Discoveries and Challenges - Using XRF for an Inorganic Pesticide Contamination Survey at the Royal Saskatchewan Museum

Timothy Greening and Alyssa Becker-Burns, Royal Saskatchewan Museum, Canada

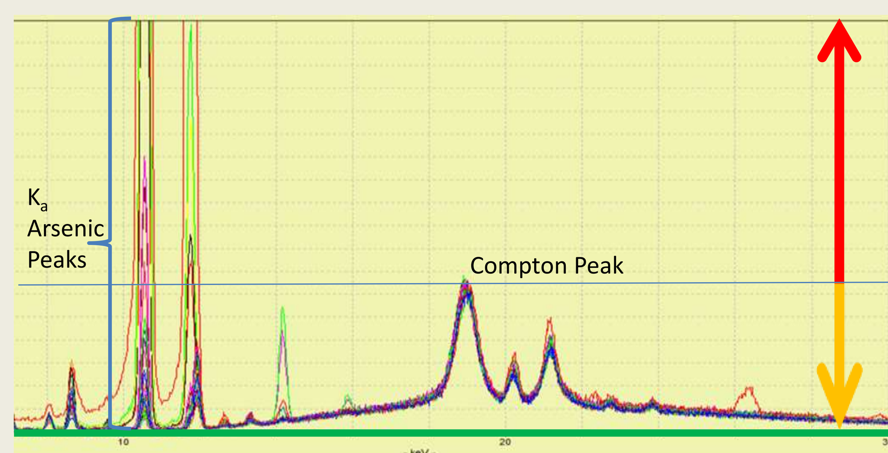
Email: timothy.greening@gmail.com Email: alyssa.becker-burns@gov.sk.ca

Abstract

XRF has become a popular technique for conservation research in recent times, particularly for determining inorganic pesticide contamination on ethnographic and natural history collections. This poster outlines our observations while qualitatively surveying natural and Aboriginal Studies collections at the Royal Saskatchewan Museum. While our pesticides were our main focus, we found unexpected elements as well. This poster also offers explanations for the unusual presence of these elements which were not associated with pesticide treatment, but offered interesting information about the makeup of the artifacts themselves.

Introduction

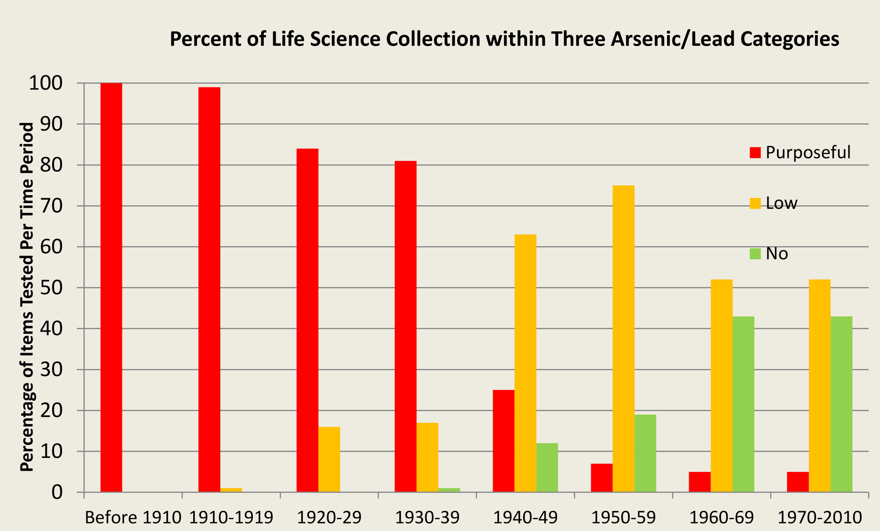
Previous testing of a small sample of objects confirmed the presence of arsenic in older natural history specimens at the RSM. This project focused on complete testing of both study skins and taxidermy collections from 1898 until 1950 and 1965 respectively. In Aboriginal Studies, we chose a objects that were amassed by collectors early in the 20th century, or were objects of uncertain provenance; we thought these were more likely to have inorganic pesticides. Our Bruker Tracer III-SD was operated using the red filter with a voltage of 40Kv, 30 microamperes of current and data collection time of 60 seconds. Up to three tests were taken on each object, depending on their size, stopping after significant arsenic was detected.



Interpreting Results

Heterogeneous test materials meant we could not quantify our results. So instead, we categorized the signals. Those above the Compton peak had "purposeful" amounts of arsenic , those with peaks below the Compton peak were labelled as "low ", and those with no peak as "no".

We then graphed these results by decade, and saw a pattern. We found a considerable drop in the number of specimens with "purposeful" arsenic after 1936 (Figure 2). This generally fits with what we expected, given a previous small survey, and what had been conveyed about in-house preparation techniques. Thus, we feel these categories give us an informative approximation of arsenic levels in the material. Our handling procedures provide a base level of protection when handling all objects, with an additional precautions taken with objects classified as "purposeful".



Date Range	Sample Size
Before 1910	20
1910-1919	247
1920-29	587
1930-39	963
1940-49	248
1950-59	444
1960-69	244
1970-2010	41

As Arsenic

Some surprises…

Arsenic on mammal skulls!
We hadn't initially included skeletal material in our survey, but tested these ones because they were housed with the study skins. The skulls that tested positive were prepared in the 1920s-40s. Arsenic was not present on our pre-1940s ornithological skeletal material.

C. F. Holmes c. 1908 Source: Sask. Archives Board R-A 21080

Variation of Technique !
Some preparators appeared to use arsenic less and less frequently over the span of their career. Some really varied their practice from day to day. And some, like early Saskatchewan naturalists, C. F. Holmes, (pictured above left c. 1908), and M.E. Barker, consistently used large quantities.

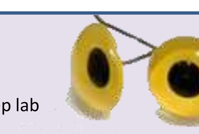
LeConte's Sparrow

Swabbing white powder on the base of a squirrel mount

Arsenic Later than 1980!
We did test a handful of more recent specimens (conveniently in a drawer with others we tested). One LeConte's sparrow specimen prepared in 1998 was an exception to our hypothesis that arsenic was not used in the late 20th century. It gave a "purposeful" signal for arsenic. Talking with the preparator revealed , however, that the use of arsenic was not on purpose! Was there a mislabeled container in the lab? Had arsenic been used (post 1980) by the collector in the field?

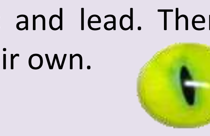
Arsenic Transfer!
This did not always happen! We used moistened cotton swabs to sample seams hidden under feathers and fur, and on outside surfaces. Arsenic was only sometimes detected on the swab. This leads us to believe that arsenic that was detected directly, was often located deeper in the object, not on the surface. When peaks did show up from the swabs, they often were relatively low, but one swab taken from a black headed grosbeak from the 1930's showed a considerable peak. Visible white powder found in drawers often tested negative - it is thought likely to be borax.

Glass

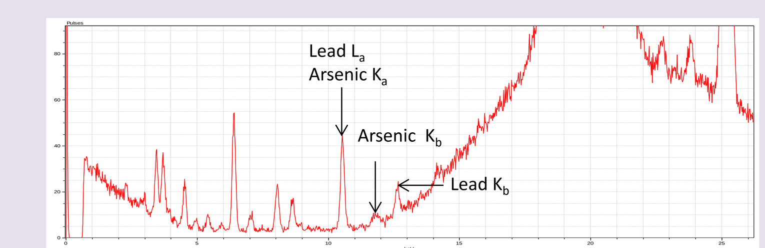


Glass eyes from the RSM taxidermy prep lab

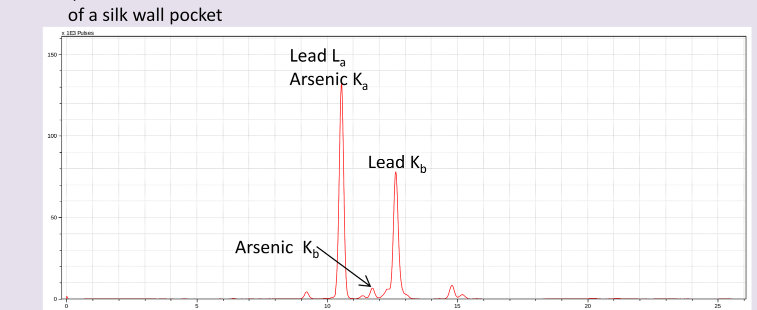
Historic glass, used in taxidermy eyes, can test positive for arsenic and lead. Therefore we never tested heads on their own.



We didn't find arsenic very often in our ethnology collection. When we did, it was thought to be inherent to the object (glass beads). We are curious, however, because we found lead and arsenic peaks in similar ratios on un-beaded areas beside the beads. Could the beads be transferring material?



Spectrum of lead with trace arsenic on a non beaded area of a silk wall pocket



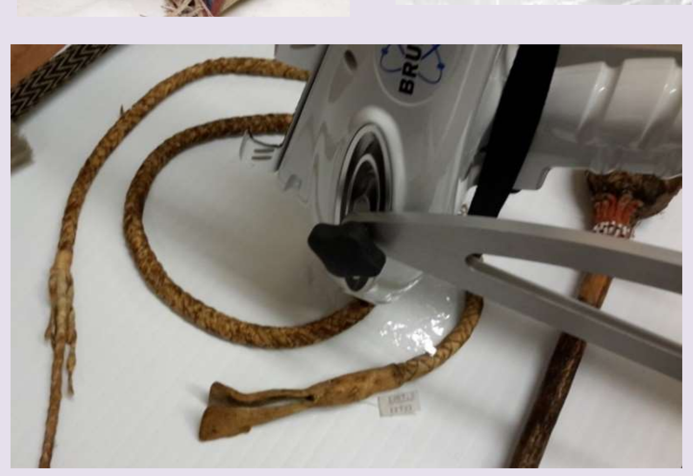
Spectrum of a glass bead

Pb Lead

Lead was routinely detected in our Aboriginal Studies collections at what appear to be higher than "trace levels", but only occasionally as "purposeful" additions. Lead (without arsenic) is thought to be from sources other than pesticides. We assume the lead we found to be from the environment (i.e. pollution or paint dust), or inherent to the object's manufacturing process.

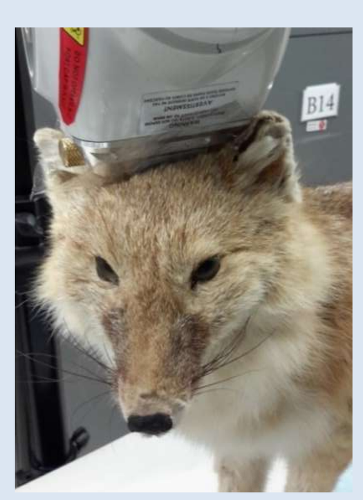
Left: The red and yellow paint on this rawhide box gave strong signals for lead, indicating these colors are not made from natural ochers, but commercial paints/pigments.

Above right: A model tipi gave strong lead signals on unpainted areas as well as painted areas. Lead could be transferred onto swabs. Could this be dust migrating from the painted areas? Nothing was visible on the swabs.



Above: Lead was used in the construction of this whip. Lead shot was put in the braid to increase its weight.

Sr Strontium

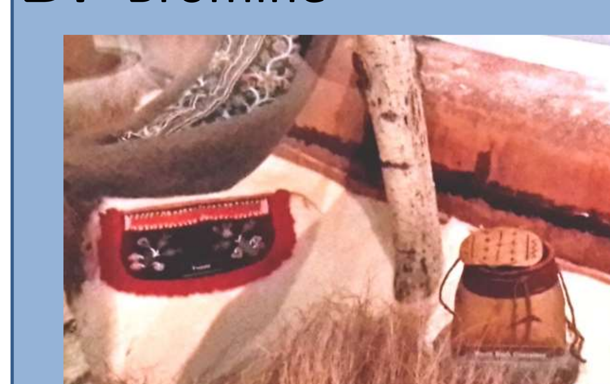


We often found strontium peaks, suggesting the presence of skeletal material inside the mount. Strontium resides in the same group on the periodic table as calcium, and is often stored in bones.

Au Gold

A Stetson Hat showed traces of gold! Had it been worn during the Klondike? The actual source of the gold turned out to be the gold leaf in the logo on the inside of the hat.

Br Bromine

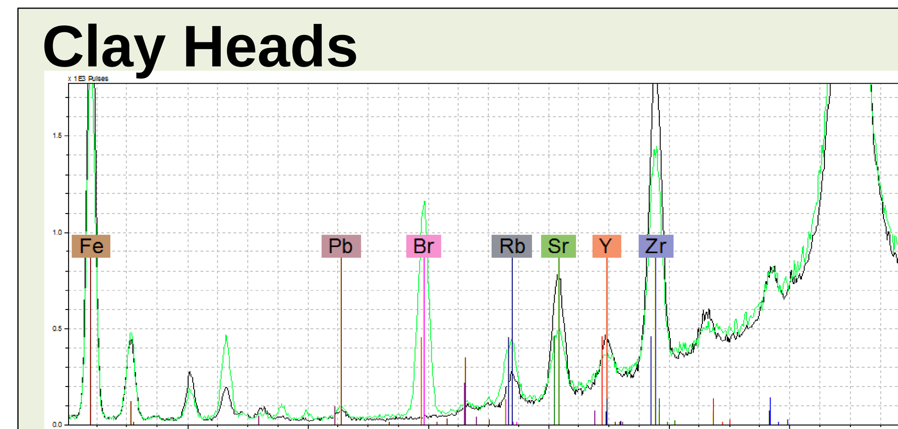


Objects in a diorama with fake "snow".

Spectra taken of Styrofoam ™

We occasionally found strong bromine signals. Possible sources include the Styrofoam™ used inside taxidermy, or the fake "snow" that is sometimes found on artifacts in our dioramas. This is because brominated flame retardants (BFRs) are added to foam products. Also, some natural history specimens may have residue from methyl bromide fumigation, or bromine inherent to the animal itself. The presence of bromine can make it hard to differentiate arsenic signals from lead, due to an overlap of peaks.

Clay Heads



We suspected the clay in the heads of some of the mounts showed up in the XRF spectra. To verify, we tested some red clay (in black, above) and compared it to the spectra of the head of a mount (in green). Both showed iron, rubidium, strontium, yttrium, zirconium and a trace of lead in a similar pattern. This particular mount also contains bromine we suspect this is from previous methyl bromide fumigation.

Sn Tin

Tin was often found in artifacts containing silk, such as this embroidered hat. Historical silk was often weighted with tin salts.

U Uranium

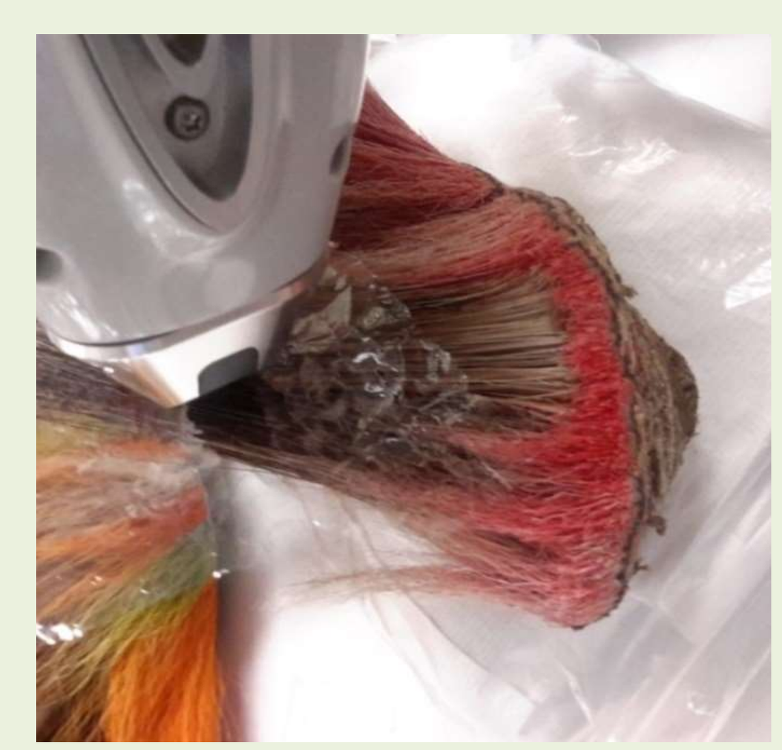
This squirrel skull showed low signals for uranium. This is probably due to where it was found (i.e. buried in a gravel pit), as sands in southern Saskatchewan can contain high amounts of uranium. This occurs because glaciers passed over uranium rich regions in northern Saskatchewan, leaving the sand deposits enriched with uranium behind in the south.

Hg Mercury

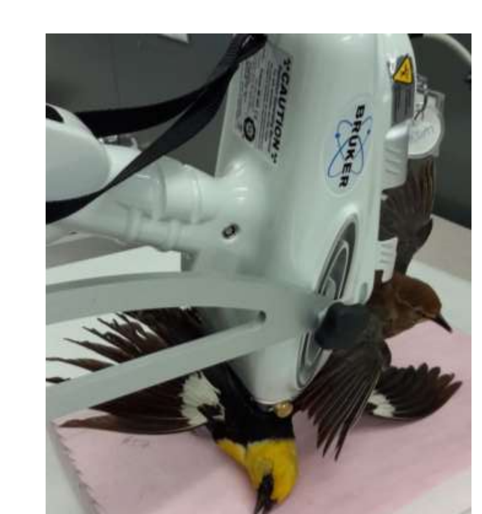
Fortunately, this was found only few times between both our Natural History and Aboriginal Studies collections.

"Purposeful" signals were found on two mounts and a study skin, all of which also showed very strong signals for arsenic.

A roach (headdress) shows a significant signal for mercury. However, since this is colored red, it is likely from the vermilion pigment.



Conclusions



…after over 3200 objects tested

Expect the unexpected when surveying a collection with XRF. Despite difficulties in quantifying results and occasional complications in interpreting spectra because of overlapping peaks, we found our survey to be informative, not only of the pest control habits of the past, but also about characteristics of the collection.

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