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Profiling Hazardous Substances in the Museum Victoria State Collection

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Abstract

The presence of hazardous substances in museum collections is a well-known problem and historically many inorganic materials such as arsenic, mercury and lead, were incorporated into collections as pest prevention systems. Methyl bromide fumigation was commonly used in the late twentieth century, leaving inorganic bromide residues. The large number of items in modern museum collections makes it impracticable to test every item for these hazards. Museum Victoria's *Materials Population Profiling Project* is designed to overcome this problem by surveying a semi-random selection of collection items, using XRF analysis. By dividing the collection into groups by material type and date of acquisition it is possible to identify specific groups of collection materials with higher levels of inorganic hazards by object, material type and date range. These results have enabled us to flag high hazard groups with in the collection. The data has been uploaded into the Museum's collection database EMu. This project has required collaboration between conservation staff, collection managers and curatorial staff and is having significant impact on the policy and procedures of Museum Victoria.

Keywords: hazardous substances, inorganic pesticides, XRF analysis, Indigenous Collection, hazard survey, museum collections

Introduction

Hazardous material in Museum Collections is a well-known problem and historically many hazardous materials were incorporated into collections as pest prevention systems. Inorganic materials such as arsenic, mercury and lead were commonly used in the 19th and early 20th centuries. These materials were used both in the museum environment and by collectors in the field (Goldberg 1996) to prevent insect pests attacking the specimens. Commonly the historical documentation of these processes is sparse and incomplete and in some cases non-existent (Nason 2001). In the second half of the 20th century gas fumigants such as methyl bromide and ethylene oxide were commonly used, while a range of organo-chemical pesticides, fumigants and rodenticides have been used in the pest management systems of museum buildings. The detection of inorganic pesticides on natural history specimens and indigenous materials is well documented and many institutions have published the findings of their investigations into this problem (Goldberg 1996, Sirois 2001, Pool et al 2005, Palmer 2006, Reunben 2006) not only identifying the hazards present but in some cases on which object types they can be found (Hamann 2006, Cross 2009, Hawks et al 2011).

Museum staff, researchers, volunteers and community members who need to access the collections on a regular basis are at risk when handling objects as analysis has confirmed that the hazardous residues can be transferred through touch. The repatriation of material to indigenous communities means the risk of harm to people could be significant if hazards are not clearly identified. Testing using portable X-ray fluorescence (XRF) has become the popular analysis technique to identify inorganic pesticides on museum objects (Sirois et al 2001, Ustun 2009). It is non-destructive, portable and easy to use and provides a quick qualitative determination of inorganic hazards. However, the size of most museum collections makes the testing of every item, even with this fast testing technique, impracticable if not impossible.

Museum Victoria has a collection of nearly 17 million items, with over 150,000 items in the Indigenous Cultures Collection. There is little or no information on past treatment of the collection, the exception being methyl bromide fumigation which was carried out on the whole of the Indigenous Collection during the 1990s when the collection was moved to the current museum site. The *Materials Population Profiling Project* was therefore instigated to survey the Museum's collection and identify key object and material types that present a higher risk of containing hazardous substances. The first stage of this project has been to carry out semi-random testing of the items in the Indigenous Collection using XRF analysis, sampling from a limited number of material types. The results of this survey indicate the material and object types where hazardous substances are most likely to be found. To establish when inorganic pesticides such as arsenic, mercury and lead have been used on the collection sampling covered items from across time.

Instrumental Method

The analysis of the collection has been carried out using a Bruker Tracer III-V+ hand held X-ray Fluorescence Analyser using settings and filters for the detection of higher elements which are the key elements used as pesticides for organic materials. The Bruker Tracer III-V+ portable XRF unit has an X-Ray tube source with a Rhodium (Rh) target and a Peltier cooled Silicon-PIN diode detector, fitted with an Al/Ti/Cu (Red) filter. Operating conditions were 40kV and 14 μA for 120 sec. Under these conditions the instrument detects elements with an atomic weight greater than 20 (Calcium). Results for four main elements arsenic (As), mercury (Hg), lead (Pb) and bromine (Br) were recorded while other elements detected were noted for further reference. The analysis results have been recorded on the collection management database EMu database for all items tested.

The results obtained from the Bruker XRF are not quantitative due to the heterogeneous nature of the objects tested and the variation of surface structure at the analysis sites. Broad assumptions can be made however about the relative level of each element and these have been used to express a semi-quantitative variation in level of inorganic pesticide determined. The analysis results are therefore reported as, Very High, High, Moderate, Low, Trace and Not Detected.

Survey protocols

The majority of Indigenous Collection items are made from natural materials such as plant, stone, shell, skin and feathers. A small number are made from processed materials such as glass, metal and ceramics. In order to simplify the identification of pesticide residues trends the collection items were therefore grouped according to fourteen material types, Table 1. The largest proportion of the Indigenous Collection items are made from plant materials which come in different forms depending on the part of the plant and any processing which the material has undergone. Plant material was divided into four categories, wood, bark, plant fibres (including processed plant material such as string or bark cloth) and resin. These materials retain hazardous materials differently due to their different surface structure. Some material types having similar surface structure and properties were grouped together, for example bone, tooth and horn. To determine if the pesticide treatments varied over time the items were further divided into 50 year time periods (based on date of acquisition by the museum). Information on the type of item was also collected so that trends for particular types could be identified. Finally the Museum has collected material from Australia as well as from overseas locations and these items are stored in separate locations. The results from these collections were analysed together and then separately to determine any differences in the two collections. The results were then tabulated into groups according to material type and date. In all 870 items were tested in the survey.

Results

The results for fourteen material types are presented in Figure 1, the number of analysis for resin and film items were too low to be statistically significant and so are not included in the graphical representations of the results. Positive results only are reported with the total number of items tested given in the x-axis description. The graphs indicate the trends in hazardous substance levels are generally much higher pre-1950.

Arsenic

The incidence of arsenic (As) on collection items is relatively low and generally found on older items acquired before 1950. As only one to five items per category were found no specific trends were observed. In some instances the arsenic could be related to the ochre paint on the items, for example six bark waist ornaments coated with thick red pigment returned trace arsenic levels. Arsenic was found as a trace element in raw ochre samples tested. The small number of these objects in the collection meant that the items could be flagged individually. Six animal skin items acquired pre-1950 were found to have trace levels of arsenic. The statistically low number of items identified with arsenic precluded the necessity to flag all of the items in this material type.

Inherent arsenic was identified in glass beads, historically both arsenic and lead were used in the glass making process. Glass items have been flagged with a warning regarding the hazard if degrading. Trace levels of arsenic and lead are also inherent in pre 1950 paper. Trace arsenic is also found in metals most likely as a trace element in the metal raw materials. The exception is Indonesian *Kris* swords and daggers which are treated with arsenic compounds in the final stages of production. Wipe tests on these items showed that the arsenic is easily removed from the surface. Mercury residues were also detected in the intricate carving at the top of these swords. *Kris* swords have been flagged in the database as arsenic and mercury risks.

Mercury

Mercury (Hg) residues were identified on a small number of material types. As discussed above mercury was found on *Kris* swords and daggers but not on other types of metal objects. It is relatively rare on other items in the collection with only one instance in the bone/tooth/horn type on the horn handle of a walking stick and this is due to pigment decoration. A small number of wood items recorded mercury residues, these are dark stained wood and the number is not significant enough to warrant a type flag in the database.

The highest incidence of mercury was found on two material types with around 50% of the skin/fur/animal fibre material type items and 42% of feather material type items analysed returning trace to high levels. The mercury is found predominantly in two time periods 1850 - 1900 and 1900 - 1950, in fact over 80 % of items in these categories pre 1930 have detectable mercury. The source of the mercury is believed to be the spraying or dipping of items with mercury chloride solution, a common pesticide practice in the 19th and early 20th centuries (Shugar 2012). Examination of the object details revealed the object types with detectable mercury belonged to the 'Head ornament' and 'Neck ornament' categories for both material types. Figure 2 is a graph of inorganic heavy metal residues found on items associated with the head and neck showing that the majority of items were acquired prior to 1930. A further interesting point regarding the way these items were treated develops when we compare the items from the Australian collection and the items from the overseas collection which are currently housed separately. The items found in the overseas collection have not been treated with mercury. This raises questions regarding different practices amongst the different collectors and curators in the early history of Museum Victoria. Sadly there are no records of how the collections were treated during this period.

Lead

Lead (Pb) presents a more complex problem for the interpretation of the analysis results. Lead is inherent as a trace element in most organic material, particularly since the advent of the industrial revolution and increased lead emissions in the atmosphere. In order to avoid inherent lead biasing the results all weak trace lead results have been ignored (where weak trace is defined as any XRF reading of less than 1000 arbitrary counts). Although it is acknowledged that many trace level results recorded are probably also due to inherent lead in the materials.

Low to high lead levels were detected in metal, glass and ceramic materials, where lead is added as part of the manufacturing processes. These are not considered hazardous unless the materials break down. Similarly historical items in the collection are painted with commercial paints which contain high levels of lead which are hazardous when breaking down, flaking or powdering. Fortunately, the Indigenous Collection has very few items painted with lead-based paint.

Bromine

Bromine (Br) residues were found on over 70% of the items tested. Methyl bromide fumigation was applied to the whole Indigenous Collection during the 1990s when the collection was moved to the new Melbourne Museum site. Studies on the residues of methyl bromide fumigation of fruit have shown that methyl bromide gas breaks down with the methyl group reacting with the organic matter in the item and the bromide forming inorganic salts (Singh et al 1976, Hansen et al 2000). The residues in these studies found very low trace levels, below the regulated tolerance levels of 20mg/kg for Australia, of inorganic bromides on the fruit after only a few days. Inorganic bromide at these levels is not considered hazardous. With XRF analysis it is not possible to differentiate between methyl bromide and inorganic bromide residues. However it is unlikely that methyl bromide would persist after tens of years and so the assumption is made that all bromide recorded will be inorganic. The results found on most of Museum Victoria's Indigenous Collection were trace levels, which for the purposes of this work were estimated to be below 100mg/kg. Organic materials such as plant and animal products were found to retain bromide residue more than inorganic materials such a stone and metals. Only a very small number of items were identified with low to high levels of bromine and no correlation with material type were detected. Trends across time were not detected because methyl bromide was applied to the whole collection in a single time period. Bromine has not been subject to trending and tagging in the museum database.

Discussion

This survey of items across the collection has reduced the number of items tested to a manageable number of items. The inorganic pesticide hazards identified in the Museum Victoria Indigenous Collection are minimal and restricted to a few material and object types. Typically materials such as stone, shell, metal and ceramic which are unlikely to be attacked by pests are free from these inorganic pesticide residues. Paper items also show little indication of pesticide treatment other than methyl bromide. Trace arsenic and lead identified on many of these items can be related to the inks used rather than pesticides. Result trends indicate that plant material-based objects are unlikely to have been treated with the inorganic pesticides arsenic and mercury.

The results of this survey have identified a strong correlation between inorganic arsenic and mercury pesticide residues and material type. A strong correlation was identified between mercury incidence and feather type items and mercury incidence and skin/fur type items. Looking at the types of objects which tested positive for mercury revealed that most of the items were intended for use on the head or neck area of the body. Time trends were also apparent for the use of mercury on these items with all items identified falling into the 1850 - 1900 or 1900 - 1950 time periods. A plot of Ornaments, head and neck, items with mercury residues versus the date collected shows that the items cover a period from the founding of the Museum collections to 1930, with the highest numbers being 1902 and before. The unexpected presence of mercury on Indonesian daggers and swords has also been noted and used to flag other items in both the Indigenous Collection and the History and Technology Collection which also has several daggers and swords of this type.

Having established material types and then object types with an increased likelihood of being treated with inorganic pesticides, the next stage of the survey was to develop a set of search criteria to identify similar items in the collection using the museum's database. One major group of items identified in this survey were the items made of or incorporating the materials type – feathers. The second important divider was found to be provenance: for feathers, only the Australian items were found to have mercury treatment. The tested items all fall into a group of object types related to the head and neck, Museum Victoria has a range of object types associated with the head and neck and so all of these are included in the search. The group could be further restricted by selecting items acquired pre-1930, a small check can also be made on items acquired post-1930 to see if they were collected by the Museum or another agency before 1930, as this increases the likelihood that they were treated with inorganic pesticides. A similar process was followed for skin/fur material types identified with high levels of inorganic substances. These items were also found to be associated with the head and neck.

The criteria used to select items for hazard tagging are outlined in Table 2. Each entry in the set of items selected using the search criteria was then tagged as being suspected of containing the hazard, the name attached to this information is the *Materials Population Profiles Project*, Figure 3. The tab is filled in with the following information, the Hazard Category, for example Poison or Flammable material, the specific Type of hazard, for example mercury or arsenic and then the Status of the identification as tested or suspected. In this way it is clear that the item is suspected of having the hazard but has not currently been tested. The yellow Hazard symbol, top right hand corner of the Materials Tab in our database appears on all tab screens, alerting all users that the item has a hazard associated with it and that the record should be checked for instructions and the relevant Safe Handling Procedure read before accessing the item in the collection store.

Conclusions

It is impossible to test every item in a collection that contains nearly 17 million items. A survey of a small proportion of the collection is possible within a finite time frame. Using the semi-random survey technique described here, items with an increased likelihood of being treated with inorganic pesticides have been identified. By using material type as the main search criteria it reduces the number of selection categories and thus reduces the number of items requiring analysis. Specific groups of collection materials with a higher likelihood of being treated with inorganic hazards were identified, and were then globally uploaded into the EMu database. This process leads to improved risk management systems, procedures and staff awareness.

References

Cross, P S, Odegaard, N, 2009, The Inherent Levels of Arsenic and Mercury in Artefact Material, *Collection Forum*, vol 23(1-2), pp23-35.

Goldberg, L, 1996, A History of Pest Control Measures in the Anthropology Collections, National Museum of Natural History, Smithsonian Institution. *Online Journal of the American Institute for Conservation,* vol 35(1), pp23-43.

Hamann, B, 2006, Testing Cultural Material for Arsenic and Interpreting the Results: A Case Study at Carnegie Museum of Natural History, *Collection Forum*, vol 20(1-2), pp13-22.

Hawks, C, McCann, M, Makos, K, Goldberg, L, Hinkamp, D, Ertel, D Jr, Silence, P, (eds), 2011, *Health and Safety for Museum Professionals*, SPNHC, New York.

Nason, J D, 2001, Poisoned Cultural Heritage: curatorial assessment and implications of pesticide residues in anthropological collections, *Collection Forum*, vol 17(1-2), pp67-81.

Pool, M, Odegaard, N, Huber, M J, 2005, Identifying the Pesticides: Pesticide Names, Classification and History of Use. *Old poisons, New problems: A Museum Resource for Managing Contaminated Cultural Materials*, Odegaard, N, Sadongei A and Associates *(eds),* Altamira Press, Lanham, pp5-31.

Palmer, P T, Martin, M, Wentworth, G, Ostini, S, Prospero, C, Fang, M, 2006, Pesticide Contamination on Native American Artefacts – Methods, Results from Six Case Studies, and Next Steps, *Collection Forum*, vol 20(1-2), pp23-32.

Reuben, P, 2006, Detection and Mitigation Strategies for Contaminated Nagpra Objects – the Seneca Nation's Experience, *Collection Forum*, vol 20(1-2), pp33-41.

Shugar, A N, Sirois, P J, Handheld XRF use in the identification of heavy metal pesticides in ethnographic collections, In Shugar, A N, Mass, J L (eds), *Studies in Archaeological Sciences*, Leuven University Press, Leuven, 2012, pp312-348.

Sirois, P J, 2001, The Analysis of Museum Objects for the Presence of Arsenic and Mercury: Non-destructive Analysis and Sample Analysis, *Collection Forum*, 16(1-2), pp65-75.

Sirois, P J, Sansoucy, G, 2001, Analysis of Museum Objects for Hazardous Pesticide Residues: A Guide to Techniques, *Collection Forum*, vol 17(1-2), pp49-66.

Ustun, O G, 2009, The Limitations of Handheld XRF Analyzers as a Quantitative Tool for the Measuring Heavy Metal Pesticides on Art Objects, *Ethnographic Conservation Newsletter*, vol 30, pp5-8.

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Biographies

Dr Rosemary Goodall is a Material Scientist at Museum Victoria investigating the hazardous substances in the collections. She has over 30 years' experience in chemical manufacture and instrumental analysis, specialising in Elemental and Vibrational spectroscopy. Her previous research interests include the study of Rock Art pigments from North Queensland and Maya pigments from Honduras.

Davina Hacklin is the former Manager of Conservation at Museum Victoria, and has a special interest in preventive conservation, hazard profiling and risk management. She graduated from the University of Canberra with a Bachelor of Applied Science (Conservation of Cultural Materials) and has worked for the Australian War Memorial, Queensland Museum and Museum Victoria. Davina has recently returned to University of Canberra.

Nancy Ladas is the Manager, Collection Information Systems and has worked at Museum Victoria for over 18 years in curatorial research, exhibition development and collection information management. Nancy oversaw the modifications to the Materials tab in the collection management system EMu and associated training manuals in order to better reflect and document hazards and the processes of identification and testing across all collecting departments.

Maryanne McCubbin is Head, Strategic Collection Management at Museum Victoria. With tertiary qualifications in history and information management, Maryanne has worked in archives and museums for thirty years. Her work has centred on the management, use and interpretation of collections, involving addressing the big, tough issues around managing a major, complex state collection.

Captions

Figure 1 Number of items versus levels of hazardous elements by time range for 12 material type categories.

Figure 2 Number of items versus date for mercury residue found on items in the Indigenous Collection associated with the head and neck.

Figure 3 The Materials Tab in the EMu database, showing the hazardous substance warning attached to the item record. The record is flagged with a yellow hazard icon in the top right corner of each tab.

Table 1 Number of items tested by XRF analysis by material type

Material Type	1850 - 1900	1900 - 1950	1950 - 2000	2000 -
Wood	47	55	77	24
Bark	6	14	11	3
Resin	4	14	4	1
Plant fibre	41	42	33	21
Skin/fur/animal fibre	25	39	34	4
Feather	17	27	13	1
Shell	5	6	14	3
Bone/tooth/horn	19	17	14	2
Paper	13	41	20	
Metal	23	14	34	1
Stone	6	14	9	3
Ceramics	5	3	18	2
Film	3	7	1	
Glass	2	4	7	1

Table 2 Material types identified with specific hazards.

	EMu Values used for search and tag				
Material Type	**Provenance**	**Object Type**	**Time Period**	**Hazard**	**Hazard Type**
Feathers, Skin/Fur	Australia	Head and Neck Ornaments	1850 - 1930	Mercury	Applied
Glass	All	Glass Beads in various object types	Pre 1950	Arsenic Lead	Applied
Metal	Indonesia	*Kris* swords/daggers		Arsenic Mercury	Inherent
Animal skin	Australia	Various object types	Pre 1950	Arsenic	Inherent

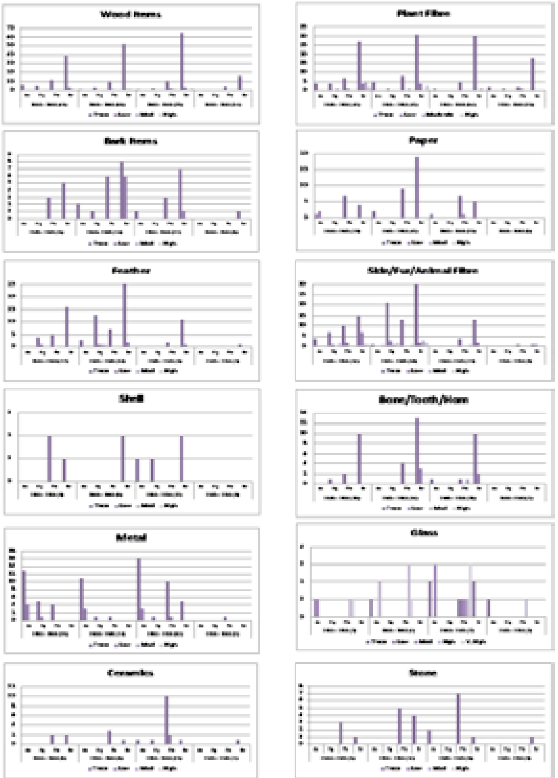

Figure 1: Number of items versus levels of hazardous elements by time range for 12 material type categories.

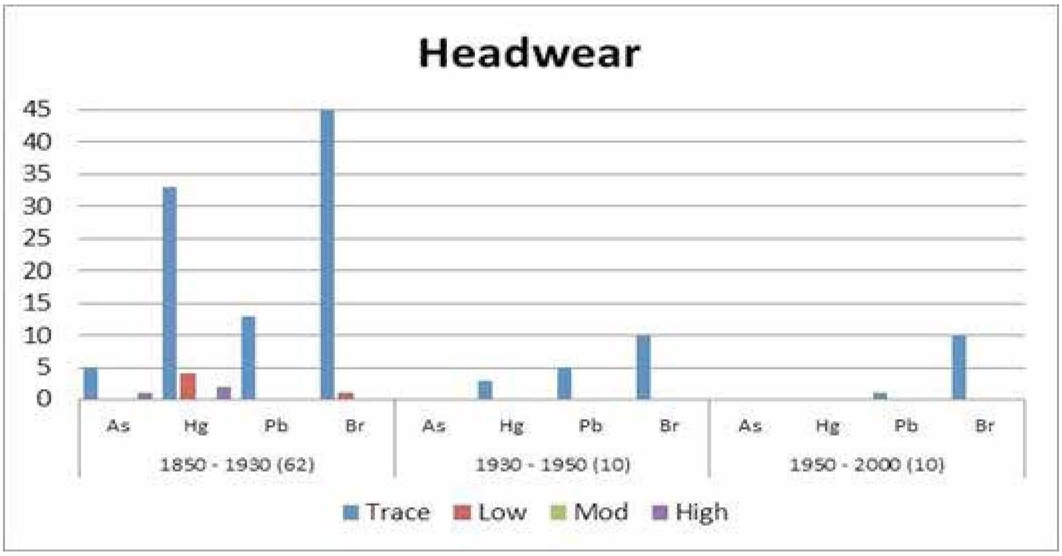

Figure 2: Number of items versus date for mercury residue found on items in the Indigenous Collection associated with the head and neck.

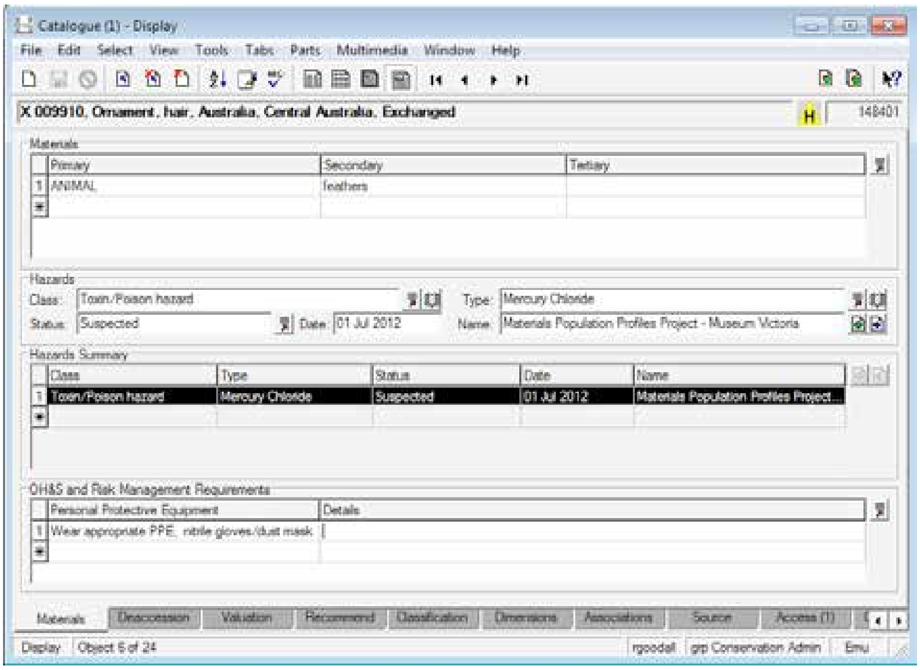

Figure 3: The Materials Tab in the EMu database, showing the hazardous substance warning attached to the item record. The record is flagged with a yellow hazard icon in the top right corner of each tab.