Sampling Strategies and Testing Procedures for Identifying Arsenic and Mercury Pesticide Residues

by Tania Collas and Allyson Lazar

Background

Arsenic and mercury salts have historically had widespread use as pesticides on anthropological and natural collections. The collections at the Natural History Museum of Los Angeles County are unfortunately no exception. As a first step in assessing and mitigating the health risk of these pesticide residues for collection staff, Allyson Lazar and I set out to develop sampling strategies and testing protocols to determine the nature and extent of contamination in the collections. These tests were initially carried out on artifacts and specimens from the Anthropology and Ornithology collections because these collections were thought to have the greatest potential for contamination. Some of the testing procedures have since been applied to the Mineralogy and Botany collections and will soon be used to test History and other collections. The approach to assessing heavy metal contamination of collection material will be illustrated with a summary of the arsenic testing in the Ornithology collection and the arsenic and mercury testing in the Anthropology collection.

Arsenic Use in Ornithological Collections

The bird skin specimens investigated in this study were prepared by removing the skin and feathers whole from the bird body. The skull and feet were usually left in place within the skin. The inside of the skin was cleaned as much as possible, then the bird was stuffed with cotton wool wrapped around a skewer stick to give the bird skin a natural form. Not surprisingly, a specimen prepared in this manner is very attractive to insects. However, ornithologists from as far back as the late 18^{th} century until as recently as the early 1970s took specific measures to prevent pest damage:

> *The inside of the skin is to be dusted with powdered white arsenic… It should never be omitted; and used with ordinary care, it offers no dangers to the health of the collector (Chapin, J.P. 1940, 6).*

This quote was taken from a respected if somewhat outdated book for bird specimen preparation. And to the credit of the ornithologists who followed this recommendation, many specimens of immense research value have survived the decades undamaged by insects.

Although arsenic has long been known to be poisonous to humans, it is only within the past decade that the health risks posed by contaminated collections have become a frequent topic of research and discussion in our field, particularly with regard to natural and anthropological collections. While most conservators do not usually work with animal specimens, the directed sampling methodology and the testing procedures that we used for the ornithology specimens would apply to ethnographic or historic objects as well.

We used the EM Quant arsenic test kit for both the ornithological and anthropological collections.[1] The kit includes arsenic test strips, zinc powder, and hydrochloric acid. The arsenic test is essentially a variation on the classic Gutzeit test for arsenic in which the arsenic in the test solution reacts to form arsine gas, which then forms a colored compound upon reaction with a metallic salt. In this case, mercuric bromide is the indicator, and it turns a range of shades from pale yellow to brown indicating the presence of arsenic. These colors correlate to amounts of arsenic in milligrams per liter on the test strip container, but in fact are only semi-quantitative at best. They give a relative sense of the degree of contamination. The arsenic test needs to be carried out in a fume hood because the arsine gas evolved is very toxic.

EM Quant Test for Arsenic

Reactions (Odegaard et al. 2000, 40):

$$Zn\ (s) + 2HCl\ (aq) = 2H\ (g) + ZnCl_2\ (aq)$$

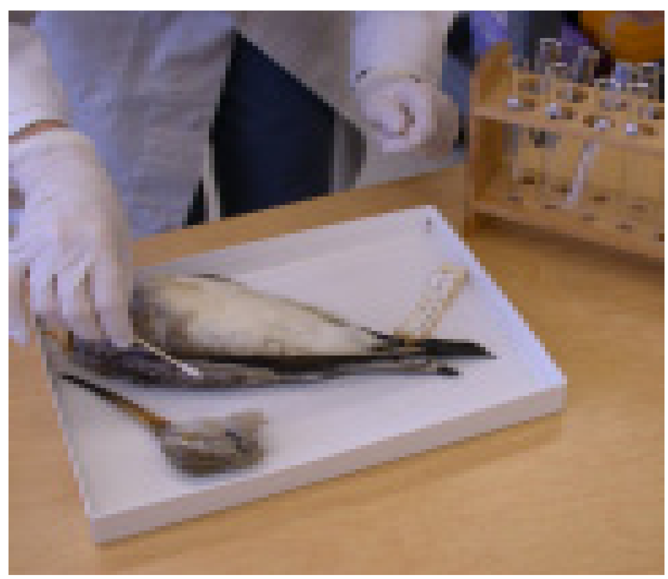
$$As^{3+}\ (aq) + 3H\ (g) = AsH_3\ (g)$$

$$AsH_3\ (g) + HgBr_2\ (aq) = As(HgBr)_3\ (aq) + HBr$$

The EM Quant test provided easy-to-read results with a couple of minor modifications to the instructions. We used a smaller amount of water to dissolve the sample and let the samples dissolve overnight. We found that other microchemical tests for arsenic, including the Reinsch test, were more difficult to interpret than the EM Quant test. The sampling and testing procedures that we followed are listed below.

Sampling Procedure

1. Swab the specimens with cotton swabs moistened slightly with distilled water. Run the swabs all over the object/specimen in such a way as to replicate normal handling.



2. Snip the swab ends off into numbered test tubes.
3. Add 2.5 ml of distilled water and let samples sit over night.
4. Prepare a known arsenic sample in the same way. (We used arsenolite – arsenic trioxide – which sometimes needed heat from a small flame to help it go into solution.)
5. Prepare a known negative sample by adding 2.5 ml of distilled water to a test tube.

Testing Procedure

1. Decant the test tube contents into numbered reaction vials. (We used flat-bottomed 20 ml glass vials with flexible snap-on lids. We had cut slits in the lids to in -sert the test strips through.)
2. Insert test strips from the EM Quant test kit into the slits in the reaction vial lids. (We cut the test strips in half, lengthwise, to increase the number of testing rounds we would be able to perform.)
3. Be sure that the test strip is inserted in such a way that it will not actually touch the solution – it tests for the presence of arsine gas, not for arsenic in solution.
4. Add one scoop of zinc powder to one of the reaction vials (scoop and zinc are both provided in the kit).
5. Add ten drops of highly concentrated hydrochloric acid to the same reaction vial.
6. Quickly and tightly cap the reaction vial.
7. Swirl gently and let sit for 30 minutes.
8. Repeat steps 4 through the 7, one reaction vial at a time, for all of the reaction vials.
9. Results are often visible within a few minutes, but it is best to let the vials sit for the full 30 minutes.

Ornithology Collection Testing

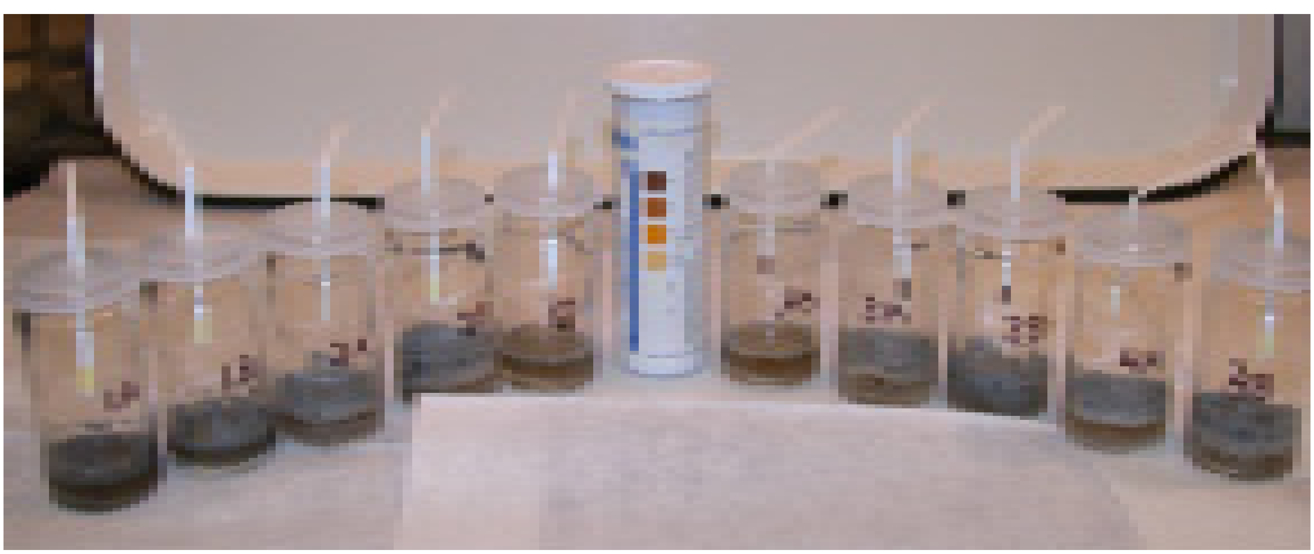
The first testing attempts within Ornithology confirmed that arsenic was present in the collection, especially in older specimens. But rather than testing each of the tens of thousands of bird skin specimens in the collection, we applied directed sampling to begin to define the scope of the arsenic contamination. With the help of the Ornithology collection manager, we defined categories of specimens within the collection to test: those dating from the late 19th century when arsenic was widely used, those prepared in the late 1950s to early 1970s when the use of arsenic was waning, and those collected and prepared in different parts of the world. The collection manager selected five birds of diverse sizes from each category.

The first group of birds to be tested was collected at the turn of the last century by Mr. Daggett, the first director of the Natural History Museum. Not surprisingly, these specimens showed consistently high levels of arsenic, evidenced by a dark brown color on the test strips. The use of arsenic does not waver over the span of twenty-three years during which the birds were collected.

The second group of birds to be tested was collected by a Mr. Partridge in 1959. The test results showed that most of the birds had detectable albeit low levels of arsenic that seem to indicate the limited and inconsistent use of the poison by this collector.

The third group of birds was collected in Kenya and Uganda during the 1960s. The point of testing these birds was to see if arsenic use persisted into recent times outside the U.S. These birds were negative or borderline positive, leaving the use of arsenic during their preparation in question. There was no correlation between the date of preparation and the presence of arsenic in these African birds.

Partly out of curiosity, we then took samples from specimens prepared at the Natural History Museum during the



1960s and early 1970s by the former collections manager, James Northern. These samples showed inconsistent low levels.

At the time of this testing, we also sampled the gloves worn by the collection manager after he had retrieved and handled the twenty specimens. They too tested positive for arsenic. At this point, we were beginning to suspect that cross contamination from heavily arsenic treated specimens, like the 19th-century ones, might be responsible for some of these borderline positive results we were getting for the late dating specimens. That is, the arsenic from the older birds was being physically transferred to the newer birds.

To test this hypothesis, we sampled five birds prepared by the current collections manager, Kimball Garrett, who never used arsenic to prepare a specimen. We chose two pairs of specimens of the same species, one older than the other. For example, two hawks that were tested had been stored in the same drawer, but one dated from 1991 and one dated from 2000. To investigate further the likelihood of cross contamination, we also swabbed the surface of a drawer liner recently placed in a cabinet with older specimens.

The high proportion of positive results obtained from specimens never treated with arsenic was somewhat surprising. The drawer liner also tested positive. The older specimens tended to have slightly higher arsenic levels than the newer specimens. Although the testing will continue, at this point, we are convinced that cross contamination from older, heavily treated specimens is responsible for the contamination of a large percentage of the museum's bird skin collection.

Anthropology Collection Testing

The first step in testing the Anthropology collections was determining which types of objects were appropriate for testing. Unlike the Ornithology collections, which consist of one type of specimen, the Anthropology collections are composed of a variety of objects made from a number of different materials, both organic and inorganic. Traditionally, only artifacts made from organic materials were treated with heavy metals. Using known dates for use of heavy metals and pesticides from the literature, we established a set of criteria for determining types of objects to test. Once the criteria were determined, to begin testing we selected five artifacts that fit each type of criteria.
The criteria were as follows:

- Organic material with strange residues
  The residues were generally white or translucent and powdery or crystalline and were discovered on leather, hide, buckskin, and wood objects from all over the world.
- Organic material in suspiciously good shape collected prior to 1950
  Due to the age of objects collected prior to 1950, it is assumed that there would be some indication of pest dam age, unless the objects had been treated with a pesticide or pest repellant. Also, objects collected prior to 1950 are more likely to have been treated with heavy metals, according to the literature.
- Organic material collected prior to 1950 from very large collections
  Very large collections are suspect because the more serious collectors would have been more likely to have taken steps to protect and preserve their objects, such as treating them with heavy metal pesticides.
- Organic material recommended for testing by the curator based on institutional memory
  One or two specific objects were recommended for test ing by the curator because she remembered a former staff member mentioning that those objects had been treated.
- Organic materials used in public programming
  We decided to test the Egyptian archaeological materials brought into the country in the 1920s because they were often requested for use in presentations to children. Using the EM Quant test for arsenic, we discovered that unfortunately some of these objects had been treated with arsenic and were therefore not safe for use in public programming.

We will continue testing for arsenic in the Anthropology collection according to the criteria listed above to determine the scope of the contamination.

In addition to the arsenic testing, we have also begun testing for mercury in the Anthropological collection. When a type of volcanic glass known as Pele's hair[2] and a piece of African rope, both housed in Riker mounts, were returned to the Anthropology Department from the Educational Lending Service, we noticed that they were labeled as having been treated with mercuric chloride. We initially tested these objects using the diphenylcarbazone test for mercury (Odegaard et al. 2000, 72) as a way of verifying our testing methods for mercury. Perplexingly, both of these objects tested negative.

After a number of rounds of testing, we learned that the diphenylcarbazone test worked very well for detecting the presence of mercuric oxide, but not mercuric chloride. Acids, which are necessary to break the bonds between the mercury and the chlorine, and chlorides, which are already present in the salt, both interfere with the test. However, when we tried a new, as-of-yet unpublished test developed by Catharine Hawks and Kathryn Makos (Stavroudis, C. 2003, 10), these artifacts did test positive for mercury vapor built up within their storage container.

This test for mercury vapor is so simple to use and interpret that we have been able to start mercury testing in the Botany and Mineralogy collections in addition to Anthropology. So far, we have found that certain older cabinets in the Botany collection, which previously housed vascular plant specimens treated with mercuric chloride, still contain some mercury residue. Fortunately, the former herbarium cabinets that are currently used to store some Anthropological collections do not.

Within the Mineralogy collection, our concern was not whether mercury was present, since we knew there were many mercury mineral specimens, but whether the specimens were giving off mercury vapor. We tested cabinets containing elemental mercury, mercury salts, and mercury sulfides. Unfortunately, all of the mercury specimen cabinets tested contained detectable levels of vapor, even where the specimens were stored in closed plastic boxes or polyethylene zip-lock bags. Some specimen drawers were then covered with Pacific Silver Cloth as a potential mercury vapor scavenger (Stavroudis, C. 2003, 11), but retesting showed no difference in results.

Thus far, we have not been able to determine whether heavy metal contamination is present in the museum collections, but this is just the first step.

Next Steps

The heavy metal testing thus far has been aimed at determining the extent of contamination in the museum's collections. But the overall goal is to begin the process of assessing the health risk to collection staff. While these tests can be used to detect contaminated objects, they cannot be used to determine if the artifacts or specimens are a health hazard. This can only be accomplished by testing the exposure of collection staff to arsenic, mercury, and other pesticides. Devices for testing worker exposure to hazardous substances include air collection tubes, glove and work surface wipe sampling, and urine tests. To accomplish this exposure testing, we will need to bring in an industrial hygienist or other occupational health professional qualified to address staff medical concerns.

While we hope that the health risks of handling the collection are minimal, we want to be sure that adequate safety measures are taken. This may involve providing personal protective gear to collection staff, such as nitrile gloves and HEPA filter respirators, or it might mean modifying the ventilation system in storage. Ornithology collection staff have expressed their fear that the results of arsenic testing will prompt the purging of the contaminated specimens from the collection. This would mean a terrible loss to ornithological research. But we are confident that better solutions to the heavy metal contamination problem will be available.

1. Before settling on the EM Quant test for arsenic, we also tried two other spot tests for heavy metals, the Reinsch and capillary tube tests, both of which we determined to be inappropriate for our purposes.

2. Pele's hair is named for the Hawaiian goddess of volcanoes and was probably treated with mercuric chloride because it is called hair and it looks like organic, rather than inorganic matter.

Acknowledgements

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EM Quant Arsenic Test Strips (100/pack) (Cat. No. M100261) includes arsenic test strips, zinc powder, and hydrochloric acid. Available from Fisher Scientific, tel: (800) 766-7000, website: www.fishersci.com.

Diphyenylcarbazone
Tri-Ess Sciences Inc., 1020 W. Chestnut St., Burbank, CA 91506, tel: (818) 848-7838, website: www.tri-esssciences.com. (Also available from most chemical suppliers).

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