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Edited by Niccolo Caldararo, Lee Davis, Peter Palmer, and Janet Waddington

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**THE CONTAMINATION OF MUSEUM MATERIALS AND
THE REPATRIATION PROCESS FOR
NATIVE CALIFORNIA:**

**PROCEEDINGS OF A WORKING CONFERENCE AT
THE SAN FRANCISCO STATE UNIVERSITY,
29 SEPTEMBER TO 1 OCTOBER 2000**

**EDITED BY NICCOLO CALDARARO, LEE DAVIS, PETER PALMER,
AND JANET WADDINGTON**

INTRODUCTION

A working conference was held at San Francisco State University (SFSU) from September 29 through October 1, 2000. The following papers were presented at the conference with the addition of papers by participants who contributed to the conference discussions. Summaries and comments made at the conference have been made available to individuals they concern for review and correction. The conference was videotaped and the tapes are available for purchase (see the website for details). The San Francisco State University information website on artifact contamination can be found at <http://bss.sfsu.edu/calstudies/arttest/>. We wish to thank Mr. Bob Spencer of Pacific Research Inc., consultant to Mr. Deron Marquez, Chairman of the San Manuel Band of Mission Indians, for preparing the initial draft of the summaries and comments.

The conference was organized by Dr. Lee Davis and Dr. Niccolo Caldararo. It focused on the contamination of Native American objects being returned to the tribes through the Native American Graves Protection and Repatriation Act (NAGPRA). The contamination of these objects with pesticides was the result of efforts to prevent the destruction of the objects by insects, pests and mold. The present problem centers around the return of these objects to the tribes and the potential health hazards they now present to tribal members in use, storage, display and study.

An artifact analysis laboratory has been developed by SFSU in consultation with the Hoopa Tribal Museum to test repatriated objects for a full range of pesticides. The results from recent tests for contamination will serve as a starting point from which a strategy to evaluate and address this national health problem will be developed. This conference provided researchers and tribal leaders with a unique opportunity to share information and allowed tribes to discuss their needs and concerns as to health and the safe use of sacred objects.

The goal of this conference was to encourage cooperation between scientists, tribal representatives, museum curators, pest control experts, and artifact conservators towards a strategy for addressing the risks to human health and to the process of repatriation. Representatives from tribes and policy agencies discussed responsibility for contamination of NAGPRA materials.

HISTORICAL SURVEY OF THE SOURCES OF CONTAMINATION OF ETHNOGRAPHIC MATERIALS IN MUSEUM COLLECTIONS

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Abstract.—From the mid-18th century onwards, pests, particularly insect pests, were viewed as the greatest threat to the preservation of collections. Initially, collectors combated pests through the use of metal salts, some aromatic herbs and oils, and possibly toxic derivatives from plants, such as strychnine. Collection growth, the use of cabinets to store specimens, and discoveries in organic chemistry eventually led to the use of gas-phase chemicals as fumigants for the contents of individual cabinets or for large-scale treatments. The legacy of pesticide use continues to pose problems for staff and various collections users, especially the recipients of repatriated objects. Modern pest control for collections focuses on prevention first, and then on treatments that do not leave lasting residues. Aside from pesticides, other potentially hazardous contaminants on collections include: residues from mold, rodent, or insect infestations; soot; asbestos from decrepitating building or pipe insulation; and powdered lead paint from old storage furniture. Efforts are underway to record the history of collections and their treatment, develop tests to identify and mitigate various contaminants, and to evaluate the risks from potentially hazardous residues. Modern practice places human safety above the safety of objects or specimens. In the long run, this approach, along with improvements in storage and display techniques should help ensure that collections will be preserved with less alteration in the future.

INTRODUCTION

It has been said that “a museum seems to represent the inheritance of one of the oldest instincts of mankind” (Ripley 1969:23). The instinct at issue is the urge to collect. Collections have been amassed, and lost to various causes, for thousands of years. It is difficult to say how long specific collections that are now known only through the records of ancient civilizations may have lasted. Certainly for many items that were formed of organic materials, long-lived collections (that is, those that survived for over a century) did not exist until fairly recent times.

By the mid 18th century, collecting cultural and natural history materials from places near and far had become an important activity for some Europeans and colonial Americans (Jenkins 1978, Kohlstedt 1991). The classification system developed by Carl von Linné (Linneaus) in the 18th century fostered study of large numbers of specimens in order to truly understand the taxonomy of flora and fauna. It became increasingly important to have not only a diversity of materials for examination, but also a series of specimens on which to base identifications. The organic materials that were part of natural science collections were vulnerable to deterioration from inappropriate temperature and humidity conditions, light, ultraviolet radiation, and pollutants. But, damage from these agents is slow and the relationship between cause and effect is not always readily obvious to a collector. On the other hand, damage from infestations happens very quickly and the causative agents can be seen at work. Collections, if they managed to survive long enough to reach the collector in the first place, might disappear within a few years as a result of pest activity (Réaumur 1748).

METAL SALTS

The realization that arsenic and mercury salts could provide long-term protection against pests led to widespread adoption of these chemicals as prophylactic treatments during the next 100 years (Hawks and Williams 1986, Hawks and Von Endt 1990, Williams and Hawks 1987). Initially, the focus was protection of natural science specimens, but ethnographic objects were also finding their way into collections, and many of these contained organic materials. In the United States, the American Philosophical Society received Native American snowshoes and a hatchet from a private donor in 1772, and a larger collection that included arrows and clothing items in 1797 (Bell 1967). In the early 19th century, the American Antiquarian Society and a private museum maintained by William Clark contained fairly extensive collections of ethnographic materials (Ewers 1967, Shipton 1967). Thomas Jefferson sent some of the Native American clothing and utensils collected by Lewis and Clark to Charles Willson Peale for display at his museum in Philadelphia (Cutright 1989). Few items from this early period survive, mainly because there was no real museum establishment at the time. When institutions foundered or lost interest in collections, the materials were dispersed (Ewers 1967, Shipton 1967). However, it may not be completely coincidental that a fair number of items from Peale's collections, which underwent many tribulations after his death, still exist at the Peabody Museum at Harvard (Cutright 1989). Peale was an early proponent of the use of arsenic for preservation (Sellers 1980). If Clark's objects are in fact the ones now in a Swiss museum (Ewers 1967), it may be because he was familiar with the use of mercury compounds for preservation. Examination of the herbarium specimens that remain from the Lewis and Clark expedition suggests that they were treated with mercury salts, probably during the course of the trip.

In the early 19th century, there were an increasing number of exploring expeditions like that of Lewis and Clark in which collecting was done by those whose primary assignment was to create maps and collect natural specimens. As a result, while ethnographic items were also collected, they were collected by naturalists, soldiers, and sailors (Kaeppler 1985). Equipped with arsenic and mercury salts to preserve the natural collections in the field or during subsequent processing, these explorers almost certainly used them on the cultural materials as well (Baird 1854, Goldberg 1996). It was not until the third quarter of the 19th century that the Bureau of American Ethnology was established and collecting became part of a systematic effort to record information on native peoples (True 1929).

The Bureau's ethnographic collections later became part of the Smithsonian's holdings. As Goldberg (1996) has pointed out in her excellent summary of pest control in the Smithsonian's anthropology collections, arsenic and mercury continued in use there until around the end of the 1800s. It is likely that similar treatments were applied to ethnographic collections at other institutions. While their use in anthropological collections seems to have ceased about 100 years ago, in some collections, particularly in the natural sciences, use of these chemicals persisted until well into the second half of the 20th century. Also, the Museum of New Mexico believes that a mothproofing spray containing sodium arsenite was used on cultural collections *ca.* 1940–1960 (Museum of New Mexico 1997). None of this is terribly surprising, in light of the fact that arsenicals had widespread

use as tonics and pharmaceuticals until after World War II (National Research Council 1977). In the 1940s, use of arsenic trioxide compounds in the U.S. as general agricultural and household garden insecticides still amounted to about 40 thousand tons annually, supplemented by tens of thousands of pounds of other arsenic compounds, and up to four million pounds of Paris green, a copper arsenite (Shepard 1951). Mercury salts, while also used as insecticides, were by no means as popular as arsenic. They were, however, very common as antiseptics (e.g., calomel, mercuric chloride, and mercurochrome), a teething powder for children (calomel) and a hospital disinfectant (mercuric chloride) until very recent times (Brady and Clauser 1991, Goldwater 1972, Windholz et al. 1983). It is unlikely that anyone believed that these were not poisons, it was simply that used in ways that were then deemed to be appropriate, they were thought to be beneficial rather than harmful.

COMPOUNDS OF BOTANICAL ORIGIN

Of course, arsenic and mercury salts were not the only pest control treatments used for ethnology and other collections during the early years of modern collecting. In the 19th century, chemicals of botanical origin such as strychnine, camphor, perfume of lemon, and tobacco, were used with collections (Goldberg, 1996), although based on the paucity of references to it, strychnine seems to have had limited use outside the Smithsonian. Other botanicals or botanical extracts reportedly used with collections include thymol, menthol, cedar oil, and oil of bitter almonds (Makos and Dietrich 1995).

OTHER ORGANIC AND INORGANIC COMPOUNDS

The past hundred years have seen several changes in museums that led to a major reliance on chemical treatments to protect collections against pests. Collections grew to great numbers of specimens or objects and tended to be enclosed in cabinets, where they were not readily visible to staff. The cabinets were constructed all or in part of wood, which could and did serve as a harborage for pests, and they rarely sealed well enough to exclude pests. The buildings that housed collections were not built with pest control in mind, and themselves served as habitats for a host of pests, from insects to rodents. The environments within these buildings were poor and tended to promote pest activity.

The use of cabinets for collection storage made case-by-case fumigation seem like a practical approach, especially for chemicals thought to be safe for humans. The development of large fumigation chambers made highly toxic gases useful for treatment of incoming collections and major infestations. In some disciplines, fumigation was a recommended routine practice (Anderson and Choate 1974). If pest control facilities were not available in house, it was suggested that ethnographic collections be treated by a commercial pest control service (Majewski 1973).

Although the 19th century was the great era of discovery in synthetic organic chemicals, the insecticidal properties of many compounds were not understood immediately. For example, naphthalene was described in 1821 (Kidd), although not as a pesticide. It was used for pest control at the Smithsonian by 1889 (Goldberg 1996). However, discussions about its efficacy, and that of the closely related compound, paradichlorobenzene, appear to have occurred, or at least continued,

much later (Abbott 1935, Arnold 1953). Both have been used as cabinet fumigants in museums for much of the 1900s, and are still used in some museums today.

The rise of large-scale farming in the 20th century seems to have led to rapid evolution of insecticides based on synthetic organic compounds (Brown 1951). In addition, there were a number of inorganic fumigants developed for commodities or structures. Often these were touted as safe when introduced and, when applied in museums, were not regarded as a potential hazard to collections staff or those who used the collections. For example, DDT was credited with nearly miraculous ability to control disease-bearing insects (Cristol and Haller 1945), and it, like many 20th century insecticides, was finally withdrawn from production not because of direct human health hazards, but because of effects on the environment. Chemicals now known to be carcinogens were routinely used in museums with no safeguards for staff who applied them to collections. Even collections that had been fumigated with gases known to be toxic were regarded as safe for handling once the collections had been aired for some period (Renshaw-Beauchamp 1978, Dawson 1981).

Chemicals that *may* have been used for pest or mold control are listed in Table 1. While this list seems formidable, it is unlikely that many of these chemicals saw any widespread use, at least in the United States. Methyl bromide, for example, was not and still is not considered an acceptable fumigant for a number of materials likely to be found in ethnographic collections (Dow 1938, Dawson and Strang 1992), which has limited its use in many museums. There was, however, still some tendency to use the same treatments for natural science and ethnographic materials. For example, at the California Academy of Sciences, Edolan U was used for both types of collections (Funk and Sherfey 1975). However, Goldberg's review (1996) of practices at the Smithsonian, based on a careful analysis of records, is an example of how the range of options can be narrowed, particularly for a specific institution and for a specific collection.

MODERN PEST CONTROL IN MUSEUMS

Today, the use of non-chemical pest control prevails in museums because there is an understanding of the importance of appropriate environmental conditions, cleanliness, and good storage and exhibit furniture in keeping pests at bay. This understanding was founded in part on fairly recent entomological research into the habitat requirements of pests, along with concern for the effects of chemical treatments on collections.

Once researchers began to examine the efficacy of fumigants when used inside cabinets (Williams et al. 1986, Williams and Walsh 1989a, 1989b), and review the often deleterious effects of the chemicals on natural and cultural materials (e.g., Ballard and Baer 1986, Baynes-Cope 1982, Brokerhof 1989, Dawson, 1986, Dawson and Strang 1992, Florian 1987, Green and Daniels 1987, Leckie and Williams 1994, Smith 1975, Tilbrooke 1978, Vingelsgaard and Schmidt 1986, Williams 1999, Williams and Walsh 1989c, Zycherman and Schrock 1988), there was interest in curtailing chemical pest control. This was reinforced by discussions of the health hazards to museum personnel and increased understanding of the regulations pertaining to pesticide use (e.g., Ballard and Baer 1986, Dawson and

Table 1. Other organic and inorganic chemicals that *may* have been used for pest or mold control.

Alcohol
Aldrin
Bendiocarb (Ficam)
Benzene hexachlorides (e.g., Lindane)
Borax
Boric acid
Carbaryl
Carbolic acid (phenol)
Carbon disulfide
Carbon tetrachloride/ethylene dichloride
Chlordane
Chlorpicrin
Chlorpyrifos (Dursban)
Diatomaceous earth
Diazinon
Dichlorodiphenyltrichloroethane (DDT)
Dichlorvos (Vapona)
Dieldrin
Edolan U
Endrin aldehyde
Endosulfan II
Ethylene dibromide
Ethylene oxide
Formaldehyde
Heptachlor
Hydrogen cyanide gas
Hydrogen phosphide
Lauryl pentachlorophenate
Malathion
Methyl bromide
Methoxychlor
Naphthalene
Orthodichlorobenzene
Paradichlorobenzene
Pentachlorophenol
Propoxur (Baygon)
Pyrethrins (synthetic)
Silica gel
Sodium aluminum fluorosilicate
Sodium fluorosilicate
Sulfuryl fluoride
1,2,4-trichlorobenzene

(Compiled from Carpenter 1985, Dawson and Strang 1992, Derrick et al. 1990, Funk and Sherfey 1975, Glastrup 1987, Goldberg 1996, Makos and Dietrich 1995, Renshaw-Beauchamp 1978, Rossol and Jessup 1996, Story 1985, Tilbrooke 1978, Vetter and Bauer 1978, Zycherman and Schrock 1988).

Strang 1992, Makos and Dietrich 1995, Muir et al. 1981, Peltz and Rossol 1983, Rossol and Jessup 1996, Smith 1975, Vingelsgaard and Schmidt 1986). The development of integrated pest management techniques that are feasible and effective for museums (Jacobs 1995, Jessup 1995, Strang 1992a), along with evidence that low heat, freezing, and controlled atmospheres could effectively treat infestations (e.g., Florian 1997, Selwitz and Maekawa 1998, Strang 1992b, 1995, 1997,

1998) have greatly diminished the use of chemical insecticides in North American museums.

OTHER CONTAMINANTS

Aside from the deliberate application of pesticides or fungicides, there are other potential contaminants on museum collections. Asbestos from decrepitating pipe or building insulation, debris (frass) from old insect attacks, finely powdered lead paint from storage case or room coatings, mold spores from infestations after floods or periods of high humidity, and soot contaminated with a host of pollutants after fires are examples of some of the residues that might occur on collections. There are objects with friable surfaces from which residues of these kinds are difficult, if not impossible, to remove without jeopardizing the object. Museums have learned this from numerous emergency salvage operations. Good examples can be found in Untch et al. (2000) and in Makos and Dietrich (1995).

It seems likely that in time we will find other residues from structures or storage furniture that were once thought to be safe, but are subsequently recognized as hazards. However, the conservation community has made an ongoing effort to evaluate building materials prior to museum renovations or new construction to help avoid unpleasant surprises.

It should be remembered that some objects are inherently hazardous by virtue of the materials from which they were fabricated, or by deliberate alteration before becoming part of a public trust collection. Hawks and Makos (2000) review some of these issues and the implications these have for collections care and use.

COLLECTION HISTORIES AND HAZARDS IDENTIFICATION

There are trends in museums that bode well for a better understanding of collection hazards of all kinds. Recording the histories of collections through research in museum records and archives and interviewing former staff is a growing practice as museums recognize the potential impact of past contamination on all types of collection use, from loans for exhibition and research, to public programs, and object repatriation.

Testing continues to be conducted to identify various contaminants (e.g., Found and Helwig 1995, Glastrup 1987, Hawks and Williams 1986, Howe et al. 1999, Knapp 1993, Makos and Dietrich 1995, Museum of New Mexico 1997, Odegaard et al. 2000, Odegaard and Sadongei 2000, Sirois 1988, Sirois and Taylor 1988). The efforts of the Museum of New Mexico (1997) and the recent conference conducted by Arizona State Museum at the University of Arizona (Odegaard and Sadongei 2000) are part of what is a growing and worldwide effort to address the identification and appropriate handling of hazardous collections (Goldberg and Hawks in press).

Efforts are also underway to evaluate the risks from pesticide and other potentially hazardous residues in collections (e.g., Burroughs pers. comm., Makos and Dietrich 1995), and to find means to remove residues from objects (e.g., Deucher et al. 2000, Hawks and Bell 1999, Spafford-Ricci and Graham 2000, Vingelsgaard and Schmidt 1986).

SUMMARY

In the natural sciences, information about collection-based hazards has been quite broadly dispersed, but in ethnographic and history collections the assump-

tion until very recently was that somehow organic materials survived without becoming contaminated: a naïve assumption given that storage and environmental conditions were the much the same across collections. One reason we can discuss repatriation today is because there is something to repatriate. It is unlikely that the objects in question could have survived in a pristine state.

The hazardous residues on collections are largely the result of well-meaning people doing the best they could with the knowledge and resources available to them at the time. Even if collections staff had understood the potential harm to themselves and their progeny, many of the treatments would still have been carried out because the accepted dictum was that the collections came first and that personnel safety was a secondary concern.

This mindset has been reassessed in recent years. Hopefully, it will never be the norm again. The new generation of museum professionals seems to have a very healthy attitude and as a consequence, human safety increasingly has priority over collections care. Perhaps a blessing in disguise, this can work to the benefit of collections. Experience has shown that poor attention to human health and safety puts collections at risk as well. In addition, collections are now much better housed at both the cabinet and building level than at any time in the past, and less invasive methods of pest control are available when infestations occur. This suggests that collections that have survived until now will undergo far less alteration in the future than has been their fate in the past.

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THE ISSUE OF PESTICIDES ON NATIVE AMERICAN CULTURAL OBJECTS: A REPORT ON CONSERVATION AND EDUCATION ACTIVITIES AT UNIVERSITY OF ARIZONA

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Abstract.—As a result of the Native American Graves Protection and Repatriation Act (NAGPRA), federally recognized American Indian tribes have begun to claim and receive certain cultural objects previously held with museums and federal agencies. Unfortunately, a wide range of pesticide substances has been applied to museum collections for the purpose of preserving them. It is the actual repatriation or the transfer of pesticide contaminated cultural objects from museums to tribes for culturally appropriate use, storage, retirement, or disposal that has brought this concern to an urgent level. This paper discusses the activities initiated by the Arizona State Museum.

INTRODUCTION

The topic of pesticide contamination on Native American objects is complex. Pesticides include herbicides, fungicides and various other substances used to prevent, destroy, repel or mitigate pests. A wide range of pesticide substances has been applied to museum collections for the purpose of preserving them. Various laws have made this a legal issue; voices from the American Indian tribes have made it a moral issue; and professional conservators have identified various ethical issues. Of critical reference is The Native American Graves Protection and Repatriation Act (NAGPRA) that was signed into law on November 16, 1990. As a result of this law, federally recognized American Indian tribes have begun to claim and receive certain cultural objects previously held by museums and federal agencies. While it is understood that a concern for chemical pesticide practices in museums extends back to a time well before the passage of NAGPRA, it is the actual repatriation or the transfer of pesticide contaminated cultural objects from museums to tribes for culturally appropriate use, storage, retirement, or disposal, which has brought this concern to an urgent level. To effectively address the pesticide residue issue, a range of specialists from a variety of fields must now combine research methods with historical information and scientific techniques to determine the nature of pesticide contaminants that are present. The medical implications for human health must be interpreted based on the quantities and qualities of pesticide contaminants actually present on cultural objects of repatriation. Finally, once the results of the research and medical interpretation are obtained, then educational responsiveness and outreach must be implemented. The responsibilities for ensuring continued attention to the educational aspect of this issue rest with museum employees, contributing specialists, and tribal people working together.

IDENTIFYING THE CONCERN

For many tribes, sacred objects and human remains have enduring symbolic qualities that are culturally and spiritually significant. American Indian people

know that these objects and remains are capable of reestablishing ancestral ties, healing tribal communities and enhancing life. As tribes gain experience in repatriation, many seek traditional methods to reduce the risk involved in handling culturally sensitive materials. These simple but effective cultural practices help to reduce the risk of spiritual harm that individuals may encounter when contact is made with human remains, funerary objects such as mortuary vessels, and other objects imbued with religious and hence spiritual significance. A critical first step in identifying the concern of residual pesticides on NAGPRA material is to acknowledge that tribes may have effective traditional methods of purification that can contribute to the resolution of this issue. This type of information can only be disclosed if tribes are actively engaged in any discussion of testing, treatment, or stabilization.

Many museum employees, based on experience or information reported in the literature, have been aware that many institutionally held objects were treated with chemical poisons to aid in their preservation. Professional conservators in particular have long held a double concern: first, that the use of chemicals may cause unpredictable, disfiguring, and irreversible changes to the objects treated, and second, that the actual access, examination, and handling of these treated objects may pose ongoing and serious health hazards to individuals. While discussions of both concerns have been widely reported, some examples referring to the human health hazard of preservative residues on objects include: (a) sources of toxic particles that may be ingested or inhaled through the nose or mouth such as biocidal treatments to objects of feather, fur, buckskin or textile with commercial pesticides; fungicidal treatments to the backs of paintings, documents, and textiles; syberizing (use of an arsenic-based mothproofing agent); and ancient biocidal treatments including copper or lead pigments; or (b) sources of toxic vapors from pesticide repellants and fumigants that may be inhaled through the nose or mouth, or irritate the eyes such as residues (Odegaard 1990).

The concept of integrated pest management (IPM) was introduced to museum use in the early 1980s when conservators began to question the widespread use of pesticide chemicals with artifacts in the absence of clear knowledge about what insects actually were present. Conservators that adopted the IPM approach to museum pest control became more knowledgeable of pesticide products, of the chemical reactions they could have on various object materials, and of the potential human health hazards they might present. IPM emphasizes the prevention of pest damage by combining monitoring and eradication methods with the least possible hazard to people, property, and the environment. Monitoring collection areas with sticky-traps followed by incorporating non-chemical techniques such as freezing, heating, and anoxic environments have become popular non-chemical alternatives to the use of pesticides. Also, during recent decades various environmental, occupational, and medical studies regarding acceptable levels of human exposure to chemicals have led to the steady removal of many pesticide products from the market place.

From a legal standpoint, it appears that the degree of potential health hazard due to historic pesticide residues remaining on an object claimed through the repatriation process was not fully recognized when NAGPRA was signed into law. A reference to pesticides occurs only once in the regulations implementing the statute. The NAGPRA regulations (43 CFR 10.10[e]) indicate that: *The mu-*

seum official or Federal agency official must inform the recipients of repatriations of any presently known treatment of human remains, funerary objects, sacred objects or objects of cultural patrimony with pesticides, preservatives, or other substances that represent a potential hazard to the objects or to persons handling objects.

Informing tribal recipients of any known treatments that may have occurred during an object's museum history is, indeed, a difficult task for most museums and federal agencies. The research necessary to fulfill the NAGPRA regulation requirement involves more than a simple checking of the museum records. Rather, a thorough review of many museum documents, archives, conservation correspondence and reports, and letters to earlier staff members that may be on file must be conducted. In 1998, the Arizona State Museum (ASM) proposed the use of a NAGPRA repatriation check sheet that would enable museum employees to record and track critical information related to the repatriation process (Odegaard and Kolaz 1998). The ASM check sheet included the following questions related to the pesticide issue:

- (1) Is there evidence of prior infestation?
- (2) Are residual pesticides indicated?
- (3) Is there evidence of museum repairs, restorations, and alterations?
- (4) Are there any written records that would suggest the use of pesticides?
- (5) Based on past storage locations, what pesticides might typically have been used on or near this object?

Since 1995, the ASM conservation laboratory has completed an in-depth review of possible pesticide residues on all ethnographic objects undergoing the repatriation process after consent and preliminary consultation from the receiving tribe.

RESEARCHING THE ISSUE

The topic of pesticide residues and museum collections has engaged many researchers who have identified a wide range of possible pesticide contaminants. Books such as Zycherman and Schrock (1988) provide lists, descriptions and discussions of pesticide products. In an effort to recover historic pesticide information, conservators such as Goldberg (1996) have undertaken institutionally focused projects. These types of projects gather and evaluate various formats of information in order to reveal the use of specific pesticides within a specific institution. There is great efficiency in having a ready list of the possible chemical products, the locations of use, and the general time periods of use within an institution when completing a repatriation claim in compliance with the NAGPRA regulations. However, producing this information is both technical and time consuming. Museum conservation laboratory files are often the first place to start as they usually house object treatment reports, technical information regarding chemicals and pesticides, as well as general literature regarding various aspects of pesticide application to objects. Unfortunately, there are relatively few conservation laboratories located in museums with American Indian collections and most of these laboratories were started less than twenty-five years ago.

Scientific testing for pesticide residues on cultural objects requires some understanding of the types of pesticides that could possibly be present, the application techniques for those pesticides, and the likely locations for residue accu-

mulation. This information may be somewhat unique within institutions and is based on the particular resources that were available at a particular time. For example, curatorial diaries from the 1950s and 1960s at the ASM indicate that a mothproofing chemical was repeatedly applied to the objects on exhibit. A review of the exhibition lists identified many objects and photographs suggested possible accumulation areas based on the object's position in the exhibit case. Material characterization techniques (sometimes called "spot tests") may be used to indicate the presence of a specific chemical or type of pesticide substance. Analytical techniques that utilize specialized instruments allow for the determination of exact quantities and qualities of a chemical substance present in a sample. Both testing techniques have application to the issue of pesticide residues on Native American objects undergoing repatriation.

The application of material characterization techniques for the detection of pesticide contaminants on museum objects is relatively recent. Protocols for arsenic testing on museum objects have been discussed by several authors including Hawks and Williams (1986), Knapp (1993), and Henry (1996) and are acknowledged to be in regular use by numerous museums. The large materials characterization project undertaken at ASM resulted in a volume of tests that detail the procedures for determining various metal, inorganic, and organic substances that may be associated with artifacts and also includes several tests of relevance to the detection of pesticides (Odegaard, Carroll, and Zimmt 2000). Expanding on the concept of characterization testing, the ASM conservation laboratory began work in 1998 on a series of residue identification test protocols devoted specifically to pesticides. Some of the tests that were discussed at the Arizona State Museum Contaminated Cultural Material in Museum Collections Workshop in April 2000 included carbamates, organophosphates and thiophosphates, chloroorganics, borates, and zinc fluorsilicates, in addition to arsenic, mercury, lead, and other heavy metals.

RESPONDING TO THE CONCERN

The Hopi Tribe first raised concerns regarding the health threat of repatriated objects in 1997 in response to a report submitted to the tribe by the Peabody Museum of Archaeology and Ethnology at Harvard University. After initiating a meeting in northern Arizona with various museum workers from the region in September 1997, the Hopi established special dialogues with several museums. In response to the Hopi concern, funds from a National Parks Service (NPS)-NAGPRA grant at The Denver Museum of Natural History (since renamed the Denver Museum of Nature and Science) were reallocated and testing for the presence of arsenic on 512 specimens was completed in 1998 (Howe 1999). Also, as follow-up to a repatriation request from the Hopi, the School of American Research undertook a testing program for the presence of arsenic on 19 specimens (Landry 1998).

Using funds from a 1998 NPS-NAGPRA grant, the Hopi Tribe proposed the use of contamination testing in their Katsina Friends Pesticide Contamination Documentation Project. The tribe engaged a multidisciplinary research team from the University of Arizona in a pilot project to develop, test, and interpret a protocol for determining the toxicity of three repatriated objects from different museums using analytical testing techniques. The testing protocols allowed for the

detection of a wide range of substances sometimes used as pesticides. Findings from the study indicated that, except for minor trace amounts of other pesticides, the only pesticide observed on these three specimens was arsenic, which occurred in two of the examples but had only been noted in museum documents for one. Preliminary results from the study suggested that all museum objects subject to repatriation should be tested for pesticide residues (Seifert et al. 2000).

In 1998, Odegaard made a presentation on the issue of pesticide contaminants on repatriated objects to representatives of the Native American Indian Advisory Group of the Arizona State Museum, a group that includes 21 tribal groups from the State of Arizona. Later that year, another presentation was made at the request of the Gila River Indian Community for members of the Four Southern Tribes in Arizona. It was evident from these meetings that more information would be considered helpful in order to fully understand the range of issue and concerns related to the topic.

Funding from a 1999 NPS-NAGPRA grant enabled the ASM to begin research and planning for a workshop entitled *Contaminated Cultural Material in Museum Collections*. Research activities of the grant included compiling historical information about the use of pesticides at the Arizona State Museum, establishing a database that identified 91 pesticides used in museums as well as information about them including: chemical name, common name, Chemical Abstract Service (CAS) number, status and dates of use, methods of application, characteristics, target pests, field half life, and persistence. In order to determine the types of information that would be most useful to tribal members, a series of consultations were held with 9 tribal communities. Finally, representatives from each of the American Indian tribes in Arizona were invited to attend the workshop held in March 2000. An informational notebook, designed to compliment the formal presentations, was prepared for each attendee. However, because there were many tribal representatives that were not able to attend, we have proposed to create a single volume that will include the content of the various presentations as well as additional information concerning the pesticide data base and details of the testing techniques. This publication should enable us to share the information with those who were not there, while maintaining the context in which the presentations were made.

MOVING THE ISSUE FORWARD

Raising the pesticide issue and notifying museum employees and Native American representatives of the potential health hazards has been important in initiating several forums for collaboration and the exchange of information. Articles and presentations by Nason (1998), Johnson (1999) and Kuwanwisiwma (Associated Press 2000) are among those that have been influential. At the suggestion of tribal representatives that attended the ASM workshop, a presentation addressing the urgency of this issue was made at the Native American Graves Protection and Repatriation Review Committee meeting held April 2-4, 2000 in Juneau, Alaska. In addition to a summary report about the workshop, several important recommendations related to the pesticide issue were offered to the Review Committee.

- (1) Communication between museums and tribes is critical. Museums need to bring this issue up during consultations and tribes need to be informed and ask questions throughout the process.
- (2) Not every object's documentation and examination reports will include bad news about potential contamination, but when the news is bad, it is probably very bad.
- (3) Current regulations promote a continued ignorance on this topic. The NAGPRA Review Committee should see the pesticide topic as important and determine a path for further clarification of the regulations (Odegaard and Sadongei 2000).

It is clear that continued attention towards the issue of pesticide contaminants on American Indian cultural objects is necessary. Museums must recognize the issue as a serious concern and begin to compile their own, unique histories of institutional pesticide use. Museums must understand that there may be particular restrictions regarding the handling of sacred objects and that these must be incorporated into any examination or testing procedures.

Despite some opinions that suggest that museum conferences have adequately covered this topic, we believe that this is not the case. We recommend that more workshops and forums for discussion be held throughout the country by national and regional museum organizations. Programs such as the Arizona State Museum's Contaminated Cultural Material in Museum Collections Workshop for Arizona tribes offer the opportunity to reach different audiences face-to-face, with information that has not been published or is not easily accessible or affordable.

American Indians must also increase awareness within their tribes and communities with meetings and workshops. Repatriation programs like the one organized by the Confederated Tribes of Warm Springs, Oregon and the National Museum of the American Indian, Smithsonian Institution, in July 2000 have included discussion of the pesticide issue.

Specialists working in related areas must be encouraged to participate in the development and improvement of testing techniques that may identify and interpret the relationship of pesticide residues on cultural objects with respect to the potential risks to human health and the environment. Program presentations and full sessions at a variety of professional meetings have brought greater awareness to this issue.

Finally, individuals participating in this issue should be mindful that they are reporting and distributing clear and accurate information and that their recommendations are within their area of professional expertise. It should be understood that the types of pesticides, their quantities and method of application, the routes of body entry (ingestion, inhalation, and absorption), and the potential storage, use, or disposal of the specific object determine the level of health risk. Museum employees should not be expected to offer medical advice related to the toxicity or human health hazard of repatriated objects without the participation of medical or industrial hygiene professionals. Similarly, conservators should not be expected to sample objects or develop treatments that decontaminate objects without the participation of tribal representatives. Collaboration is the key to moving ahead on this issue.

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THE EFFECTIVENESS OF COMPRESSED AIR IN REMOVAL OF PESTICIDES FROM ETHNOGRAPHIC OBJECTS

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Abstract.—Objects from the Danish National Museum and from the Danish Museum of Arms and Uniforms, originally stored in areas that are known to have been treated with pesticides in the past, were analyzed using gas chromatography. It is shown that many of these objects still contain pesticides. Cleaning of the objects with compressed air results in a maximum removal of 40 percent of the pesticides, however the overall level of pesticides on the objects is significantly lower after cleaning. Personnel are at risk of exposure to pesticides during the cleaning process and when handling objects before and after cleaning. However, also in this case the exposure level is significantly lower after cleaning.

INTRODUCTION

At the Danish National Museum during the 1950s and 1960s it was common practice to prevent insect attacks on museum objects by spreading pesticides liberally throughout the stores and in exhibitions. Today the use of pesticides is considered a health risk and it is desirable to have as much as possible of it removed. In Denmark DDT (1,1,1-trichloro-2,2-bis(p-chlorophenyl)-ethane) has been totally banned since 1982, and in the United States the use is restricted to “cases of public health emergency.” The threshold limit value (TLV) for DDT dust in air is one milligram per cubic metre in Denmark.

In order to facilitate the cleaning of museum objects, a specially designed fume cupboard was constructed, in which compressed air was installed and used to clean the objects of common dust and pesticide crystals sitting on and in the objects. The fume cupboard was under constant negative air pressure and exhaust filters were installed to prevent pesticides from entering the environment.

The scope of this work is to demonstrate the effectiveness of using compressed air to remove pesticides from the objects, with respect to both the amount of residue removed and the transfer of pesticides from the objects to the personnel handling the artifacts before, during and after the cleaning process.

EFFECTIVENESS OF COMPRESSED AIR

Museum artifacts, especially fur and fabric objects, can easily hold quantities of pesticides greatly exceeding generally accepted limits. Sixteen museum objects from the Ethnographic Department, most consisting of fur and skin objects from Greenland that were known to have been treated with insecticides in the past, were chosen for examination and cleaning in the fume cupboard. Samples were scraped or cut off, typically between five and ten milligrams of leather, parchment or fur as described by Glastrup (1987), before and after cleaning, in order to test whether the cleaning had an effect on the pesticide content on the objects. Previous results (Glastrup 1987) show that the distribution of pesticides is never uniform in the objects. Care was therefore taken to ensure that samples were

Table 1. The concentrations of paradichlorobenzene (PDB), naphthalene, DDT and methoxychlor found by gas chromatographic analysis of samples taken before and after cleaning with compressed air in a fume cupboard. The numbers given are in $\mu\text{g/g}$ material analysed. Detection limits are: PDB, 62 $\mu\text{g/g}$; Naphthalene, 5 $\mu\text{g/g}$; DDT, 39 $\mu\text{g/g}$ and Methoxychlor, 21 $\mu\text{g/g}$.

Sample number	PDB		Naphthalene		DDT		Methoxychlor	
	Before	After	Before	After	Before	After	Before	After
1	0	140	110	100	4,030	7,060	5,000	4,610
2	0	0	60	50	2,770	2,220	2,860	2,990
3	420	500	590	480	50	0	0	0
4	800	780	800	460	190	160	0	0
5	0	0	0	0	0	0	0	0
6	710	360	330	1,500	4,300	2,600	630	620
7	1,620	1,810	1,110	1,600	0	0	0	100
8	220	270	360	920	870	610	0	410
9	390	230	1,000	900	2,610	2,660	0	320
10	0	0	100	100	0	0	180	160
11	0	0	10	10	50	0	500	720
12	130	150	420	350	1,500	1,110	260	0
13	1,460	250	4,190	630	5,060	240	790	70
14	110	130	150	210	260	120	230	170
15	90	0	450	110	1,050	1,190	670	400
16	90	0	50	10	770	370	260	0
x_{av}	380	290	610	370	1,470	1,280	710	660

removed from the same general area before and after cleaning. The samples were deliberately chosen from a variety of surfaces.

The "Before" sample was taken immediately before cleaning, after which the object was cleaned with compressed air (60 psi) using a hand held air pistol. Dust was seen coming off the objects and whirling around in the fume cupboard. The process was continued for from one to ten minutes until no more dust was seen coming off the objects. Cleaning was stopped and a second sample "After" was taken.

Paradichlorobenzene, naphthalene, DDT and methoxychlor (1,1,1-trichloro-2,2-bis[p-methoxyphenyl]-ethane) were found in concentrations shown in Table 1. In view of the potential toxicological risk for personnel or owners when handling the objects after such a cleaning, the results are somewhat disappointing. Just 40 percent of naphthalene and less than 25 percent of the other three pesticides were removed. On the other hand, it was easily seen that considerable amounts of dust came off the objects. It should be noted that, even though great care was taken to ensure close proximity of samples taken before and after, some samples showed a larger content of pesticides after than before cleaning. This may reflect the repositioning of pesticides during cleaning, but it may also reflect large concentration variations on the samples, even over very short distances.

RISK OF EXPOSURE

A "dirty glove" measurement was also performed, to measure the transfer of pesticides from the objects to a prerinsed (soxhlet extracted) cotton glove before, during, and after the cleaning of the objects in the fume cupboard. The prerinsed

Table 2. Analysis of gloves used in the cleaning of the 12 uniforms before, during and after the cleaning process in the fume cupboard. All numbers given are μg DDT found in a single pair of gloves.

Sample number	Working time with objects (minutes)			Analysis of DDT gloves before, during and after cleaning		
	Before	During	After	Before	During	After
1	01:00	02:10	01:00	38	33	31
2	01:00	04:30	01:00	24	61	16
3	01:00	07:40	01:00	18	92	26
4	01:00	10:06	01:00	16	25	<7
5	01:00	06:01	01:00	17	50	<7
6	01:00	05:30	01:00	18	15	<7
7	01:00	05:40	01:00	23	16	<7
8	01:00	15:00	01:00	16	23	16
9	01:00	02:42	01:00	22	<7	14
10	01:00	05:42	01:00	7	25	14
11	01:00	16:16	01:00	17	65	19
12	01:00	00:45	01:00	<7	<7	<7
				x_{av} 20	36	15

cotton gloves were tested by gas chromatography to ensure that no pesticides of interest could be found in these before use in the test.

Twelve uniforms from the Danish Museum of Arms and Uniforms, known to have been treated in the past with DDT, were chosen for cleaning. The uniforms were examined for exactly one minute with a prerinsed pair of cotton gloves over a thin vinyl glove. The cotton gloves were then taken off, and a new pair of gloves was used during the actual cleaning/examination period. This process typically lasted from one to five minutes, depending on the cleaning required. After the cleaning the cotton gloves were again taken off and a third pair of gloves used during the final handling/packing, which again took exactly one minute.

All cotton gloves used in the working process were transferred directly from the hand to a soxhlet filter tube that could be transferred to the soxhlet extraction apparatus. A soxhlet is a glass device, which continuously pours freshly distilled and warm solvent over the sample in order to extract any soluble components. An internal standard (1-chloroanthracene) was added to the solvent. The amount of internal standard added was adjusted to give a suitable signal compared to the other components found. This made it possible to quantify the absolute amount of pesticide adsorbed by each pair of gloves. The gloves were extracted in CS_2 for at least four hours, with each washing cycle lasting less than four minutes. This equals at least eighty washings before a sample was taken for analysis. Recovery tests have not been done on the extraction procedure, and the extracted amounts are therefore minimum estimates.

Again the results showed only moderate removal of the DDT present (Table 2). On average, the content of DDT in each pair of gloves was 20 μg before cleaning, 35 μg during cleaning/handling (however, this result is not directly comparable because of the variable length of the cleaning procedure), and 15 μg when handled after cleaning of the objects.

CONCLUSION

Cleaning of ethnographic objects is sometimes necessary because of previous use of pesticides. However, only a few methods are practicable when handling diverse objects; one of these is the use of compressed air. This method is undoubtedly capable of removing dust from the objects, however, it should be noted that once objects have become contaminated, pesticides are not easily removed. On the contrary, it seems that most of the pesticides remain on the objects and that subsequent handling still poses a potential health risk for the personnel involved. Therefore, measures should be taken to avoid unnecessary exposure of personnel who are in contact with these objects. Expecting that the pesticide distributions follow a Gauss distribution on the objects it is possible to perform a paired single sided *t*-test on the concentrations found before and after cleaning. This results in a null hypothesis probability of $P_{\text{PDB}} = 0.568$; $P_{\text{Naphthalene}} = 0.290$; $P_{\text{DDT}} = 0.407$ and $P_{\text{Methoxychlor}} = 0.483$, and the effect of cleaning is therefore not significant in any of the four cases. However, again assuming that the mean concentrations of the four pesticides follow the Gauss distribution, a *t*-test can be performed on the average concentrations before and after cleaning. The null hypothesis is now found to be $P_{\text{overall}} = 0.040$, and we can therefore assume that there is significant difference in the overall level of pesticides in the objects before and after the cleaning process. As seen in the tables there are large variations in the amounts of pesticides in the analysed samples. This probably reflects the methods chosen for applying the pesticides and therefore a relatively large number of samples may be necessary in order to get an impression of the general pesticide level in a collection. Furthermore there are indications that the pesticides may be more evenly spread over the objects after the cleaning. It is notable that the numbers in Table 1 show that in seventeen out of seventy-two cases the pesticide concentrations are higher after cleaning than before, even though the average concentration is smaller. Considering the cleaning method this may not be too surprising.

Comparing the "Before" and "After" results in the dirty-glove experiment, with a null hypothesis that there is not any difference between the concentrations and assuming a "worst case" concentration of 7 μg DDT on gloves which were below the detection limit showed a $P = 0.043$. The amount of DDT collected on the gloves is therefore significantly lower after the cleaning process than before. This does not, however, imply whether the level is acceptable or not.

It should be noted that the cleaning procedure continued until no more dust could be seen coming off the objects. Nevertheless the transfer of DDT to the gloves after cleaning was only lowered by 25 percent, which is on the level of pesticides in the objects after cleaning. This indicates that transfer of DDT is not only the result of loose dust, but also of transfer directly from the objects to the working environment.

The work presented here is a preliminary study and more work should be done to confirm the cleaning efficiency using compressed air as well as the exposure risk when handling objects contaminated with pesticides.

LITERATURE CITED

- Glastrup, J. 1987 Insecticide analysis by gas chromatography in the stores of the Danish National Museum's Ethnographic Collection. *Studies in Conservation* 32:59-64

OPEN DISCUSSION 1

- One speaker said a large alarm has gone off throughout Indian country.
- Catharine Hawks said it was possible to train people to clean repatriated materials. She said some tribes might not want outside people handling their objects.
- Monona Rossol said that since 1997, all people cleaning toxic objects were required to undergo full training.
- Monona Rossol said that vacuuming cannot remove all the very small particles of hazardous materials.
- Catharine Hawks said that asbestos flaking off museum building walls and insulation can also be a real contamination problem in museum collections. She said that HEPA vacuuming has been quite effective for reducing asbestos contamination. She does not recommend the use of compressed air as that embeds asbestos and pesticide fibers deeper into the artifacts. She also suggested that HEPA vacuuming may be effective in reducing powder forms of arsenic.
- One speaker urged tribes who don't have a member trained to clean objects to contact their regional EPA office.
- Nancy Odegaard said that handling objects for cleaning was different from handling objects for cultural reasons and that caution should be exercised in interpreting cleaning studies.
- Yolanda Chavez said that if tribes started working with repatriated items in their own tribal museums, they would be faced with the daunting task of disposing of the hazardous waste materials (such as HEPA vacuum filters, asbestos particles, cleaning rags, protective clothing, gloves, etc.) that would be generated by their activities.
- Catharine Hawks replied to Yolanda by saying that EPA guidelines govern the disposal of hazardous waste.
- Niccolo Caldararo said that in some cases, people trying to treat contaminated items had contaminated the treatment area.
- One speaker asked why the government could not take responsibility for cleaning the objects before they are given back to the tribes.
- A museum employee said attitudes in museums were beginning to change and that he now wore gloves and a mask when handling objects.
- Alyce Sadongei said that tribal NAGPRA coordinators must be educated in this issue, and that museums are morally responsible for informing tribes of all the pesticide treatments on tribal collections.
- Nancy Odegaard said that her experience with the Arizona tribes has shown her that standard museum techniques for handling and cleaning contaminated objects have not been consistent with tribal beliefs and practices for the handling of sacred materials.
- Monona Rossol said that if you want to make a real difference, you should make museum administrators stick to the law. She said OSHA developed arsenic and lead standards many years ago. She said if museums had met the laws, there would have been 20 years of data to work from already. She said museum administrators do not have a clue about gases, vapors and dust.

Many lawsuits are being filed against museums with gag orders attached to them.

- Monona Rossol said people were often given cotton gloves to protect the object being handled, but that cotton gloves do not protect from pesticides. Because of the risk of allergic reaction to latex, nitrile gloves are recommended.
- Pauline Gerber-Montoya of the Mendocino Tribes said she was appalled and concerned by what was being said. She said the burden of responsibility needs to be placed back on the federal government, which should provide more money to museums and tribes to deal with this issue.
- Monona Rossol said that under OSHA regulations no one should wear respirators until they had undergone medical tests. She said these laws had also been in existence for years.
- Victoria Purewal said that since no one knows what pesticides are on each artifact, development of a testing program should be a high priority. Until that time we should treat every untested object as if it is contaminated, maximizing protection to our health and reducing the risk of exposure.
- Alyce Sadongei said there was a need for everyone to work together on the issue.
- Nancy Odegaard said that there needs to be a coming together of the government agencies, museum workers, and native communities around this issue.

TESTING AT THE SAN FRANCISCO STATE UNIVERSITY NAGPRA LAB (SUMMARY)

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Fentress reported on testing conducted at the San Francisco State University Laboratory. The materials tested included storage containers and animal bones. Mercury was found in all of the items tested. The ramifications of the testing are complex; for example, where did the mercury come from and how many other poisons are there?

A REVIEW OF ANALYTICAL METHODS FOR THE DETERMINATION OF MERCURY, ARSENIC, AND PESTICIDE RESIDUES ON MUSEUM OBJECTS

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Abstract.—The historical use of arsenic, mercury, and various organic pesticides for preservation of museum objects has led to justifiable and valid concerns regarding the potential health risks of humans coming in contact with them. As the past treatment of specific objects within individual collections is for the most part unknown and undocumented, chemical analysis represents the most reliable means for determining whether an object has been contaminated and the level of contamination. It is important that museum professionals and other interested parties understand the analytical methods that can be applied to this problem, the details involved in designing and effecting a study, and the relative advantages and disadvantages of each technique. This paper outlines the various stages involved in a chemical analysis, reviews the sundry analytical methods for the determination of arsenic, mercury, and organic pesticides, and provides a framework which will hopefully assist non-experts in determining which method is most appropriate for a specific application.

INTRODUCTION

The past practice of applying mercury, arsenic, and various solutions of pesticide agents to museum pieces was intended to protect these objects from damage by rodents, insects, and microorganisms. Several excellent papers document the history and use of the methods used to treat these objects (Goldberg 1996, Hawks and Williams 1986). Given the lack of records documenting the treatment of objects in individual collections, chemical analysis represents one of the few reliable means for ascertaining whether or not an object has been contaminated with these agents.

Although such analyses have been performed on objects in various collections, only a few references and case studies on these analyses are reported in the literature. Out of these references, few if any provide details on the relative merits and deficiencies of specific methods, their limits of detection (LODs), selectivity and reliability, and necessary equipment and costs, and none provide a thorough review of the various methods that can be brought to bear on this problem. Additionally, it should be noted that no regulatory agency is responsible for developing standardized protocols or methods for this application. Hence, it is understandable that there is much confusion as to how to best effect these analyses.

The purpose of this article is to provide a framework on these issues from the perspective of an analytical chemist. It describes the various steps involved in a chemical analysis: defining the problem, selecting and refining a method, sampling, data acquisition, interpretation, and reporting the results. It goes into detail on the various analytical methods for the analysis of heavy metals and pesticides, and discusses their applicability and utility for measuring these contaminants on museum objects.

While it is understood that much of this information is of common knowledge to experts in chemical analysis, museums, and forensic laboratories, the same

Table 1. List of acronyms and abbreviations.

AAS	Atomic absorption spectrophotometry
AES	Atomic emission spectroscopy
BP	Boiling point
ECD	Electron capture detector
EPA	Environmental Protection Agency
FAAS	Flame atomic absorption spectrophotometry
FID	Flame ionization detector
GC	Gas chromatography
GC/MS	Gas chromatography/mass spectrometry
GFAAS	Graphite furnace atomic absorption spectrophotometry
HCL	Hallow cathode lamp
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
LC	Liquid chromatography
LOD	Limit of detection
MS	Mass spectrometry
ng	Nanogram ($=10^{-9}$ gram)
NIST	National Institutes of Standards and Technology
pg	Picogram ($=10^{-12}$ gram)
ppb	Part per billion
ppm	Part per million
ppt	Part per trillion
SEM	Scanning electron microscopy
SIMS	Secondary ion mass spectrometry
TCD	Thermal conductivity detector
XES	X-ray electron spectrometry
XPS	X-ray photoelectron spectroscopy
μg	Microgram ($=10^{-6}$ gram)
μL	Microliter ($=10^{-6}$ liter)

cannot be said for other museum professionals and collectors. It is hoped that this article will hence provide much needed background information to assist non-experts in defining the objectives of their analyses and understanding the sundry and complex factors involved in this process. A summary of the many acronyms and abbreviations used in this article is provided in Table 1.

THE ANALYTICAL PROCESS

The processes associated with effecting a chemical analysis can be broken down into several distinct stages as shown in Figure 1. The first and most important involves *defining the problem*. This involves interaction between the customer requesting the analysis and the analytical chemist responsible for performing it. Before any sampling or analyses are performed, a variety of questions must be addressed using the best available data or knowledge on the samples:

- What is the sample (where did it come from, is it solid, liquid, or gas, a mixture or relatively pure substance)?
- How much of it is available (is sampling to be destructive or nondestructive, how much can be taken for sampling, is the analysis to be done on-site or at a remote lab)?
- What are to be the analytes (heavy metals, volatile organic compounds, dioxins or polychlorinated biphenyls, particulates, etc.)?

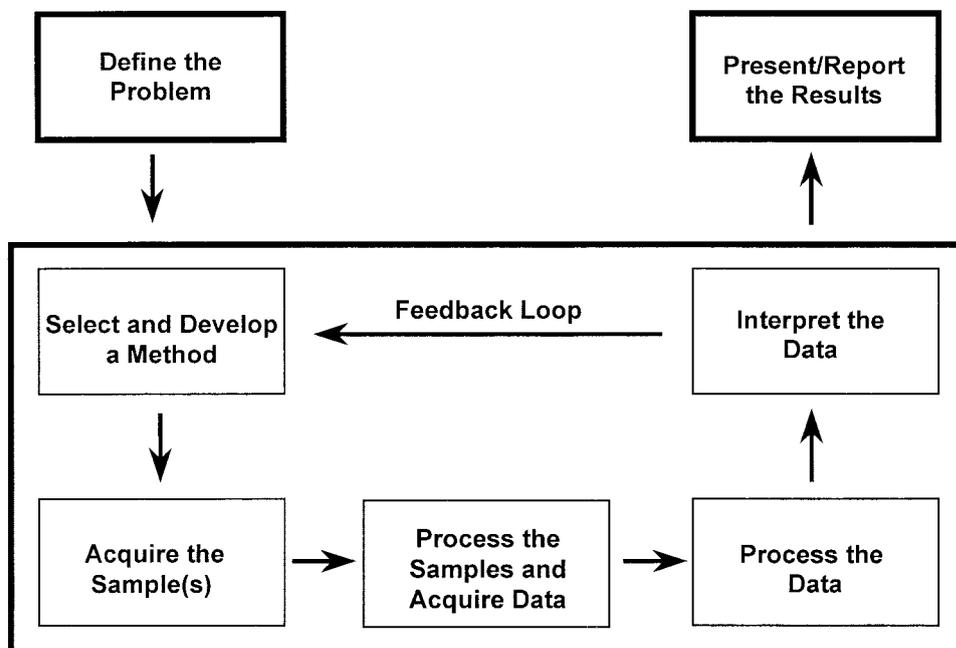


Figure 1. The analytical process, depicting the various stages involved in the chemical analysis of a sample.

- What is the expected range of concentrations of analytes in the sample and what LODs are required (is the analysis required to be performed at ultra trace levels, trace levels, or percent levels)?
- What are the reproducibilities or level of precision required (is the scope to be to provide precise measurements or simply to screen for the presence of a substance)?
- How soon are the results needed (how long a time is permitted between sampling and providing the results)?
- What are the budgetary limitations (with respect to time, personnel, instrumentation, and other resources)?

At this stage of defining the problem, the customer often begins to realize the original question was not so simple. Perhaps analytical chemists are to blame here for not making their audiences appreciate the knowledge and effort required to answer such questions, but popular media have also played a role in trivializing such measurements (note that tricorders exist only on Star Trek!). Defining the problem is an ongoing process; initial analyses can provide information to help guide subsequent analyses as will be discussed later.

Once the desired information is known, the next step is *selecting an appropriate method* to obtain this. An introduction and background on these methods is provided in various texts on quantitative and instrumental analysis (Enke 1999, Harris 1998, Skoog et al. 1996). Various analytical methods for the determination of heavy metals and pesticides are discussed in greater detail further on.

The next step is *developing a specific analytical method* for the application in question. In many cases, there is no need to “reinvent the wheel”, and this process may involve employing either an existing method or a variation on it to effect the desired outcomes. In some applications, a specific method is called for to meet regulatory requirements. A host of analytical methods are available for such purposes. These include methods for the analysis of water and wastewater (Clesceri et al. 1998), methods for the analysis of food and beverages (Horwitz 2000), and methods for environmental pollutants (Keith 1995, Unknown 1996). Additional, emerging, and novel methods are continually reported by the Environmental Protection Agency (EPA) and in various peer-reviewed journals, such as *Analytical Chemistry*, *Environmental Science and Technology*, and *Analytica Chimica Acta* to name but a few. The development of such methods is an ongoing task in academia, industry, and government laboratories, as new applications continually arise and new technologies constantly improve the ability to perform ever more sensitive, selective, and faster chemical analyses.

The next step is *sampling*, which is a process that is often given cursory attention, yet is critically important as improper sampling can lead to misrepresentative data. Sampling can be broadly divided into two major types: random and judgmental (Keith 1992). Random sampling involves the use of techniques to provide non-biased and statistically valid information on the sample. Judgmental sampling is used more often as it requires fewer numbers of samples, and implies lower costs for the analyses, but may lead to biased results. The sampling process is inherently fraught with pitfalls. One of the more important principles of science, the Heisenberg uncertainty principle, states that to obtain a more accurate measure of an electron's position, one must accept a large uncertainty in its momentum and vice versa. This principle has implications on sampling as well. Clearly, the process of taking a sample has the potential to disturb and even contaminate the sample. The materials used for taking a sample and the sample collection devices must be clean. Care must be taken not to cross contaminate the samples. Often, field, trip, or sampling blanks (the term blank refers to the assumption that this standard will contain “zero” levels of the analyte) are used to ensure that these media contain negligible levels of the analytes.

The next steps are *processing the sample and acquiring the data*. This may involve weighing of the sample, addition of reagents, digestion or extraction, filtration, dilution, and finally performing the measurements. Note that standards are often used here to provide a response function to enable determination of the levels of analytes in the unknown. Again, special method blanks should be analyzed to ensure that this process does not contribute significant levels of analyte to the samples. Typically, several samples and standards are analyzed to aid in determining the uncertainty or precision associated with the analysis.

The next step is *interpreting the data*. This may involve the development of a response function or calibration curve to relate some physical property that can be measured to the concentration or amount of analyte. An important point to note here is that often the desired results are not available at the first time through the analytical process. For example, the concentrations of the analytes in the sample extract may be too high or low in relationship to the standards, and hence the resulting extrapolation of the calibration curve may lead to unacceptable uncertainties. The presence of some other component in the sample matrix can cause

the response to deviate and can lead to erroneous results. The sample workup procedure may require modification to achieve improved results, and higher purity standards may be needed for improved quantitation. The analytical method may be inappropriate for the application and an entirely different method may be required. The possibilities are endless, but the bottom line is that rarely if ever are the desired results obtained on the first run through this process for a complete unknown. This is reflected in Figure 1 by the incorporation of a *feedback loop* in the analytical process. The purpose of this feedback is to employ the results of the initial analyses to guide subsequent analyses.

The last step in the analytical process is *reporting the results*. This can range from tabulated numbers, standardized report forms from analytical service laboratories, publications intended for lay people, or detailed and highly specialized publications for peer-reviewed journals. The requirements for each depends on the context.

METHODS FOR THE DETERMINATION OF ARSENIC AND MERCURY

This section focuses on analytical methods for determining arsenic and mercury on objects from museums or personal collections. Similar methods can be employed in the analysis of samples of ambient air samples in storage areas, and biological samples taken from human subjects. While such analyses and their results are of obvious significance from toxicological and industrial hygiene perspectives, the specialized sampling methods and analytical instrumentation for these applications are beyond the scope of this article. For the most part, sampling solid objects is relatively straightforward and involves nondestructive imaging-based methods, wipe or swab-based methods, or more destructive sampling methods requiring removal of a piece of the object. The various instrumental methods for determination of arsenic and mercury can be broadly categorized into spot tests, spectroscopic methods, mass spectrometry (MS) based methods, and radiation or surface analysis methods. It should be noted that this discussion is not intended to be an exhaustive review of such methods, but to provide some information and insights into the relevant techniques.

Spot Tests

A variety of simple and effective tests exist for the determination of heavy metals (Feigl and Anger 1972). These are often referred to as spot tests, as they typically involve swabbing a spot on a sample, adding reagents, and observing a color change that is related to the analyte concentration. The Merckoquant 10026 kit-based method for determination of arsenic is mentioned here to illustrate the details and typical application of these methods (Henry 1996). In brief, this test involves swabbing the object with deionized water, placing the swab in a flask containing deionized water, and adding zinc powder to a portion of this extract. A portion of the resulting solution is transferred to a test tube and a solution of hydrochloric acid is added. The tube is capped with a plug containing an indicator strip that serves as a visual indicator of the analyte concentration. The method is simple and elegant insofar that it uses chemical reactions to convert the targeted species into a colored form to permit estimation of its concentration. It should be stressed that *careful control of the chemistry* is essential for this method to work properly.

Even with such control and an experienced user, one cannot rule out the possibility that some other component in the sample matrix or a contaminant in the reagents may interfere with any of these reactions and lead to erroneous results. Constanzo (1999) showed that the arsenic spot test consistently underestimated the actual concentration of arsenic compared to more reliable methods. Landry (1988) reported a negative response (indicating no arsenic present) was obtained for arsenic standards used as a reference in determining the concentrations of the samples. This necessitated further study into identifying and correcting the causes, as this spot test is rendered useless if it cannot provide a positive response for arsenic standards. After consulting with the vendors of this kit, the problem was traced to a nitrate ion interference caused by the use of nitric acid in preparing the standards. Once the preparation of standards was modified to exclude this reagent, the test kit gave satisfactory results and was successfully used to positively identify between 0.1 and 0.5 part-per-million (ppm or mg/L) of arsenic in three of the 19 samples. In a comparative study on bird and mammal specimens, Found and Helwig (1995) showed spot test results for arsenic gave eight percent false positives (meaning arsenic was identified as present when it actually was not) and five percent false negatives (meaning arsenic was identified as absent when it actually was present). Clearly, the results from these spot tests vary from study to study and operator to operator, and their reliability has been called into question on several occasions.

The advantages of spot tests versus other methods for determination of arsenic and mercury are their low cost, ready availability in kit form, simplicity in their implementation, and the fact that they can be used by non-experts with minimal training. Their major deficiency is that they are inherently semi-quantitative and can provide erroneous results due to interferences and matrix effects in certain situations. Lastly, their use is somewhat time consuming given a minimum one hour reaction time per sample.

Atomic Spectroscopy Methods

Atomic spectroscopy is perhaps the most widely used method for the determination of metals in a variety of matrices. Compared to spot tests, atomic spectroscopy-based techniques require expensive and complex instrumentation, more involved sample workup procedures, and calibration curve-based data analysis. They are nevertheless employed much more frequently than spot tests as they have lower detection limits, are much less prone to interferences, and provide much more reliable results.

The selectivity of atomic spectroscopy stems from its use of specific wavelengths to serve as "probes" for individual metals. Each metal has a characteristic line spectrum and a particular metal can be identified and quantified by monitoring the light intensity at a characteristic wavelength that is chosen to minimize the possibility of interferences from other metals. Most often, atomic spectroscopy involves the use of absorption of characteristic radiation for a metal. This variation is termed atomic absorption spectrophotometry (AAS). Alternately, it can involve measuring the emission of this radiation, and this variant is termed atomic emission spectroscopy (AES). Both techniques can be used for the determination of most of the metals in the periodic table of elements at trace and even ultra-trace levels, depending on the sample introduction system.

An AAS instrument requires a source of the characteristic radiation of the target metal. This source, referred to as a hollow cathode lamp (HCL), utilizes a cathode made out of an alloy of the metal in question. The light generated by the HCL is focused in the form of a beam through an atomizer to a monochromator and detector. The atomizer can be a flame, graphite furnace, or inductively coupled plasma as described below, and uses heat to convert any metallic species in the sample into atomic form so that they can then absorb the characteristic radiation from the HCL. The monochromator and detector provide a measure of the attenuation of the characteristic radiation of the target metal as it passes through the sample. This absorption of light from the HCL is directly proportional to the concentration of the metal (a relationship commonly known as Beer's law) and provides a basis for developing a response function for quantitative analysis.

Flame Atomic Absorption Spectrophotometry (FAAS)

FAAS represents the most common form of AAS. It requires some sample preparation to convert the sample into an appropriate extract solution prior to analysis. Typically, this involves taking a sample, digesting it with nitric or hydrochloric acid, filtering it to remove particulate or undigested matter, and diluting it to a known volume. Accurate metal standards of precisely known concentrations must be prepared to enable accurate quantitation. Both samples and standards are analyzed under identical conditions using a flame atomizer, in which the sample extract solution is sucked into a mixing chamber, mixed with fuel and oxidant gases, and converted into a mist for subsequent combustion in the flame to enable identification and quantitation. FAAS is capable of detecting ppm levels of metals in extracts, and is very selective due to the use of both a characteristic wavelength for a metal and a technique called background correction to minimize the possibility of interferences from other components in the sample matrix. The sample preparation represents the most time consuming portion of this analysis, and once the samples and standards are prepared and the FAAS instrument is tuned, samples can be analyzed at the rate of approximately 60 per hour. Compared to spot tests, FAAS provides much better accuracy and precision, but does require expensive instrumentation and significant operator training.

Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS)

GFAAS represents another variation on AAS. The sample preparation and instrumentation required for GFAAS are nearly identical to FAAS with the exception of the sample introduction system and atomizer. In GFAAS, a discrete amount of sample extract is deposited in a specially constructed cuvette. This cuvette is purged with a pure inert gas such as argon and subjected to a temperature program to gently boil off water and dry the sample, char and break down any salts or organic species present in the sample, and volatilize the metals. Once again, these atoms will then absorb light from the HCL, and a measure of this absorbance provides a means for quantitation. GFAAS is often two to three orders of magnitude more sensitive than FAAS, meaning that metals can be determined to levels as low as a part-per-billion (ppb or $\mu\text{g/L}$). It is more complex and expensive in its implementation, and its throughput (as measured as number of samples that can be analyzed per hour) of approximately 20 samples per hour is lower than FAAS due to the time required for the atomization process.

Cold Vapor Mercury/Hydride Generation Atomic Absorption Spectrophotometry

Yet one more variation on AAS involves the use of selective chemistry to generate a vapor containing the metal of interest. For mercury, this involves reduction of ionic mercury to the zero oxidation state. Mercury, a rather unique metal, has a significant vapor pressure at standard temperature and pressure, and when converted to gaseous form can be swept from the sample through a cell where its absorbance can be monitored. This technique is referred to as cold vapor mercury AAS. Similarly, selective chemistry can be used to convert ionic arsenic to arsine hydride, and this gas can be purged from the sample through a cell where its absorbance can be determined. This technique is referred to as hydride generation AAS. Both techniques require similar apparatus and are exquisitely sensitive, with LODs approaching part-per-trillion levels (ppt or ng/L). They require additional hardware, involve more time in effecting the chemical reactions on each sample and standard, and careful attention to minimization of trace levels of analytes in the reagents, glassware, and sample containers.

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)

The emission of characteristic radiation can be used to determine the types and relative amounts of metals. In this technique, referred to as AES, a flame represents the source, in that its heat is used to promote atoms into an excited state where they undergo subsequent emission of photons. Quantitative analysis is achieved by monitoring the intensity of this emission at a characteristic wavelength. The most common variant of AES is inductively coupled plasma AES (ICP-AES). Here, the flame is created by entraining the sample into a flow of argon that is then converted to a plasma (a mixture of high-energy ions and atoms) through the use of a radiofrequency coil. This coil excites the argon atoms and creates temperatures that approach 10,000 degrees Kelvin. The high energies associated with this hot plasma convert metal species into atomic forms, promote them into excited states, and hence provide a source for emission of the metal's characteristic radiation. The advantages of ICP-AES are its wide applicability to nearly every metal in the periodic table, its sensitivity with LODs that approach those for GFAAS, and most importantly the fact that this technique is much more amenable to simultaneous multielement analysis. For applications requiring determination of several metals, ICP-AES can provide more rapid information on a suite of metals in a sample compared to FAAS and GFAAS which usually require each targeted metal to be measured individually or in succession. ICP-AES is subject to interferences, most notably spectral interferences, in which the wavelength of light used to quantify a metal is close to that of some other species in the sample matrix, and ionization interferences, in which the metal atoms are converted to ions, changing the electronic configuration and resulting emission spectrum of the metal. When used with care by a trained operator, ICP-AES can provide sensitive, selective, and reliable determination of trace levels of metals.

Other Methods

Several alternate methods for determination of heavy metals include mass spectrometric methods and radiation or surface analysis-based methods. A technique referred to as ICP-MS is a variation on ICP-AES in which the ICP is used to provide a source of ions to a MS detector. This detector likewise permits simul-

taneous multielement analysis and is very sensitive with LODs approaching ppt levels. Although such instrumentation is certainly appropriate for this application, the instrumentation required for effecting such analyses is quite complex and very expensive to purchase and maintain.

Radiation-based methods most often employ X-rays to probe the composition of a sample. Although these techniques are simply another variation on spectroscopy, and the same principles of absorption and emission apply, the difference between these techniques and AAS is that the radiation falls in the X-ray rather than the visible portion of the electromagnetic spectrum. The most common such method is X-ray electron spectrometry (XES), a variation of scanning electron microscopy (SEM). The details and instrumentation associated with this technique are described in more detail by Sirois elsewhere in this volume. XES has numerous advantages that render it very attractive for determination of arsenic and mercury on museum objects. It is sensitive, selective, and requires minimal sample preparation. Although it is semi-quantitative and cannot distinguish between external and internal contamination, it can be used to rapidly screen a collection for the presence of these metals (Sirois reported its use to analyze up to 100 objects in an 8-hour time period). More importantly, it is a nondestructive technique and portable versions of such instruments are available, meaning that objects need never leave a museum and the instrumentation can be brought to bear on the problem and not vice versa.

Even more complex, expensive analytical techniques are possible; these are based on various surface analysis techniques such as X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). These are capable of providing information which is difficult to derive via other methods, such as providing a visual image of the extent of heavy metal contamination on an object, and even depth profiling showing the impregnation of contamination into an object. The techniques are beyond the scope of this article and are not discussed further here.

METHODS FOR THE DETERMINATION OF PESTICIDES

A wide variety of pesticides have been applied through the years to protect museum objects from degradation (Goldberg 1996, Hawks and Williams 1986). In some cases, the pesticides were applied as mixtures containing several active agents. As more modern pesticides such as DDT were developed, these were applied as needed to objects in various collections. Eventually, as considerations of bioaccumulation and long term toxic effects on various organisms led to the banning of DDT, newer pesticides were occasionally applied.

Historical information provides a priori information that can be used to develop a more comprehensive list of target pesticides (Goldberg 1996). This list includes a wide range of chemicals and represents a daunting analytical challenge. Nevertheless, some of these chemicals can be eliminated from consideration in a pesticide residue analysis. For example, certain chemicals such as methyl bromide and carbon tetrachloride are gases at standard temperature and would in most circumstances not be detectable several years after their application. The scope of a pesticide analysis must be defined prior to an analysis, and in this case the discussion is limited to a much shorter list of pesticides that were used most frequently in the past. Table 2 provides a list of these pesticides and some of their

Table 2. Some common pesticides and their chemical properties.

Common name	Formal name	Molecular formula	Molecular weight	Density (g/mL)	Boiling point (°C)
p-Dichlorobenzene	1,4-dichlorobenzene	C ₆ H ₄ Cl ₂	147.00	1.458	174
Naphthalene	Naphthalene	C ₁₀ H ₈	128.17	1.162	218
Thymol	2-methyl-5-isopropyl-phenol	C ₁₀ H ₁₄ O	150.22	0.965	233
Lindane	1,2,3,4,5,6-hexachloro-g-cyclohexane	C ₆ H ₆ Cl ₆	290.83	1.06	223
Dieldrin	N/A	C ₁₂ H ₈ Cl ₆ O	380.92	1.75	N/A
DDT	2,2-bis(4-chlorophenyl)-1,1,1-trichloroethane	C ₁₄ H ₉ Cl ₅	354.49	N/A	N/A

chemical properties. This list is not intended to be all-inclusive, and indeed other pesticides have been used on museum artifacts in the past. Nevertheless, these compounds are appropriate in this context to illustrate how their chemical properties make them amenable to various analytical methods. Despite their high boiling points (BPs), these compounds have a small but appreciable volatility that to some extent is a prerequisite for their intended function as a pesticide. These particular pesticides are generally considered to be persistent although it is possible that these pesticides can be degraded or volatilized off an object given sufficient time, elevated temperatures, high flowrates of air, and sunlight. Given the persistence of these pesticides, one may employ an appropriate analytical method to confirm whether or not they were applied to specific objects in a collection in the past. The fact that the method must be capable of detecting several pesticides, any one of which may or may not be present in a sample, implies the need for some technique that simplifies the analysis of a mixture. One of the best means for achieving this is chromatography.

The most common chromatographic techniques are liquid chromatography (LC) and gas chromatography (GC). Although LC has been used for determination of pesticides, it is generally reserved for chemicals with higher BPs or more reactive and/or unstable species that are generally unamenable to GC. Since the compounds listed in Table 2 have reasonably low BPs (i.e., less than 300°C), and the compounds are relatively stable at these temperatures, they are hence more amenable to GC. The following discussion is limited to GC and the various detectors that can be used in conjunction with this mixture analysis technique for identifying and quantitating trace levels of pesticides. The sampling techniques most often involve either swab or wipe-based sampling or removal of a piece of the object. The sample workup typically employs an organic solvent to extract the pesticides from the sample, filtering the sample, and diluting it to a known volume prior to analysis. As with spectroscopic techniques, standards containing accurate and precisely known concentrations of pesticides must be prepared and analyzed under the same conditions as the samples. The analysis involves the use of GC in conjunction with a specific detector to provide a means for selective determination of several pesticides in one analysis. The bulk of this discussion describes the various GC-based techniques to achieve this end.

Gas Chromatography (GC)

GC is based on the use of a column with specific properties that enable separation of complex mixtures. In a GC analysis, a sample is injected onto a column

and immediately volatilized in an injector held at an elevated temperature. A low flowrate of a carrier gas, typically helium or nitrogen, is used to maintain a constant flow through a column. The column in most cases is a small inner diameter capillary column which contains what is referred to as a stationary phase, representing a polymeric species that has been coated or chemically bonded onto the walls of the column. The various compounds in the sample are separated on the basis of their differing affinities for the stationary phase. In general, more volatile species with lower BPs spend more time in the mobile phase and will exit the column first. The column, which is placed in a temperature-controlled oven, is heated and the less volatile compounds will exit the column over the course of an analysis.

Detection can be achieved by several means. More common, general-purpose detectors include the thermal conductivity detector (TCD) and flame ionization detector (FID). The TCD detects species based on their different resistivities compared to the carrier gas using a Wheatstone bridge circuit. The FID “burns” the column effluents in a flame of air and hydrogen, and the generation of current from the combustion products results in a small electric current that can likewise be sensed by appropriate circuitry. One additional detector often used in pesticide analysis is the electron capture detector (ECD). The ECD uses a radioactive beta (electron) emitter, and responds to changes in current from the emitter in response to the elution of organic compounds with high electron affinities (which typically includes most chlorine-containing compounds). TCD is a simpler, more universal detector and has LODs in the low ppm range. FID requires gases to support the flame but is several orders more sensitive than TCD. ECD is even more selective and sensitive with LODs that can approach ppt levels.

When using GC in conjunction with any one of these detectors, compounds in an unknown are identified by comparing their retention times (time between sample injection and elution off the column) to those determined from the analysis of known standards. For example, naphthalene should elute at nearly the same retention time, providing all other parameters (i.e., flowrate, temperature, etc.) are held constant. This is illustrated in Figure 2, in which DDT has been tentatively identified in an unknown extract from a museum object on the basis of a retention time match from this analysis to that obtained from a DDT standard. It should be noted that a retention time match does not provide definitive proof that that compound is present. It is possible that other components of the sample matrix may also come off the column at the same retention time. Analysis of the same sample on another column that contains a different stationary phase and a subsequent retention time match on this second column would provide nearly conclusive identification of that compound. However, rarely are such additional analyses performed, and hence it should be noted that although unlikely, GC can be prone to interferences unless the target compounds are confirmed by some alternate technique or additional analyses.

Gas Chromatography/Mass Spectrometry (GC/MS)

The combination of GC with its ability to separate complex mixtures, in conjunction with MS with its ability to identify trace levels of organic compounds, represents a very powerful technique for mixture analysis. MS is a much more complex detector than those mentioned previously, and necessitates a vacuum

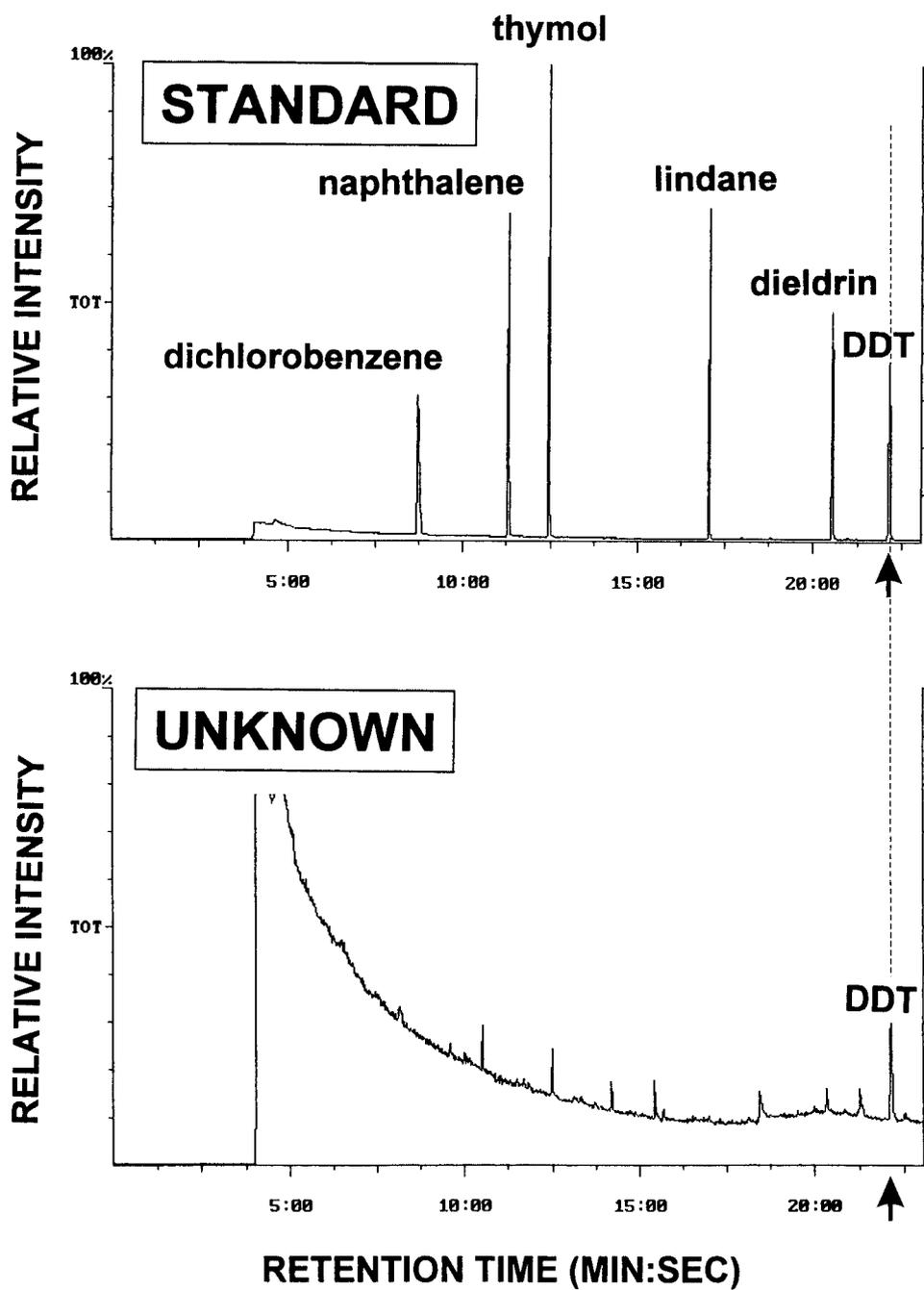


Figure 2. Tentative identification of DDT by a retention time match. The top plot shows a peak in the chromatographic analysis of an extract from a museum object. The bottom plot shows a peak in the chromatographic analysis of a DDT standard. The retention times from the two analyses, measured as elapsed time between sample injection and the peak maximum, match to within one second.

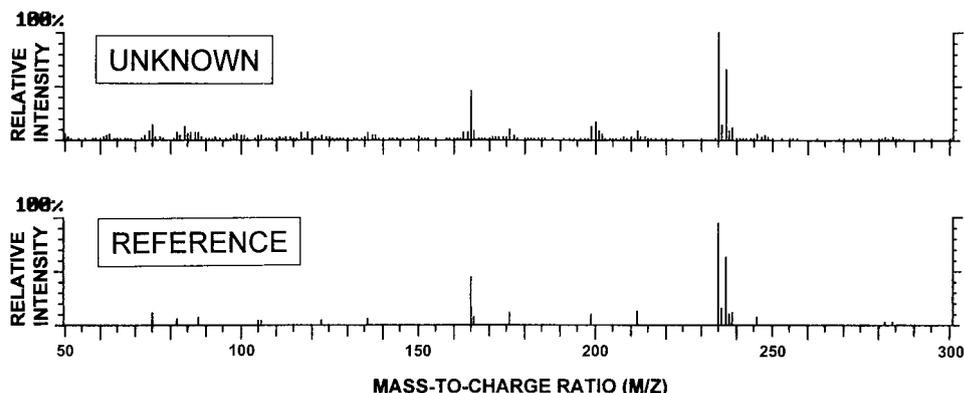


Figure 3. Tentative identification of DDT by a mass spectral match (or library search). The top plot shows the experimental mass spectrum from peak in the chromatographic analysis of an extract from a museum object. The bottom plot shows the reference mass spectrum of DDT from the NIST library of mass spectra.

system and significant accompanying hardware and control systems. An MS detector typically requires the sample molecules be converted into gaseous form, where they are subsequently bombarded with a stream of electrons that break the molecules into pieces of various sizes (more properly referred to as ions). The result of this process is a mass spectrum, which represents a plot of the relative intensity of ions as a function of their mass-to-charge ratio (m/z). Under proper control of experimental parameters, this mass spectrum is often considered to be a “fingerprint” for that molecule, and the ions and their relative intensities can be used to deduce the identity of that compound.

GC/MS is one of the most widely used analytical methods for the analysis of trace levels of organic compounds. The MS detector provides excellent sensitivity, with LODs frequently approaching one picogram ($=10^{-12}$ grams). The calibration curves from GC/MS are often linear over five orders of magnitude. This wide dynamic range implies that the calibration curve can hence be used to analyze unknown extracts spanning a wide range of concentrations (i.e., one $\text{pg}/\mu\text{L}$ to 100 $\text{ng}/\mu\text{L}$). Unlike a GC in conjunction with TCD, FID, and ECD, in which a peak in the resulting chromatogram simply indicates a response to a compound coming off the column, GC/MS detector provides three dimensions of information: m/z value, intensity, and time. A plot of intensity as a function of time provides an picture of the separation of various components of the mixture and is often termed a chromatogram. The mass spectrum at a specific point in time corresponding to a compound coming off the column provides both qualitative and quantitative information. Compound identification is most often achieved by matching the experimental mass spectrum against a library or reference mass spectrum.

An example of the use of MS to aid in identifying a specific pesticide in a sample extract is shown in Figure 3. The top plot in this figure represents a mass spectrum from a specific peak from the analysis of a sample extract of a museum object via GC. The bottom plot represents the reference mass spectrum of DDT from the mass spectral database provided by the National Institutes of Standards and Technology (NIST). Humans are inherently good at pattern and image rec-

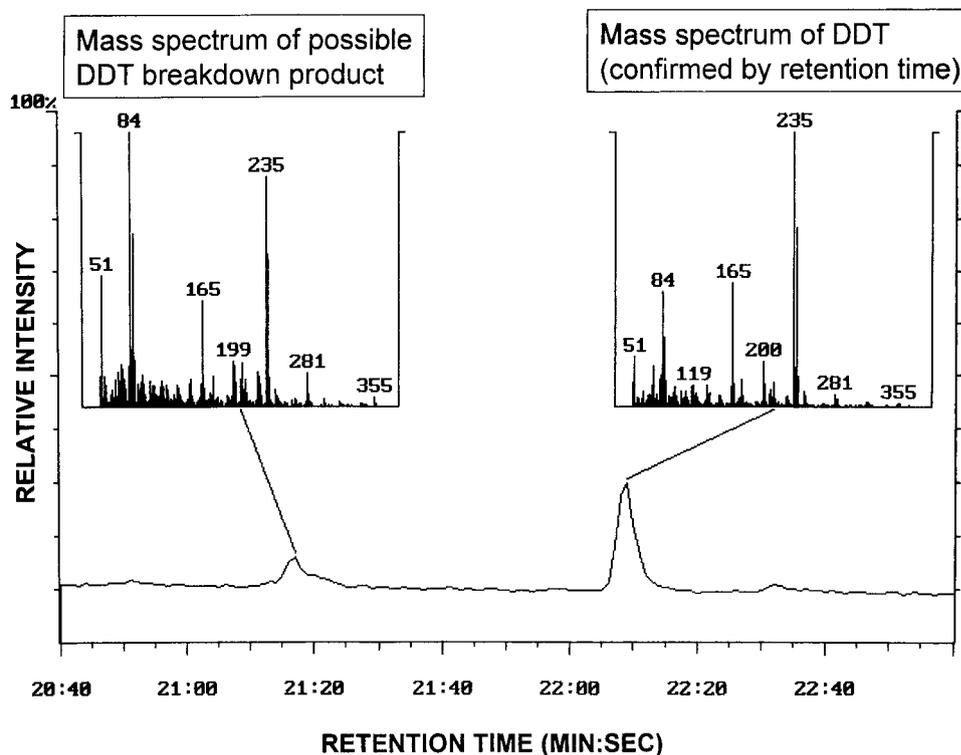


Figure 4. Tentative identification of a DDT breakdown product by GC/MS. The plot shows a portion of the total ion chromatogram which shows the total MS response as a function of time. The two mass spectra inserts represent the plots of the experimental mass spectra of the suspected breakdown product (shown on the left) and DDT (shown on the right, with its identity confirmed by both a retention time and mass spectral match).

ognition, and it is obvious from visual inspection of these two plots that the mass spectra are quite similar, and that it is highly likely that DDT is present in this sample. Just as with retention time matching, library searching is not proof positive as to the identity of the compound. For example, the mass spectra of terpene isomers are quite similar to one another, and it is difficult to definitively identify a specific terpene isomer from a mass spectrum alone. But the combination of a retention time match and library match on a particular compound provides near conclusive identification. Indeed, GC/MS has been used in this manner in the Olympics to test for steroids and banned substances in athletes, and is considered the "gold standard" in legal settings for the determination of drugs of abuse. Another example of the utility of GC/MS is to provide information on unanticipated or heretofore unidentified compounds. The mass spectrum of an unidentified component in a sample is shown in Figure 4. This compound eluted shortly before DDT and may represent a breakdown product of DDT. Although this compound was not a target compound, it may be toxicologically significant, and MS can be used to facilitate its identification and its subsequent quantitation.

While GC/MS is widely used for a variety of environmental, biological, and other applications, it is expensive and the interpretation of the resulting data can

be complex and time consuming. While many laboratories have such instrumentation, the use of it for this application is not trivial. Significant time and effort must be put into configuring the instrument for the analysis of these pesticides. Standards must be prepared for each target compound. The GC temperature program must be optimized to provide efficient separation of these compounds. The response function must be determined from the analysis of the standards. The entire process is prone to numerous pitfalls such as contamination, carryover, and misinterpretation of the data. Clearly, the use of this technique requires significant operator training and expertise. However, once the method for determining the pesticides has been established and implemented, a sample analysis can be completed in less than an hour, and modern GC/MS data systems can be used to automate compound identification and quantitation.

Other Methods

The analysis of pesticide residues can be achieved through the use of alternate techniques. For example, spectroscopic techniques based on the use of light or radiation can use selective absorption to indicate the presence of pesticide on an object. Additionally, a highly specialized MS technique referred to as time-of-flight secondary ion MS can be used to sputter pesticides off a sample of an object and into an MS instrument for subsequent detection. These techniques are prone to interferences as they analyze the sample in bulk, and may not be able to provide reliable quantitative information due to the lack of good reference materials.

CONCLUSIONS

This paper has reviewed a variety of analytical methods for the determination of heavy metal and pesticides on museum objects and other artifacts. In the absence of any records documenting the treatment of specific objects or collections, these analytical methods represent the *only* means for definitively answering the question of whether or not an object has been contaminated with these substances. Such analyses are neither simple nor inexpensive, and many factors come into play in selecting the most appropriate sampling method and analytical method. It should be noted that *there is no one single method that is best for this application*; in some cases a single method may suffice, and in others several different sampling techniques and analytical methods may be warranted.

In effecting these analyses, the most important questions to address are “*what is the intended purpose of the analysis*” and “*what are the relevant constraints?*” If money and cost are the driving factors, and the scope is simply to determine if an object or several objects in a collection are contaminated with arsenic or mercury, spot tests are perhaps the easiest option so long as appropriate training to the operator is provided. If the intended purpose is to screen large numbers of objects for the determination of arsenic and mercury, then XES is appropriate given its high throughput. If the purpose is to precisely measure the concentrations of these metals on objects, then AAS, ICP-AES, and ICP-MS are appropriate. If the purpose is to accurately and reliably determine a variety of pesticides on a sample, then GC/MS is the best method for providing such data. If information on the extent of contamination on the surface or into an object is desired, then radiation or surface analysis techniques are needed to provide such data.

It should be noted that while an array of techniques such are available for determination of metals, GC/MS represents one of the few methods for determining a range of pesticides on such objects. Nevertheless, to date to the best of this author's knowledge, only one case study on the application of GC/MS to the analysis of pesticides on museum artifacts has been reported to date in the literature (Glastrup 1987). The author has performed two case studies to date for the determination of pesticides on museum objects, but these results will not be published until some later date.

When one considers the historical value of the objects in various museums and personal collections, nondestructive sampling is certainly more desirable than destructive sampling. However, it should be noted that such sampling may not provide reliable quantitative results, either due to the nature of the technique (i.e., imaging or scanning techniques are in some cases inherently semi-quantitative) or the sampling method (i.e., swab tests may not efficiently remove all of the contaminants on a given surface area). Destructive methods involving sample removal, homogenization, digestion, or extraction, may provide better or more reliable quantitative results but may diminish the value of the object unless micro-sampling techniques are used. The choice of a specific sampling method depends on the application and intended results, and inevitably involves compromises.

Interpretation of the significance or meaning of the final results and concentrations for pesticide contamination on museum objects is even more complex. Widely variable results are often obtained from replicate analyses of the same object. It should be noted that this is not a result of the uncertainty of the analytical method so much as the *inherent variability of pesticide contamination on the object* as a result of the application processes used. This implies that careful considerations should be made in developing a sampling protocol and strategies to provide the desired information on the extent and level of contamination on the objects. Interpretation may also involve consideration of the toxicological significance of the results. Although government agencies have set occupational exposure limits for toxic substances, no such standards exist for objects in museums or personal collections. Moreover, the standard techniques used to develop such limits often do not take into account long term exposure to low doses of such chemicals, and the highly variable toxicological effects observed in higher risk groups such young children and older people.

Without question, the various issues involved in this application bridge many disciplines and are quite complex. The parties involved with initiating these analyses must take into account these and many other factors to decide what information is desired, how quickly it is needed, and how much in terms of either personnel or monetary resources they are willing to commit to these analyses.

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Pete Palmer thanks editor Janet Waddington for the extra time needed to prepare this manuscript. He gratefully acknowledges the significant roles played by both Lee Davis and Niccolo Caldararo in involving and collaborating with him in the development of these methods. He acknowledges Catherine Hawks, Nancy Odegaard, and Jane Sirois for their leadership and extensive prior work in this area.

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OPEN DISCUSSION 2

- Yolanda Chavez suggested that the information be published and circulated to tribes in simple language that everyone could understand.
- Joseph Moreno asked what happens when repatriated artifacts are re-buried. Dr. Palmer said that toxic metals could leach into the groundwater.
- Mr. Moreno said some tribes were planning to lay remains to rest by burning them. Dr. Palmer replied by warning that burning materials that contain mercury is dangerous, because the mercury would be released into the air and endanger people's health.
- Another attendee said he was concerned about the danger of repatriated artifacts that were going to be used in cultural or religious ceremonies, especially if they were to be used by children.
- Lee Davis said it was only human for people who had just learned about this issue to be afraid and angry, but we could come together and decide what to do about it.
- Joseph Moreno asked if scientists had correlated the relationship between pesticide exposure levels to specific consequences for human health.
- Monona Rossol replied to Mr. Moreno that OSHA publishes the correlation between the thresholds of occupational exposure levels and human health hazards. She said that gathering this information, enforcing the law, and informing employees about this issue, are all the responsibility of the employer.
- Monona Rossol said that 'exposure' is a complex issue and that it is up to the government to educate the tribes about the dangers of toxic exposure and health hazards.
- Victoria Purewal advised the tribes to buy dosimeters, which record the presence of mercury vapor, for their members who work with museum materials, in order to monitor exposure compared to limits set by various governmental agencies such as NIOSH and OSHA.
- Another attendee cautioned that the use of dosimeters can give a false sense of security if the right chemicals are not targeted
- Victoria Purewal discussed the different effects of short term and long term exposure to pesticides. For instance, breathing air contaminated by burning materials, such as that produced during the cremation practices of some tribes, could easily result in exposure levels 25 to 30 times over the legal limit for occupational exposure. At the other end of the spectrum, the amount of exposure in dose per contact may be low in an average one-time handling situation.
- An industrial hygienist in the audience said that the legal dose limit for pesticides as established by OSHA are based on studies of male workers in industrial settings, and don't apply to women, children, the elderly, or the infirm. The OSHA guidelines also cover only industrial or factory types of exposure, and are not applicable for the very different type of exposure routes experienced in a museum or tribal setting, for example, ceremonial dancers whose body temperature is high, whose skin is heavily perspiring, wearing

a contaminated headdress directly upon the skin of the forehead for a period of several hours.

- David Goldsmith discussed exposure routes. Body weight and exposure must be factored into the effects of pesticide exposure, especially as regards children.

MORE THAN MAGIC: PESTICIDES ON NAGPRA SACRED OBJECTS (SUMMARY)

MONONA ROSSOL

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Ms. Rossol gave a presentation on the health risks to humans resulting from contact with these hazardous chemically treated materials. She explained the differences between gases, vapors, fumes, dust and mists, and how contaminants in these various forms enter the body by skin contact, inhalation, and ingestion. The potential medical effects of pesticide and preservative chemicals were covered. Special care should be taken with artifacts because the people who are exposed can be considered a high-risk population. It will take work on both sides of this issue to establish a reasonable and workable safety protocol.

Collection Forum 2001; 16(1-2):43

CHEMICAL CONTAMINATION OF REPATRIATED NATIVE CALIFORNIAN NAGPRA MATERIALS: PRINCIPLES OF RISK ASSESSMENT FOR ACUTE AND CHRONIC HEALTH EFFECTS

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Abstract.—An overview of the components of risk assessment (hazard identification, dose-response evaluation, exposure assessment and risk characterization) facilitates a discussion of the potential acute and chronic health effects from exposure to contaminated repatriated native Californian NAGPRA materials. The presentation encompasses terminology (carcinogen classification, dose-response curve, reference dose, hazard index, and minimal risk levels) and limitations of risk assessment of hazardous chemicals. It provides a general survey of the acute and chronic health effects of hazardous materials used by museums that may have contaminated tribal materials including: arsenic, DDT, dieldrin, lindane, mercuric chloride, carbon tetrachloride, carbon disulfide, borax, naphthalene, paradichlorobenzene, and thymol. The chemical and physical characteristics, sources, uses, potential routes of exposure, cancer classification and toxic exposure levels are provided for each chemical respectively. The acute and chronic health effects are put in context with respect to target organ, dose and duration of exposure, and grouped by chemical and toxicity categories: heavy metals (arsenic, mercuric chloride), organochlorine pesticides (DDT, dieldrin, lindane), halogenated solvents (carbon tetrachloride), repellents (naphthalene, paradichlorobenzene), and other antiseptics and disinfectants (borax, thymol, carbon disulfide). This will provide a framework for future discussions and risk assessments of materials of known contamination levels and exposure circumstances.

BACKGROUND

The use of pesticides on artifacts collected for museums has been chronicled for the nineteenth and twentieth centuries (Goldberg 1996, Hawks and Williams 1986). While museum collectors have most recently converted to “chemical-free” means (e.g., freezing, vacuum cleaning, sticky traps, etc.) to preserve artifacts from destruction by insects, a variety of pesticides and application techniques were utilized over the past two centuries. Unfortunately, the types of pesticides and their respective application techniques on museum artifacts have created a risk of residues and the possibility of contamination of individuals handling such artifacts. In particular, pesticides that are resistant to biodegradation (organochlorines, heavy metals) and may persist for many decades were extensively applied to museum artifacts. Furthermore, these pesticides may tightly bind to biological materials (animal furs, feathers, nails, claws, plant fiber, wood) commonly present in tribal artifacts.

TYPES OF PESTICIDES AND APPLICATION TECHNIQUES

The types of pesticides utilized on museum artifacts have varied over the past two centuries and paralleled the technological advances in pesticide availability and application. During the nineteenth and early twentieth centuries, tobacco, camphor, strychnine, carbolic acid or phenol, “flour of sulphur” or elemental

sulfur, “corrosive sublimate” or mercuric chloride, thymol, naphthalene, carbon disulfide, and several forms of arsenic (arsenous acid, arsenic trioxide or white arsenic, sodium arsenite, potassium arsenate or Macquer’s salt, and potassium arsenite in Fowler’s solution) were used. Later in the twentieth century (circa 1950) emerged newer classes of pesticides including the organochlorines (DDT, dieldrin, lindane or benzene hexachloride), fumigants (ethylene dichloride, ethylene dibromide, methyl bromide, ethylene oxide, and sulfuryl fluoride), organophosphates (dichlorvos or DDVP) and repellents (p-dichlorobenzene). Of these, Lindane (for the treatment of lice and scabies), methyl bromide (fumigant on soil, perishable foods and in buildings), ethylene oxide (sterilizer of medical supplies), p-dichlorobenzene (moth repellent) and sulfuryl fluoride (structural fumigant for termites) are in common use today.

The application techniques varied considerably and depended on the type of specimen or artifact, physical form and solubility of the pesticide, and technical capabilities of the applicators. The heavy metal-containing pesticides, arsenic and mercury, were rubbed, painted or brushed, sprinkled and sprayed on the surface of the artifacts. They were also used in mixtures (e.g., arsenic and carbolic acid) and as solutions for dipping or immersion of the artifacts. Some were then sealed and impregnated with wax. Later in the twentieth century, the use of fumigants and special chambers or “fumatoriums” evolved. The fumigant pesticides, carbon disulfide, ethylene dichloride, ethylene dibromide, and methyl bromide, were highly volatile and may have been mixed with other solvents (e.g., ethylene dichloride, dibromide, and carbon tetrachloride in Dowfume®). Some were impregnated in resin strips (DDVP in No-pest Strips®) or dispersed in a fogger (DDT in kerosene). Due to the high acute toxic potential of the fumigants, this practice was abandoned in the 1980s.

The critical issue and result of these practices is the current level of contamination and residues of pesticides on museum artifacts. This is extremely difficult to predict due to the numerous factors that impact residue levels including the chemical properties and “persistence” of the pesticide, the application process and vehicle for the pesticide, the constituents or material comprising the artifact, and storage environment (e.g., access to air and moisture). Unfortunately, some of the pesticides used on the artifacts have tremendous persistence or resistance to degradation. For example, organochlorines, such as DDT, may persist for several years after one application to soil (Kearney et al. 1969).

RISK ASSESSMENT

The initial components of risk assessment include a hazard estimate or identification and a dose-response evaluation. The goal is to determine (a) whether the suspect chemicals are capable of causing an adverse health effect and (b) the relationship between the amount of exposure (dose) and the severity of the adverse health effect. This may be followed by an exposure assessment to determine or predict the level of exposure (or dose) of the chemical given a particular exposure circumstance. The final step in this process is to integrate the information and characterize the risk and then decide whether the risk can be controlled or managed (e.g., by use of protective gear) or is acceptable.

The first step in estimating a hazard is to identify the chemical or poison. This is a pivotal issue and in most routine poisonings is determined by several sources:

a history from the victim or others, labeling, Material Safety Data Sheets (MSDSs), and computerized databases. However, in the circumstance of contaminated artifacts, it may be difficult to accurately identify a pesticide contaminant based on the availability and accuracy of the records of the collector or museum. Furthermore, artifacts may have been preserved in the field prior to reaching a museum or the final collector or repository and this information may not be recorded. Therefore, the only definitive method may be a targeted (based on records and other historical facts) or a comprehensive toxicology screen or analysis of the artifact or specimen to obtain a qualitative and quantitative assessment of contamination. Toxicology practices and laboratory capabilities vary by region. In California, the model for toxicological investigation usually includes an investigative team. For example, the investigation is initiated after a patient exhibits health effects from exposure to a drug, chemical or commercial product. This may be reported to the poison center that then provides medical guidance to the patient or the medical caregiver. Contingent upon the nature of the chemical or contaminant, and its potential as a public health hazard, a federal or state governmental agency (e.g., Food and Drug, Department of Agriculture, Centers for Disease Control) may be notified and serve as the lead investigative agency. The laboratory assessment of a specimen by a private or public sector laboratory may occur as directed by the lead agency or toxicologist. However, few laboratories exist that have the capability to perform comprehensive screens on contaminated museum artifacts. This is the basis for the policy recommendation in the conclusion of this paper.

The next step is to review the dose-response information available on the chemical or substance. An important tenet in toxicology is that the dose makes the poison. As stated by the fifteenth century physician, Paracelsus, "All substances are poisons; there is none which is not a poison. The right dose differentiates a poison and a remedy." There are also several routes of exposure for chemicals, including oral or ingestion by mouth; inhalation or breathing fumes or vapors; placing on or in the eyes and skin; and by injection. Each route may have a defined toxic dose and a special concern for local effects (e.g., irritation) as well as potential for absorption into the body. The most common route for general poisonings is by ingestion and is usually estimated in milligrams (of chemical) per kilogram of body weight of the victim. The dose of a poison received by other routes is more difficult to predict due to the variability in its absorption. However, many pesticides (heavy metals arsenic and mercury, organochlorines, organophosphates) are significantly absorbed and can cause poisoning by exposure to intact skin. The general published index of acute toxicity is the LD 50 (lethal dose) and is defined as the dose required to produce death in 50 percent of test animals exposed to it. This can be used to provide a general comparative index between substances as shown in Tables 1 and 2. For example, the smaller the number for the LD 50, the more hazardous the substance.

The problems with the LD 50 value as an index of toxicity are that it only accounts for a one-time or acute exposure, does not consider other parameters that influence a patient's susceptibility to toxic effects (age, other diseases and medications), assumes that animals can predict effects in humans, and only considers the end-point or final effect of death. Other indices or values have been determined that may be more meaningful to the assessment of risk and are sum-

Table 1. Examples of oral LD 50 values.

Substance	LD 50 (mg/kg)
Botulinus toxin	0.00001
Dioxin	0.001
Nicotine	1
DDT	100–200
Sodium chloride	4,000
Ethyl alcohol	10,000

marized in Table 3. Again, a low number indicates a hazard (with the exception of a Hazard Quotient); a very high number indicates a relatively harmless chemical.

The development of cancer is a special form of toxicity. The risk assessment for carcinogens (cancer-producing chemicals) does not include threshold doses as discussed previously. There are mathematical models to estimate the probability (or lifetime risk) that cancer will develop. This reflects the complex nature of carcinogens. There may be a multistage process in the damage that occurs to genetic material and the development of cancerous cells. Some carcinogens may initiate this process (“initiators”) and some may act at later stages of the process (“promoters”). There may be a delay of many years before the onset of disease. The cancer risk and ratings are based on a combination of human and animal experiences and data.

The foremost authority on evaluating the carcinogenic potential of chemicals in humans is the International Agency for Research on Cancer (IARC) under the World Health Organization (WHO). The IARC ratings are also based on human and animal data. In addition, other agencies may provide carcinogen risk classifications. Table 4 summarizes carcinogen risk classifications by agency. These classifications can be accessed through electronic databases, governmental agencies by telephone or websites, and toxicology references. Most databases and agencies are readily accessible through the internet, for example:

- Agency for Toxic Substances and Disease Registry (ATSDR <http://www.atsdr.cdc.gov>);
- International Agency for Research on Cancer (IARC <http://www.iarc.fr>);
- National Library of Medicine (NLM <http://www.nlm.nih.gov>);
- Environmental Protection Agency (EPA <http://www.epa.gov>);
- National Toxicology Program (NTP <http://www.ntp.niehs.nih.gov>);
- Occupational Safety and Health Administration (OSHA <http://www.osha.gov>);

Table 2. Example of a toxicity rating scale.

Rating	LD 50 (oral)
Extremely toxic	<1 mg/kg
Highly toxic	1–50 mg/kg
Moderately toxic	50–500 mg/kg
Slightly toxic	500–5,000 mg/kg
Practically nontoxic	5,000–15,000 mg/kg
Relatively harmless	>15,000 mg/kg

Table 3. Exposure level indices, thresholds and limits for non-cancer effects.

Index	Agency	Definition
Minimum Risk Level (MRL)	ATSDR (Agency for Toxic Substances and Disease Registry)	Daily human exposure to hazardous substances likely to be without risk of adverse non-cancer health effects over a specified duration (Acute-Chronic)
No Observed Adverse Effect Level (NOAEL)	EPA (Environmental Protection Agency)	In a dose-response experiment, the highest experimental dose at which there was no statistically or biologically significant increase in a toxic effect of the chemical being tested
Lowest Observed Adverse Effect Level (LOAEL)	EPA	In a dose-response experiment, the lowest experimental dose at which a statistically or biologically significant increase occurs in a toxic effect of the chemical substance being tested
Reference Dose (RfD)	EPA	An estimate of the daily exposure to the human population that is likely to be without appreciable risk of deleterious effects during a lifetime
Hazard Quotient (HQ)	EPA	The ratio of a chemical's exposure level to its reference dose. If <1, then no significant risk of toxicity
Threshold Limit Value (TLV)	ACGIH (American Conference of Governmental Industrial Hygienists)	Workplace exposure guidelines. Exposure limit for 8 hours a day, day after day with no adverse effect. Expressed as TWA (Time Weighted Average)
Immediately Dangerous to Life or Health (IDLH)	NIOSH (National Institute for Occupational Safety and Health)	Any atmosphere that poses an immediate hazard to life or immediate irreversible debilitating effects on health

National Institute for Occupational Safety & Health (NIOSH)
<http://www.cdc.gov/niosh>.

These websites provide hotlinks between agencies and other national and international groups, the ability to search by substance or chemical, and updated monographs regarding substance specific toxicity and cancer research. There are also clinical handbooks and textbooks that can be utilized as quick reference guides such as Olson (1999).

The next step in risk assessment is to estimate the level (or dose) of exposure specific to the circumstance of exposure. Estimating the amount of exposure from an acute exposure, particularly with ingestions involving pharmaceuticals, is usu-

Table 4. Summary of carcinogen risk classifications.

Agency	Classification/ Rating	Cancer Risk/Designation
International Agency for Research on Cancer (IARC)	IARC 1	Human Carcinogen
	IARC 2A	Probably carcinogenic to humans
	IARC 2B	Possibly carcinogenic to humans
	IARC 3	Not classified
American Congress of Governmental Industrial Hygienists (ACGIH)	A1	Confirmed human carcinogen
	A2	Suspected human carcinogen
	A3	Animal carcinogen
Occupational Safety & Health Ad- ministration (OSHA)	OSHA CA	Regulated as a carcinogen
National Institute for Occupational Safety & Health (NIOSH)	NIOSH CA	Potential human carcinogen

ally straightforward. However, the level of exposure may be more difficult to estimate by other routes of exposure such as skin and if contact to the chemical is prolonged or repeated. This assessment would require quantitative results for the level of contamination of an artifact. The frequency, route, and duration of contact by the individual would need to be determined. This data would then be considered with the characteristics of the chemical (for example, its ability to penetrate skin) and any precautions taken by the individual (use of gloves, respirator, washing). This would be analogous to a workplace assessment by an industrial hygienist.

The final step is to integrate the data from the previous steps and characterize the risk to allow the development of policies for risk management. The determination of a medical hazard (capable of causing injury to a patient) requires that two factors be present: (1) that the substance be toxic; and (2) that a significant exposure has occurred or can occur. A medical hazard does not exist if either one of these factors is missing. For example, some commercially available pesticides for ants contain a toxic form of arsenic, arsenic trioxide. However, the pesticide is internally incorporated into the ant stake and the toxic ingredients are not accessible with surface contact. Therefore, it is unlikely that significant exposure can take place and handling such ant stakes is not considered a medical hazard. However, if a potential medical hazard is present, then it must be determined if the health concern is (a) an acute toxic hazard (usually refers to immediate effects with initial exposure), (b) sub-acute or chronic toxic hazard (may be delayed or sub-clinical effects from lower levels and prolonged contact), or (c) a risk of cancer. Table 5 provides a health hazard summary by target organ, characteristics and uses, safe exposure levels, and cancer classification of selected pesticides that may contaminate museum artifacts. The Minimum Risk Level (MRL) is utilized as the index for safe levels because it is promulgated by the Agency for Toxic Substances and Disease Registry (ATSDR) with discussions and a rigorous review process involving scientists from several agencies. These values are derived when reliable data exists to identify the target organs of effect and the most sensitive health effects relevant to humans. These effects are specified for a given duration and route of exposure for a given substance. Collectively, MRLs may be the most applicable index for the screening of contaminated museum artifacts.

Table 5. Characteristics and health hazard summary for selected pesticides.

Pesticide name & category	Chemical & physical characteristics	Sources & use	Potential routes of exposure	Acute & chronic effects by target organ	Minimum risk level (MRL) ¹	Cancer classification
Arsenic <i>Heavy metal pesticide</i>	Silver-gray, shiny, brittle, crystalline metalloid; darkens to black with moisture. May dissolve in water	Element found in ores & ground water. Used in metallurgy, glass manufacture, pigment, electronics & broad spectrum pesticide and preservatives	All routes, including ingestion, intact skin & inhalation	Irritant; cellular poisoning with multi-organ effects for acute & chronic	Oral, chronic, 0.0003 mg/kg/day	IARC 1 (Skin, liver & respiratory tract cancers)
DDT [1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane] <i>Organochlorine pesticide</i>	Colorless or white to slightly off-white powder with no odor or taste. Poor water solubility for all organochlorine pesticides	Synthetic. Banned pesticide in the US (may be used in other parts of world) due to wildlife & environmental damage	All routes, including ingestion, intact skin (poorest with DDT) and inhalation	Irritant; nervous system (acute & chronic) & liver (chronic). Bioaccumulation (levels accumulate in body with repeated exposures)	Oral, acute, 0.0005 mg/kg/day	IARC 2B EPA Group B
Dieldrin <i>Organochlorine pesticide</i>	Colorless, white to light tan (impurities) powder with mild chemical odor	See DDT above	See DDT above	See DDT above	Oral, acute, 0.00007 mg/kg/day; chronic, 0.00005 mg/kg/day	IARC 3 (liver & adrenal cancers in animals)
Lindane (gamma-hexachlorocyclohexane) <i>Organochlorine pesticide</i>	White to cream colored odorless crystal with a bitter taste & musty odor	Synthetic. Used as a human pharmaceutical for scabies & lice	See DDT above	Irritant; nervous system (acute & chronic)	Oral, acute, 0.01 mg/kg/day; intermediate, 0.00001 mg/kg/day	Equivocal

Table 5. Continued.

Pesticide name & category	Chemical & physical characteristics	Sources & use	Potential routes of exposure	Acute & chronic effects by target organ	Minimum risk level (MRL) ¹	Cancer classification
Mercury <i>Heavy metal pesticide</i>	Elemental or metallic mercury is shiny, silver-white color, odorless liquid. Inorganic salts are white powders or crystals	Naturally occurring metal; organic mercury formed in water & soil by bacteria. Used in thermometers, batteries, dental treatments, skin creams, and to produce chlorine gas	Elemental mercury is absorbed by inhalation of vapors. Mercury salts are absorbed by ingestion and application to skin. Organic mercury may be absorbed by any route	Irritant, kidney & nervous system; effects may be acute or chronic	Mercuric chloride; Oral, acute, 0.007 mg/kg/day; Intermediate, 0.002 mg/kg/day	Not classified (lack of human data)
Carbon Disulfide <i>Disinfectant & fumigant</i>	Colorless to light-yellow liquid with sweet ether-like odor. Commercial grade has rotten egg odor	Used as a solvent, production of cellophane, vacuum tubes, optical glass and intermediate for adhesives	Poisoning generally occurs after inhalation, but absorbed by any route	Irritant: nervous system (acute); cardiovascular (chronic); & liver (acute or chronic) Strongest of solvents	Oral, acute, 0.01 mg/kg/day. Inhalation, chronic, 0.3 ppm	Not classified (lack of human data)
Carbon Tetrachloride <i>Halogenated solvent</i>	Clear, colorless heavy liquid with an ether-like odor	Banned from most commercial uses in the US. Used in the production of fluorocarbons. Was used as a degreasing solvent, dry cleaning agent, and grain fumigant	May be absorbed by any route	Irritant: nervous system, liver & kidney (acute or chronic effects)	Inhalation: acute, 0.2 ppm; intermediate, 0.05 ppm. Oral: acute, 0.02 mg/kg/day; intermediate, 0.007 mg/kg/day	ACGIH-A2

Table 5. Continued.

Pesticide name & category	Chemical & physical characteristics	Sources & use	Potential routes of exposure	Acute & chronic effects by target organ	Minimum risk level (MRL) ¹	Cancer classification
Naphthalene <i>Repellent</i>	White crystalline flakes or solids with a strong "moth ball" or coal tar odor	Occurs naturally in essential oils of <i>Radix & Herbaonidis</i> . Chemical intermediate for indigo and other dyes and other products. Most commonly used as a moth repellent and in air freshener and toilet bowl deodorizers	May be absorbed by any route	Irritant: liver (acute or chronic) Hemolytic anemia in patients with a specific enzyme deficiency (G6PD) (acute)	Oral, acute, 0.05 mg/kg/day; Intermediate, 0.02 mg/kg/day Inhalation, chronic, 0.002 ppm	Not classified (lack of human data); may be associated with laryngeal & intestinal carcinoma
Borax (anhydrous sodium tetraborate) <i>Antiseptic & disinfectant</i>	White to light gray odorless solid	Used in pharmaceuticals, cleansers, & cosmetics	Absorbed by ingestion, mucous membranes and abraded skin	Irritant with small acute exposures; skin (exfoliative rash) & kidney with large exposures	Not classified (lack of human data)	Not classified (lack of human data)
Paradichlorobenzene <i>Repellent</i>	White to colorless crystals with a penetrating camphor-like odor	Replaced naphthalene as safer ingredient in moth repellents and diaper pail deodorizers	Absorbed by ingestion & inhalation	Irritant: nervous system, blood & liver (mild), all chronic	Not classified (lack of human data)	Animal carcinogen
Thymol <i>Antiseptic & disinfectant</i>	Aromatic oil with characteristic odor of the spice thyme	Essential oil from thyme. Used as a disinfectant, deodorant, in mouthwashes, & in dentistry	Unknown; potential for all routes	Irritant; nervous system (acute)	Not classified (lack of human data)	Not classified (lack of human data)

¹ Duration of exposure for MRLs are acute (1–14 days), intermediate (15–364 days), and chronic (365 days and longer).

Recommendations

In conclusion, the policy considerations for repatriation of NAGPRA objects should support the risk assessment process as enumerated. This will require the expertise and resources of several state and federal agencies, most notably the National Park Service, Environmental Protection Agency and Agency for Toxic Substances and Disease Registry at the federal level and possibly HESIS (Health Evaluation System and Information) and Department of Health Services at the state level for California. The establishment of a centralized Artifact Analysis Lab, as created at San Francisco State University, is a critical first step. The risk management approach should be individualized and tailored to the specific circumstance (e.g., tribal burial or interment, burning, handling or donning artifacts) and contingent upon the level and type of contamination of NAGPRA objects, as well as the options available to tribes to control exposures among their members (e.g., avoid or minimize direct contact with object during ceremonial customs, ability to use protective equipment).

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PUBLIC HEALTH ISSUES INVOLVED WITH IMPLEMENTING NAGPRA LAW (SUMMARY)

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Manzanilla provided an overview of the EPA Pesticide Program. The EPA provides money to the state and to tribes to develop environmental programs. He explained how tribes are able to influence EPA policy through the Regional Tribal Operations Committee (RTOC), the Tribal Operations Committee (TOC), the Tribal Pesticide Program Council (TPPC), and the National Environmental Justice Advisory Council (NEJAC). He said the issue is very perplexing, as it does not fit routinely into other EPA operations or programs. The issue needs to be raised at the national level. Tribes need to be advocates for requesting the resources necessary to address this issue.

Discussion Following This Presentation

- One attendee said she would like to see the EPA take a more active role in this issue.
- Another attendee said that Indian Health Services should be involved.
- Another attendee suggested that a resolution be sent to the EPA and to tribal representatives on the various committees and councils.

**THE HOOPA TRIBAL MUSEUM'S EXPERIENCE WITH
CHEMICAL CONTAMINATION OF REPATRIATED
MATERIALS (SUMMARY)**

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The group gave a presentation on the Hoopa Tribal Museum's experience with chemical contamination of repatriated materials. Hostler said he now has mixed feelings about repatriations. Two years ago he contacted the Peabody Museum at Harvard for a copy of their inventory. When he got there he was unaware of contamination and was told to wear gloves and a mask. He did not know how to react. Each room was secured with locks and when the doors were opened he could smell odors. Some artifacts were not being stored according to Hoopa religious practices, and he did restore them properly for the Peabody staff. The museum met with tribal elders about the return of some artifacts.

During the 1800s many loads of artifacts were hauled away by collectors. The artifacts are living spirits who cry to come to the ceremonies back home and dance with "their people." That is why the repatriation subject is so emotional. Hostler said the tribe asked for 52 very religious items but only 17 items were returned by the museum. A report from the museum warned that the artifacts might contain arsenic, mercury and other poisons. The artifacts were double wrapped and in a container. Later, during a Jump Dance, the artifacts were placed on a table at the ceremonial grounds, at some distance from the regalia that was to be worn in the dance, so that they could once again be with the other spiritual beings that come to the dance grounds. One head roll was made out of humming birds that would have taken years to collect. These materials are irreplaceable. Hostler said the Peabody Museum was unfamiliar with the tribe's beliefs, and all artifacts to do with women were left out.

Kane said she would like to see the issue taken to the next level. Information should be shared nationally. She, Hostler and Davis also went to the Smithsonian and were given the same information about possible contamination.

PESTICIDE TESTING OF HOOPA TRIBE REPATRIATED REGALIA: TAKING THE SAMPLES

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Abstract.—Seventeen items of regalia repatriated under NAGPRA by the Hoopa Tribal Museum from the Peabody Museum at Harvard were reported as being contaminated by pesticides. The Hoopa Museum Director worked with faculty from San Francisco State University (SFSU) to develop a method for taking samples from these precious objects so they could be tested for pesticide contamination at in the SFSU Chemistry Lab. Sample sizes were chosen to provide sufficient mass for scientific analysis in an acceptable ethical manner from the perspective of the Hoopa Tribal Museum.

INTRODUCTION

Benedetti-Pichler, one of the great analysts of this century observed that “sampling and analysis are related as question and answer are” (Benedetti-Pichler 1965). We think this is a poignant place to begin addressing the issue of pesticides on Native American and other artifacts. The original text of the 1990 Native American Graves Protection and Repatriation Act (NAGPRA) only provides for the return of museum objects to the tribes, without mention of their possible pesticide contamination. The NAGPRA regulations later added a requirement for museums to inform tribes at the point of actual return items, of any known chemical applications that the museum had historically used anywhere in the museum. Since this time the question which tribes must first have answered is, “Are these objects contaminated and with what chemicals?” Once this question is answered, the potential health hazard can be assessed depending on the concentration of pesticides present, the intended use of the objects, and the potential routes and frequency of exposure of humans to these objects.

In 1997 after three years of negotiation, the Hoopa Tribe of California received seventeen items of religious regalia from the Peabody Museum at Harvard, along with a letter stating that the material was probably contaminated with a variety of pesticides used in the Museum over hundreds of years.

Hostler and Kane of the Hoopa Tribal Museum contacted Davis, San Francisco State University (SFSU) professor and NAGPRA consultant for the Hoopa tribe, to discuss the possibilities for testing these materials and for removing contaminants. To address these questions, Davis recruited Caldararo, a museum conservator, to find appropriate analytical testing services. Initially, we contacted commercial pesticide laboratories but found that they were ill prepared to provide the specialized services for testing sensitive religious materials. The SFSU Chemistry Department had the experience and resources to carry out the required analyses

and Palmer was interested in the application of scientific methods in the service of the public good.

Over the next year our team, Hostler, Kane, Davis, Caldararo, and Palmer, would work together to examine the repatriated materials in order to determine the type of testing methods that would provide reliable information on the presence of pesticides. It became clear that testing was the only way to identify specific pesticides on each item before the tribe could evaluate how it would manage the museological, religious, and health issues raised by contaminated regalia.

It was agreed that SFSU would develop a testing laboratory for tribal materials, as a collaborative project between the tribe and the university. The SFSU scientists explained various options for sampling methods and analysis. The Hoopa Museum staff explained the importance of the regalia and their role in Hoopa life. The laboratory workers would learn to understand the meaning and use of the objects. The Hoopa people would become knowledgeable in the workings of the laboratory. The SFSU scientists began by conducting preliminary tests on artifacts and packing materials from the Treganza Museum on campus and the campus NAGPRA laboratory. These tests were necessary to calibrate laboratory equipment and furthermore provided examples of the levels of artifact contamination to compare with Hoopa objects.

SAMPLING CONTEXT

The Hoopa-SFSU team decided that the taking of regalia samples for destructive testing could best be carried out on the Hoopa reservation, so the SFSU staff traveled to Hoopa to take samples, isolate them, and return with them to SFSU for analysis. In the fall of 1999 Palmer, Caldararo, and two graduate students in Chemistry traveled to Hoopa. The Hoopa Tribal Museum is located on the Hoopa Valley Indian Reservation in Humboldt County, California. At the Hoopa Museum, Hostler and Kane showed their SFSU colleagues the exhibits and storage areas. It was in the context of this knowledge that sampling and testing took place.

The taking of samples occurred in a room near the Hoopa Tribal Museum. The seventeen repatriated items remained in their storage bags until ready for sampling, and were then moved to one of several tables set up for examination. All the instruments used in taking the samples were cleaned with de-ionized water and methylene chloride between each sample to remove residues and minimize cross-contamination. All participants used gloves, latex or nitrile, and each sample was placed in a separate container for each sampling procedure. We had not anticipated high levels of contamination, and so were not fitted with lab coats, but the individual doing the sampling wore a respirator (Combination Cartridge R51HE type for organic vapors, mists of paints, lacquers & enamels, dusts, fumes, asbestos, pesticides, radionuclides and radon daughters). Ideally people taking samples should do so under a fume hood to protect themselves from exposure to toxic materials. There was no fume hood in the Hoopa Museum, so we took other precautions. The person doing the sampling was careful not to touch any of the objects, but to section only the areas that were then directly placed into collection tubes. The objects did give off considerable dust during the operation, and it was feared that this dust was arsenic. The tables became covered with the dust between

sampling and an effort was made to avoid these areas for each subsequent sample. In addition to masks for use in sampling on-site or other handling of artifacts known or believed to be contaminated, the use of a PACE extractor Evac 250 system might be advisable. The samples taken were quite small—a centimeter at most in many cases. The sample containers were standard similar to Urisystem tubes with tight-fitting plastic lids. Each sample was labeled separately.

Hostler, Caldararo, and Palmer examined the structure of each item to determine the best location from which a sample would be taken. The size of the sample to be taken was a delicate issue for all present. A sufficient mass of each sample was needed for accurate testing, but the goal was to take from each item the absolute smallest quantity necessary to achieve the testing requirement. It was also important to leave the object's appearance unchanged. An important consideration of Hostler was to test an item at the locations of most potential harm, the place on the item where it touched the skin of a ceremonial participant. The scientists needed a variety of physical materials (feather, skin, etc.) as testing samples to determine the extent of the contamination (Table 1). The discussion about the size of samples was centered around two issues: first, the concern for the integrity of the objects, and second, the amount of sample and a randomized nature to sampling locations, which would be sufficient to provide a reliable test result. The mass of feathers is quite small given the bulk of material making up a feather, with the rachis and calamus containing the greatest mass. This meant that more feather needed to be removed than, say wood or leather. We therefore decided to attempt a balance between sample size and loss in bulk to the object and damage to its cultural integrity. Samples were chosen from feathers under tufts, from previously broken areas, or damaged vanes and barbs of feathers, from straps, ends of shafts of wood and inside of construction, especially ends of sewing or tied off elements.

That evening, the university staff were invited to a Deerskin Dance ceremony, in which regalia similar to those sampled earlier in the day were brought out for the ceremony.

SAMPLING METHODS

The sampling process was part of a larger context in which the scientists were able to experience how similar ceremonial objects were used. This context was kept in mind as the sampling process evolved. The samples were now separated from the objects and yet they carried on as some part of them, a part that would provide the Hoopa with answers to the dilemma they faced.

We often speak of samples as being representative of the object or material to be studied. Leo Biek (1963) noted that there are three considerations that must be addressed in this process: choice, sampling, and reliability. One must choose where to take the sample, how much to take, and be confident of the quality of the sample taken. Sample size and destructive testing have been a significant concern in conservation and anthropological research (Wouters 1992). In taking the sample one must be sure that the sample is not contaminated with other materials after it has been removed. Thus, after the sample is isolated, it must remain so to establish a "chain of evidence" relationship with the sampling context (Maloney 1980). Finally, one must be sure that the sample is sufficient for testing which will produce results that are significant.

Table 1. Summary of samples taken from Hoopa artifacts for analysis.

ID #	Artifact description	Sample description	Analysis method
R0a	N/A	Trip blank for metal analyses	As/Hg via AA
R0b	N/A	Trip blank for pesticide analyses	Pesticides via GC/MS
R1a	Ringtail dance hide	Leather hide with fur from top	As/Hg via AA
R1b	Ringtail dance hide	Leather hide with fur from top	Pesticides via GC/MS
R1c	Ringtail dance hide	Leather hide with fur from bottom edge	As/Hg via AA
R1d	Ringtail dance hide	Leather hide with fur from bottom edge	Pesticides via GC/MS
R2a	Ringtail dance hide	Leather hide with fur from edge	As/Hg via AA
R2b	Ringtail dance hide	Leather hide with fur from edge	Pesticides via GC/MS
R2c	Ringtail dance hide	Red fabric from top edge	As/Hg via AA
R2d	Ringtail dance hide	Red fabric from top edge	Pesticides via GC/MS
R3a	Jump dance basket	Leather from bottom of basket	As/Hg via AA
R3b	Jump dance basket	Leather from bottom of basket	Pesticides via GC/MS
R3c	Jump dance basket	Straw from interior body of basket	As/Hg via AA
R3d	Jump dance basket	Straw from interior body of basket	Pesticides via GC/MS
R4a	Morning feathers	Wood handle shavings	As/Hg via AA
R4b	Morning feathers	Wood handle shavings	Pesticides via GC/MS
R4c	Morning feathers	Yellowhammer (flickers) feathers	As/Hg via AA
R4d	Morning feathers	Yellowhammer (flickers) feathers	Pesticides via GC/MS
R5a	Ceremonial eagle feathers	Wood handle shavings	As/Hg via AA
R5b	Ceremonial eagle feathers	Wood handle shavings	Pesticides via GC/MS
R5c	Ceremonial eagle feathers	Straight feathers, taken from middle	As/Hg via AA
R5d	Ceremonial eagle feathers	Fluffy feathers, taken from end	Pesticides via GC/MS
R6a	Unfinished basket	Straw from bottom of basket	As/Hg via AA
R6b	Unfinished basket	Straw from bottom of basket	Pesticides via GC/MS
R7a	Head roll	Hide strap	As/Hg via AA
R7b	Head roll	Hide strap	Pesticides via GC/MS
R7c	Head roll	Twine used to hold strap on headband	As/Hg via AA
R7d	Head roll	Twine used to hold strap on headband	Pesticides via GC/MS
R8a	Head roll	Leather from middle edge	As/Hg via AA
R8b	Head roll	Leather from middle edge	Pesticides via GC/MS

Table 1. continued.

ID #	Artifact description	Sample description	Analysis method
R8c	Head roll	Leather from outer edge	As/Hg via AA
R8d	Head roll	Leather from outer edge	Pesticides via GC/MS
R9a	Head roll	Leather from inside edge	As/Hg via AA
R9b	Head roll	Leather from inside edge	Pesticides via GC/MS
R9c	Head roll	Leather from inside edge	SURFACE ANALYSIS
R10a	Wood rod to store headbands	Wood shavings	As/Hg via AA
R10b	Wood rod to store headbands	Wood shavings	Pesticides via GC/MS
R11a	Hookman's head band	Leather from inside headband	As/Hg via AA
R11b	Hookman's head band	Leather from strap	Pesticides via GC/MS
R11c	Hookman's head band	1 sq cm leather area swabbed w/methylene chloride	Pesticides via GC/MS
R12a	Donut head roll	Leather with fur from inside headband	As/Hg via AA
R12b	Donut head roll	Leather with fur from inside headband	Pesticides via GC/MS
R13a	Deer hoove necklace	Twine	As/Hg via AA
R13b	Deer hoove necklace	Twine	Pesticides via GC/MS
R14a	Head net	Leather from headband	As/Hg via AA
R14b	Head net	Leather from headband	Pesticides via GC/MS
R14c	Head net	Twine from body of headband	As/Hg via AA
R14d	Head net	Twine from body of headband	Pesticides via GC/MS
R15a	Head net	Leather with fur from headband	As/Hg via AA
R15b	Head net	Leather with fur from headband	Pesticides via GC/MS
R15c	Head net	Cuticles and feathers	As/Hg via AA
R15d	Head net	Cuticles and feathers	Pesticides via GC/MS
R16a	Head net	Leather from headband	As/Hg via AA
R16b	Head net	Leather form headband	Pesticides via GC/MS
R16c	Head net	Feathers	As/Hg via AA
R16d	Head net	Feathers	Pesticides via GC/MS
R17a	Head blind	Twine from body of headband	As/Hg via AA
R17b	Head blind	Twine from body of headband	Pesticides via GC/MS
R17c	Head blind	Leather from inside edge	As/Hg via AA
R17d	Head blind	Leather from inside edge	Pesticides via GC/MS

In most cases, taking a sample requires a certain knowledge of the object to be studied. This allows for a firm basis in sampling, especially when one cannot return to take more samples. In conservation, we are generally limited to very small samples due to the intrinsic value of the objects studied and the expectation that samples may produce some reduction in the object's integrity or structure. Most reports of the use of instrumentation in conservation for analysis are more concerned with the limits of detection and identification of pigments, etc. than in the nature of the sample as being representative (for example, see Mairinger and Schreiner 1982, Billmeyer et al. 1982, Mills and White 1976, Clottes 1993). However, in the last decade considerable progress has been made in the development of sampling strategies (for example, see Schneider 1995). In our case, since the objects had survived in tact with little or no evidence of damage, it seemed assured that they were contaminated (Hawks and Williams 1986); hence we were forced to test for metals (arsenic and mercury) as well as organic pesticides in general. Palmer spent the spring and fall fine tuning, identifying, and detailing specific analytical methods for testing for metals and organic pesticides. At first, we decided to focus on the metals as the pesticide data was so complex and made problematic by the breakdown products some pesticides degrade into. The analytical methods used on the samples are listed in Table 1. While minimal sample sizes (mass) have been reported to produce results, we desired to have some margin of confidence in our samples in case we had problems with equipment, etc. So while a few grams sufficed in most cases, the ability to identify specific masses of materials was a problem. Nevertheless, we were able to measure sample masses in the laboratory and after running all the samples found that we had taken sufficient sizes of all the samples to achieve the desired detection limits for metal tests.

When dealing with ceremonial objects, there is an additional requirement: not only one of sensitivity to the meaning of the object and its regard by others, but one must also be sensitive to the fact that the object is a spiritual being—to remove some part of it is to participate in an enterprise that is both momentous and contradictory. A variety of interpretations exist for approaching this situation (for example, Crick 1988, Firth 1996). For our group, the immediate task, however, required a personal exploration based on a familiarity developed between those involved.

We say "contradictory" because we have an arbitrary goal fixed by the instruments we are using; they require certain masses of substance to be able to produce the reliable results we need to be able to provide answers to questions. Certainly in taking blood as a sample the individual can produce more blood, and we have not changed the person by removing the blood. Also, when we take samples from a painting, the painting is changed in so far that we have reduced its mass by the amount of pigment taken at a certain location, usually without affecting the design. In the removal of a piece of ceremonial object for testing we are entering a world which is separate from us, unknown, and our task is one which can only be guided by those who are the familiars of such unknown territory. (Crick 1988, Firth 1996).

CONCLUSION

The sample sizes were sufficient for reliable results, and metals and pesticides were detected; arsenic and pesticides were found in all cases. This supported the

initial hypothesis that the objects had been treated with pesticides. The results were also given to the Peabody Museum to use in their NAGPRA consultations. A beneficial result of this process was the creation of a cooperative approach between the Hoopa Tribal Museum and SFSU. A method was devised that produced a sensitive handling of the objects within the spiritual context of the Hoopa religion.

In the future we would recommend that all personnel wear protective clothing, gloves and respirators. The gloves should be changed between each sample and the tables should be cleaned between each sample procedure. We isolated and marked the samples to produce a “chain of evidence” in order to support test results in the future if litigation results over the responsibilities of various agencies concerning mitigation of the pesticides on the objects or the health consequences to the Hoopa Tribal Museum staff or tribal members participating in their ceremonies who use these objects. Difficulties arise in sampling ethnographic art and producing results specific to objects. Storage facilities (shelving, containers, walkways, etc) are often contaminated. In addition, an intimate knowledge of the fabrication of objects is necessary to make sure test results do not reflect native metals present in pigments and other components of manufacture.

We will need to have a considerable number of test results from a variety of locations, storage facilities, and types of objects and a differing age to be able to understand the extent of the problem of contamination. We will also need a number of well designed experiments to be able to characterize the degradation steps and products of pesticides on ceremonial objects and how other factors such as conservation treatments affect this process. It is possible that institutions have unpublished reports of the analysis of objects, which might include data on pesticide content, concentration, degradation products and possible interactions with conservation treatments or materials of fabrication. We are aware of pesticide testing at the Field Museum, the Denver Museum of Natural History, the Smithsonian Institution, the Peabody Museum at Harvard, the Hearst Museum, and the Treganza Museum at SFSU. There are certainly more museums that have instituted or will institute a testing program for their collections. An international effort to gather such data would be of value as would long term studies of the health of museum workers exposed during their careers to the doses contained in artifacts. Linnie (1993) collected data from the international community on pesticide use. A similar inquiry is in order for health effects on museum workers.

Discussion Following This Presentation

- Monona Rossol recommended that a third party with no vested interest in the samples should do the testing
- Niccolo Caldararo added that it was important to note that preliminary testing in the NAGPRA lab indicated significant levels of mercury contamination not only of artifacts, but also of packing and storage materials associated with the artifacts. He offered to provide the results of these analyses to anyone who was interested.

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NAGPRA ARTIFACT REPATRIATION AND PESTICIDES CONTAMINATION: HUMAN EXPOSURE TO PESTICIDE RESIDUE THROUGH HOPI CULTURAL USE (SUMMARY)

MICAH LOMA'OMVAYA

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Loma'omvaya gave a presentation on contaminated artifacts and health risks of human exposure through Hopi cultural practices. The tribe has an Office of Cultural Preservation, which is responsible for repatriating artifacts and objects to the tribe. More than 60 items have been returned to the tribe prior to notification of potential contamination. Few tribal members were ever warned of contamination by museum staffs. The tribe still has 400 or more objects that it intends to repatriate from museums. Loma'omvaya has spoken to the EPA about medical monitoring for tribal members involved in repatriation. Each tribe is unique and will approach repatriation in a different manner.

For a full account of this issue, see Loma'omvaya (Collection Forum, in press) NAGPRA artifact repatriation and pesticides contamination: Human exposure to pesticide residue through Hopi cultural re-use.

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OCCUPATIONAL HEALTH INFORMATION ON PESTICIDE CONTAMINATION (SUMMARY)

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Goldsmith gave a presentation on occupational health parameters of the most commonly used pesticides in repatriated artifacts, and the most common signs and symptoms of illness. While the issue is giving everyone serious concerns, he wanted to make sure everyone has a credible base of knowledge about these chemicals.

In the state of California it is wise to become familiar with the department of pesticide regulation (DPR) in Sacramento, and their vast expertise on pesticides and health. He also urged tribes to get to know their regional EPA representatives, because they (with DPR) can provide access to programs related to pesticides. In particular, Region 9 (covering California, Arizona, Hawaii and Nevada) has a vital tribal pesticide program, which includes native leaders in this field. An ex-

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ample is Micah Loma'omvaya from the Hopi Tribe who is supported by the Region 9 EPA program. UC Davis is a nationally recognized center which could benefit both tribes and museums—the NIOSH agricultural health & safety program.

The pesticides of concern are arsenic, mercuric chloride, DDT, strychnine, naphthalene mothballs, paradichlorobenzene mothballs, and dichlorvos (DDVP). The routes and targets of exposure among tribal members are dermal, and the contamination of food and clothing. The routes and targets of exposure for conservators are inhalation, dermal and indirect contamination. This could also be a serious problem for children if they are exposed to parents who work in repatriation or museum programs.

Arsenic is a well-known poison and preservative. Strychnine is also a very serious hazard to children and may have been used in the past to protect artifacts from rodents. The record keeping of pesticide use was poor and we now must determine what is on the artifacts. In the past 40 years museums have moved to much less toxic methods for preservations. In order to reduce exposure and lower risks, it is important to examine the history of repatriated items and test them for pesticide residues, and to wear protective clothing and eyewear. Pesticide health professionals should be consulted and exposure to artifacts by children should be limited.

Prevention approaches recommended include: consultation with pesticide and public health experts; communication with tribal members, museum staff and management about the chemicals used in repatriation; recognition of the different cultural perceptions and re-consecration of the lives of Indian religious treasures and symbols; and “education, education, education.” Prevention is always better than cure, especially with the cultural sensitivity of the returned tribal artifacts.

Although current exposures may not appear “high,” there should be consideration of future studies including surveillance of exposures and of illnesses and epidemiological research of chronic health conditions and possible reproductive studies. Future research studies should also include surveys of tribal exposures and better characterization of exposures related to repatriation. Past uses of older pesticides on preserved native artifacts may have placed Native Americans at risk. Public health thinking also suggests that control of exposures and prevention of unnecessary risks must begin by taking a cautionary approach to handling objects and by cooperating with tribes and sharing information.

THE ANALYSIS OF MUSEUM OBJECTS FOR THE PRESENCE OF ARSENIC AND MERCURY: NON-DESTRUCTIVE ANALYSIS AND SAMPLE ANALYSIS

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Abstract.—Many natural history specimens and First Nations artifacts have been prepared or treated using a wide range of pesticides and biocides, including arsenic and mercury compounds, to prevent insect damage. These compounds can be toxic to humans so it is important to identify them. The Analytical Research Laboratory of the Canadian Conservation Institute has analysed a representative selection of natural history specimens in five museums, as well as a collection of First Nations masks and a varied anthropology collection in two other museums, to determine the presence of arsenic and mercury compounds. The artifacts were analysed on-site using a portable X-ray energy spectrometer, a cadmium-109 radioisotope x-ray source and a lithium-drifted silicon x-ray detector. This technique permits the non-destructive analysis of a 3-cm-diameter area, and can detect elements above atomic number 19 (potassium) in the periodic table. Although the technique cannot determine whether the arsenic is present in the interior or exterior of the specimen, samples can be taken for further analysis if residues are noticed on the surface of a highly contaminated specimen. Approximately 80 percent of the natural history specimens examined contained arsenic, mercury, or both (arsenic was encountered far more frequently than mercury). The incidence of arsenic and mercury in the First Nations and anthropology artifacts analysed to date was 23 percent.

INTRODUCTION

There are many kinds of museum collections where pesticides, particularly arsenic and mercury, may be found. Arsenic and mercury are routinely found in mammalogy and ornithology collections; however, objects in the following collections may also contain arsenic and/or mercury:

- herbarium collections (Briggs et al. 1983, Hawks and Bell 1999);
- anthropology collections which may contain traces of arsenic, and/or mercury from pesticides or may be painted with mercury-containing pigment (Sirois et al. 2000);
- archival collections where graphics materials which contain mercury, in particular self-toning boards used for drawings reproduced in newspapers and magazines, may be found (Moffat and Sirois 1999);
- mineral collections which contain arsenic and mercury containing minerals such as realgar (As₂S₃), orpiment (As₂S₃) and cinnabar (HgS) (Waller et al. 2000);
- fine and decorative arts collections where arsenic and mercury containing pigments such as emerald green (copper aceto-arsenite) and vermilion (HgS) may be used; and
- scientific collections where scientific instruments may contain mercury.

Many pesticides have been identified on natural history specimens and in anthropology collections. Extensive surveys of the possible chemicals on museum ob-

jects are in the literature (Glastrup 1987, Goldberg 1996, Hawks this volume, Rossol and Jessup 1996, Williams and Hawks 1987).

Since the 18th century, many highly toxic materials have been used to protect taxidermy specimens from infestation and putrefaction. The review by Williams and Hawks (1987) on the subject reveals that the list of different chemicals used and the variety of application methods is long and varied. Arsenical soaps and corrosive sublimate (=mercuric chloride) solutions (HgCl_2) were commonly used in taxidermy along with many other chemicals to prevent infestation of the specimens by insects. These compounds were also used, to a lesser extent, in the treatment of anthropological material such as wool, fur and leather objects. Arsenic, mercury and bromine have been identified in anthropology collections.

Arsenic compounds were widely used as chemical preservatives for natural history specimens during the 1800s and early 1900s (Brown 1833, Farber 1977, Hornaday 1905). The most popular form of this insecticide was arsenical soap, but powders and solutions were also used. The soaps and powders were generally applied to the inside of the skin, and solutions were brushed onto the outside surface of infested specimens. Another procedure involved burying skins in sand saturated with arsenic or corrosive sublimate solutions (HgCl_2) for 12–24 hours (Davie 1894). As a result, many museum specimens contain large amounts of arsenic. The use of arsenic has been recommended for the preservation of natural history specimens as recently as 1985 (Hangay and Dingley 1985).

In *Taxidermy and Zoological Collecting*, Hornaday (1905) suggested applying a solution of arsenic acid and alcohol, carbolic acid, strychnine, and naphtha to the specimens. The application of an arsenic solution to fur using a watering pot was an old method cited by Hawks and Williams (1986) as was applying arsenic to the inside of the skin as a paste or using dry arsenic which the preparators “should ‘shovel’ into bird skins.”

Another popular chemical used was mercuric chloride (also known as corrosive sublimate). This compound (HgCl_2) was rubbed on the inside of bird skins or applied as a solution to the interior and exterior surfaces (Hawks and Williams 1986). This compound was also applied to the surface of badly infested specimens, generally as a solution in alcohol and water and it was also used along seams in the specimens. It was not used as frequently as arsenic because of its high toxicity to humans.

HEALTH CONCERNS

A major problem that is encountered with natural history collections is the lack of treatment and preparation records available for many older specimens. For health reasons, it is important for anyone who comes in contact with specimens to know what chemicals they contain so that proper handling and storage precautions are taken.

Arsenic can be introduced into the body by inhalation, absorption through the skin, and ingestion. Chronic toxicity can result from constant handling of treated material. Long-term inhalation of small concentrations of arsenic dust or fume may eventually cause poisoning and constant exposure of the skin to arsenic may cause ulceration (Bretherick and Muir 1981). The intake of small amounts of mercury compounds by inhalation, skin absorption, or ingestion over a long pe-

riod of time may cause nervous disturbances, including tremor of the hands, insomnia, loss of memory, irritability and depression (Bretherick and Muir 1981).

One of the first published studies investigating potential health hazards in natural history collections was undertaken at the Bristol Museum (Muir, Lovell and Peace 1981). High concentrations of arsenic were detected in some of the natural history specimens, with concentrations of up to 10,000 ppm (or 1.0 percent). Arsenic detected in the air was less than $0.2 \mu\text{g}/\text{m}^3$ which is below the recommended standard of $10 \mu\text{g}/\text{m}^3$ in Ontario which is a time-weighted average exposure (Ontario Ministry of Labour Reg. 836 as amended by O. Reg 508/92. 1994). Approximately 0.01 ppb arsenic was detected on the gloves worn by staff.

The Park Museum in Banff, Alberta undertook an air quality study for arsenic in conjunction with Health Canada and AGAT Laboratories Ltd. in 1992 after swipe tests revealed high concentrations of arsenic on nine out of 37 natural history specimens examined (Feniak 1995). The air tested was determined to be well within public health standards however (Morrow 1993).

Another air quality and wipe test survey was done at the Redpath Museum, McGill University, Montreal, on a selected number of ornithology specimens in 1998. The results showed that the air quality from particulate, airborne arsenic was not a health hazard, however the arsenic present on the surface of the specimens could transfer to the work surfaces and to the hands of the individuals working with the objects (Costanzo 1999).

METHODS OF ARSENIC AND MERCURY ANALYSIS

Non-Destructive Techniques: REXES

Radioisotope excited X-ray energy spectrometry (REXES) was used in the on-site surveys in museums A to I. The artifacts analysed in these studies were selected by the museum staff. Six hundred and fifty-six natural history specimens from five natural history collections were analysed using REXES. The specimens were collected between 1875 and 1985. Approximately 100 to 200 specimens were analysed during each of the five three-day visits (museums A to E). Three surveys of selected anthropology artifacts from different collections (museums A, F and G), and two smaller groups of repatriated masks (museums H and I) were also analysed. No samples are taken for these analyses. X-ray energy spectrometry is a quick non-destructive, qualitative and semi-quantitative method of simultaneously determining the presence of arsenic and mercury in natural history specimens. The lower limit of detection for this technique was determined experimentally to be comparable to a 0.05 percent standard of arsenic, prepared as arsenic trioxide in Chemplex[®] x-ray mix. A typical analysis takes between 200 and 300 seconds. A surface area of approximately three square centimetres is examined with x-rays that can penetrate the feathers and fur to detect arsenic in the skin of a natural history specimen. The instrumentation used to analyse specimens on-site is a Canberra Packard Inspector, a portable x-ray energy spectrometer equipped with a lithium-drifted silicon x-ray detector. A Cd-109 radioisotope is used as the source of x-rays. REXES is predominantly a surface technique that indicates the presence of arsenic and mercury but may not accurately indicate the amount present in the object. The presence of a thick layer of fur or feathers

between the contaminated area and the detector can result in the underestimation of the amount of arsenic present in the skin.

The semi-quantitative results from the REXES surveys are divided into the five groups listed below to indicate relative amounts:

- negative, which indicates that the element in question is below the detection limit;
- trace, in which a specimen has a spectrum comparable to that of a standard between 0.05 percent and 0.1 percent;
- minor, in which a specimen has a spectrum comparable to that of a standard between 0.1 percent and 0.95 percent;
- high, in which the specimen has a spectrum comparable to a standard between 1.00 percent and 5.00 percent; and
- very high, where the arsenic concentration is comparable to a standard above 5.00 percent.

Techniques Requiring Samples: X-ray Microanalysis

When it was not possible to visit the museums within the existing time constraints, samples were removed from the artifacts by the museum conservator and examined in a lab off-site. The sample size for skin, fur, textiles or leather was: a one to two square millimetre sample of skin, a few pieces of hair, the tip or base of a small feather, scrapings of powder samples of an area approximately one square millimetre, or a few fibers of textile. The sample sizes varied between institutions. Hair and feather samples from as close to the skin as possible were requested. The samples were prepared by mounting them on a carbon planchet with double-sided carbon tape and carbon coating. X-ray microanalysis was performed using a Hitachi S-530 SEM (scanning electron microscope) integrated with a lithium-drifted silicon x-ray detector and a Noran Voyager II x-ray microanalysis system. The SEM was operated at an accelerating voltage of 20 kV. Using this technique, elemental analysis of volumes down to a few cubic micrometers can be obtained for elements from boron (B) to uranium (U) in the periodic table down to concentrations of approximately 0.1 to 1.0 percent. In a previous study using this instrumentation, the lower limit of detection for arsenic was determined experimentally to be 0.2 percent (Sirois and Taylor 1989).

Analysis of Swab Samples

Swab samples were taken from selected specimens which contained high concentrations of arsenic to determine whether the arsenic was present on the inside or outside. The techniques used for the analysis of these samples were:

- Fourier transform infrared spectroscopy (FTIR) to identify some organic and inorganic compounds;
- x-ray diffraction (XRD) to identify crystalline compounds;
- scanning electron microscopy with x-ray microanalysis to detect elements from boron (B) to uranium (U) in the periodic table; and
- polarized light microscopy to identify particles.

Table 1. Percentage of museum artifacts/specimens with arsenic, mercury (Hg) and bromine (Br) as identified by x-ray energy spectrometry (REXES).

Museum collection and type of artifacts analysed	Number of artifacts analysed	Percentage of artifacts/specimens where arsenic was detected	Percentage of artifacts/specimens where arsenic >1% was detected	Percentage of artifacts where Hg was detected	Percentage of artifacts where Br was detected
Museum A, natural history and anthropology					
Ornithology	43	81%	26%	2%	19%
Mammalogy	41	78%	29%	12%	10%
Anthropology	24	33%	—	17%	46%
Other	2	50%	—	—	—
Total	110	68%	19%	8%	22%
Museum B, natural history					
Ornithology	130	81%	40%	4%	2%
Mammalogy	43	25%	7%	1%	23%
Total	173	67%	32%	5%	8%
Museum C, natural history					
Ornithology	128	95%	43%	4%	1.5%
Mammalogy	2	—	—	—	—
Total	130	95%	47%	4%	1.5%
Museum D, ornithology	114	98%	29%	3%	—
Museum E, natural history					
Ornithology	144	74%	12%	6%	5%
Other	11	55%	—	—	18%
Total	155	73%	11%	5%	6%
Museum F, anthropology	71	42% (15% minor)	—	18%	86%
Museum G, aboriginal collection, masks					
	111	9% (trace)	—	1%	19%
Museum H, aboriginal collection, masks					
	6	33% (trace)	—	33% (paint)	—
Museum I, aboriginal collection, masks					
	8	13% (trace)	—	—	—

RESULTS AND DISCUSSION

X-ray Energy Spectrometry (REXES) Analysis

The results in Table 1 report the percentage of artifacts analysed where any arsenic was detected (trace to very high groups) and also where high concentrations of arsenic were detected (> one percent, high and very high groups). The presence of mercury and bromine (present or absent only) is also reported as these two elements are generally present as a result of an earlier pesticide treatment. There are some instances, however, where the mercury is present as part of the object itself (i.e., paint).

Natural history collections.—Overall, 81 percent (530/656) of the specimens in natural history collections tested positive for arsenic (range = 25 to 98 percent)

and 5 percent (39/656) tested positive for mercury. Of the birds analysed in Museum B, none collected after 1964 contained arsenic. Mammal specimens from Museum B showed the highest occurrence of bromine (23 percent). Only one of the mammalogy specimens examined in Museum B dating post 1964, a pika skin prepared in 1976, contained any arsenic. Arsenic was detected in most of the bird specimens examined in Museums C and D. These two museums were smaller regional museums with collections containing a substantial amount of material from the late 1800s to the first half of the 20th century.

Of the ornithology specimens which were in the high or very high category in Museum D, several occurrences are worth mentioning. Eleven specimens identified in the high to very high category were from a single collection that dated from 1928 to 1933. Two other groups which had several specimens with high arsenic concentrations were those from the Democratic Republic of Congo in 1938 (five specimens) and others collected in the 1930s in Costa Rica. The high arsenic concentration in three collections dating from the late 1920s to the early 1930s suggests that specimens from this time within these specific collections should be treated with caution. Specimens collected at the same time in hot countries also contained high concentrations of arsenic.

Anthropology collections.—In total, 186 anthropology artifacts were analysed non-destructively. In general, the data from the two larger museums F and G show very different results. In Museum G, 9 percent of the collection contained levels of arsenic less than 0.1 percent (trace). The total percentage of artifacts where either no arsenic was detected or a “trace” of arsenic was found was 91 percent. In the objects from Museum G, bromine was detected in 19 percent of the artifacts. When it was detected, bromine was generally found in the hair portion of the masks.

In Museum F, 71 objects were examined. One interesting feature was that in many of the false face masks the hair attached to the wooden mask contained both arsenic and mercury while the wooden mask did not. This result would imply that the hair was treated with a solution which would have been either brushed or sprayed onto the objects. The results obtained to date from the analyses of aboriginal artifacts, suggest that each museum had its own “pesticide program” and that different results would most likely be obtained for different institutions.

Variability of Arsenic Distribution within Natural History Specimens

Examination of multiple areas on large bird specimens in Museum B illustrated that the arsenic concentration was variable throughout the object, often with the head or the base of the tail containing higher amounts. Approximately two thirds of the specimens analysed had higher concentrations of arsenic in the head and/or tail regions than in the body.

To determine whether the arsenic concentration varied throughout the bird, multiple areas of 17 of the larger bird specimens in Museum D were analysed. Almost half (47 percent) of the 17 bird specimens showed highest concentrations of arsenic in both head and tail regions, 47 percent had greater amounts of arsenic in the body, and six percent had higher concentrations of arsenic in either the head or tail areas. These two surveys illustrated the variability of the arsenic within each specimen as well as differing practices from collection to collection.

Table 2. Percentage of bird and mammal specimens with arsenic and mercury identified by x-ray microanalysis.

Museum collection	Number of samples analysed	Percentage of artifacts/specimens where arsenic was detected	Percentage of artifacts where mercury was detected
Museum J: natural history (Found and Helwig 1995)			
Mammalogy	24	17%	8%
Ornithology	37	76%	—
Total	61	53%	3%
Museum K: natural history			
Mammalogy	31	7%	3%
Ornithology	112	32%	—
Total	143	28%	1%

This has implications for sampling as the results for each sample may differ from location to location.

X-ray Microanalysis Surveys

A total of 204 bird and mammal specimens from two museums were analysed for trace amounts of arsenic and mercury (Table 2). The results from Museum K are noticeably lower, both overall and in the ornithology samples, than the other museums. Whether this is a result of analysing samples taken from the outside of the specimens and not analysing the objects as a whole, or whether the collection is in fact lower in arsenic than most of the collections studied is not certain. Any technique which uses samples is very dependent on the sample taken. Different areas of the same object often contain very different concentrations of a particular compound (Found and Helwig 1995). Samples taken from different locations of both a quetzal and shrike and subjected to spot tests gave results ranging from negative (no arsenic detected) to a very strong positive response on the same artifact (Sirois and Taylor 1989). Examination of surface dust samples and swab samples (see Tables 3 and 4 below) often show far lower levels of arsenic present than is detected through REXES analysis.

From a health and safety point of view the survey did show whether the surface fur or feathers contained arsenic, an important issue for both the conservator and any staff member or member of the public who would come in contact with the collection.

Surface Samples

Some of the swab or dust samples taken contained varying concentrations of arsenic. The remaining samples contained materials such as borax, cornstarch, calcium carbonate, salt, clay or Epsom salts. To date, most of the specimens analysed have contained arsenic on the inside of the specimen or the arsenic has been detected in the fur or feathers from a specimen. It has not generally been present as a pure arsenic dust on the surface, however that is not always the case. In one instance, arsenic was detected by x-ray microanalysis as the major chemical element present in surface powder samples from nine natural history specimens

Table 3. X-ray microanalysis results from dust and swab samples—Museum C.

Sample description	Elements detected by X-ray microanalysis
Control (clean cotton swab)	(Al)
Swab from ornithology specimen #8 (~10% As)	Ca , Si, S, Fe, K, (As)
Swab from ornithology specimen #16 (~10% As)	Ca , Si, S, Fe, K
Swab from ornithology specimen #17 (~10% As)	Ca , Si, S, Fe, As, Cl, K, (Ti/Ba)
Swab from ornithology specimen #24 (~10% As)	Ca, (Fe, Si, As, Pb)
Swab from ornithology specimen #25 (~10% As)	Ca , Fe, Si, (As, Al, S)
Swab from ornithology specimen #80 (~5% As)	Ca , Si , (S, Al, Ti/Ba, Fe, Zn)
Swab from ornithology specimen #83 (~5% As)	Ca, (Si, K, Ti/Ba)
Swab from ornithology specimen #84 (~10% As)	(Ca, Ti/Ba)
Swab from ornithology specimen #89 (~5% As)	Cl
Swab – base of display case	Ca , Fe , Si , S, K, Ti

Chemical Abbreviations Used: Al—aluminum, As—arsenic, Ba—barium, Ca—calcium, Cl—chlorine, Fe—iron, K—potassium, Pb—lead, S—sulphur, Si—silicon, Ti—titanium.

Bold type indicates a major concentration of the element, normal type indicates a minor concentration and () indicates trace amounts. Where spectral overlaps between elements occur, (such as Pb and S or Ti and Ba), both elements are listed in the results table in the following way: Pb/S which indicates Pb and/or S. When low concentrations of these elements are present in the sample it may not be possible to distinguish between the two elements with the x-ray detector used.

donated to a public school. The samples were removed by brushing loose powder from the specimens (Helwig 1994).

In the 11 swab samples from specimens in Museum C, four contained low levels of arsenic in the surface accumulation on the specimens (Table 3). Arsenic was not detected in the remaining seven samples. The major element detected in ten of eleven swabs was calcium.

The examination of the dust samples from museum C, shows that in this instance, while the arsenic concentration present inside the birds is very high, the arsenic in the dust was either not detectable (therefore <0.2 percent) or present at lower levels in the dust (see Table 3). The results from the other samples examined ranged from the identification of arsenic trioxide as a pure substance to the identification of white powders as borax, Epsom salts, starch, plaster, and calcium carbonate (see Table 4). Other compounds which have been identified in powders present on the outside of two artifacts are organic pesticide residues such as DDT which was identified on a bear paw pouch (Miller 1984) and lindane which was identified on a fly catcher (Helwig 1996).

These results indicate that the presence of a white powder on the surface of artifacts can range from highly toxic materials to routine household products. With this in mind, objects should be handled cautiously (Rossol and Sirois 2000) until the identity of the powder is known.

SUMMARY

Six hundred and fifty-six natural history specimens from five natural history collections were analysed non-destructively by x-ray energy spectrometry. Overall, 81 percent of the natural history specimens analysed tested positive for arsenic and five percent tested positive for mercury. Ornithology specimens had the highest occurrence (86 percent) of arsenic.

Table 4. Results of dust samples, Museums D and E.

Sample description	Elements detected	
	SEM/X-ray microanalysis	XRD and FTIR
<i>Museum D</i>		
Ornithology specimen—Nycticorax Ornithology specimen #RM 5211	As Na, (Si S)	As ₂ O ₃ (arsenic trioxide) NaB ₃ O ₅ ·2H ₂ O (sodium borate hydrate) unidentified compound
Ornithology specimen—Rallus/ porzana	Na, (Si, Fe)	Na ₂ B ₄ O ₇ ·5H ₂ O (sodium borate hydrate) probably sodium fatty acid salt (soap)
Ornithology specimen #RM 5821	Na, K, (S)	NaB ₅ O ₈ ·0.95H ₂ O (sodium borate hydrate) K ₂ S ₂ O ₇ (potassium pyrosulphate)
Dust—parrot drawer	Na, Cl, Ca, K, (S, Si)	CaCO ₃ (calcium carbonate)
Ornithology specimen #RM 153	As, Si, S, (K, Fe)	As ₂ O ₃ (arsenic trioxide), starch
Ornithology specimen #RM 363	S, Mg	MgSO ₄ ·6H ₂ O (epsom salt)
Ornithology specimen #RM 146	(Cl, As/Pb, K)	Possibly borax, unidentified compound
Ornithology specimen #RM 365	Na, Cl, Ca, Mg, Si, S	Starch
Ornithology specimen #RM 5404	Na, Cl	Na ₂ B ₄ O ₇ ·5H ₂ O (sodium borate hydrate)
<i>Museum E</i>		
Specimen #L-92-159-Hi white powder	S, Ca	CaSO ₄ ·0.5 H ₂ O (calcium sulphate hemihydrate)
Specimen #L-92-159-Hi yellowish powder	S, Ca	CaSO ₄ ·0.5 H ₂ O (calcium sulphate hemihydrate)
Specimen #L92-58-Hi white powder	Na (S, Cl, K)	
Specimen #X-92-21-Hi white residue	S, Na, (Si, K, Ca)	
Specimen #L-92-190-Hi white powder	As (Sb)	

Chemical Abbreviations Used: As—arsenic, Ca—calcium, Cl—chlorine, Fe—iron, K—potassium, Mg—magnesium, Na—sodium, Pb—lead, S—sulphur, Sb—antimony, Si—silicon.

Bold type indicates a major concentration of the element, normal type indicates a minor concentration and () indicates trace amounts. Where spectral overlaps between elements occur, (such as Pb and S or Ti and Ba), both elements are listed in the results table in the following way: Pb/S which indicates Pb and/or S. When low concentrations of these elements are present in the sample it may not be possible to distinguish between the two elements with the x-ray detector used.

Two surveys where multiple areas on large bird specimens were examined illustrated the variability of the arsenic within each specimen as well as differing practices from collection to collection. One survey illustrated that the arsenic concentration was variable throughout the object, often with the head or the base of the tail containing higher amounts. A second survey showed higher concentrations of arsenic in both head and tail regions in half the specimens, while the other half of the specimens had greater amounts of arsenic in the body. This has implications for sampling as the results for each sample may differ from location to location.

In total, 186 artifacts from anthropology collections were analysed non-destructively. In general the data from different museums show very different results. In one museum, nine percent of the collection contained levels of arsenic less than

0.1 percent (trace) and bromine was detected in 19 percent of the artifacts, usually in the hair portion of the masks. In another museum 86 percent of the artifacts showed the presence of bromine, 42 percent contained traces of arsenic, and 18 percent traces of mercury. One interesting feature was that in many of the false face masks the hair attached to the wooden mask contained both arsenic and mercury while the wooden mask did not. The results obtained to date from the analyses of artifacts from anthropology collections, suggest that each museum had its own "pesticide program" and that different results would most likely be obtained for different institutions

Swab samples were taken from selected specimens which contained high concentrations of arsenic to determine whether the arsenic was present on the inside or outside. Some of the swab or dust samples taken contained varying concentrations of arsenic. The remaining samples contained materials such as borax, cornstarch, calcium carbonate, salt, clay or Epsom salts. In one instance, arsenic was detected by x-ray microanalysis as the major chemical element present in surface powder samples from nine natural history specimens donated to a public school.

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OPEN DISCUSSION 3

- An attendee said she feared that the pesticide issue would be used to stop the repatriation program.
- Penelope Edmonds, Senior Conservator, Museum of Victoria, Australia, said that similar issues were being faced with aboriginal artifacts.
- Steve Henrickson, Curator of Collections for Alaska State Museum, Juno, said the issue of contamination is much on the minds of native Alaskans. He said there was less of a need to douse Alaskan artifacts with pesticides because the state has fewer bugs. Because the population of native Alaskans is high, museums there have always had a good working relationship with them.
- Dale Ann Sherman of the Yurok Tribes, a NAGPRA representative, said it was a good thing for everyone to come together and talk about the issue. She said it is even better to look for solutions.
- Yolanda Chavez said she first became interested in the pesticide issue in 1992 while attending a workshop at the Smithsonian. She said this issue would not stop the repatriation process. She represented six tribes at the conference that want to get as much information as possible in order to make informed decisions. She was happy that this was being made a national issue. California tribes have been invited to develop part of the agenda for the May 2001 NAGPRA Review Committee meeting at Clear Lake, California.

THE IDENTIFICATION OF FOUR PERSISTENT AND HAZARDOUS RESIDUES PRESENT ON HISTORIC PLANT COLLECTIONS HOUSED WITHIN THE NATIONAL MUSEUM AND GALLERIES OF WALES

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Abstract.—Natural history specimens can remain contaminated with pesticide residues years after the chemical was originally applied. The problem facing conservators and curators is that the collections may pose a risk to health through working with the collections. Analysis was conducted to identify whether the National Museum of Wales (NMW) Herbarium posed such a threat. The results identified four residues and established high concentrations. Quantitative and qualitative results were attained through Atomic Absorption Spectrophotometry (AAS), Tandem Mass Spectrometry (MS-MS), Flow Injection Mercury System-AAS (FIMS-AAS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Mercury (Hg), arsenic (As) and barium (Ba) were found in high concentrations e.g., one specimen held 1000 PPM of mercury. Naphthalene (C₁₀H₈) was also identified but not quantified. Biological monitoring has indicated that staff members handling the collections had become contaminated with arsenic and mercury. The possible routes of contamination are through inhalation, ingestion and absorption. Safe standard procedures were implemented to reduce the contamination through working on the collections. Within one year the biological monitoring provided evidence that all previously elevated levels had returned to normal in all members of staff.

Because of the organic nature of most museum collections, there has been the need to protect the material from biological attack. If a specimen or object has not been damaged through biodeterioration in over twenty years, then it is probable that the object has been treated with a toxic chemical. It is unlikely that many of the natural history specimens or ethnographic materials of museum collections would have survived the last three hundred years without the aid of pesticides and fungicides.

Natural science curators have concocted numerous chemical recipes to provide successful pest and fungal eradication. Mercuric chloride has been applied as a fungicide by many of the larger botanical institutions. Cambridge University Herbarium painted plant specimens with ethanol, phenol and mercuric chloride (Briggs et al. 1983). Bird and mammal skins frequently had chemicals applied such as arsenical soaps to aid cleaning and fat removal. Specimens have been treated with a range of chemicals and their use has rarely been documented. This problem could be compounded by their subsequent exposure to a variety of other pesticides over the course of their lifetime through reapplication. The problem faced today by curators and conservators is that the collections may be contaminated with the remaining chemical residues and these may pose a risk to health. Data very rarely accompany the object/specimen with regards to its chemical history. Occasionally a stamp would state the word POISONED or show the "skull and cross bones," but the chemical may have been applied many years

ago. It was common practice in the larger UK institutions to repeat applications since corrosive sublimate, for example, was reported to become inert over time, necessitating fumigation or re-poisoning (Merrill 1948). The problem now arising is that common applications and the re-applications of mercuric chloride and arsenic trioxide are producing high concentrations of mercury and arsenic after many years, as the heavy metals do not dissipate over time. Another important issue is the possibility that the pesticide applied may have altered through time. Metals such as mercury and arsenic can be methylated naturally over time. In the case of mercuric chloride this would give rise to methyl mercuric chloride, which is extremely toxic. Chlorinated compounds can break down and become altered; for example DDT can degrade to DDE. This presents another problem, as the accurate identification of a pesticide is only possible if the compound being identified is suspected prior to analysis.

Since 1988 The Control of Substances Hazardous to Health (COSHH) has prohibited the use of a number of pesticides including mercuric chloride in the UK. These regulations were aimed to protect workers and were introduced under the Health and Safety at Work Act of 1974 within the forum of the Health and Safety Commission. Before using any chemical, its possible risk must be assessed and its use, storage and disposal have to be fully documented by the user by completion of a COSHH form. Gaining this information has become easier since it is now common practice in the UK for manufacturers of chemicals to send out risk assessment data with each new chemical purchased. Environmental Health booklets published by the Health and Safety Executive (HSE), such as EH40 (HSE 2000), also produce information relating to the levels of safe exposure of banned and permissible chemicals. The Environmental Protection Agency (EPA) and the Occupational Safety and Health Administration (OSHA) provide this data for Canada and the United States.

Staff members and some visitors tend to be in close contact with specimens and the lack of documentation can prevent the correct precautionary measures being taken when handling or studying these specimens. Another source of concern regards genetic work on zoological or botanical material. It would be beneficial to know which chemicals were applied, as certain chemicals such as arsenic compounds and chromates affect both extraction and amplification of DNA (Hall et al. 1997).

The National Museum and Galleries of Wales (NMGW) Department of Biodiversity and Systematic Biology is home to the National Museum of Wales (NMW) Herbarium. (The museum was given gallery status in 1994 but the herbarium remains as NMW as published in *Index Herbariorum*.) The herbarium houses approximately 500,000 specimens dating back to the 1700s. Arsenic and mercury pesticides and fungicides were first applied around this time and because of the stability and toxicity of these metals they still pose a threat to health and safety today.

The NMW herbarium has no documentation accompanying the collections that have been donated to the museum or regarding its own methods of preservation. However, a metal coal bunker style building was used as an area for specimens to be placed for fumigation with carbon disulphide. It was used from about 1970 until 1977 when its use ceased (T. Tipper pers. comm.). From 1930 onwards it is

Table 1. Results from literature search and survey on chemicals stated as being used on herbarium material by 22 institutions from 12 countries.

Chemical applied	Number of institutions using the chemical	Chemical applied	Number of institutions using the chemical
1 Arsenic trioxide	2	9 Mercuric chloride	5
2 Barium fluorosilicate	1	10 Methyl bromide	6
3 Carbon disulphide	4	11 Naphthalene	7
4 Carbon tetrachloride	1	12 Paradichlorobenzene	6
5 DDT	2	13 Phosphine	3
6 Ethylene oxide	3	14 Pyrethrum	5
7 Lauryl pentachlorophenate	2	15 Hydrogen cyanide	1
8 Lindane	0	16 Vapona/Dichlorvos/ Dichlorodimethylvinyl phosphate (DDVP)	3

thought that paradichlorobenzene was applied to the zoological specimens and naphthalene was placed within botanical cabinets (T. Tipper pers. comm.).

A condition survey was conducted on the botanical collections in 1993 to ascertain the condition of a small collection of gymnosperms housed in a temporary location. Grey spots and yellow tidemarks were present on several of the specimens surveyed. These were not believed to be organic applications. Senior curators within the department suggested that the stains were most probably arsenic or mercury applied outside of the institution. Since both mercury and arsenic are extremely toxic and stable, a method of confirming their presence was essential. Before analysis could begin, it was imperative to determine which chemicals might have been applied to the collections. A comprehensive list of the possible pesticides used in the history of plant collecting was drawn up through a literature search. From this information a survey form was produced that was distributed to key botanical institutions in the UK and abroad. Thirty institutions were approached and 22 responses were received (Table 1). This information served as a basis although it is possible that many more chemicals were applied to the collections. The institutions did not state whether the chemicals were still in use, although 10, 11, 12, 14 and 16 are still used in the UK. (10 is shortly to be discontinued.)

ANALYSES AND RESULTS

In 1996 a research opportunity arose with the University of De Montfort, Leicester, and analysis of the collections began for their pesticide and/or metal content.

Simple tests such as the revised Gutzeit test for mercury (Feigl and Anger 1972) and for arsenic (Hawks and Williams 1986) were employed for the simple identification of these heavy metals. The arsenic spot tests have been successful with zoological material (Found and Helwig 1995) but were not sensitive enough for analysis of paper samples (the herbarium sheets). Zoological specimens generally have so much residue present that it is visible as a white powder. NMW botanical specimens have no such residues lying on the surface; instead it has soaked into the paper. To obtain some of the residue from the paper more sensitive

methods were required, involving the digestion or extraction of the sample as swabs were not effective.

Through collaboration with the University of Derby it was possible to use a wide range of analytical instruments. The findings and usefulness of the equipment has been tabulated (Table 2). All methods were destructive but X-ray Fluorescence (XRF), Energy Dispersive X-ray (EDAX) and Tandem Mass Spectrometry (MS-MS) were capable of analysing the paper without any preparation. The paper samples were cut to size and inserted for analysis, which reduced sample preparation time and possible errors from solvent dilution, contamination, and evaporation.

The analysis identified four main chemicals on a cross section of botanical material: arsenic, barium, mercury and naphthalene. Naphthalene was expected, as it was known that the NMW herbarium applied this to the cabinets, and mercuric chloride and barium fluorosilicate were well-known fungicides and pesticides within herbaria. It was not foreseen that arsenic would be present as it was applied more regularly to zoological than to botanical collections. Several different methods were used and served to identify the best and most accurate analytical instruments for the purpose.

Table 3 shows the variation in results for four different methods of analysis. Based on the XRF analyses, six samples would give rise to 4905.8 $\mu\text{g/g}$ (ppm) of mercury. The risk of exposure from handling this material is therefore very high. Toxicology data for the four targeted pesticides are given in Table 4. Because of the high concentration of mercury found on some of the sheets it was vital to inform all members of staff and heads of department. The herbarium was closed down for three months and notices were displayed in all areas (Fig. 1). Air quality control was carried out and key herbarium workers were biologically monitored for arsenic and mercury contamination. A part-time staff member who had been in contact with one collection (ca. 1800s) for three months and complained of itchy, sore skin on their hands and a tingling in their fingers was found to have elevated arsenic levels.

An external analyst was employed to monitor the air quality around the botany department. In this instance only mercury vapour was investigated. An air pump calibrated by standard bubble meter was employed to draw air through the monitor at a rate of 2 litres per minute for a period of three hours. The air is drawn through a 0.8 μm mixed-cellulose ester membrane (MCE) filter. If mercury is present in the air sample it will bind to the filter. The filter is then removed, digested in acid and analysed using a cold vapour-atomic absorption spectrophotometer (CV-AAS). Nine sample sites were analysed including work areas and the interior of herbarium cabinets. All of the sites showed levels below 0.0001 mg/m^3 , which were well below those recommended in the Health and Safety Executive guidelines (TWA 0.025 mg/m^3). The qualitative and quantitative detection limits for the analytical procedure were 0.01 μg and 0.02 μg respectively.

The NMGW herbarium is in a large area with an aged but adequate ventilation system. The air circulation within the herbarium together with the constant use of the collections prevents the build up of mercury vapour from the specimens within the work area and cabinets. Similar institutions such as Cambridge and Oxford University Herbaria have had very high mercury vapour readings due to the lack of a satisfactory ventilation system. These institutions employed external

Table 2. Results of paper analysis for organic and inorganic residues.

Analytical process	Specifics	Identifies	Results and comments
*Arsenic spot test	Requires reagents, potassium, hydroxide, zinc, hydrochloric acid and copper (I) chloride	Arsenic	Surface technique, not sensitive enough for this work. No conclusive results.
*Mercury spot test	Surface technique requires reagent 1,5-diphenyl hydrazone and nitric acid	Mercury	Surface technique, not sensitive enough for this work. No conclusive results.
Energy Dispersive X-ray (EDAX)	Scanning electron microscope with EDAX Cambridge 250, Mark 3	Inorganic species	Indicates presence or absence. Surface technique. Produced results for arsenic. No preparation required.
Cold Vapour Atomic Absorption Spectrometry	Perkin Elmer Flow Injection Mercury System (FIMS)	Mercury	Recommended method for mercury. Sample digestion and filtering required before analysis.
Tandem Mass Spectrometry (MS-MS)	VG TRIO 3	Specified organic and inorganic species	Very fast and accurate method. Recommended for specified organics. No preparation required. Analyses solids.
Inductively Coupled Plasma Mass Spectrometry (ICP-MS)	PE-SCIEX Elan 6000	All inorganic species in one run	Recommended method for unknown inorganics. Sample digestion and filtering required before analysis.
Inductively Coupled Plasma Atomic Emission Spectrophotometry (ICP-AES)	Perkin Elmer Plasma 40	A specified metal	Highly erratic results for mercury due to carry over from subsequent runs. Preparation of standards, sample digestion and filtering before analysis.
X ray Fluorescence (XRF) Spectrometers	SPECTRO XEPOS bench top EDP-XRF	All inorganic species in one run	Easily interpretable results, very fast, 12 samples in 20 minutes. No preparation required. However, there may be interfering metals leading to errors (see table 3). Use in conjunction with AAS or ICP-MS.
Atomic Absorption Spectrophotometry (AAS)	Perkin Elmer 1100B	Specified metals	Cheap, fast, readily available and accurate. Preparation of standards, sample digestion and filtering required before analysis.
Gas Chromatography Mass Spectrometry (GCMS)	TRIO-1 MS attached to Hewlett Packard 5890 gas chromatograph	Specified organics	Slow, 40 minutes for a conclusive run. Preparation requires sample extraction and filtering before analysis.

* These results are both revised Gutzeit methods (Feigl & Anger 1972) developed for natural history specimens by Steven Weber at the University of Pittsburgh. Only the arsenic technique has been published (Hawks & Williams 1986); however, the mercury test has been upgraded since and published (BDH 1996).

Table 3. Results of mercury concentrations showing comparisons with different instrumentation.

Sample number	AAS μg/g (ppm)	FIMS μg/g (ppm)	MS-MS	XRF μg/g (ppm)	ICP-MS μg/g (ppm)
A	Not tested	1021	Not tested	3090	717.4
B	Not tested	0.96	Not tested	Not tested	5.82
C	Not tested	1.2	Present	19.6	6.42
D	Not tested	3	Not tested	34	27
E	Not tested	0.5	Not tested	3.4	1.9
2	423.69	3	Not tested	1750	Not tested
4	3.98	Not tested	Not tested	8.8	Not tested
Detection limits	≅2.5 ppm	≅10 ppb	—	≅17 ppb	≅0.01 ppm

ppm = Parts per million

ppb = Parts per billion

The variation in results is attributed to the sensitivity and suitability of the instrument and to the sampling method. The herbarium sheet to be analysed may not have an even distribution of residue throughout, so each sample could give varying results, also in some cases it was not possible to see where the pesticide had originally been applied.

analysts to monitor the herbarium air quality and staff also wore personal air monitors to determine TWA over an eight-hour day. Other such devices that can provide immediate detection of mercury vapour include mercury sniffers, mercury vapour indicators, mercury badges and dosimeters (dosemeters in UK). Badges and dosimeters can be worn on the lapel and the period of wear is timed. A colour change will indicate whether the mercury vapour level has been exceeded within that set period of time. Taking temperature and humidity into account, the badges give accuracy within 15–20% (Walton pers. comm.). These devices may not be accurate, but they do give indications of the presence or absence of mercury vapour. Mercury vapour indicators and sniffers are battery operated, hand-held devices that draw ambient air through the instrument by aid of a pump. The air is analysed by an ultra violet technique and a reading is given instantly. These instruments are calibrated but error is within 10%. The one drawback of this instrument is that petrol fumes will interfere with the mercury detection (Walton pers. comm.). The mercury passive sampler is a hand held device that pumps air through a copper manganese oxide mixture. This absorbs the mercury onto it and the whole device is then sent away to be analysed. This method is by far the most accurate as an exact TWA can be achieved.

The NMGW health centre recommended that blood and urine samples were taken and analysed for both arsenic and mercury. Blood samples give information on contamination within a five-day exposure of organic mercury whereas urine will provide information relating to the past three months of possible exposure to, and contamination from inorganic arsenic, organic and inorganic mercury. For an accurate baseline result it is important to avoid fish of any sort seven days before the test, as this can interfere with the final result, since fish can be a high source of these heavy metals. Two members of staff were found to have slightly elevated levels of both mercury and arsenic above the normal levels set by the Super Regional Assay Laboratories in accordance with the Health and Safety Executive (UK), but not sufficiently high to cause serious alarm. It was recommended that they were referred for further tests after a period of six months,

Table 4. Toxicology data for the residues found on the botanical collections.

	Mercuric chloride mg/m ³	Arsenic trioxide mg/m ³	Barium fluorosilicate mg/m ³	Naphthalene	
				mg/m ³	ppm
STEL	0.015	0.002	—	80	15
LTEL	0.025	0.01	0.5	53	10
Routes of entry into system	Absorption through skin Inhalation Ingestion	Absorption through skin Inhalation Ingestion	—	Absorption through skin Inhalation	
Short term effects	Eye contact = irritation, burns, even permanent damage. Central nervous system damage. Breathing = lung irritation, coughing, possible pulmonary oedema	Hoarse voice, irritation of nose, eyes, skin and mucous membranes Nausea, vomiting, diarrhoea, weakness, loss of appetite, coughing, chest pain, giddiness, headache, breathing difficulty	Barium poisoning results in a rapid onset of paralysis, gastrointestinal symptoms, cardiac dysrhythmias, hypertension, and often severe hypokalemia. The acute syndrome can be fatal*	Irritation of nose, eyes, skin and throat	
Long term effects	Sore gums, shakes, memory loss, weakness, loss of teeth, poor appetite	Damages the heart, brain, lungs, gastrointestinal tract and kidneys. Eventual skin, bone marrow and peripheral nervous system damage. 1 ppm = serious illness	Repeated or chronic exposures have been reported to cause osteosclerosis, as with fluoride	Clouding of the eye lens. Damage to the red blood cells, liver and kidneys. Skin allergy. Fatigue headaches, and nausea	
Minimum lethal exposure in adults	300 mg/L excreted in urine represents mercury poisoning	120–200 mg	Barium compounds range from 29–226 ppm	2–15 g	
Acute effects	Headache, flu symptoms, fever, dry mouth and throat. Gastrointestinal symptoms	Delayed hair loss, convulsions, tremors, vomiting and diarrhoea	—	Eye irritation	
Chronic effects	Tremors to hands and arms, lips and tongue, lack of self control, loss of memory, vascular collapse, lesions and death	Melanosis, facial edema, skin cancers, vomiting and diarrhoea	—	Severe haemolytic anaemia	
Carcinogen	Possible	Class A oncogen	—	Not tested	
Reproductive problems	Foetal damage and genetic mutations	Malformations of mice/rat offspring	—	—	

This data has been accumulated from Ellenhorn et al. (1997) and courtesy of the Welsh National Poisons Unit, Llandough Hospital, Cardiff, Wales, UK.

STEL = Short term exposure levels usually within a 15 minute period (HSE 2000).

LTEL = Long term exposure levels usually within an 8 hr day, 5 days a week. (HSE 2000).

— Denotes no information available at present.

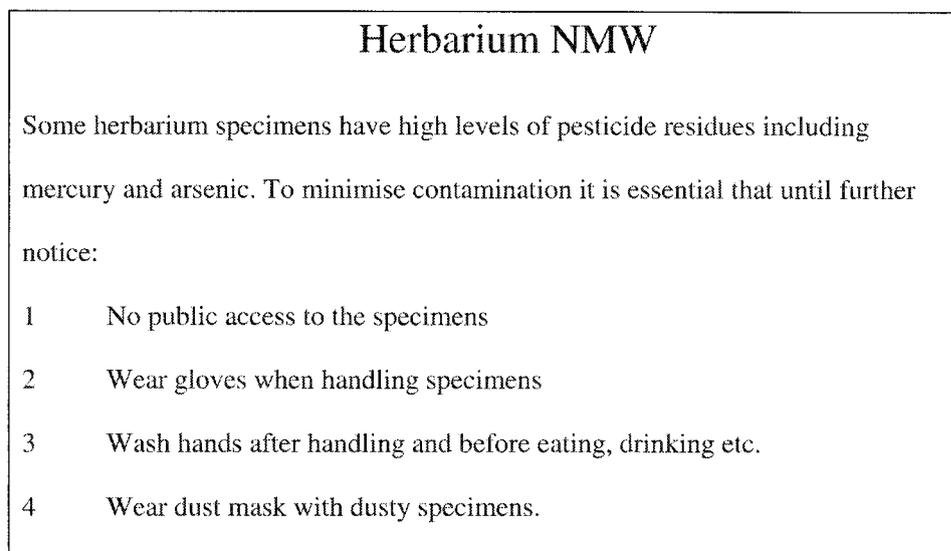


Figure 1. Notice to herbarium workers regarding the possible risk of contamination.

however this was not authorised and the re-tests commenced sixteen months later. One of the two staff members was only in employment for three months and so their results could not be obtained. Due to the confidential nature of the material only a small proportion of the data could be published.

Mercury and arsenic analysis was a relatively new field for the museum health centre and unfortunately only three out of six complete results were kept and recorded. Staff members A and B work on a mixture of botanical material but mainly historic; C is responsible for collecting, identifying and curating fresh material, but there is periodic contact with historic material; D was working on a historic collection for three months only and therefore was not in employment for the final test.

Normal working practice resumed up until the test. The only precaution taken was to avoid fish and seafood for seven days before the test. The biological monitoring results (Table 5) show a significant amount of mercury and arsenic in the urine; however the air quality results proved negative. It is reasonable to assume that in this case mercury and arsenic are entering the system through other means than inhalation such as ingestion and absorption. The initial tests were conducted in November 1998, with re-testing in March 2000. Blood samples were taken from the first staff members to be tested but as the levels were so low this procedure was not repeated. After sixteen months of safe standard procedures, all arsenic and mercury levels had returned to well within the normal guidelines recommended by the Health and Safety Executive UK.

The wearing of nitrile gloves when working with the collections has become standard practice. After use these are disposed of. It is obligatory not to eat, drink or smoke with the gloves on and hands should be washed after the removal of the gloves and after handling material. Work on collections should only take place in well-ventilated areas and close work should be minimised; for example a microscope would replace the use of a hand lens.

Table 5. Results of biological monitoring before and after safe standard procedures were implemented.

Staff members and test date	As/creatinine $\mu\text{g/g}$	As normal levels $\mu\text{g/g}$	As industrial concern $\mu\text{g/g}$	Hg/creatinine $\mu\text{g/g}$	Hg normal levels $\mu\text{g/g}$	Hg industrial concern $\mu\text{g/g}$
A 1998	12	10	50	9.75	8.125	32.5
A 2000	5			2.8		
B 1998	6			7		
B 2000	1			2		
C 1998	1			0.1		
C 2000	2			1.4		
D 1998	11	↓	↓	Not detected	↓	↓

These reference levels have been established in the UK by the Supraregional Assay Services Laboratories within the National Health Service in collaboration with the Health and Safety Executive.

RECOMMENDATIONS

Health monitoring, such as attaching a personal vapour detector to the clothing, would give an accurate level of exposure to the worker within an 8 hour day. A dosimeter badge would give an immediate visual indication of mercury concentration (Ellenhorn et al 1997:1592). Dosimeters and mercury vapour indicators are a simple and effective method of monitoring the presence of mercury vapour but more sensitive instrumentation will provide more accurate results. Wearing nitrile gloves and ensuring that the working environment is well ventilated is now standard; however further precautions can be taken.

One recommendation could be to work on the collections within a fume cabinet. This removes any contamination of gas/vapour or particulates through inhalation and ingestion. Placing activated charcoal or Microchamber[™] board within cabinets will attract the toxic vapours onto the surface of the charcoal thus removing it from the air. Microchamber[™] paper could be placed in contact with an object that may come into direct contact with the skin.

Heat treatments have been developed with regards to organic decontamination and the subsequent reduction in PCP's (pentachlorophenols) and Lindane has been successful (Rotberg et al. 1997). This approach could also be applied to reducing naphthalene/paradichlorobenzene that has permeated collection cabinets.

CONCLUSION

The results have shown conclusively that the collections are holding high concentrations of chemicals that are able to contaminate staff and visitors that come into contact with the collections. The toxicological information stresses the hazards that the contaminants pose and therefore safe standard procedures must be implemented if work is to continue on the collections. The NMW Herbarium is still being accessed. It is too important a resource not to be used and so a strategy had to be implemented that allowed staff and visitors to protect themselves. Information relating to the possible hazard has been placed within the herbarium. All staff and visitors must read and then sign a form indicating that they have read, understood and will comply with the procedures of the herbarium to keep themselves safe.

Further research is necessary to identify the extent of contamination of the entire collection continuing with inorganic and organic residues. Research into this area is now being undertaken with De Montfort University. Carbon disulphide and naphthalene will be expected but it is quite possible that other residues will also be present.

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RESOURCES

Further information can be obtained on the analytical techniques from a number of websites including the following:

- FIMS and AAS can be found at <http://www.semiconductoronline.com/storefronts/perkin-elmer.html>
- XRF and EDAX at <http://www.kratos.com/XRF/EDX7001.htm>
- GC-MS at <http://www.shsu.edu/~chemistry/primers.gcms.html>
- ICP-MS and MS at <http://www.astm.org/DATABASE.CART/PAGES/E1024.htm>

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PHOTODESTRUCTION OF MALATHION ON SURFACES

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Abstract.—At least twenty years ago it was learned that excimer laser radiation in the ultraviolet portion of the spectrum can be used to destroy and/or remove toxic and hazardous chemicals from surfaces of skin, fabric, plastic, rubber, paint, wood, and metal without damaging those surfaces. The investigation reported herein was performed to determine whether ultraviolet radiation from a simple and inexpensive xenon flashlamp is equally effective. Tests were performed with an ultraviolet flashlamp to remove and destroy Malathion on glass plates and painted surfaces. Destruction rates, Malathion fragment species, and surface damage character were all noted. As flashlamp-induced decontamination of the test surfaces was found to be comparable to that determined previously with lasers, it is probable that flashlamp effectiveness on organic and porous materials will be analogous to that determined with lasers. It is concluded that flashlamp radiation may be effective in decontaminating Native American museum artifacts with as few as three flashlamp pulses at a flux of about 3 J/cm². However, proof tests will have to be performed on authentic historic materials in order to validate this extrapolation.

INTRODUCTION

In bulk form insecticides and other toxic chemicals are usually disposed of through high-temperature incineration. On surfaces decontamination is frequently accomplished through vigorous washing with caustic chemical solutions (Smee 1982). Obviously, unique and fragile museum artifacts that have become contaminated with dangerous substances cannot be subjected to either of these remedial measures without considerable risk of alteration, damage, or destruction.

It has long been known that organic molecules can be broken down through exposure to sunlight. This is most often observed as fading or bleaching. Although solar decontamination can be effective (e.g., in large-scale oil spills), it is a very slow process. Further, just as solar radiation breaks down toxic chemicals, it decomposes organic materials such as the dyes, fibers and textiles that comprise much of the fabric of many museum collections. The common fading and deterioration of everyday wearing apparel is in part a consequence of this solar effect.

With the invention of high-performance ultraviolet (UV) excimer lasers over twenty years ago it became technically feasible to accomplish high-speed photodecontamination. Laser technology made it possible to apply arbitrarily high UV fluxes to surfaces so that chemical decontamination could be accomplished rapidly. The UV photon, the unit of energy imparted here, is ideally suited for the destruction of toxic molecules. It is slightly larger than the energy holding these molecules together in their lethal form. Imparting this much energy to the chemical dramatically increases its reactivity. It may fall apart, rearrange, or react in order to deal with its energy content. It is thereby denatured. Further, a laser's parameters (viz., wavelength and pulse length) may be adjusted to minimize or avoid damage or alteration to the surface being exposed to the ultraviolet light. In the decade of the 1980s this procedure was developed to counteract the chemical warfare threat posed by countries such as Iraq. Laser systems were developed that, after a chemical attack, could safely decontaminate human skin, fabric uni-

forms, buildings, furniture, windows and canopies, weather stripping and ordnance equipment (Outterson and Prociv 1980).

Laboratory experiments performed in response to the perceived chemical warfare threat (Radziemski 1981) revealed that pulsed ultraviolet (PUV) energy could rapidly and efficiently destroy chemical nerve agents such as GD ($C_2H_{16}PO_2F$), EA 1699, and VX as well as agent simulants such as bis (2-ethylhexyl) hydrogen phosphite, 2-chloroethyl-ethyl sulfide, and di-isopropylflourophosphonate. As these chemical nerve agents (effective against humans) are chemically similar to pesticides (nerve agents against insects), it is plausible to assume that high-power PUV (Pulsed UV) light may be effective in destroying insecticide residues on the surfaces, as well. Further, it should be possible to safely decontaminate with flashlamps as there is an extensive record of successful, damage-free, laser cleaning of delicate museum artifacts with UV fluxes and fluences comparable to those used in the military to decontaminate human skin, communication equipment, and computers.

LASER MALATHION EXPERIMENT

To prepare and calibrate for the flashlamp experiments and in order to evaluate the hypothesis that PUV laser radiation ought to be able to denature insecticides on surfaces, a series of irradiation experiments was performed with the familiar pesticide Malathion (O,O-Dimethyl dithiophosphate of diethyl mercaptosuccinate with Trade name Cythion, American Cyanamid Co., and used as ingredient in museum and domestic sprays and dusting insecticides from the late 1950s to the late 1980s) as a test case.

For the initial experiments a KrF excimer laser at a wavelength of $0.25 \mu\text{m}$ was operated in a single-shot mode and adjusted to a pulse energy of one joule and a spot size of one square centimeter incident on a glass slide. Analytical grade Malathion was applied to the 1cm spot on the slide by dissolving $500 \mu\text{g}$ in CH_2Cl_2 , applying a drop, and allowing the solvent to evaporate before firing the laser. The photodestruction of the Malathion was tracked by measuring with a UV photodiode, as commonly employed in military contamination monitors, the fluorescence emitted from the irradiated zone during each laser pulse. The results are shown in Table 1.

The approximate data presented in Table 1 from cursory probative experiments establish that PUV radiation has comparable effectiveness in Malathion decontamination as has been observed with chemical nerve agents. Elsewhere, it has been extensively demonstrated that for surface cleaning, laser fluences and fluxes in this range can be applied to representative museum artifacts without causing damage (Asmus 1987, Gaetani and Santamaria 2000, Kautek et al. 2000, Kolar et al. 2000, Wiedeman et al. 2000). Thus, it appears that the application of PUV

Table 1. Malathion decontamination by pulsed ultraviolet (PUV) irradiation.

PUV source	No. of pulses	Total fluorence (J/cm^2)	% Removal
KrF LASER	1	1	60
KrF LASER	2	2	90
KrF LASER	3	3	100

radiation to the surfaces of contaminated museum artifacts may be a plausible route to their decontamination.

DECONTAMINATION WITH XENON FLASHLAMP RADIATION

The military decontamination program focused on the use of excimer lasers. This approach presents several impediments to implementation in the museum field. These stem directly from the character of the excimer laser. Specifically, they are large, complex, inefficient, and expensive. Thus, they are an impractical tool to be introduced into a museum or conservation environment (for anything other than the most precious of artworks).

There is a widely utilized alternative route to the production of high-power PUV radiation. This is the xenon flashlamp that has been the key technology in "flash" and "strobe" photography for more than a half century. Advances in the strength of glass-to-metal seals and the purity of fused-silica (quartz) tubes that transmit UV have led to the development of flashlamps that are efficient and powerful PUV sources.

Although decontamination with UV lasers has been shown to be primarily a thermal effect, rather than a photochemical effect, the light radiation does contribute somewhat to decomposition of the vaporized chemicals. In this regard, the polychromatic light produced by flashlamps is advantageous relative to monochromatic light produced by lasers. Monochromatic light tends to break only those chemical bonds that are activated by wavelengths of the particular laser line. The breaking of particular bonds in certain toxic chemicals that may occur when exposed to monochromatic (laser) light may produce daughter chemicals that are also toxic. Broadband radiation (e.g., flashlamp light), on the other hand, would be expected to photochemically decompose a wider range of chemical bonds and to fragment the contaminant into more elementary units, which are less likely to be toxic.

In summary it appears that PUV from xenon flashlamps may be both more cost effective and more thorough than excimer lasers in decontaminating surfaces. The only advantage accompanying the use of a laser would be its ability to send a highly collimated beam over great distances. This, of course, is not relevant in a laboratory environment. Thus, experiments were performed to determine the prognosis for flashlamp insecticide decontamination for application in the museum and/or conservation laboratory.

XENON FLASHLAMP FEASIBILITY EXPERIMENT WITH MALATHION

A test program was formulated to explore the effectiveness of flashlamp PUV for the decontamination of surfaces with pesticide contamination. Accordingly, closed cells were built out of a short segment of aluminum tube and two quartz windows, one-sixteenth inch thick and three inches diameter, sealed on the ends of the tube by rubber O-rings. Their interiors were cleaned to analytical standards and 500 μg of analytical grade Malathion was deposited on the inside of the bottom window and the solvent was allowed to dry completely before the cells were sealed.

Two cells were irradiated at a flashlamp distance of 6 cm. A first cell was irradiated once and a second one ten times. A third cell, to be used as a control, was not irradiated. Immediately after the irradiation an optical calorimeter was

placed at the same location as the cell and the optical energy density was measured as 2.9 J/cm^2 over a circular aperture 3.8 cm in diameter centered on the middle of the five inch linear flashlamp (13 mm bore).

The two irradiated cells and the control were then analyzed by gas chromatography/mass spectroscopy (GC/MS). This was accomplished by washing each disassembled component of each cell with CH_2Cl_2 to detect the Malathion remaining on the bottom window and any that could have redeposited on the walls or cover window. Samples of gas extracted from the cells were also analyzed by GC/MS. It was determined that 15 percent of the Malathion was removed by one pulse, 10 percent of that amount was found redeposited on the walls of the cell. After ten pulses 75 percent of the Malathion was removed from the bottom window, and none was detected on other portions of the cell. The gas from the cell exposed to one pulse contained CO_2 and diverse organic polymers such as $\text{C}_2\text{H}_5\text{OH}$ and $t\text{-C}_4\text{H}_{10}$. The gas from the cell exposed to ten pulses contained CO_2 and diverse organic polymers such as $\text{C}_2\text{H}_5\text{OH}$ and $i\text{-C}_3\text{H}_7\text{CH}_3$. Microscopic examination of the substrate failed to reveal any damage.

A second test series was performed in order to determine whether a higher flashlamp intensity would increase the rate of Malathion destruction. Unfortunately, operating flashlamps at higher intensities reduces lamp life, which entails more frequent lamp replacement and a correspondingly higher overall decontamination cost. By increasing the power supply voltage to the flashlamp the energy density at the Malathion surface was more than doubled to 6.4 J/cm^2 . At this irradiation level 33 percent of the Malathion was removed by one pulse and none was found redeposited on the cell walls. The second cell received two pulses and 80 percent of the Malathion was removed. Again, no Malathion was detected on the other surfaces indicating that it was destroyed rather than being merely moved around. Again, no substrate damage could be detected.

DECONTAMINATION OF A PAINTED SURFACE

Having demonstrated that Malathion can be removed from, and destroyed, when applied to quartz glass, it is of interest next to know whether it is possible to decontaminate a surface more representative of a museum artifact without inflicting damage. For such a proof-of-principle test gray epoxy spray paint was applied to a sheet of aluminum. A thick layer of commercial Malathion was smeared onto the surface and allowed to air dry for two hours. The resulting film was easily visible to the naked eye.

At a setting of 6.4 J/cm^2 one pulse was sufficient to remove most of the visible Malathion. No funds were available for analytical work for this series; however, some slight etching of the epoxy coating was evident. The experiment was repeated at 2.9 J/cm^2 . At this level two pulses were required to remove most of the visible Malathion. But at this 2.9 J/cm^2 flux level the two pulses did not appear to etch the paint layer at all.

The efficiency of flashlamp Malathion decontamination of the very thick films at these relatively modest fluences suggests that the presence of the colored epoxy actually improves the process. It is probable that the enhanced absorption of the paint over that of the glass in the initial experiments leads to higher transient vapor temperatures so that the photochemical decontamination is augmented by thermal decontamination. However, as these fast phenomena are non-LTE (Local

Thermodynamic Equilibrium) transient conditions, one cannot necessarily conclude that surface damage is more likely.

CONCLUSIONS

The probative experiments recounted herein have shown efficient removal of Malathion as well as virtually complete denaturization at all but the lowest flash-lamp fluences. The irradiation levels for decontamination were found to be commensurate with those used routinely for damage-free cleaning in art conservation. As the bulk of the work reported here was performed more than 20 years ago, and numerous technical advances have emerged in the interim, the intent of this report is not to present a decontamination recipe, but to stimulate a further examination of the potential decontamination role of PUV in the museum conservation field.

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INSECTICIDE CONTAMINATION AT THE NATIONAL MUSEUM OF DENMARK: A CASE STUDY

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Abstract.—At the National Museum of Denmark many different insecticides have been used historically to protect artefacts against moths, woodborers and other pests. In 1983, prompted by the need to transfer artefacts to Greenland, the first artefacts were examined for insecticides. All the samples contained DDT in various concentrations. Procedures were developed for cleaning the artefacts. Late in the 1980s the whole museum was tested for the presence of insecticides, including DDT, Lindane, and methoxychlor. The museum's Safety Department set up work procedures and instructed the employees on how to remove hazardous insecticides from artefacts, exhibition rooms and stores. Today after many years work the task is now as good as completed and the National Museum will be pleased to make its experience available to other museums. The process used to detect insecticides is described in detail.

The Danish National Museum has customarily treated artefacts to protect them from attack by insects. A wide variety of insecticides have been used, from flower extracts, through various heavy metals, to metal salts and more modern organic compounds. As a result, we are today in possession of comparatively well-preserved, unique collections.

It was already known in ancient times that certain substances had a harmful effect on humans. For example, a relationship was proven between the use of mercury in cosmetics and certain diseases. Mercury, lead and arsenic were very widely used in the past to combat insect attack. When people became aware of the associated health effects in the 19th century, other forms of insecticides were developed. Many of these substances have a high vapour pressure; they evaporate relatively quickly and therefore do not remain lying as a latent toxic hazard in the places where they have been used. Dichlorodiphenyltrichloroethane or DDT was developed in the mid 1930s. This substance proved extremely effective against numerous insects and was a major component of almost all insecticides until around 1987. Like many other chlorinated substances, DDT has a low vapour pressure. It is quite stable, with a half-life in nature of about 35 years. Unfortunately the half-life is considerably longer if the substance lies in dark, unventilated rooms.

Studies have shown a relationship between the use of DDT and lung and throat cancer, brain damage, damage to the central nervous system and some liver diseases. Therefore, in October 1984, Denmark banned importation and production of the substance; however, residual stocks could still be used. DDT therefore continued to be used at the National Museum and elsewhere for a short time.

The National Museum became aware of the hazards of insecticides in the beginning of the 1980s, when mention of the problems appeared in the literature and the press. When large amounts of spray had to be used at the museum, masks and gloves were worn in some cases, but no consistent records were kept of the use of DDT because the dangers were still not fully recognised by either the authorities or the users.

In 1983 in connection with the conservation of Eskimo artefacts that were to be repatriated to the Landsmuseum in Nuuk, Greenland (later the Greenland National Museum and Archives), a number of sample scrapings from the artefacts were taken and analysed by means of gas chromatography. All the samples contained DDT in various concentrations. Procedures were developed for cleaning the artefacts. The instructions were approved by the Danish Working Environment Service (now the Danish Working Environment Authority), which gave permission for the work to continue.

A major museum expansion project, 'The National Museum and the Future', from 1988 till 1992, required workers to spend extended periods of time in potentially contaminated areas. In 1987 traces of DDT were found in the stores and collections of the Department of Modern Danish History. Knowing that spray agents containing DDT had been used almost everywhere at the National Museum and that the substance was on the list of carcinogens, the museum's management decided that all work on the museum's collections should cease on 13 April 1988 and should not recommence until the problems had been properly assessed and documented. The management decided to use an impartial, outside firm for this task. Together with safety representatives, the firm took samples in all exhibition rooms and storerooms in which it was suspected that there might be traces of insecticides. The samples were analysed for methoxychlor, Lindane, aldrin, dieldrin, DDT, and heptachlor. The rooms found to be contaminated were closed until they and the artefacts in them could be cleaned.

DETECTION PROCESS

Collection of Samples

Dust samples from simulated work situations were collected by means of a high-flow pneumatic pump (NIOSH-SKC) with adjustable airflow calibrated at 3.5 litres per minute, fitted with a Millipore glass-fibre filter AP 40037, 37 mm, and set for a flow of 10.2 litres per minute, the rate at which people breathe during moderate work. For all the work-simulation samples, the pumping time was 15 to 30 minutes, depending on the dust load. In selected places, dust was raised using controlled compressed air and collected by means of pumps with the filters worn in the breathing zone. Dust was stirred up more strongly than during normal work with the objects in order to allow for the worst conceivable work scenarios.

To test individual objects for insecticides, samples were scraped from a surface area of about ten square centimetres using a glass slide. The scraped dust was collected on inert tissue and then transferred to test tubes with Teflon lids.

To determine whether a collection of objects had been treated with insecticides, selected objects were micro-vacuumed. The dust was collected on micro pore filters inside the vacuum cleaner.

Analysis

Filters from the micro vacuuming and the simulated work situations were weighed on a Sartorius research electronic scale with an analytical sensitivity of 0.00001 g. All specimens were extracted with glass distilled grade acetone for 18 hours. Samples were analysed using a Shimadzu Gas Chromatograph GC-9A with Shimadzu C-R3A Chromatopac Integrator; wide-bore capillary column of the type

SBP-5 15 m with an inside diameter of 0.53 mm; carrier gas in the form of hydrogen, column flow 6 mm/ml per minute; and an EC Detector (Electron Capture Detector) with specific sensitivity to halogenous compounds.

The analyses were carried out with the temperature programmed to rise by 5°C per minute from initially 200°C to 250°C. The analyses were duplicated. External standards of six insecticides in concentrations of 0.00167 grams per millilitre were used: Aldrin, dieldrin, DDT, heptachlor, Lindane, methoxychlor.

Linearity was found in the measuring range. Where the pesticide content of the samples exceeded the linear measuring range, dilution was carried out.

CLEANING

Large quantities of personal protection aids were purchased: breathing masks, disposable suits, gloves, boots and dust extractors with appropriate filters and discharge to the outside. Artefacts were cleaned using compressed air within fume cupboards designed with appropriate exhaust filters. Specially designed vacuum cleaners were also used, with micro filter and exhaust outlets connected to the fume cupboard's filter systems. Especially trained conservators from the Conservation Department carried out the cleaning process, assisted by technical staff.

Systems were established for disposal of the "DDT" dust collected, together with dust bags, cloths, disposable gloves and suits, and courses were held to teach the personnel how to use the personal protection aids and not least how to clean the contaminated rooms properly. At first all surfaces in the room were thoroughly vacuumed, then all surfaces were washed with water and detergent and dried with disposable towels. The most heavily contaminated rooms were cleaned by a firm that specialised in removing asbestos dust from buildings. Since working in protective clothing and wearing a face mask is extremely tiring, even when fresh-air equipment is used, various social measures were introduced. They included making soft drinks available and extra breaks during the day.

After cleaning, artefacts were sampled again either by scraping or micro vacuum cleaning. If the amount of insecticide detected exceeded one tenth of the Danish threshold limit value, the artefact was cleaned again. Artefacts for instance made from baleen and feather were often impossible to clean satisfactorily. Those were sealed in polypropylene plastic labelled 'Very toxic: poison.'

After cleaning the rooms, more dust samples were taken to ensure that pesticide levels were acceptable. Subsequently, samples of dust collected during one month's normal vacuum cleaning, i.e., from the daily used vacuum cleaners, were examined in order to ensure the continuing level of decontamination of the rooms. Dust samples from the vacuum cleaner bags were weighed and then tested for insecticides in the same way as samples from the micro vacuum cleaners. Again, the permissible amount of insecticide in the vacuum bags was one tenth of the Danish threshold limit value.

CONCLUSIONS

The task is now as good as completed. It has been an extremely time-consuming and costly exercise, but looking back over the years in which the work took place, one sees that very little of it could have been done differently. At the same time, the National Museum has gained extensive and useful experience in removing insecticides from artefacts, exhibition rooms and stores: experience that was not

available elsewhere. All rooms and showcases in the museum are clean and safe. Nearly all inorganic artefacts in the museum are now uncontaminated but there will always be problems with the organic materials, especially wood, feather, skin and fur. Even if the surfaces have been carefully cleaned the insecticides inside the artefacts may migrate towards the surface. Those artefacts have to be handled with gloves and it is necessary to repeat cleaning of the surface after some years. Instructions have been made for the staff so they know how to handle organic material that might still contain insecticides.

Parts of the foregoing come from memoranda from 1988 and 1998 that were distributed to the National Museum's personnel.

RECOMMENDED ACTIONS REGARDING THE PESTICIDE CONTAMINATION OF MUSEUM MATERIALS

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STATEMENT OF PROBLEM

According to historic documents, museum records, interview evidence from museum employees, and the few available test results, we assume that most if not all museum collections of organic materials have been treated with pesticides and other hazardous chemicals.

Scientific research published in peer-reviewed journals and presented at professional conferences has shown that significant levels of pesticides exist in particular collections as well as in museum working environments, and that according to medical literature these pesticides are harmful to human health.

Because museums kept incomplete and inconsistent records documenting the specific application of pesticides; because pesticides were also known to have been applied to artifacts by field collectors, dealers, etc. before they arrived at the museum; because personal recipes of mixed pesticides were concocted and applied to collections; and because collections were commonly moved from location to location (sold, donated, loaned, re-housed within the museum, etc.), no assumption about the pesticide content of any specific item can be made without testing.

Museum environments as well as museum artifacts may contain pesticides, for instance, in the air of collection storage areas and on working surfaces, and may have been spread widely through building air conditioning systems to exhibit areas, offices, and non-collection areas of the building. Therefore museum environments may also pose risks to human health.

While most museum collections remain in a museum environment, the notable exceptions are the Native American materials that are to be returned to tribes under the Native American Graves Protection and Repatriation Act (NAGPRA). These materials are handled differently in the tribal setting than they are in the museum setting, and therefore have the potential to pose different and in many cases greater health risks to tribal people than they do to people in the museum setting.

RECOMMENDED ACTIONS

Health

Safety guidelines for handling museum collections should be publicly posted and enforced in museums, given to people entering the museum collection areas, and provided to all American Indian tribes (see Appendix: Safety Guidelines for Handling Museum Collections).

National Institute for Occupational Safety and Health (NIOSH) should research and make recommendations regarding the hazardous materials exposure in museum working environments. NIOSH is the Federal agency responsible for conducting research and making recommendations for the prevention of work-related disease and injury. NIOSH is part of the Centers for Disease Control and Prevention. The present risk levels for pesticide exposure as established by the Occupational Safety and Health Administration (OSHA) have proven not to be useful in museum conditions. OSHA risk levels are based on industrial work environments, while museum pesticide exposures have consistently been found to be below the OSHA risk levels. Because of this, we recommend NIOSH as the lead research agency that will study and develop risk standards for museum environments.

All new museum employees should be given a baseline medical examination upon hiring and then undergo regular medical monitoring during employment, with special attention to effects of pesticide poisoning. Current studies have called into question whether baseline blood and urine test for pesticides provide reliable results. However until more studies are done on the effectiveness of these tests, we continue to recommend that museum employees be given blood and urine test for pesticides upon hiring and at each regular medical monitoring thereafter.

Epidemiological studies of museum workers past and present should be conducted. The studies should address the routes of exposure, the concentration of hazardous materials, and associated health risk factors such as age of employee, length of time working in the museum, length of time working in the collection areas, and so on. Although there are no baseline tests for the long-term employees, the test results should be examined for patterns of disease.

Basic medical research (not done in the museum setting as above) should be conducted to examine the short term and long term effects on human health of the pesticides known to have been used in museums. Each pesticide should be correlated to health risks, as they vary with exposure to different doses, with different routes of exposure as experienced in the museum environment, and after exposure over different lengths of time. This will be especially important in gaining a better understanding of the long-term health effects of chronic exposure, as related to different types of disease, chronic illness, fertility and disability.

Testing for Contamination

All museum items that are to be returned back into a tribal community should be individually tested for the presence, type, and concentration of pesticides, if the tribe so wishes. This applies to all NAGPRA items before they are returned to tribes. The tribe involved should be provided with complete information about the testing procedures. The decision as to whether to test, the method for taking a sample, what tests are done, and by whom, should be made by the tribe involved.

Research should be conducted to develop methods for taking samples of valuable materials (human remains, ceremonial objects, and so on) to be used in artifact testing.

If samples are collected away from the testing lab, they should be transported to the lab with a documented chain of possession, to ensure the accuracy of the results.

A nationwide database should be developed that tracks the results of contamination studies in museums. It should be made available to the public.

Soil, air, and ground water should be pre-tested for pesticide contamination before repatriated human remains and burial goods are re-interred or burned, with monitoring to continue over time, if the tribe so wishes.

Removal or Reduction of Contamination on Artifacts

Research should be conducted to develop methods that will reduce the amount of pesticides on objects and in museum environments.

Research should be conducted to develop methods for removing pesticides from objects as well as from museum environments.

Education

An educational program should be developed for tribes that explains the risks of pesticide exposure during the repatriation process. The program should include history of pesticide application in museums, the health effects of pesticide exposure, the specific risks posed by human remains and grave goods being returned under NAGPRA, the specific risks posed by sacred materials returned under NAGPRA, the environmental risks posed to air, soil, and water, the ways that Indian people can become exposed to pesticides with their repatriated materials, and so on.

An educational program should be developed for tribes that explains how they can protect themselves from the health and environmental risks posed by pesticide contamination of repatriated museum materials. The program should include information on how to reduce the risk of exposure, how to store repatriated items, how to limit the handling and use of these materials in display, storage, etc.

An educational program should be developed for tribes that explains the options available for taking samples from repatriated materials for use in pesticide testing. Educational materials should be developed that correlate the amount of the item needed for each test with the types of test results that can be achieved. This information will assist the tribes in choosing which tests they would like done on their NAGPRA materials.

Research should be done with the tribes, to develop various strategies to continue with the repatriation process, laying out actions that can be taken when the presence of pesticides is known and when the presence of pesticides is not known. These repatriation options should be carefully recorded and presented to all tribes for their own use and adaptation.

Collaboration, Policy, and Financing

Because pesticide contamination of museum sites and materials may cause health risks to museum workers, visitors, and tribes receiving repatriated materials, it would be desirable for representatives of these groups to work collaboratively in addressing this problem.

Because the problem of artifact contamination falls under the umbrella of various laws and public agencies, it would be desirable for those agencies to work together to develop an integrated approach to addressing this problem.

The NAGPRA law or its guidelines should be amended to address the artifact contamination issue.

Allocation of public funds will be necessary to address the various aspects of this problem. The extent of the problem is vast, existing as it does in thousands of museums with millions of collection items. The cost for testing, basic research, education, and removal/reduction is far outside the financial capacity of any museum or tribe to pay for. There are public health issues for museum workers, visitors and especially for tribes. For all these reasons, we recommend that the state and federal governments address the policy and fiscal obligation that artifact contamination poses.

APPENDIX: POST THIS THROUGHOUT THE MUSEUM WORKPLACE

Safety Guidelines for Handling Museum Collections

<http://bss.sfsu.edu/calstudies/arttest>

Prepared on Oct. 6, 2000 by:

Monona Rossol (Conservation Scientist, Arts, Crafts, and Theater Safety)

Jane Sirois (Conservation Scientist, Canadian Conservation Institute)

- ✓ If you do not have information on any treatments applied to your artifacts, assume that hazardous pesticides are present.
- ✓ Wear nitrile gloves (not cotton nor latex gloves) while handling your artifacts.
- ✓ When removing gloves, do so such that your hands do not touch the exterior surface of the gloves.
- ✓ Always discard gloves and wash hands with soap and water after handling objects, and especially before eating or smoking.
- ✓ Wear a lab coat or other protective clothing to keep dust off clothing. Remove the lab coat when out of the areas or no longer handling contaminated material. Assess your work area. If there is visible surface dust, you should also wear shoe and hair coverings.
- ✓ Keep lab coats clean so as to avoid transferring dust and dirt.
- ✓ If possible, work with your material in a well ventilated area. For example, examine objects in an area outside of the storage location, (i.e., conservation lab with proper ventilation or fume hoods).
- ✓ Make sure you have medical certification to wear a mask or respirator and that you have an up to date fit test for your device. Assess your working situation, and choose an appropriate type of respirator and cartridges.
- ✓ Eating or drinking in the store room/around artifacts should be prohibited.
- ✓ Ensure that work surfaces are well cleaned after they have been in contact with artifacts. Sponge-clean or wet-mop floors with soap and water.
- ✓ If there is any chance dust has gotten onto your clothing, remove your clothes as soon as you get home, bag and launder separately from other clothing.
- ✓ If you have any concerns about exposure, consult a board certified occupational medical doctor or toxicologist.
- ✓ If you have questions, email Monona Rossol at <Actsnyc@cs.com>

ERRATUM

The following replaces Table 2 in *Collection Forum* 15/1–2, “Disaster Recovery in the Herbarium” by Debra S. Baker and Caleb A. Morse, p. 31.

Table 2. Condition of herbarium specimens after recovery from damage.

DAMAGE	RESPONSE	RECOVERY	<i>Agrostis</i>	<i>Artemisia</i>	<i>Asclepias</i>	<i>Convolvulus</i>	<i>Erigeron</i>	<i>Impatiens</i>	<i>Opuntia</i>	<i>Pinus</i>
fire	wait 24 hours	air dry	+++++	+++++	+++++	+++++	+++++	+++++	////	////
fire	wait 24 hours	press dry (heat)	+++++	+++++	+++++	+++++	+++++	+++++	////	////
fire	freeze	press dry (no heat)	////	+++++	+++++	+++++	+++++	+++++	////	////
fire	freeze	press dry (heat)	+++++	+++++	////	+++++	////	+++++	////	////
mud	wait 24 hours	air dry	////	////	////	////	////	////	////	////
mud	wait 24 hours	press dry (heat)	+++++	+++++	+++++	+++++	+++++	+++++	////	////
mud	freeze	press dry (no heat)	+++++	+++++	+++++	+++++	+++++	+++++	+++++	+++++
mud	freeze	press dry (heat)	////	+++++	+++++	+++++	////	+++++	+++++	+++++
mechanical	wait 24 hours	air dry	////	////	////	////	////	////	////	////
mechanical	wait 24 hours	press dry (heat)	////	////	////	////	////	////	////	////
mechanical	freeze	press dry (no heat)	////	////	////	////	////	////	////	////
mechanical	freeze	press dry (heat)	////	////	////	////	////	////	////	////

- Specimen requires no further repair.
- Herbarium sheet should eventually be replaced, but specimen can remain as it is in the mean time.
- Herbarium sheet replaced during triage due to extensive damage. Specimen now requires no further repair.
- Exsiccate requires repair and immediate transfer to a new herbarium sheet.
- Specimen is not recoverable (due to severe burns).

REVIEWERS

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