of emissions in the β

(beta) bands (As: $K\beta$ 11.73 KeV, Pb: $L\beta$ 12.61 KeV). The analyzer is programmed to use these β emission bands to differentiate between the two elements, but because of the high concentration of lead, and the corresponding high margin of error in the resulting data, it is possible for the analyzer software to misinterpret the results for arsenic. By using the instrument to view the actual spectra for the glass, it was possible to verify that arsenic was indeed present due to the marked emission spike at 11.7 KeV (see image). It would be possible to use the intensity values at this peak to calculate the actual concentration of arsenic present; however this data was not pertinent to the pesticide survey. The spectra were stored in the museum database for future analysis.

Ultimately, the presence of the glass beads thwarted our attempts to test for arsenic and lead based pesticides with the XRF. Unless there was a bead-free area on an object large enough to allow sufficient clearance for the head of the analyzer (approximately 3 x 7 cm, although the actual sampling area is only about 5 x 8 mm), accurate testing was impossible. Wipe tests and alternative chemical analyses should be considered where heavily beaded objects are suspected of being contaminated with pesticides.

Mercury in Blue Wool Stroud Cloth. The C.M. Russell collection contained a number of objects made of blue and red wool cloth with a white un-dyed selvedge. This textile type is commonly referred to as Stroud cloth, for the original place of manufacture in Stroud, England, (though the term is loosely applied to all early trade wools of European manufacture), and is also known as Saved List cloth. During the survey, the XRF analysis revealed unusually high levels of mercury in the blue Stroud, but not in the red. The concentrations averaged in the 700-1000 ppm range ± 20 ppm. There was no detectable mercury in areas of the objects not containing this blue wool cloth. It was therefore considered unlikely the mercury was from a pesticide, rather, an artifact of the cloth manufacturing process.

Research into the historic dyes for the time period revealed a likely source for the mercury in the blue wool cloth. Up until the late 1800s, natural indigo was the primary blue dye used in the textile industry.

A method for the production of synthetic indigo was developed in 1880, but the process was too inefficient to allow for large scale production. The first step in the synthesis of indigo was to oxidize naphthalene (available in great abundance as a byproduct of the coal tar industry), to phthalic acid, which is converted to phthalic anhydride. However, this reaction was very slow and yielded too little anhydride. By accident, a BASF chemist broke a mercury thermometer in the reaction vessel one day and discovered that the reaction was greatly accelerated in the presence of the mercury. The elemental mercury reacted with oxygen and sulfuric acid to make mercuric sulfate, a catalyst for the rapid conversion of phthalic anhydride. The result was a method of producing synthetic indigo at a much cheaper cost than that of the natural dye, and large scale commercial production began by the late 1890's. The accidental broken thermometer changed the entire dye industry; within ten years the production of natural indigo in India alone had dropped by 75%. (Nagendrappa, 2003).

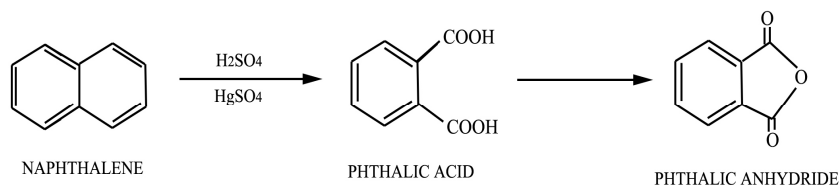


Figure 2. Synthesis of phthalic anhydride.

It is entirely likely that the mercury observed in the blue wool cloth is a byproduct of the synthetic indigo production process. If indeed the mercury is residual from the anhydride synthesis, one would expect to see Hg(II) as mercuric sulfate (HgSO₄) and other mercury salts. It is interesting to note that the mercury

catalyst was replaced by vanadium pentoxide (V_2O_5) in commercial phthalic anhydride production sometime in the 1930s or 40s. This suggests the handheld XRF might have applications as a tool for identifying and dating textiles dyed with synthetic indigo. Namely, the presence of mercury in blue cloth might be used as an indicator that a particular textile was produced between the late 1890's and the 1930s.



Figure 3. A portion of a Plains saddle bag decorated with glass beads and vermilion paint. X-ray fluorescence spectra shows high concentrations of lead, arsenic, and mercury, but no pesticides are present.

Chrome Yellow and Vermillion on Plains Indian Leather Goods. The ethnographic collection surveyed included several leather objects that originated from the people of the Southern Plains - Kiowa, Apache, and Comanche. Typically these objects were made of tanned deer hide tinted yellow with a powdered pigment; a practice that is characteristic of their art even today. On most of these objects, XRF readings for lead averaged in the 5000-6000 ppm range ± 30 -50 ppm. One example tested over 20,000 ppm lead. Arsenic levels were below detection limits, so it was unlikely that the lead was from the pesticide lead arsenate.

Curious about the source of this lead, the author asked a Kiowa acquaintance about the history of these pigments, and the response was “Ask any Kiowa who purports to know anything about old ways and they'll tell you its earth pigment from Paloduro Canyon in Texas” (Jennings, 2006). Lead ore in the American west most often occurs in conjunction with ores of zinc, silver and copper (Samans, 1949). All three elements were easily detectable by the analyzer in the soil analysis mode, but the concentrations of all three were beneath the limits of detection on the sampled objects. The high concentration of lead in a bright yellow powder without these other elements present suggested the use of something other than a naturally occurring pigment. The element chromium was present on all these objects in the range of 1300-1700 ppm, ± 70 -80ppm.

Records of early trade goods indicate that chrome yellow ($PbCrO_4$) was introduced to the Plains Indians in the first half of the nineteenth century, (Hanson, 1981). This yellow pigment, along with verdigris (copper acetate), chrome green (Cr_2O_3), Prussian blue (Iron II) and Iron(III) cyanoferrate compounds), and Chinese vermilion (HgS) were all popular commodities throughout the fur trade and well into the early twentieth century.

Carl and Vanessa Jennings of Fort Cobb, Oklahoma graciously loaned the author samples of old paint pigments for comparison. These earth paints had belonged to Vanessa's Kiowa grandfather. The powder pigments were spot tested for lead using Plumbtesmo test papers (Odegaard et al, 2000). One sample, a bright yellow powder stored in a very old beaded leather bag, tested positive. The Jennings' yellow pigment and samples from the Russell objects will be submitted for further chemical analysis to verify the presence of chrome yellow.



Figure 4. A collection of old Kiowa paint pigments in their original bags, dating from the early 1900s. Yellow pigments spot tested positive for lead.

As mentioned above, vermilion, or mercuric sulfide, was another material much favored by the Indians. It was used to decorate objects and also, rubbed onto the skin as body paint. Vermilion was present on a number of rawhide containers and a painted saddle bag in the Russell collection. The XRF spectrometer readings showed greater than 10% mercury on these objects when sampled directly in the pigmented areas.

Several objects in the collection were composed of various combinations of glass beads, yellow pigmented leather, vermilion paint, and blue wool Stroud. The XRF readings showed high levels of mercury, lead, and arsenic on these objects, and yet none of these elements were from pesticide residues. In the presence of these artifact materials the handheld XRF was rendered useless for identifying metallic pesticides. Alternative means of chemical analysis must be employed in order to survey such items for pesticides.

Environmental Sources. Unique to the collections at the museum are a number of objects personally owned by Charles M. Russell. Russell lived in Great Falls most of his adult life until his death in 1926. He was fond of collecting Indian clothing, weaponry, horse trappings and cowboy gear, and these he displayed on the walls of his log studio which still stands at its original site on the museum grounds.

All of Russell's 'studio' objects were tested for pesticides during the course of the XRF survey. Over 90 percent of these objects had lead levels in 100-400 ppm range, $\pm 6-10\%$. Even though these levels are relatively low, they would still be considered well above background levels. The fact that the levels were so consistent across the entire collection was very unusual. Research into the history of the Great Falls area revealed a possible source for the lead. From 1893 to 1980, a metals refinery complex and large smelter operated on a 250-acre piece of land just north of the city, approximately 1.5 miles from Russell's studio. The smelter was shut down in 1982, and is now designated as a "Superfund" hazardous waste site by the Environmental Protection Agency. Soils in the area are contaminated with lead, arsenic, and other toxic metals. The lead observed on the studio objects is most likely residual from the operation of the nearby smelter.

Apparently it is not uncommon for smelter and refinery residues to be detected by XRF spectroscopy. During a conversation with the author, Mr. David Walters, sales representative for the Innov-x company, explained that he was demonstrating the use of the XRF analyzer in an area where there was a large mining and smelting operation in progress. To show the presence of metals in the immediate environment, he ran his fingers down some window glass inside a classroom. With a piece of scotch tape he lifted the material from his fingertips and placed the piece of tape over the x-ray port of the analyzer. The readings from the XRF showed levels of metals well above normal background levels, presumably from the mining operation nearby. It is therefore quite possible that the elevated lead levels in Russell's studio collection are attributable to the smelter that operated north of the city during his lifetime.

Conclusion. The handheld X-ray fluorescence spectrometer is an effective tool for conducting surveys of ethnographic collections for the presence of metallic pesticides, with some caveats. Unique materials found on ethnographic objects may result in readings for arsenic, mercury and lead that can be misinterpreted as pesticide residue, and it is important that these materials be taken into consideration when conducting pesticide surveys. Alternative analytical methods may be necessary when materials such as glass beads and lead and mercury based pigments are present on objects. Environmental influences such as regional factories and refineries may contribute detectable levels of these metals as well. The versatility and ease of use of the handheld XRF analyzer makes it valuable not only for detecting pesticides, but for revealing more about the chemistry and the history of ethnographic collections.

References

“25 years later: End of Refinery Ruinous”, *Great Falls Tribune*, Sept 29, 2005.

Corey, Carolyn, “Coveted Stripes: The Origin of “Stroud” and “Saved List” Cloth for the North American Trade”; *People of the Buffalo*, Vol. 2, pp. 131-146, Tatanka Press, Germany, 2005.

Davison, C., Giaouque, R., Clark, J., “Two Chemical Groups of Dichroic Glass Beads from West Africa”, *Man*, New Series, Vol.6, No.4. (Dec., 1971) pp. 645-658.

Hanson, Charles, Jr., “A paper of Vermilion”, *Museum of the Fur Trade Quarterly*, Vol.7, No.3, Fall 1971, pp. 1-3.

Hanson, Charles, Jr., “Paint Pigments in the Fur Trade”, *Museum of the Fur Trade Quarterly*, Vol. 17, No. 4, Winter 1981, pp. 1-6.

Jennings, Carl, personal correspondence, September, 2006

Kurkjian, Charles K. and Prindle, William R., “Perspectives on the History of Glass Composition”; *Journal of the American Ceramic Society*, Vol. 81, No.4 1998 pp. 795-813.

“Missouri River Trail at Great Falls Polluted”, *Great Falls Tribune*, May 18, 2002.

Morey, George W., “The Composition of Glass”, *The Scientific Monthly*, Vol. 42, No 6, June 1936, pp. 541-554.

Nagendrappa, G., “Chemistry Triggered the First Civil Disobedience Movement in India; Indigo in Indian Independence - Role of a Broken Thermometer”, *Resonance Journal of Science Education*, Indian Academy of Sciences, March 2003.

Odegaard, N., Carroll, S., and Zimmt, W., *Materials Characterization Tests for Objects of Art and Archaeology*, Archetype Publications, 2000.

Roberts, R. M., *Serendipity (Accidental Discoveries in Science)*, Wiley and Sons, New York, 1989.

Samans, Carl H., *Engineering Metals and Their Alloys*, Macmillan Company, NY, 1952.

Walters, David, personal correspondence, September 2006, December, 2006.

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