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The use of inductively coupled plasma mass spectrometry to quantify chemical hazards in natural history collections: As and Hg in taxidermy bird specimens

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The earliest record relating to the use of arsenic in the preservation of taxidermy specimens belongs to Wolfgang Helmherd Baron von Hohberg¹ (1612–1688). However, it is the invention of arsenical soap by Jean-Baptiste Bécoeur in the mid-1700s and the publication of its recipe in 1800 that made arsenic a popular pesticide used in the collections, until it was phased out in the second half of the 20th century. Since 1770, alongside arsenic (often in a form of arsenical soap, arsenic trioxide, potassium arsenite or arsenic sulfide), mercury (as mercury chloride, also known as “corrosive sublimate”) was widely used in taxidermy, in herbaria and in the preservation of museum collections in general. Arsenic poisoning was recorded among both herbarium workers and taxidermists and fatal cases² are known.

Few records exist with reference to the methods of preservation applied to the taxidermy specimens in heritage collections, including the use of pesticides to control any immediate or ongoing risk of infestation. Specimens would have been routinely treated with pesticides, and retreated as required.

Arsenic and mercury are still commonly identified in taxidermy and herbarium specimens in the museum collections

using spot tests, and, more recently, X-ray fluorescence (XRF) spectrometry. Spot tests are semi-quantitative at best. Tests for As have been reported to give false positives and false negatives,³ however, the method is generally found to be reliable,⁴ while a spot test for Hg is reported as being unsuitable for testing the collection materials.³ Arsine (AsH_3), a gas more toxic than As(III) or As(V), present in the materials used for preservation treatment is formed during testing so that the use of a fume cupboard is required and the resulting waste needs to be treated as a hazardous material due to mercury present in the test paper. Handheld XRF is a useful non-destructive technique to screen the collections for elevated concentrations of toxic elements, however, due to the nature of specimens and heterogeneity of contaminant distribution the results should be considered to be qualitative.

There are several reasons why quantitative (rather than qualitative) information on trace metal concentrations in animal specimens preserved in museums is important:

- To better assess potential hazards existing in the collections and provide the necessary background information for risk assessing the activities of

collection staff, visitors and contractors.

- For an informed decision to be made about whether an object is safe for handling by members of the public, for example, in “hands on” displays.
- Life science collections and their curated metadata are now seen as potential archives of environmental levels of trace elements.⁵ As a result, changes in metal concentrations, e.g., in feathers induced by conservation treatment has now become an important research subject.⁶

Quantitative analytical methods, such as atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) are seldom applied to the study of pesticide residues in natural history collections. This is likely to be due to the cost of instrumentation and the level of expertise involved, as well as a reluctance to apply a destructive sampling technique. However, the low detection limits and multi-elemental capabilities of modern techniques, e.g., ICP-MS, make destructive collection of small (1 mg or less) samples a practical alternative to non-destructive methods, especially when

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1 fully quantitative data collection is
2 required or preferred.

3 The aim of the study discussed in this
4 article is to provide quantitative back-
5 ground for the assessment of chemi-
6 cal safety of bird taxidermy specimens
7 (mounted birds, skins or wings) for use
8 in learning centres and similar "hands on"
9 displays.

10 Bird specimens

11 Eleven bird specimens (mounted birds,
12 wings and a study skin) represent-
13 ing species widespread in the UK were
14 selected for testing with a view of using
15 them in educational displays. None of
16 the bird specimens had associated with
17 them any background information on
18 the conservation methods used and
19 only two specimens were dated. One
20 or two feathers (see, for example, Figure
21 1) were collected from each specimen
22 from areas most likely to be touched by
23 visitors when the specimen is displayed,
24 but having in mind minimising damage
25 to the specimen. Feathers (0.6–11.5 mg)
26 were weighed using an MC6 Sartorius
27 microbalance ($d=0.001$ mg).

28 Determination of As, Hg 29 and Pb in feathers by 30 ICP-MS

31 Feathers were transferred into 60 mL
32 Savillex® fluoropolymer vessels, 2.5 mL
33 HCl, 0.5 mL HNO₃ and some ultra-pure
34 water were added and the vessels heated
35 at 70°C overnight. Samples were diluted
36 with ultra-pure water to 50 mL and further
37 diluted for ICP-MS analysis using 2%
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hydrochloric acid (HCl) when necessary.
ICP-MS analysis was conducted using an
Agilent 7700x instrument.

Inorganic mercury at low levels is not
stable in HNO₃ solutions without suffi-
cient concentration of chloride ions,
which is why HCl was selected as an acid
matrix even though it can cause inter-
ferences with ⁷⁵As due to the formation of
⁴⁰Ar³⁵Cl⁺. To minimise polyatomic inter-
ferences, the instrument was run with
5 mL min⁻¹ He (99.9995% purity) in the
collision-reaction octopole cell (CRC)
as well as with no collision gas entering
the CRC. Pb was determined in the "no
gas" mode (average of ²⁰⁶Pb, ²⁰⁷Pb and
²⁰⁸Pb) while As (⁷⁵As) and Hg (²⁰²Hg)
were determined in the "He mode".
The limit of quantification (LOQ) for As
in 2% HCl is only about 0.02 μg L⁻¹ and
the LOQ for Hg and Pb are less than
0.01 μg L⁻¹ and 0.003 μg L⁻¹, respectively.
The actual method detection limits (per
weight of the solid sample) depend on
the dilution and the tailing of the signal
due to the memory effects after higher
concentrations, which is a very impor-
tant factor for As and, especially, Hg
determination.

31 Arsenic contamination

32 One of the mounted bird specimens
33 analysed, a common kingfisher (*Alcedo
34 atthis*) was found to contain up to 1.44%
35 As in feathers. The chronic Minimal Risk
36 Level⁷ (MRL) by ingestion is considered
37 to be 0.0003 mg As kg⁻¹ body weight
38 and the acute MRL is 0.005 mg As kg⁻¹
39 body weight, which means that only

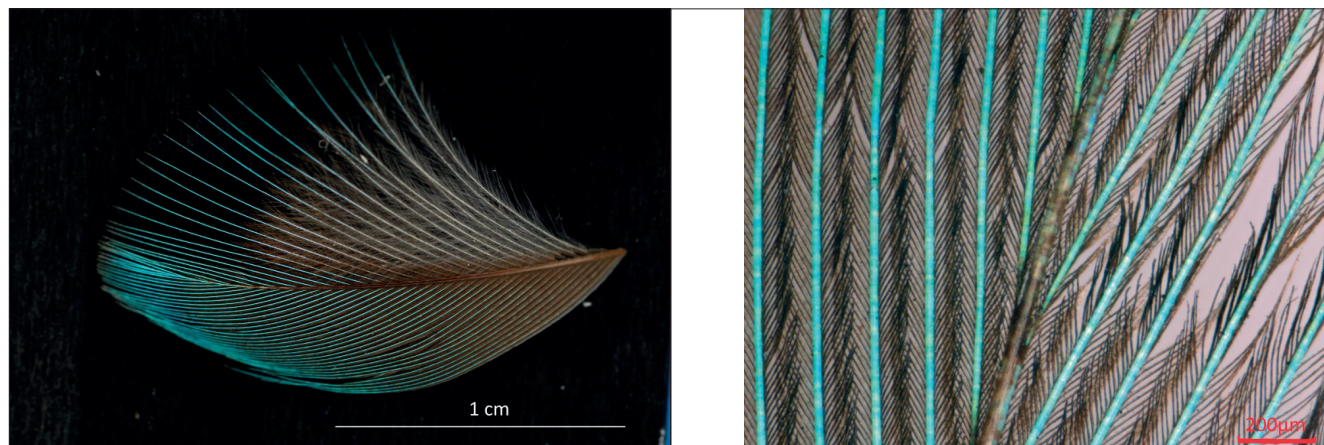
about 7 mg of these contaminated
feathers would contain enough As to
exceed the acute MRL for a 20 kg child.
Scanning electron microscopy (SEM)
with energy dispersive X-ray analysis
(EDX) has shown that vanes and barbs
of the feather are covered with particles
containing As and Ca (see Figure 2), but
As is also present in particle-free areas
of the shaft.

Mercury contamination

One of the bird specimens analysed, a
wing of kestrel (*Falco tinnunculus*), was
found to contain up to 1.85% Hg in the
feathers. The intense MRL⁷ by ingestion
is considered to be 0.002 mg Hg Cl₂ kg⁻¹
body weight and the acute MRL is
0.007 mg Hg Cl₂ kg⁻¹ body weight, which
means that a single feather weigh-
ing 8 mg would contain enough Hg to
exceed the acute MRL for a 20 kg child.
The same specimen was found to be
contaminated with As (0.28%) and Pb
(0.17%). A high concentration of Pb indi-
cates that lead arsenate might have been
used as one of the components (among
other arsenic compounds) of the pesti-
cide treatment.

31 Conclusions and risk 32 assessment

33 The solution-based ICP-MS analysis
34 provides fully quantitative information
35 on bulk contents of toxic elements in
36 taxidermy specimens. Using an ICP-MS
37 equipped with a CRC allows the deter-
38 mination of a number of target elements
39 simultaneously, including As and Hg,



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56 **Figure 1.** Photomacro- and photomicrograph of the feather fragment of a common kingfisher used for testing for toxic elements.

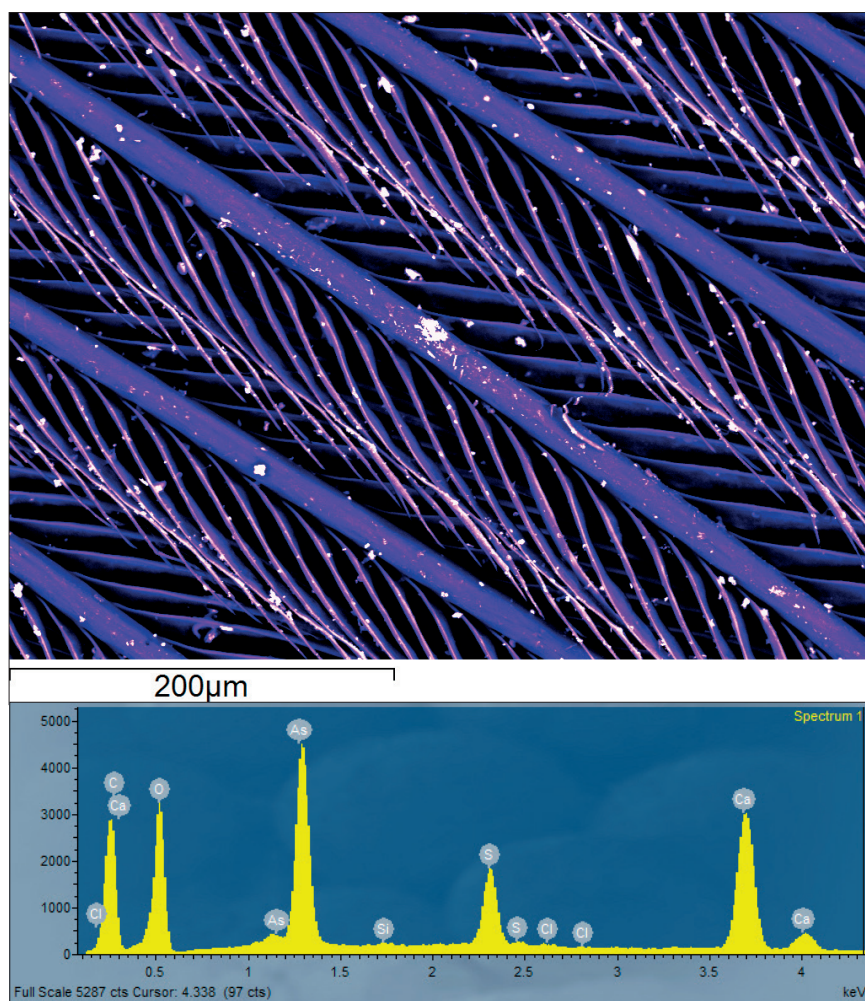


Figure 2. Top: Backscattered electron image of a feather of the kingfisher specimen showing pesticide residues on vanes and barbs. Bottom: the EDX spectrum of the particle in the centre of the image showing the presence of As and Ca. The sulfur peak is probably coming from feather keratin.

using a single digestion protocol. As this approach requires careful destructive sampling and is labour-intensive, it may not be the first method of choice for bulk assessment of chemical hazards in large collections, where non-destructive handheld XRF can be used in preference. However, unlike XRF or spot testing, the ICP-MS method gives quantitative bulk concentration of As and Hg, which is necessary to estimate the potential toxic element intake from contact with the specimen. This is invaluable when risk assessing the use of a specimen in "hands on" displays when the chemical risks should ideally be fully quantified and compared with respective MRLs. In assessing chemical risk for chil-

dren, behavioural factors must also be considered. The normal hand to mouth activity of young children may result in an increase in toxic metal intake from pesticide particles potentially present at the surface of taxidermy specimens. The combination of ICP-MS with SEM-EDX analysis can also reveal not only the level of pesticide contamination, but what compounds were likely to be used and so help to put taxidermy objects with unknown or unclear history into context. The inherent level of As and Hg in bird feathers can be used to assess whether the specimen has been treated with pesticides or cross-contaminated from other specimens in the collection. This can be estimated as below $10 \mu\text{g g}^{-1}$

As and $25 \mu\text{g g}^{-1}$ Hg.⁸ The specimens containing less than $15 \mu\text{g g}^{-1}$ As and less than $100 \mu\text{g g}^{-1}$ Hg (seven out of eleven specimens tested) are considered by us as either having natural levels of these metals or slightly elevated levels due to cross-contamination, but safe to handle (only with respect to toxic metals as we have not done testing for organic pesticides) and specimens containing more than $1000 \mu\text{g g}^{-1}$ (0.1%) of either metal (two specimens) are treated as hazardous. Two more specimens were found to have elevated levels of As (between $100 \mu\text{g g}^{-1}$ and $1000 \mu\text{g g}^{-1}$) and are not recommended for using in "hands on" displays.

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