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pXRF Analysis of Arsenic When Lead Is Present: A Cautionary Tale

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Although the InnovX Alpha Series portable X-ray fluorescence device we used to qualitatively analyze ceramics pigments and Lowry Pueblo Kiva white paint repeatedly reported As (in hundreds of measurements) whenever significant amounts of PB were present, there were in fact no significant amounts of As present in those samples. Obviously, care must be taken when using that device to determine As when there are significant amounts of Pb present in the samples.

Portable X-ray fluorescence spectroscopy (pXRF) is beginning to be used more and more in art, conservation and archaeology (*1-11*) to list a few. We wish to point out a potential difficulty with the use of pXRF when analyzing for As (As) in the presence of significant levels of Pb. In particular, we have faced that situation in two projects we are currently working on: pigment analysis of the decorations of some ceramics from the Colorado Plateau and some white paint on the painted kiva walls at Lowry Pueblo.

Our pXRF analyses indicated that hundreds of the ceramic pigments and

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some of the kiva wall paint layers contained elevated levels of Pb and As. When significant Pb signals were seen in samples, As was also always detected at elevated levels. As an example of the problem, we will concentrate on one of the Lowry Pueblo Kiva B paint layers here. Paul Martin, the excavating archaeologist, reported Kiva B overall had up to 2 inches thick plaster with multiple layers (12). Our sample is obviously only a small part of what he saw and had six layers of brown plaster, separated by white paint layers. Our analyses of five of those paint layers indicated that Pb and As were prominent in at least one of them, along with Zn.

Experimental Procedure

For our initial analyses, we used a battery operated InnovX Systems Alpha Series, portable, hand-held, nondestructive pXRF device for measurements of the elemental signal of the white paints used in the Lowry Kiva wall paints and Colorado plateau ceramics. The spectrometer works by irradiating the sample with an X-ray tube that emits primary X-rays that strike the target, in our case the surface pigments associated with individual ceramic design elements and Lowry Pueblo white painted Kiva walls. These primary X-rays sometimes strike an orbital electron in an atom (say Fe) of the sample being analyzed with enough energy to knock out the electron from the inner electron shell of the element. The removal of such an electron from an element is accompanied by the emission of secondary X-rays in the atom's attempt to re-stabilize itself. The energies and numbers of secondary X-ray emissions are measured. The energy of a secondary electron is specific for a given element, and essentially different from all others *with a few exceptions*. Thus, ideally the technique qualitatively detects the atoms that are present in the pigments. Then, with proper calibration and software, the approximate (semi-quantitative) abundances of the elements present can be calculated by measuring the intensities of the radiations of particular energies. Abundances in *uniform*,

homogeneous samples as low as 10 parts per million (ppm) are possible for some elements. The elemental analysis on the InnovX instrument is displayed on the miniature iPAQ computer as parts per million for a given element. In the situation here, we recorded measurable signals from the pigment elements Pb and As (as well as Zn in the kiva wall paint), and Fe, Cu, Mn, Rb, Sr and Zr (present in the ceramics and the plaster that separates the Kiva paint layers). But we emphasize that the method is not even semi-quantitative in the application to ceramic and wall paint pigment analysis; we do not get accurate measures of the *abundance* (ppm, e.g.) of the elements for a number of reasons: (1) the pigment often does not cover the entire area of the target primary X-rays; (2) the paint/pigment is thin, but not of uniform thickness; and (3) the pigment is not necessarily uniform in the paint/pigment layer. These factors combine to render the method *qualitative* with at best a rough indication of the presence at lower vs. higher levels. Nonetheless, we will see that the analyses are useful in spite of these difficulties. We are, at this stage, primarily interested in determining what elements were used as pigments in the paints.

With these difficulties in obtaining quantitative concentrations, one might ask, õWhy use pXRF at all?ö The advantages are significant. Importantly, *nondestructive* in situ analysis is possible. Second, the device is easy to use ó just point and shoot. Third, each analysis is fast ó typically just 10 - 30 seconds per analysis will indicate clearly the dominant pigment elements used in a paint, pottery design element; etc. For better statistics in some applications, up to 300 second counts were used. Data reduction takes longer. One can analyze hundreds of samples; so the device is very applicable for survey work. Fourth, the instrument is light enough that it can be carried to remote sites. It is *generally* reliable for *qualitative* analysis, i.e., the presence numerous elements in this study. But extreme caution must be exercised at times, as in the case of the As supposedly detected in this study.

Figure 1 shows one example of a pXRF analysis, one of hundreds of pigmented ceramics where Pb and As were reported on the screen of the InnovX Alpha series handheld X-ray fluorescence spectrometer (pXRF).

Figure 1. A photograph showing analysis of black pigment painted on a white ceramic from the Colorado Plateau. Readout indicated the presence of Pb and As in the pigment. That As was typical of all ceramics where Pb was indicated as a major component of the pigment. That is, in every case when high levels of Pb were recorded, lesser amounts of As were also reported on by the pXRF.

Results and Discussion

Table I shows a table of the average of five determinations from the iPAQ handheld computer readout on the InnovX pXRF device for a typical result yielding high levels of Pb and As (and Zn). The other elements detected are almost certainly due to the underlying plaster layer. In our experience, every

time a sizable Pb peak was seen, an elevated As signal was invariably seen as well. Because of the overlap between the Pb and As peaks at 10.6 keV, and that peak is apparently used for both Pb and As determinations in the InnovX software, we became concerned whether the As results were valid, or were an instrumental software artifact. We therefore consulted the InnovX brochure concerning the peak overlap problem between Pb and As. The Innov-X User Manual Version 2.1, Soil Appendix 14 reads, õExample 1: Lead and Arsenic. Most XRFs are calibrated for lead and arsenic. Lead interferes with arsenic (not vice-versa though). The net effect is a *worsened detection limit for arsenic, and poorer precision. The XRF handles the correction automatically, but the precision is affected. The loss of precision is also reported by the XRF*.ö The italics were added by us for emphasis. That this is the position held by InnovX was confirmed by a telephone call to them. However, because we invariably õdetectedö significant As signals whenever we detected substantial indications of Pb, we continued to be wary. High Pb measurements were accompanied by significant As in several hundred ceramics samples (*13, 14*).

Table I. The table contains an average of five, 300 second determinations from the iPAQ handheld computer readout on the InnovX pXRF device. We bold faced Pb and As, those being the elements of interest here. The pigment here contains principally Zn, Pb & As. Other elements are likely from clay fabric.

Innov-X Results	Kiva B Paint	Innov-X Results	Kiva B Paint
Ti	1002±223	Hg	86 ± 11
Ba	2406 ± 139	**As**	**3329 ± 43**
Cr	172 ± 42	Se	102 ± 7
Mn	120 ± 23	**Pb**	**23496 ±231**
Fe	8461 ± 111	Rb	84 ± 2
Co	244 ± 22	Sr	88 ± 1
Cu	57 ± 11	Zr	242 ± 4

Zn	57983 ± 570	Cd	78 ± 6

To examine the problem further, we utilized a Bruker Tracer III-V pXRF device at the Conservation Laboratory of the Museum of New Mexico, Santa Fe, NM. With that instrument, unlike our InnovX device, it is easy to display and manipulate the scale for the raw spectra taken. Figure 2 shows a pXRF spectrum of the sample of Lowry Pueblo Kiva B outer paint layer (shown in Figure 3) taken with the Bruker pXRF device, showing the major peak overlap between Pb and As at the asterisked peak at 10.6 KeV.
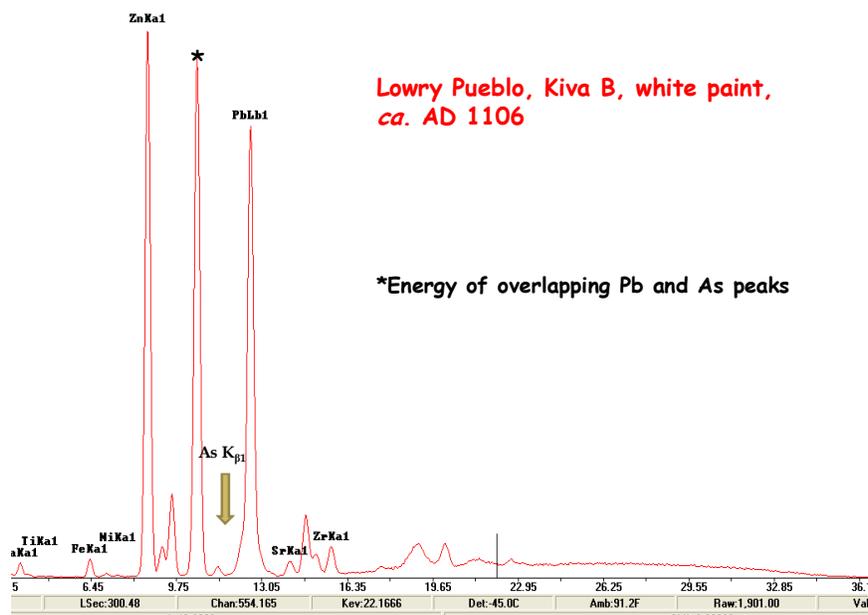

Figure 2. PXRF spectrum of the Lowry Pueblo Kiva B white paint. The asterisk above the peak at ~ 10.6 keV indicates where both the Pb L_{a1} and As K_{a1} occur, i.e., overlap, a potential problem. Unfortunately, the algorithm for determining the abundance of As on the InnovX device uses this peak. The yellow arrow points to the position of the As $K_{\beta1}$ peak of As, a peak that is not interfered with by the Pb.

Figure 3. Photograph of the sample of the outer white paint layer from the Lowry Pueblo Kiva B. Other layers are visible on the edge views.

To evaluate this suspected õAsö problem more carefully, we examined the K_1 peak of As at 11.7 keV, which is not coincident with a Pb peak. That is a more definitive means of seeing whether there is significant As present in a measurement or not. Figure 4 shows the spectrum with the y-axis expanded to investigate the As K_1 peak in detail. As can be seen from Figure 4, there is no substantial As observed in the sample. For every case we checked (amounting to many replicate measurements of the Kiva B wall paint, as well as hundreds of measurements on Colorado Plateau ceramics), we did not find evidence for substantial As at the As K_1 peak even though As was reported on the iPAQ computer screen of the InnovX pXRF every time in considerable abundance.
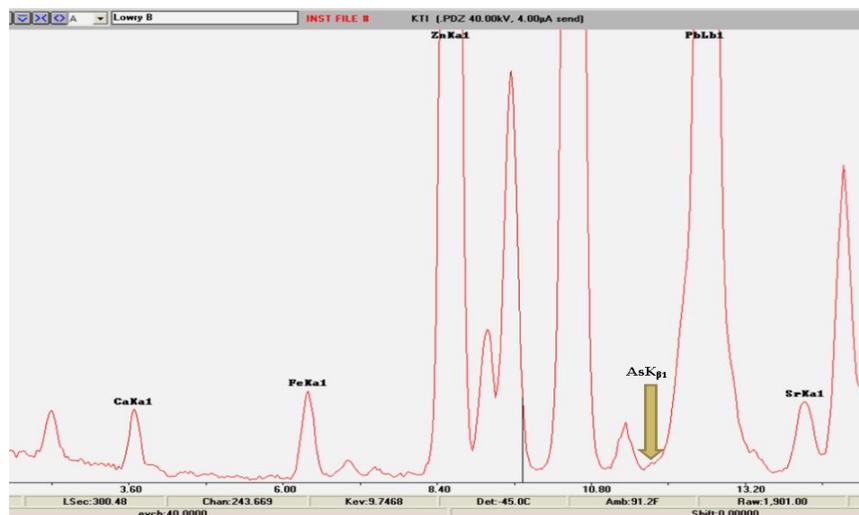
Figure 4. *The figure2 pXRF spectrum of the Lowry Pueblo Kiva B white paint shown on an expanded scale. The asterisk above the peak at ~ 10.6 keV indicates where both the Pb $L_{\alpha 1}$ and As $K_{\alpha 1}$ occur, i.e., overlap, a potential problem. Unfortunately, the algorithm for determining the abundance of As on the InnovX device uses this peak. The yellow arrow points to the position of the As $K_{\beta 1}$ peak of As, a peak that is not interfered with by the Pb. Even with a strongly expanded scale, there is no evidence seen for more than a very minor shoulder to indicate the presence of As at the As $K_{\beta 1}$ peak.*

And finally, to question further whether there was significant As present in the Kiva B white paint sample, we also examined a small sample of the white paint using scanning electron microscopy (SEM) equipped with energy dispersive X-ray fluorescence analysis that yields qualitative chemical information similar to pXRF. The device used was a Scanning Electron Microscope Model Quanta 400 by FEI Company (USA), operated at Texas A&M University - Qatar, Doha. The SEM-EDX software distinguishes As from Pb by looking at secondary lines, the 1.28 keV L-alpha for As and the 2.35 keV M-alpha for Pb. Thus, we can tell if there is both As and Pb present by looking at the L-line for As and the M-line for Pb. There are also several other Pb L-

lines (L-beta-1, L-beta-3, etc) that are not overlapping any of the As K-lines, further indicating the presence of Pb. A spectrum of the analysis is shown in Figure 5. Although there is clear indication for Pb and Zn in the paint, as well as C, O, Mg, Si, Ba, and Ca from the plaster layer underlying the thin paint layer, there is no indication of As.
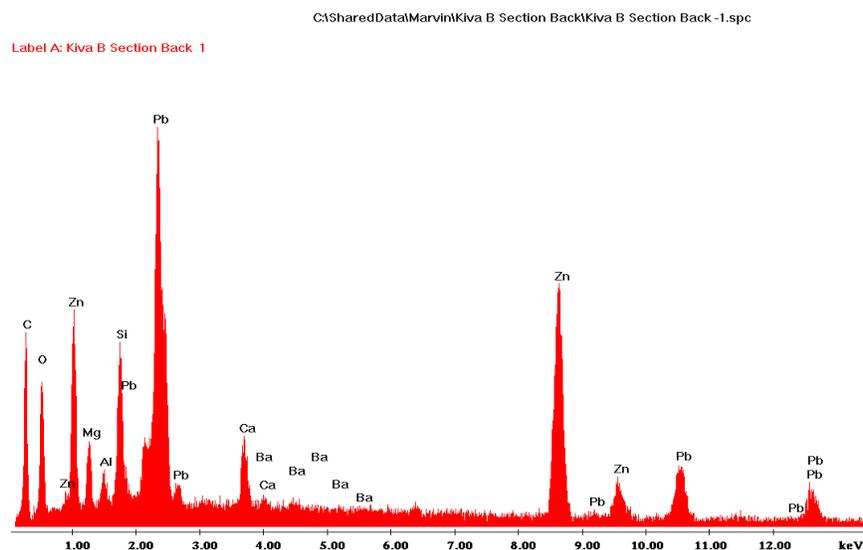

Figure 5. A scanning electron microscopy spectrum of a small white paint sample from the Lowry Pueblo Kiva B painted wall. Although the pigment obviously contains both Pb and Zn, there is no indication for any As.

Conclusion

We conclude from the measurements discussed here that there is no significant As content in either the hundreds of ceramic pigment designs we examined (this was confirmed in ~100 ceramics samples using the Bruker device described above). Nor is As present in elevated levels in the numerous analyses of paint from the Lowry

Pueblo Kiva B sample we examined. Therefore, if Pb is present at significant levels in any sample, it is essential to examine the raw X-ray fluorescence spectrum, or to use another technique (such as scanning electron microscopy used here), in order to be able to ascertain whether or not As is also present. From the raw XRF spectra we examined, one can readily determine the presence or absence of As by examination of the K_1 peak of As, a peak that does not overlap with Pb. Alternatively, SEM clearly shows whether As is present or not as well. In our experience, the InnovX handheld computer *always* indicates elevated As is present if there is substantial Pb present. Thus, the handheld display of our InnovX device, As results appear to be almost invariably wrong (always in our cases) when measured in the presence of substantial Pb.

Acknowledgments

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