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INVESTIGATION OF SOLID PHASE MICROEXTRACTION SAMPLING FOR ORGANIC PESTICIDE RESIDUES ON MUSEUM COLLECTIONS

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Abstract.—Solid-phase microextraction (SPME) in combination with gas chromatography/mass spectroscopy (GC/MS) analysis offers a simple and sensitive option for analyzing objects that have been contaminated with volatile and semi-volatile organic pesticides. In this project, items from the National Museum of the American Indian (NMAI) were placed in plastic bags and allowed to sit overnight. A SPME fiber was then inserted into the bag, exposed for approximately one hour, and analyzed by GC/MS. Naphthalene and para-dichlorobenzene were found on several objects. It may also be possible to detect other semi-volatile pesticides. A privately owned piece of reproduction trade cloth was studied more extensively to evaluate equilibrium times and reproducibility. Raising the humidity within the bag substantially increased the release of pesticides from the cloth. This preliminary project demonstrated that this simple setup is practical. Its ease of use and minimal effect on the object make it attractive to museum staff and may make it more attractive to Native constituents who have concerns beyond preserving the physical material of the object. Quantitative analysis appears feasible but will require further study.

INTRODUCTION

A wide variety of volatile organic pesticides have been used on museum collections in an attempt to protect the material from insect infestation and damage (e.g., Williams et al. 1986). These pesticides were used throughout the museum community during the 20th century and in some places are still commonly applied. Concerns about contact with these pesticide residues on collections from the National Museum of the American Indian (NMAI) are especially acute due to repatriation and loan policies in the museum. These objects may be worn by Native individuals in ceremonies and dances. In addition to the possible health risks to people, there are also concerns about the damage these chemicals may have caused to the objects. Identifying residues of pesticides on items that are examined for condition may help explain some of the deterioration seen on NMAI collections.

BACKGROUND AT NMAI

NMAI acknowledges Native cultures as the living, first person voice of the National Museum of the American Indian. Our approach to work in the conservation lab is to develop and organize projects that support the needs of our Native constituency through an evolving collaborative process (e.g., Heald and Ash-Milby 1998, Kaminitz et al. 2005, Johnson et al. in press). The focus of pesticide

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research on NMAI collections has been identification of pesticides on collections being repatriated or loaned to Native communities (Johnson and Pepper Henry 2002). To date, this work has primarily been to identify heavy metal pesticides in our collections (Johnson et al. 2005).

Conservators at NMAI have had experiences where volatile organics are released from collections objects at high enough levels to cause complaints from individuals. When conservators have worked with individuals who wear items in collections during ceremonies or consultations and when conservators have used humid and wet treatment techniques, they have noticed that the smell of pesticides becomes much more prominent.

For example, a volunteer developed a migraine during a wet-cleaning procedure for a wool shawl. The object was in a surfactant bath for 25 minutes followed by four rinses. Although there is good fume extraction equipment in the lab, the smell of mothballs was pronounced the entire time the object was wet. In another case, a Bear Crest hat of the Tlingit Bear Clan of Klukwan was photographed being worn by the Tlingit house leader for an exhibition photomural. As hot studio lights heated up the room and the house leader perspired in the hat, the smell of mothballs coming from the hat became more and more apparent. This hat was later repatriated to the community.

Organic Pesticide Contamination at NMAI

Prior to the move of all of NMAIs objects to their current storage in the Cultural Resources Center in Suitland, Maryland, objects were stored at the Research Branch facility in the Bronx, New York. It is known that collections were repeatedly treated with a variety of pesticides; however, what was used was not well-documented. A 2001 historical review (Pool 2001) of archival records gave us the following information on organic pesticide use on NMAI collections:

The primary pesticide applied to the collection throughout the 20th century appears to have been naphthalene. It was routinely used between 1917 and 1975 with sporadic use after 1975 until 1984. At times, artifacts were packed with naphthalene mothballs or stuffed with naphthalene flakes if they were found to be infested. In 1987, all remaining drums of naphthalene at the Research Branch were removed as toxic waste.

In 1975, Phyllis Dillon, the first staff conservator, advocated stopping the use of naphthalene out of health concerns. However, small quantities continued to be used until 1984. She suggested using Dichlorvos as an alternative. Both Dichlorvos bombs and enclosed chambers with Vapona strips were used. The last recorded use of Dichlorvos was in 1987.

In 1985, the Research Branch building was tented and Vikane (sulfuryl fluoride) was used on the entire collection. Until the end of 2004, Vikane was used to treat very large objects, such as totem poles, that could not be treated in other ways. Freezing was first used at the museum in 1988. NMAI purchased a CO_2 bubble in 2003. These latter two techniques will be used to treat any future infestations.

NMAI began research into identifying volatile organic residues through a collaborative project with Dr. Rolf Hahne of the University of Washington (Bosworth et al. 2002). Although successful in extracting and identifying organic pesticides, the technique, which required removing air from a bag, replacing it with nitrogen

and heating the object, was considered unacceptable from both a physical and metaphysical perspective. The nature of our collections and our relationships with our Native constituency compelled us to look for an alternative strategy for sampling. Luckily, presentation of this project led to the collaboration with the National Archives and Record Administration (NARA) reported in this paper. Although NARAs predominantly paper-based holdings are very different from NMAI, previous use of pesticides is an issue for both institutions. For decades NARA systematically fumigated all newly accessioned records (Minogue 1943). There is also concern that new accessions that NARA receives may have been exposed to pesticides prior to coming to the Archives.

Solid Phase Microextraction (SPME)

An alternative analysis method that avoids many of the objections to the previous approach is solid-phase microextraction (SPME). Introduced in 1989, it has attracted attention in large part due to its simplicity and ease of use (Pawliszyn 1998, 1999, Vas and Vekey 2004). In one solvent-free step a SPME fiber concentrates the sample and prepares it to be injected into a gas chromatograph/mass spectrometer (GC/MS). SPME allows the sensitivity and versatility of GC/MS analysis to be utilized without the use and associated risks of solvents (Sirois and Sansoucy 2001). This economical method is sensitive and in many cases is more accurate than other standard procedures (Koziel and Pawliszyn 2001). In addition to environmental analysis, SPME has been used in a wide range of applications (Supelco 2004). In the conservation field, SPME has primarily been used to analyze gaseous pollutants and volatile degradation products (Rhyl-Svendsen and Glastrup 2002, Lattuati-Derieux et al. 2004). Plasticizers associated with laminated documents have also been studied (Ormsby 2005). This work led to the current project.

The goal of this study was to develop an easy-to-use setup for SPME analysis that minimized risk to the objects while being sensitive enough to evaluate the potential health risks of a range of pesticides. Although few institutions can afford a GC/MS, arrangements might be made with local colleges or labs where the instruments are common. It may also be possible to sample the objects in-house and send the fibers elsewhere for analysis (Xiong et al. 2003). Individual fibers cost less than $100 and are reusable.

SPME Sampling Procedure

The basic procedure for collecting a sample using SPME is illustrated in Figure 1. The SPME fiber is mounted inside a syringe-like device. When the plunger is depressed the fiber extends from a hollow needle to expose a quartz fiber with a polymer-coated tip. The sample is sorbed onto the tip. After a suitable exposure time the fiber is removed and then injected into the GC/MS. The heated injector vaporizes the sample from the fiber. The GC separates the mixture of compounds into individual components which are ionized and fragmented by the MS. The resulting mass spectra are identified by comparison with reference spectra in a database. The fiber can then be reused.

The sample can be collected by exposing the fiber to a liquid (direct immersion, DI) or to the air in the headspace (HS) above an object. Both methods have been used in environmental studies of pesticides (Lee et al. 2002, Musshoff et al. 2002,

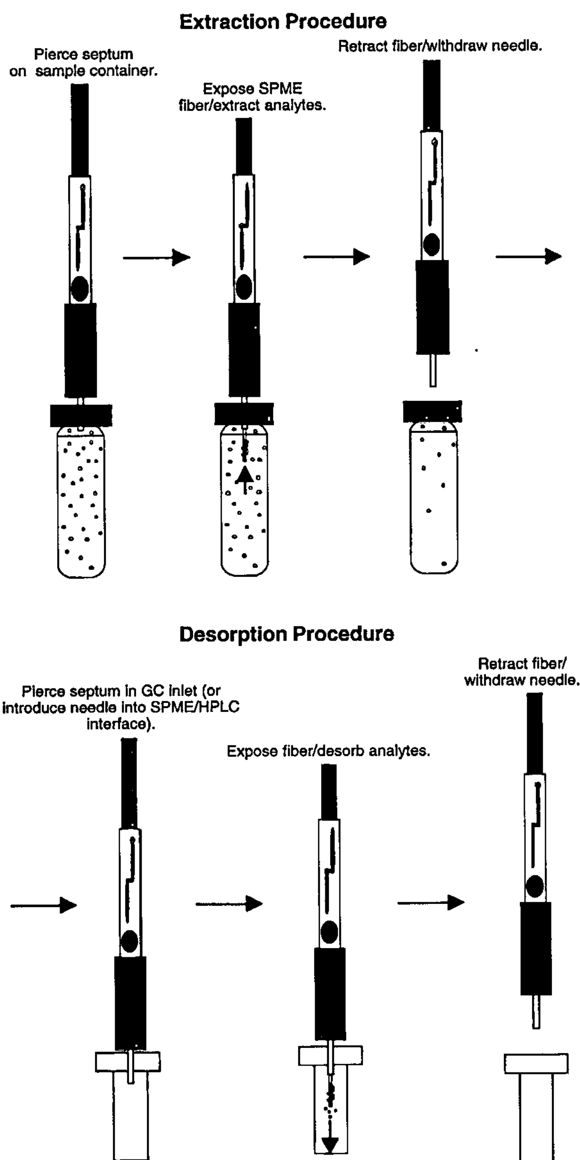

Figure 1. The process for collecting a sample with a SPME fiber is shown in the top row, and the bottom row illustrates the procedure for desorbing it in the GC/MS injector port. Figure used with permission of Supelco, Bellefonte, PA 16823 USA.

Sanusi et al. 2003, Ferrari et al. 2004, Sakamoto and Tsutumi 2004, Supelco 2004). Sampling can also be performed with the air or liquid flowing (dynamic) or stagnant (static). In most published studies dynamic sampling has been used because of its advantages in terms of control, sensitivity, and ease of calibration (Razote et al. 2002).

The goal of this project was to develop a simple setup that did not require pumps, tubing, and other equipment needed for dynamic sampling. Also, HS

sampling was preferable because it would not expose the objects to liquids as in DI sampling. Therefore, static sampling was tested using bags made from DuPont Tedlar polyvinyl fluoride sheeting. This polymer is commonly used to collect gas samples because of its inertness and resistance to permeation (Lee et al. 2002). Other types of plastic sheeting may also be suitable.

The amount of sample collected on the SPME fiber depends on a number of factors (Supelco 2001). As with GC columns, a fiber coated with a polar polymer is more sensitive to polar compounds, and non-polar coatings are more suitable for detecting non-polar compounds. Thicker polymer coatings are generally preferable for collecting more volatile compounds. The temperature, relative humidity, headspace volume, and exposure time during sample collection also affect the results. Finally, desorption of compounds from the fiber depends on the temperature of the GC/MS injector, the time, the gas flow, and the depth at which the fiber is inserted in the port.

Seven types of polymer coatings are available on commercial SPME fibers (Supelco 1999). Based on published studies (Lee et al. 2002, Sanusi et al. 2003) and the compounds expected to be encountered (Pool 2001, Palmer et al. 2003), polydimethylsiloxane and carboxen/polydimethylsiloxane (CAR/PDMS) fibers were selected for this project. Preliminary tests indicated that the CAR/PDMS fiber was more sensitive for this application. The CAR/PDMS fibers have the added advantage of acting as a trap for volatiles. These fibers minimize sample loss, making them suitable for field use (Xiong et al. 2003). All of the data shown in this report were taken with CAR/PDMS fibers.

Data Collection

Bags were made by cutting a length of the plastic to an appropriate size to hold an object. The sheet was folded in half over the object and heat sealed with a welder. Double seals were made on each of the three open sides to reduce the possibility of leaks. Ten objects were studied in different tests. The bags most commonly used contained roughly two liters of air, but larger bags were needed for some items.

Objects were sealed in bags and allowed to equilibrate at room temperature for roughly 24 hours. A pin was used to make a small hole in the bag, through which the SPME fiber was inserted and exposed for one hour. Preliminary tests indicated that these equilibration and exposure times produced an adequate signal over a convenient time period. An empty bag was used as a control to detect compounds originating from the polyvinyl fluoride or the laboratory air. Bags were not reused because of possible carryover between exposures. The fibers were initially conditioned following the procedure recommended by the manufacturer. Between fiber exposures a blank run was made to check for carryover of pesticide peaks. If necessary, additional blank runs were made until the carryover was minimized.

Analysis was performed on an Agilent HP6890N/5973 Inert GC/MS with a 30-meter HP5-MS (5%-phenyl)-methylpolysiloxane column. A narrow-bore inlet liner optimized for SPME was installed in the injection port. A splitless injection was made with the injector port at 310°C. The carrier gas was helium at 1 ml/min in the constant flow mode. The oven temperature was 40°C for the first two minutes. It was heated at 12°C/min to 250°C and held at the final temperature for two minutes. Mass spectra were collected using electron ionization and a quad-

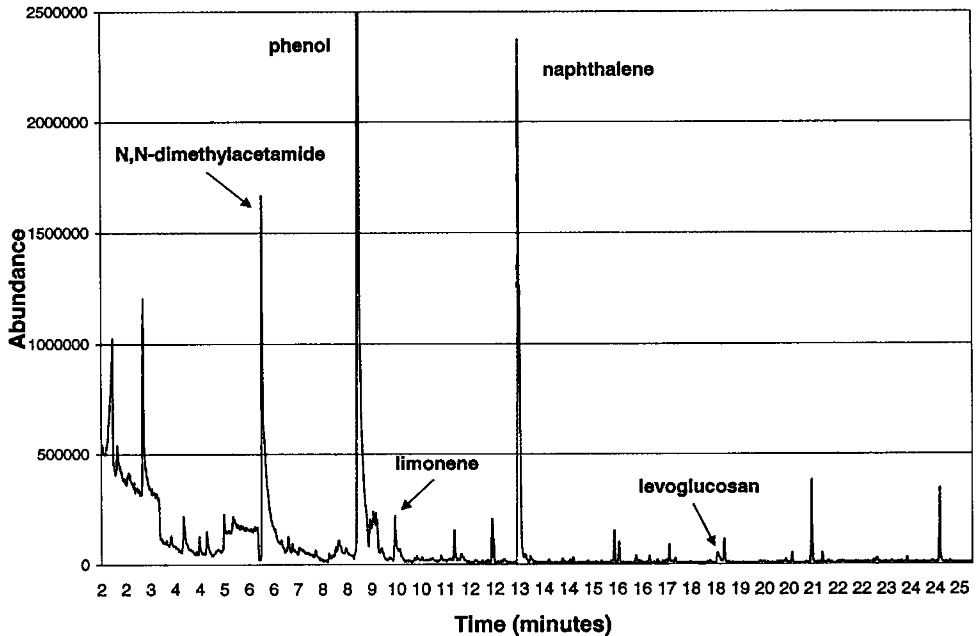

Figure 2. The mixture of compounds from the Tlingit Clan Bear Crest hat that adsorbed onto the SPME fiber are separated into peaks by the GC/MS. Pesticides and background peaks from the bag are shown.

rupole mass filter. The MS source, quadrupole, and detector temperatures were 230°C, 150°C, and 280°C, respectively. A standard spectra autotune using perfluorotributylamine was performed for comparison with a mass spectral library. For spectra collected in the scan mode the mass range was 29–420 atomic mass units. In the selected ion monitoring (SIM) mode mass fragments were selected for Dichlorvos (109, 185), pDCB (146), and naphthalene (128). Since the SIM data focused on naphthalene and pDCB the oven temperature program was modified to reduce the analysis time. After the initial two minute hold at 40°C the oven was heated at 12°C/min to 150°C. It was then heated at 35°C/min to 275°C and held at the final temperature for one minute.

Results

Data from a Bear Crest hat of the Tlingit Bear Clan are shown in Figure 2. (Note: this data is from preliminary work using an older GC/MS with the same column type but slightly different instrument settings.) The large phenol and N,N-dimethylacetamide peaks are background from the polyvinyl fluoride bag. These compounds might be reduced by flushing the bag using nitrogen or purified air. Three pesticides were observed: naphthalene, pDCB, and limonene (the pDCB peak is obscured by the phenol). The levoglucosan might be due to exposure to smoke from burning wood (Simpson et al. 2004). The other peaks are background from the bag, the fiber, or unknown. Results from other objects were similar. Dichlorvos was not detected on the ten objects that were studied.

Further tests were performed to explore the effect of varying the fiber exposure time and to study the change in pesticide concentration within the bag over a

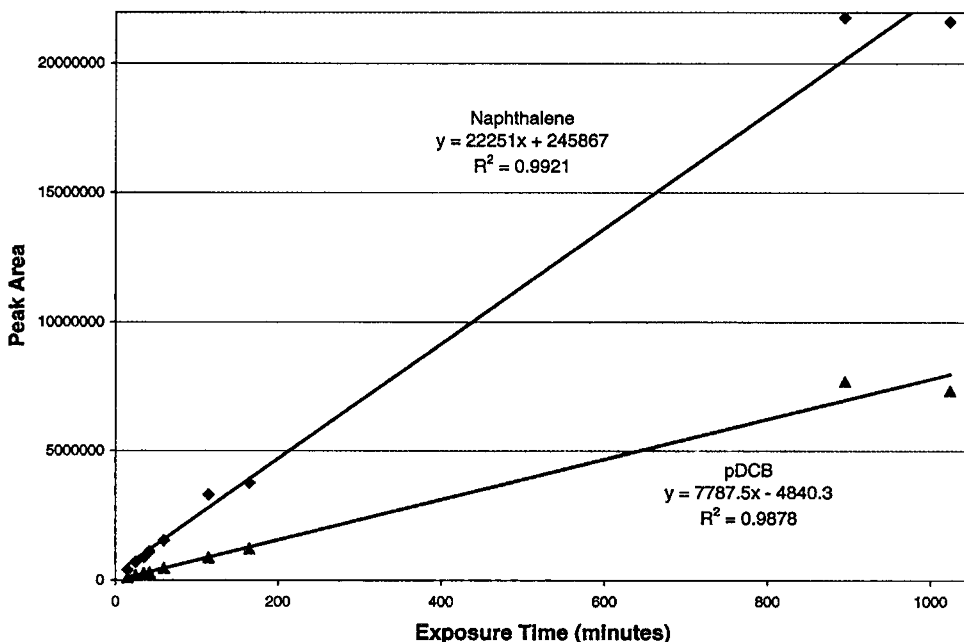

Figure 3. Peak areas of naphthalene and pDCB are shown as a function of SPME fiber exposure time. The reproduction trade cloth had been in the bag for 22 hours before the first measurements were made.

period of days and weeks. To improve the sensitivity to naphthalene and pDCB the MS was set to SIM mode so that it monitored mass fragments specific to these two compounds rather than scanning over a broad range. This mode was used to more carefully study the changes in the amount of pesticide detected over time. A strip of a wool reproduction trade cloth smelling like mothballs, from a personal collection, was placed in a bag and monitored over several weeks. To compare the amount of pesticide detected, the naphthalene and pDCB peak areas were calculated.

As illustrated in Figure 3, several measurements with different fiber exposure times were made over a 48 hour period. The wool reproduction trade cloth had been sealed in the bag for 22 hours when the first measurements were made. The graph shows the change in the peak area as the fiber exposure time is increased. A linear relationship was found for both compounds as indicated by the lines fit to the data and the R^2 values near 1 (a perfectly linear relationship has a value of 1). This result agrees with that expected from theory assuming that the object has reached equilibrium in the bag so that the pesticide concentrations are constant during the time over which the measurements are made (Koziel et al. 2000). This assumption is explored further below. Because of their porous structure, CAR/PDMS fibers take longer than other fibers to reach equilibrium, so the linear range over hours of exposure is reasonable. This linear range also indicates that displacement due to competitive adsorption is not significant (Tuduri et al. 2001).

The results of numerous pDCB measurements made over a two week period to study the equilibration of the cloth with the air in the bag are shown in Figure

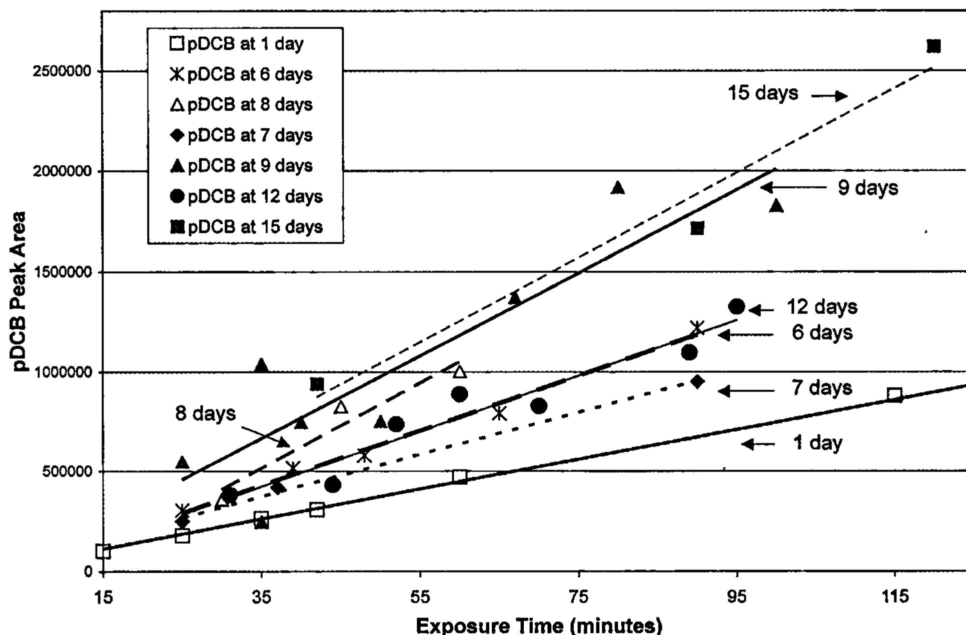

Figure 4. Fibers were exposed several times a day over a two-week period. pDCB peak areas from the reproduction trade cloth are shown.

4. During this time the enclosed cloth was kept in a drawer in the laboratory. Several measurements with different exposure times were made on separate days. After one hour the pDCB concentration was too small for the peak area to be calculated accurately. Measurements made the next day showed that the concentration had increased. Generally, the concentration rose over the two week period, but there were large fluctuations. The data for naphthalene was similar.

It is not clear from the data presented in Figure 4 if the pesticide concentrations are approaching equilibrium. Possible explanations for the large fluctuations include temperature and humidity variations and leaks in the bag. In addition, Lee et al. (2002) reported that pDCB concentrations in polyvinyl fluoride bags decreased 14% in the first 2 hours and an additional 27% in the following 9 hours. This loss was attributed to diffusion through the bag or adsorption on it. The data shown in Figures 3 and 4 do not reflect such losses. If they are occurring, they may be offset by increased release from the cloth.

To evaluate the effect of humidity, two small pieces of blotter paper were soaked with deionized water and sealed in a bag with the cloth. The bag was stored in a laboratory drawer at approximately 20°C. The humidity was estimated at 70–80% in the bag with the deionized water. The graph in Figure 5 compares the concentrations measured with and without humidification over two week periods. Based on the peak areas the amount of naphthalene and pDCB detected was roughly 50–60 times greater in the humidified bag.

Naphthalene and pDCB are nonpolar compounds as is illustrated in Figure 6. As such, they are only weakly bound to the wool cloth. When the humidity is increased the water molecules in the air will be attracted to the hydrophilic wool and form hydrogen bonds that are stronger than those binding the pesticides. Over

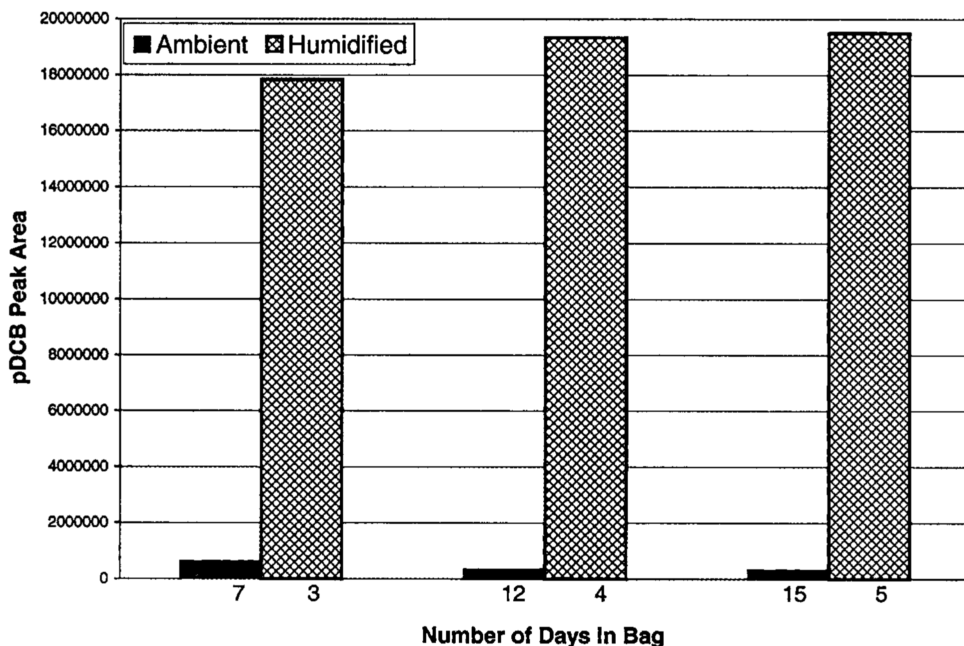

Figure 5. Measurements were made over two two-week periods with the cloth at ambient conditions and with dampened blotter paper enclosed in the bag.

time the concentration of pesticides in the air will increase relative to the concentration on the cloth. Cellulose objects would exhibit similar behavior.

Discussion

The work thus far has not attempted to calibrate the chromatograph peak areas to calculate concentrations such as parts per million of naphthalene. Generating known concentrations of the pesticides in a static environment (a bag or a sample vial) is difficult, and issues such as adsorption on the container walls and the effect of relative humidity must be explored (Tuduri et al. 2001). The surface area of the object relative to the volume of the bag is also an important variable (Ryhl-Svendsen 2000). Alternative approaches for calibration, including time-weighted average SPME (Martos and Pawliszyn 1999), stepwise SPME (Xiong et al. 2003), and on-site application of standards to the fiber (Chen and Pawliszyn 2004) may address these issues.

The technique may be applied in other ways to detect pesticides in cabinets,

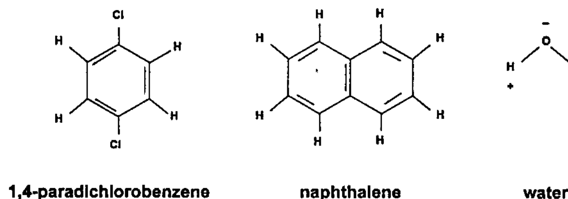

Figure 6. Naphthalene and pDCB are non-polar compounds that are more weakly bound to the surface of objects than water, a polar compound.

drawers, or rooms. If objects are washed or treated with solvents it may be possible to detect compounds in the liquid, including less volatile pesticides (Sakamoto and Tsutumi 2004). SPME fibers have also been used for personal exposure monitoring (Martos and Pawliszyn 1999) and might be used in a similar manner for pesticides.

Even with quantitative data, interpreting the SPME results in terms of personal exposure risk is a complicated issue (Makos 2001). Since items from the NMAI collection may be worn for dances, performances under hot spotlights, etc., it would be useful if the data taken at room temperature can be used to indicate risks under other conditions. With further work it may be possible to develop standard testing methods using SPME.

Conclusion

This project has demonstrated that enclosing objects in polyvinyl fluoride bags and sampling the headspace with SPME fibers is a practical, simple, and inexpensive method that provides valuable information on semi-volatile organic pesticide contamination. The method poses minimal risk to the objects and requires little staff time. Naphthalene and pDCB were detected on a number of objects. More extensive studies of a wool reproduction trade cloth showed that the amount of pesticide adsorbed by the fiber increased linearly with time. Raising the relative humidity within the bag greatly increased the amount of pesticides in the headspace. With further work to better understand issues of equilibrium and calibration the method may be very useful for evaluating contaminated collections.

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TESTING CULTURAL MATERIAL FOR ARSENIC AND INTERPRETING THE RESULTS: A CASE STUDY AT CARNEGIE MUSEUM OF NATURAL HISTORY

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Abstract.—One hundred and seventy-one objects in the process of repatriation from the Carnegie Museum of Natural History to the Hopi Tribe were screened for the presence of arsenic pesticide residue using a commercial spot test. One hundred and three objects (60%) produced positive results, but unexpected positives led to suspicions that arsenic-containing pigments were responsible for some of the arsenic that had been detected. Analysis of pigment samples from four representative objects resulted in the identification of the commercial artist's pigment emerald green (a copper acetoarsenite) and a native iron earth pigment that might contain arsenic naturally. A statistical analysis of the test results and object information, such as fabrication materials, previous locations within the museum, and absence/presence of green paint, was undertaken to determine whether correlations among certain factors could explain patterns in the test results or predict the sources of arsenic on objects within the test group as a whole. The study identified a correlation between positive test results and two early exhibitions, but in the end it was difficult to predict with certainty whether the source of the detected arsenic for particular objects was inherent or acquired. This project provides an example of the difficulties in interpretation that can result from the presence of arsenic-containing pigments when testing for pesticide residue.

INTRODUCTION

In 1997, the Carnegie Museum of Natural History (CMNH) was asked by the Cultural Preservation Office of the Hopi Tribe to undertake sampling and testing for pesticide residue on Hopi objects that were in the process of repatriation from the museum under the conditions of the 1990 Native American Graves Protection and Repatriation Act (NAGPRA). This request was prompted by the recent discovery that some objects already repatriated to Hopi communities from other museums might have been treated with pesticides and could still be contaminated with hazardous residues (Loma'omvaya 2001).

In order to formulate a strategy for testing, a history of pesticide use in the Section of Anthropology was compiled. Although routine chemical pest control had not been practiced in the Section since 1979, 95% of these Hopi objects had been in the museum since 1907 or earlier and it was expected that the pesticides used historically on collections in other museums might have been employed at CMNH as well (Goldberg 1996, Pereira and Hammond 2001). As anticipated, reviews of the museum's annual reports, searches of departmental files, and interviews with current staff revealed that pesticide treatment of Anthropology collections at CMNH during the twentieth century had included carbon disulfide, chloroform, arsenic, naphthalene, dichlorvos, ethylene dichloride-carbon tetrachloride, and one instance of sulfuryl fluoride.

No records concerning the application of pesticides to Hopi objects were encountered, although the possibility existed that this material could have been treated without documentation or indirectly exposed. Based on the reported use of a white arsenic powder on unspecified Anthropology collections in storage and on

Table 1. Accession groups tested for arsenic pesticide residue.

Accession number	Collector	Accession year	Quantity tested
1529	Thomas Varker Keam	1900	44
1579	Frank D. Voorhies	1900	33
3165	George A. Dorsey for The Fred Harvey Company	1906	72
3264	*	1907	13
6601	*	1921	1
9331	*	1932	1
32803	*	1985	4
Z-9	No Data	Pre-1980	3

* This donor is not a public figure and the name is withheld for the purposes of this paper.

exhibit from the mid-1930s to the mid-1950s, it seemed likely that some of the Hopi objects might be contaminated with arsenic. Several Native American objects had been tested for arsenic in 1994 and had produced positive results. Work surfaces in Anthropology storage, vacuum cleaner bag dust, and examination gloves also tested positive at that time.

Because of the specific concern expressed about arsenic in the request from the Cultural Preservation Office, the decision was made to test the Hopi objects for that element first and to use a commercial spot test kit. The use of a kit would allow the testing project, which had been delayed for nearly three years by personnel changes at the museum, to begin immediately, with the staff and financial resources available at the time.

Between January 2001 and January 2003, sampling and testing was carried out for 171 objects from eight accession groups that had been acquired by the museum between 1900 and 1985 (Table 1). Six of the objects were made primarily of stone or ceramic, but the remainder were fabricated from a variety of organic materials, including untanned skin (with and without hair), semi-tanned and tanned leather, feathers, horsehair, antelope hooves, turtle shell, wood, and woolen or cotton cloth. Most of the objects were painted.

This paper summarizes the results of the arsenic testing and describes subsequent efforts to interpret them. Out of respect for the nature of the objects, with very few exceptions, they will not be discussed by name.

Test Kit

Testing was carried out using the Merckoquant® 1.10026.0001 Arsenic Test. The reaction and detection mechanisms are a variation on the classic Gutzeit test for arsenic (Feigl and Anger 1972). Arsenic in the sample is converted to arsine gas (AsH_3) by the addition of powdered zinc metal (Zn) and dilute hydrochloric acid (HCl). The arsine reacts with the mercuric bromide-treated paper ($HgBr_2$) on the test strip, forming a compound whose color is dependent upon the concentration of arsenic (Merkoquant® 1.10026.0001 Arsenic Test Instructions).

Because the kit is designed for testing liquid samples such as water and prepared biological material (Merckoquant® 1.10026.001 Arsenic Test Instructions), the manufacturer's directions must be modified in order to use the kit with samples from museum objects. The procedure employed for the testing project generally

followed the modified instructions provided by Henry (1996) and by Odegaard et al. (2000).

Sampling and Testing

Sterile cotton swabs, slightly moistened with de-ionized water, were gently rolled over representative surfaces and materials of each object. Special attention was paid to protected areas, such as inside creases, where arsenic powder would be likely to remain even if it had been lost from the rest of the object through handling or superficial cleaning. A maximum of five swabs was used on each object, with each swab being replaced once it had accumulated an excess of dust or soot.

After sampling, the cotton swab tips were cut from their wooden sticks and dropped into a glass beaker holding 15 ml of de-ionized water. After fifteen minutes, five ml of test-water was withdrawn from the beaker and placed in a glass reaction vessel, to which the HCl and Zn powder were added. A test strip from the kit was inserted in the top of the reaction vessel and held in place with a stopper. During each day of testing, negative controls (de-ionized water alone) and positive controls (arsenic trioxide in de-ionized water) were tested periodically in order to confirm the cleanliness of the glassware and the performance of the test strips.

Recording the Test Results

After thirty minutes, the color on the strip was compared with the kit's color scale, which provides detection levels of 0, 0.1, 0.5, 1.0, 1.7, and 3.0 milligrams per liter (mg/L) of trivalent (As^{3+}) or pentavalent (As^{5+}) arsenic ions. Lack of color change from white signifies that no arsenic ions were detected in the sample, while a change through yellows and oranges to brown indicates the detection of a quantity of arsenic ions equal to or greater than 3 mg/L.

Because the amount of surface that was sampled for each test could vary with the size and nature of the object, the concentration of arsenic in the test-water was partly an artifact of the sampling process. The detection levels from the kit's color scale were recorded in the project database, but the results are presented here as negative or positive.

Spot Test Results

Of the 171 objects tested, 103 (60%) produced positive results. For 68 objects (40%), no arsenic was detected. Objects occurring in pairs were sampled and tested separately, but are counted here as one object. Results for paired objects never differed qualitatively from each other.

Influence Of Pigments

Although care was taken not to remove pigment during the sampling, loose particles were sometimes picked up on the swabs. As testing of the 34 dance wands from accession group 3165 proceeded, suspicion grew that an arsenic-containing pigment was contributing to the strong positive results. Samples of four colors from one wand were submitted to Orion Analytical LLC, Williamstown, Massachusetts, for identification.

A portion of each sample was analyzed for molecular composition using infra-

red microspectroscopy (IMS). The white was found to consist of kaolin clay and quartz, while the yellow and red were identified as the synthetic organic colorants naphthol yellow S, and acid red or orange, respectively. The green was determined to be the commercial artist's pigment emerald green and the identification was confirmed by polarized light microscopy (PLM) (Hamann and Martin 2003). Also known as Paris green and Schweinfurt green, this pigment is a copper acetoarsenite with the formula $3Cu(AsO_2)_2.Cu(CH3COO)_2$ (Scott 2002, Fiedler and Bayard 1997).

A green sample that was darker and duller than the first was taken from a second dance wand and analyzed in order to determine whether emerald green was present in more than one shade, making its visual identification more problematic. This sample was also identified as emerald green by means of IMS and PLM (Hamann and Martin 2003). The difference in the color field may have been due to the blue pigment particles that were detected in that design area, although impurities, crystal shape and size, or recipe variations can also be responsible for variations in the color of emerald green (Scott 2002, Fiedler and Bayard 1997).

There was no visual or documentary evidence to indicate that the emerald green had been applied at the museum as part of a repair or restoration. Commercial pigments and dyes were generally available to the indigenous people of the southwest by 1880 (Odegaard 1998) and an early ethnologist among the Hopi observed the use of synthetic yellow, red and green dyes for painting dance wands in 1892 (Stephen 1936).

The potential of the arsenic-containing pigments emerald green, orpiment (As_2S_3) and realgar (As_2S_2) to interfere with pesticide analysis by x-ray fluorescence spectroscopy has been noted by Sirois and Sansoucy (2001), but published examples of the actual complication of analytical results—whether spot test or instrumental—had not been encountered.

Discussion Of Spot Test Results

Accession Groups

Figure 1 shows the test results graphed by accession group. The differences among the result profiles from the project's three largest and oldest groups were unexpected. One potential explanation—that the negative test results had been produced by objects left untreated because their materials were not vulnerable to insect damage—was found not to be generally applicable. Within group 1579, for example, eight of nine spare mask parts, composed entirely of painted wood or gourd, tested negative, as might be expected. However, within group 3165, ten of eleven masks, containing significant quantities of feathers, horsehair, fur, or wool, also produced negative test results. Another explanation—that objects tested negative because they had been cleaned prior to the testing—was not generally supported by the visual evidence of the objects themselves.

Possible False Negatives

The pesticide lead arsenate, which is insoluble in water and in HCl, would remain undetected by this test procedure. Successful detection of this compound, which is soluble in caustic alkalies (Budavari 1996), would be ensured by a spot test procedure that employs potassium hydroxide (Hawks and Williams 1986, Knapp 2000). Both sodium arsenite and sodium arsenate are readily soluble in

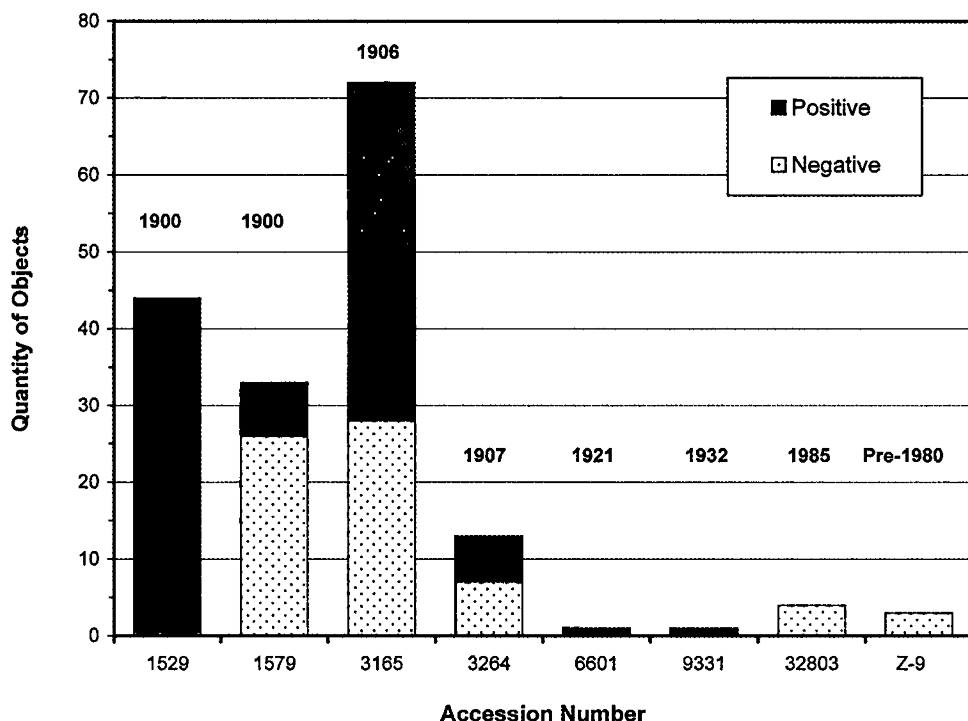

Figure 1. Positive and negative arsenic spot test results sorted by accession group number. The number at the top of each bar is the year the group was accessioned into the museum's collection.

water (Budavari 1996), and arsenic trioxide (As_2O_3), which was the arsenic compound most commonly used in the preparation of dry arsenical powders (Goldberg 1996), is soluble in dilute HCl.

False negative results could also be caused by the reported tendency of arsenic to adhere strongly to keratins (Hawks and Williams 1986, Bertholf 1985), which might inhibit sampling by swabbing. However, during this project arsenic was detected in swab samples from objects consisting entirely of feathers, hair, or turtle shell.

Positive Test Results

While the negative results demonstrated no apparent trends, the positive test results showed strong correlations with two particular sets of objects: the dance wands in group 3165 (31 out of 34 tested positive) and the entire contents of accession group 1529 (all 44 objects tested positive). Of the 103 positive objects in the test project, 75 (or 73%) belonged to those two categories. The confirmed presence of emerald green on two of the dance wands suggested one source of the arsenic detected in that set, although the presence of an arsenic-based pesticide remained a possibility. Very few objects from 1529 were painted with green, but 39 objects from this group had been on exhibit together for nearly a century and had only recently been placed into storage. It was thought likely that these objects had tested positive due to a pesticide treatment that was related to their exhibition.

The positive results in accession group 1579 were produced by painted and

unpainted objects and presented no apparent trends. Nothing was known of their museum history or of what they might have in common with the positive objects from the other two large accession groups.

Statistical Analysis Of The Test Results And Object Data

In an effort to identify what factors might be possessed in common by objects that produced similar test results, a study using the Statistical Program for the Social Sciences (SPSS) was undertaken. The hope was that these factors, once identified, could be used to explain the patterns of test results within the project group or to predict occurrences of pesticide contamination or emerald green usage on other Native American artifacts in the Section's collection. The twenty variables coded for each artifact included accession and catalog number, object name, storage and exhibit locations over time, presence/absence of green paint, primary and secondary construction materials, records of cleaning or other conservation/restoration work, and arsenic test result. Univariate, bivariate, and *chi* square analyses were performed. Multivariate analyses were not carried out.

Results

The most significant variables in relation to positive arsenic test results were determined to be previous display within two particular exhibitions and the presence of green paint (Thompson 2004). Negative test results were associated most strongly with a lack of exhibition history. Figure 2 shows the spot test results distributed according to these factors.

Discussion Of SPSS Correlations

Additional spot testing and instrumental analyses were carried out following the completion of the SPSS study in an attempt to determine whether the correlations could be explanatory or were simply descriptive. This work is described below.

Snake Dance Case and Accession Group 1529

All 39 of the objects from the Snake Dance Case tested positive and all of these objects belong to accession group 1529. Only six of these objects have areas of green color, but 19 are extensively colored with a powdery red pigment. The use of red iron earth pigments by the Hopi was particularly connected with a certain set of ceremonial objects (Hough 1902), to which this accession group corresponds. It has been suggested in a summary of a similar screening project that positive spot test results from certain red-colored objects might be due to arsenic that can occur naturally in association with the mineral hematite (Howe 1999). Nancy Odegaard, Conservator at the Arizona State Museum, who brought the ceremonial significance of the red pigment to the author's attention, reports that arsenic has been detected in traditional iron oxide pigments from excavations at a Hopi ancestral site (Odegaard pers. comm. 2005).

In an attempt to determine whether the source of the detected arsenic on objects in this exhibit case was a pesticide or a pigment, loose particles from two red-colored leather objects and from the skin side of two unpainted, untanned foxskins were submitted to the Canadian Conservation Institute. Portions of each sample were analyzed using x-ray microanalysis (SEM/XES), x-ray diffraction (XRD),

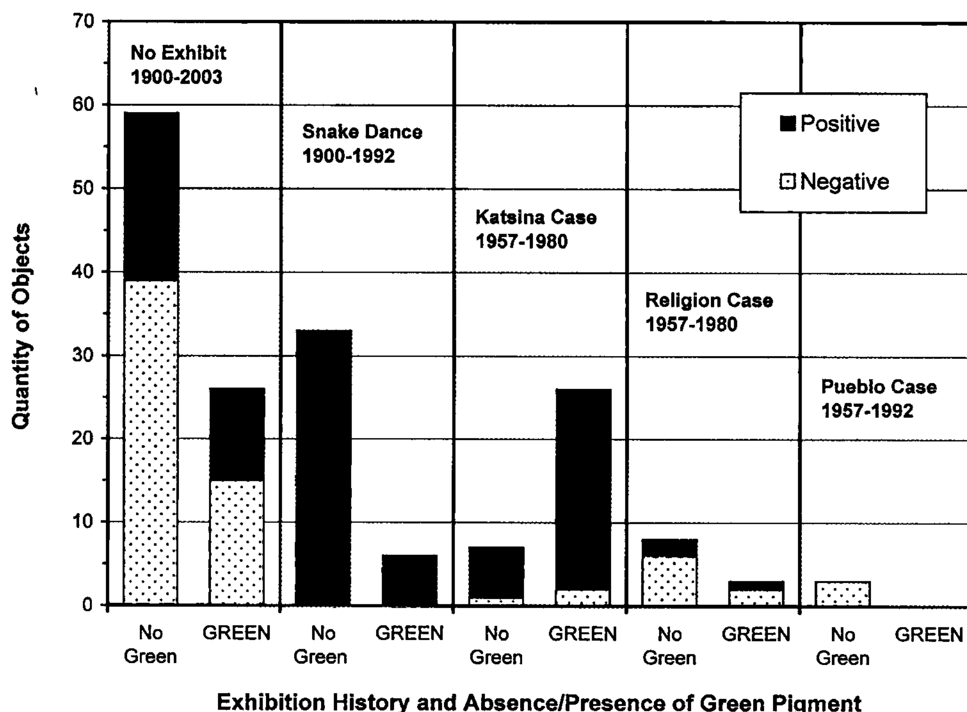

Figure 2. Positive and negative arsenic spot test results sorted by exhibition history and absence/presence of green pigment. Beneath each exhibit name inside the graph are the years of its existence.

Fourier transform infrared spectroscopy (FTIR), and polarized light microscopy (PLM) (Sirois and Moffatt 2005).

In the samples from the two red-colored objects, iron was detected with SEM/XES, hematite was identified with XRD, and the presence of red iron earth pigments was confirmed using PLM. A trace level of arsenic was detected with SEM/XES in the sample from one red object, although both objects had produced positive spot test results. In the samples from the two unpainted foxskins, minor levels of arsenic were detected with SEM/XES. The arsenic compound was not identified in any of the samples, and so it remains to be determined whether the correlation between the positive spot test results and the Snake Dance Case was due to an exhibition-related pesticide application, the presence of the iron earth pigment, or a combination of the two. The fact that this accession group tested 100% positive and was the only group to do so might be an indication that it had been treated by the collector before it entered the museum.

Hopi Katsina Case and Accession Group 3165

The objects in the Hopi Katsina Case that were tested for this project were 33 dance wands from accession group 3165. Thirty (91%) produced positive results and 26 of 33 (79%) had areas of green color.

In addition to dance wands, the Hopi Katsina Case had contained 77 katsina dolls from the same accession group. The dolls had not been requested for repatriation and had not been screened during the project. If the positive results for

the dance wands in this exhibit case were due even partly to arsenic powder applied in connection with the exhibition, it might be expected that a high percentage of these katsina dolls would test positive as well. To investigate this hypothesis, samples from twelve of those katsina dolls were tested using the same procedures: eleven produced negative results and one gave a very slight positive (<0.1 mg/L). The museum's conservation treatment records, which have been kept since the year this case was de-installed, do not record any cleaning of the dolls. Their spot tests suggest that the correlation between the positive results and the Hopi Katsina Case is actually with the dance wands and their emerald green component and not with an exhibit-related pesticide application.

No Exhibition History

Of the 85 objects that had never been on long-term display, 54 (64%) tested negative. By contrast, of the 86 objects with an exhibition history, only 14 (16%) produced negative test results. Among the negative objects within the "no exhibition" category are objects that seemed likely candidates for pesticide treatment: artifacts from the earliest accession groups that are also made of materials extremely susceptible to insect attack. The SPSS correlation could be interpreted as evidence that arsenic powder had been applied to Anthropology collections in storage less extensively than to collections on exhibit and according to criteria that are not always directly related to an object's degree of vulnerability.

However, if the objects in the Snake Dance Case and the Hopi Katsina Case tested positive primarily because of the presence of arsenic-containing pigments, the correlation between negative test results and lack of exhibition history does not in fact represent a contrast in pesticide application practices between stored objects and exhibited objects.

Summary and Conclusions

During 2001–2003, 171 objects in the process of repatriation from Carnegie Museum of Natural History to the Hopi Tribe were screened for the presence of arsenic pesticide residue using a commercial spot test kit. One hundred and three objects (60%) produced positive test results. Because of the reported historical use of an arsenical powder on unspecified Anthropology collections in storage and on exhibit over a two-decade span, positive test results had been expected. But the patterns of contamination within the test group led to suspicions that arsenic-containing pigments had been responsible for some of those positive results. Analysis of samples from four representative objects using IMS and PLM resulted in the identification of the commercial artists' pigment emerald green, which is a copper acetoarsenite, and a traditional red iron earth pigment, which may be a source of naturally occurring arsenic. The strong correlation between positive test results and the presence of green paint suggested that emerald green was present on many more objects than the two dance wands on which it was identified.

A study of the spot test results and object catalog information using SPSS revealed a correlation between positive test results and two previous museum exhibitions, suggesting an exhibition-related use of arsenic, although the pigments on the objects in those exhibit cases might also be a source of the detected arsenic. The transfer of pigment particles or pesticide residue from one object to another

through handling, or as a result of proximity during storage or transport, might be responsible for some of the positive results. However, the research that was carried out for the SPSS analysis revealed that extant museum records do not contain the level of detail necessary to draw many inferences about cross-contamination of specific objects.

Given the current state of our knowledge about the objects in this test group, it would be difficult to predict with certainty whether the source of the detected arsenic for a particular object is inherent or acquired. If identification of the arsenic-containing compounds on individual objects would be required for decisions regarding remediation or future use, more extensive application of quantitative analytical techniques would be necessary. This project provides an example of the difficulties in interpretation that can arise from the known or suspected presence of arsenic-containing pigments on objects that are screened for arsenic pesticide residue using a spot test.

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PESTICIDE CONTAMINATION ON NATIVE AMERICAN ARTIFACTS—METHODS, RESULTS FROM SIX CASE STUDIES, AND NEXT STEPS

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Abstract.—This work describes several case studies involving the determination of pesticide contamination on objects from the Treganza Museum at San Francisco State University, the Phoebe Hearst Museum of Anthropology at the University of California at Berkeley, and the Elem Pomo, Hoopa, Karuk, and Yurok tribes of California. The focus of these studies was determination of arsenic and mercury via Flame Atomic Absorption Spectrophotometry and determination of six organic pesticides via Gas Chromatography/Mass Spectrometry. Mercury was detected in 31% of the samples at concentrations up to 16.6% by weight. Significant contamination was found in several different collections, with mercury and DDT concentrations at levels that may be of toxicological significance. DDT was detected in 44% of the samples with concentrations as high as 2,900 parts per million (ppm) or 0.29% by weight. Native Americans, museum professionals, and anyone handling potentially contaminated objects should continue to take appropriate measures to minimize exposure. In the future, it is hoped that government granting agencies will facilitate efforts to provide for free testing of pesticide contamination for tribes and museums, and that researchers will develop improved sampling techniques, analytical methods, and exposure and risk assessment data that more definitively address people's concerns about their safety.

INTRODUCTION

In the past, it was standard practice for museums to treat artifacts in their possession with arsenic, mercury, and other pesticides (Goldberg 1996, Hawks 2001). The purpose of this was to protect the objects from possible destruction by fungi, insects, and rodents. Museum staff working with these pesticides, handling contaminated objects, or breathing the air in rooms where they are stored may be exposed to these potentially toxic chemicals. Despite numerous symposia and publications on this issue, there is surprisingly little published work which shows the extent of this contamination within specific museums; only one study reported an evaluation of the potential health hazards of DDT exposure within a museum in the U.S. (Pryor 1982). To the best of the knowledge of the primary author, there are no published epidemiological studies that retrospectively evaluated the health of museum workers who may have been exposed to these pesticides.

Passage of the Native American Graves Protection and Repatriation Act (NAGPRA) in 1990 allowed for repatriation of artifacts to federally recognized tribes. While tribes may be aware that these items could be contaminated, there is often little or no a priori information as to the types and levels of contamination that may be present. In most cases, no records were kept to document the types, quantities, and frequency of pesticide applications to each object within a collection. Hence, chemical analysis represents the only means for determining whether or not an item has been contaminated. Two publications provide a thorough review

of the various analytical methods that can be used for this purpose (Palmer 2001, Sirois and Sansoucy 2001).

Many tribes are actively pursuing repatriation of sacred artifacts, and the most common question encountered in this process is whether or not their items are contaminated. While some tribes and museums have resorted to the use of relatively inexpensive spot tests for this purpose, these tests often yield false positives (Found and Helwig, 1995) and spot tests for organic pesticides such as naphthalene or DDT are not available. Palmer and his students at San Francisco State University (SFSU) have been performing these analyses *gratis* or for a nominal charge to cover the cost of the supplies and standards. They have completed six case studies to date including analyses of items from the Treganza Museum at SFSU, the Phoebe Hearst Museum at the University of California at Berkeley, and the Hoopa, Elem Pomo, Karuk, and Yurok tribes of California. This manuscript describes the various methods used for sampling and analysis, summarizes the results from the six case studies, and concludes with some suggestions for future work.

Methods

The artifacts of interest in this work included items such as baskets, headdresses, deerskin aprons, and baskets. In each case study, the issue of sampling has been an important consideration (Caldararo et al. 2001). From the standpoint of the tribes, an artifact is sacred and hence should be sampled in a manner consistent with their beliefs. For some tribes, this does not preclude the use of destructive sampling, in which a small amount of the artifact is removed for subsequent testing. For some case studies, nondestructive sampling methods using swabs and/or wipes were employed so as to minimize damage to the objects. While it should be understood that nondestructive sampling can underestimate the amount of contamination present, as it will neither remove 100% of the surface contamination nor be able to assess subsurface contamination, it may be an acceptable means for providing a sample that can answer the question as to whether or not the item is contaminated.

Another important consideration is where to sample the artifact. If possible, more than one sample from each artifact is desirable, as pesticides may not have been applied to the entire object. Ideally, a composite sample representing several locations on an object would be used as the most cost efficient means of determining whether or not an artifact was contaminated via a single analysis. Where both heavy metal and organic pesticide contamination were to be assessed, a separate sample was required for each of the two different types of analytical methods required.

In each case study, sampling was performed in accordance with the wishes of the tribes and/or museums. Where destructive sampling was used, a small piece of an artifact was removed from an inconspicuous area with typical sample sizes of a few square millimeters and sample masses on the order of a few milligrams. Where nondestructive sampling was used, several swabs wetted with an appropriate solvent (water for arsenic and mercury analysis and acetone for organic pesticide analysis) were rubbed over a 10-cm^2 sized area of the artifact. Once acquired, the sample was placed into a clean vial, which was sealed and sent to SFSU for subsequent analysis.

The analytical methods used in this work are described in more detail elsewhere (Palmer 2001, Palmer et al. 2003). Briefly, Flame Atomic Absorption Spectrophotometry (FAAS) was used to measure arsenic and mercury, and Gas Chromatography/Mass Spectrometry (GC/MS) was used to measure organic pesticides. The scope of the GC/MS analyses was limited to no more than six organic pesticides, which included p-dichlorobenzene, naphthalene, thymol, dieldrin, lindane, and DDT. All of these analyses were performed by undergraduate students majoring in chemistry, biochemistry, or environmental studies at SFSU. A number of quality assurance and quality control (QA/QC) procedures were followed to ensure generation of reliable data. Standard operating procedures (SOPs) were developed for sampling and analysis. Each student was trained in the relevant analytical methods. Certified reagents were used to prepare the standards used as the basis for quantitation. Method, field, and trip blanks were analyzed to ensure negligible levels of contamination in the media used for sampling (i.e., vials, swabs, solvents). Precision was assessed via replicate measurements of samples and standards. Limits of quantitation (LOQs) and limits of detection (LODs) were computed to qualify results where sample concentrations fell below the limits of reliable quantitation and detection, respectively. In some cases, separate standards and spikes of sample extracts were performed to assess accuracy of quantitation. Finally, each and every analytical result was verified and validated by Palmer prior to documenting them in a report to the tribe or museum.

Case Study Results

The results from six case studies completed to date are shown in Tables 1 to 3, which provide summaries of mercury testing via FAAS, organic pesticide testing via GC/MS, and cumulative results from all six studies. In some of the case studies, only metal analyses or organic pesticide analyses were performed due to the limited number of samples available. Note that arsenic was not detected in any of the samples in these case studies. While this does not preclude the presence of arsenic in these samples at concentrations below the LODs, these results indicate that arsenic was not used for preservation of these particular objects. It should be noted that QA/QC procedures demonstrated both accurate detection and quantitation of arsenic. For confirmation of accurate detection, a "blind" check standard was analyzed and found to give positive detection for arsenic. For confirmation of accurate quantitation, either a blind check standard prepared by M. Fang was analyzed and found to give an experimentally determined concentration of arsenic within 5% of the true value, or a sample was spiked with a known concentration of arsenic, analyzed, and gave a percent recovery close to theoretically expected value of 100%.

The first case study involved the analysis of arsenic and mercury on five items in the Treganza Museum collection at SFSU in 1999, which included a musical instrument, a fossil, cotton packing, debris, and a bag from a drawer where these items were stored. Here, destructive sampling methods were employed and a total of nine samples were acquired from these items. The musical instrument showed the highest level of contamination with 2.7% mercury (on a weight-weight basis) detected in the sample. The presence of mercury on the other items demonstrates that mercury was either applied to the entire contents of the drawer and/or migrated to other items.

Table 1. Summary of mercury analyses. Where destructive sampling was used, concentrations are reported on weight/weight basis in units of percent; where swab sampling was used, concentrations are reported in units of $\mu g/cm^2$.

Case study	Pesticide agent	Number of samples	Frequency of detection	Range of concentrations
SFSU	mercury	9	100%	0.4%–2.7%
Hoopa	mercury	28	32%	ND–16.6%
Elem	mercury	25	0%	ND
Yurok	mercury	22	73%	ND–3.3%
UC Berkeley	mercury	25	4%	ND–47 $\mu g/cm^2$

Table 2. Summary of organic pesticide analyses. Where destructive sampling was used, concentrations are reported on weight/weight basis in units of ppm; where swab sampling was used, concentrations are reported in units of $\mu g/cm^2$.

Case study	Pesticide agent	Number of samples	Frequency of detection	Range of concentration
Hoopa	p-dichlorobenzene	29	17%	ND–130 ppm
Karuk	p-dichlorobenzene	20	0%	ND
Yurok	p-dichlorobenzene	22	5%	ND–3 $\mu g/cm^2$
Hoopa	naphthalene	29	77%	ND–1830 ppm
Karuk	naphthalene	20	0%	ND
Yurok	naphthalene	22	10%	ND–88 ppm
Hoopa	thymol	29	3%	ND–10 ppm
Karuk	thymol	20	0%	ND
Yurok	thymol	22	0%	ND
Hoopa	lindane	29	7%	ND–30 ppm
Karuk	lindane	20	0%	ND
Yurok	lindane	22	0%	ND
Hoopa	dieldrin	29	0%	ND
Karuk	dieldrin	20	0%	ND
Hoopa	DDT	29	40%	ND–130 ppm
Karuk	DDT	20	55%	ND–2900 ppm
Yurok	DDT	22	67%	ND–1698 ppm

Table 3. Summary of results from all six case studies.

Pesticide agent	Number of samples	Frequency of detection	Range of concentration
mercury	105	31%	ND–16.6%
arsenic	105	0%	ND
p-dichlorobenzene	71	8%	ND–130 ppm
naphthalene	71	34%	ND–1830 ppm
thymol	71	1%	ND–10 ppm
lindane	71	3%	ND–30 ppm
dieldrin	49	0%	ND
DDT	71	44%	ND–2900 ppm

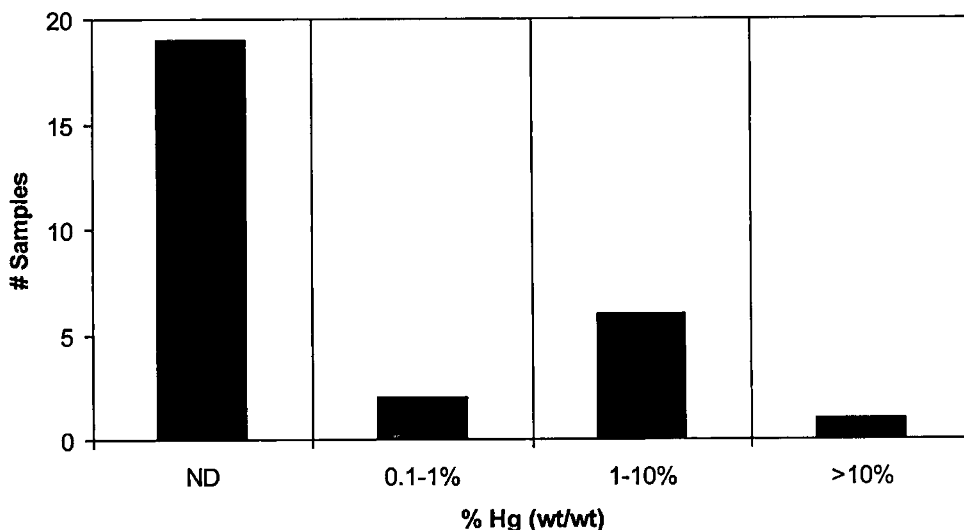

Figure 1. Results from Hoopa case study showing the frequency distribution of mercury in the samples. For the six samples where mercury was detected, the mean concentration was 4% with the standard deviation of 5%.

The second case study involved analysis of arsenic, mercury, and six organic pesticides on 17 items repatriated to the Hoopa tribe in 1999. Full details on this study including methods and results are provided elsewhere (Palmer et al. 2003). Here again, destructive sampling methods were used with the permission of the Hoopa curator responsible for repatriation of these objects (Caldararo et al. 2001). A total of 58 samples were acquired: 29 for arsenic and mercury analyses and 29 more for GC/MS analyses. Mercury was detected in nearly a third of the samples (32%) at concentrations as high as 16.6% for some of the smaller samples of feathers. Naphthalene was detected on nearly 80% of the samples with concentrations as high as 1800 parts per million (ppm) (equivalent to 0.18%). DDT was detected in 40% of the samples at concentrations as high as 130 ppm. Figures 1 and 2 show frequency distributions for mercury and naphthalene, and indicate the typical concentrations found and the variability in the data. For the nine samples where mercury was detected, the average concentration was 4% with a standard deviation of 5%. For the 23 samples where naphthalene was detected, the average concentration was 202 ppm with a standard deviation of 412 ppm. These results show wide variability in the concentrations detected, which is understandable given the heterogeneity of the pesticide application process and the different types of materials sampled.

The third case study focused on analysis of arsenic and mercury on 25 items from the Phoebe Hearst Museum at the University of California Berkeley (UC Berkeley). One sample from each object was acquired using *either* destructive or swab-based sampling for subsequent FAAS analyses at SFSU. Several additional swab samples were acquired from each object for subsequent spot tests by Fang. Mercury was not detected via FAAS, with the exception of one swab sample in which 47 $\mu g/cm^2$ of mercury was found. Of particular interest in this study was comparison of FAAS results with those from spot tests. FAAS results did not

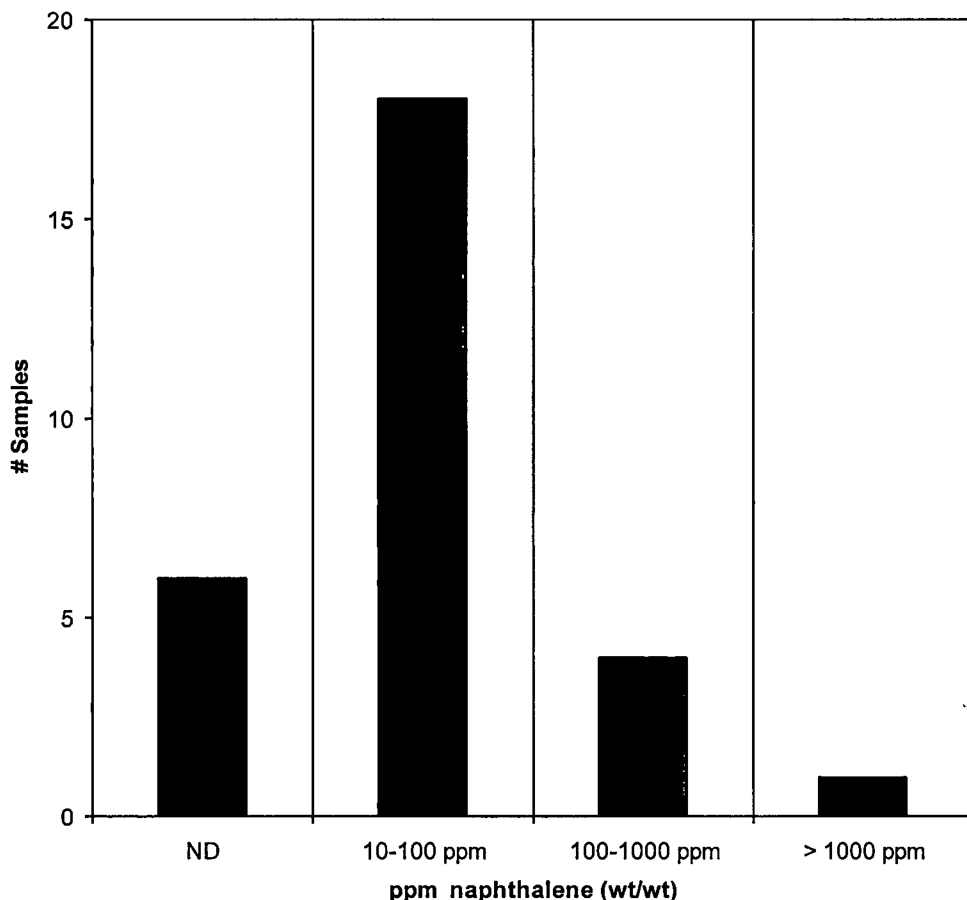

Figure 2. Results from Hoopa case study showing the frequency distribution of naphthalene in the samples.

show the detection of measurable levels of arsenic in any of these samples, whereas spot tests indicated the presence of arsenic in trace amounts in five samples (<0.025 mg/L in three samples and 0.1 mg/L in two samples). Assuming the arsenic spot test to be reliable (Found and Helwig 1995), these conflicting results may be due to the differenct LODs of the methods: typical LODs from FAAS were approximately 0.2 ppm whereas the LODs from spot tests were less that 0.1 ppm. FAAS and spot tests for mercury on four of these same samples agreed in that no mercury was detected on all but one of the objects. Here, FAAS indicated 47 $\mu g/cm^2$ whereas the spot test showed no detection. The negative spot test result may well be the result of a desensitizing type of interference (Found and Helwig 1995). While it is possible that FAAS results may be incorrect, QA/QC data indicated accurate detection and quantitation of arsenic and mercury via FAAS in two blind unknowns prepared by Fang, and it is generally accepted that FAAS provides greater selectivity based on the use of a selective wavelength of absorption for detection and quantitation based on this method's greater selectivity. Clearly, the difficulties in correlating results from spot tests to those from FAAS

points out the need for a more rigorous intercomparison between these two methods.

The fourth case study involved determination of arsenic and mercury on 16 objects to be repatriated from the California Department of Parks and Recreation Museum in Sacramento to the Elem Pomo tribe. The tribe agreed to acquisition of 25 samples via destructive sampling. Neither arsenic nor mercury was detected in any of the samples. QA/QC data showed recoveries near 100% on samples spiked with known levels of arsenic and mercury, again indicating the reliability of quantitation, in this case within the sample matrix. While these results do not show arsenic or mercury contamination, this does not preclude the possible presence of organic pesticides on these objects.

The fifth study involved determination of six organic pesticides on 12 Karuk objects in the Hearst Museum at UC Berkeley at the request of the Karuk tribe. A total of 20 samples were acquired via either destructive or swab-based sampling. DDT was detected in 55% of the samples, with concentrations as high as 0.29% (2,900 ppm), which corresponds to the highest concentration found to date in these studies. Of particular interest here is comparison of GC/MS results with museum records that indicated the use of DDT via a small green dot on some of the objects. GC/MS results and historical data were in agreement on either detection or non-detection of DDT in 14 samples. In three samples, DDT was detected via GC/MS where historical data did not indicate its presence, suggesting that DDT has somehow migrated onto these objects or that the original marked tags may have been removed or detached. In the three remaining samples, DDT was not detected via GC/MS when historical data indicated its usage, suggesting that DDT was not applied to this particular sample location or that its concentration was reduced below the LOD via time, degradation, and/or volatilization.

The sixth case study involved determination of arsenic, mercury, and five organic pesticides on 12 objects repatriated to the Yurok tribe. A total of 48 samples were acquired via destructive sampling plus one more via swab-based sampling. Dieldrin was excluded from these analyses, as a standard was not available at the time these analyses were performed. Mercury was detected in 73% of the samples at concentrations ranging as high as 3.3%. DDT was detected in 67% of the samples at concentrations as high as 0.17% (1,698 ppm). P-dichlorobenzene and naphthalene were detected in only a few samples.

Conclusions and Next Steps

The results of these case studies spanning the period 1999 to 2004 have also been evaluated from the standpoint of developing recommendations for future work in this area. It should be noted that many Native American tribes do not have access to the expensive instrumentation required for this work and may not have the funds needed to use contract laboratories for these analyses. Although these labs certainly have the capability to do these analyses, they may be unaware of the special sampling considerations and typically charge approximately $100 per sample for heavy metal analysis and $500 per sample for pesticide analysis. University-based laboratories hopefully represent an unbiased third party that can provide objective and reliable data, in some cases free of charge or at costs well below that of contract labs.

In regards to sampling, nondestructive sampling is usually preferred from a

conservator's viewpoint but destructive sampling is preferred from an *analytical* standpoint given its near 100% extraction efficiency for either metals or organic pesticides. Nevertheless, nondestructive sampling methods based on the use of swabs give useful data showing whether or not an object has been contaminated. Very little work has been done comparing results from both destructive and non-destructive sampling methods, and such data will not be easy to obtain unless a uniform pesticide application process is employed. Assuming the goal of the study is to determine *if* an object has been contaminated, composite sampling is preferable as a sample taken from only one small area on an object may yield misleading results, as pesticide(s) may not have been applied to this particular location. Assuming the goal is to determine which *parts* of an object are contaminated (i.e., feathers, leather, etc.), replicate sampling is needed. Clearly, the issue of sampling is more complicated than it might seem, and the sampling strategies employed in a particular study will depend on a number of factors including cultural issues, conservator input, analytical data required, etc. Finally, some discussion of experimental error is appropriate in this context. While false positives and negatives can occur (especially when using spot tests) and errors can be attributed to a number of sources (i.e., analytical method, analyst, etc.), the major source of variability in the data results from the sampling process and the objects themselves. Once an object has been sampled using wipes or swabs, subsequent sampling at the same locations will result in lower concentrations of a given pesticide. More importantly, pesticides may not have been applied uniformly on an object, and this should be kept in mind when comparing data from replicate analyses of the same object.

FAAS appears to give good quality data and sufficient sensitivity to detect percent levels of arsenic and mercury contamination in samples. One concern for destructive sampling is acquiring a minimal sample weight to ensure sufficiently low LODs in the sample. For example, given an LOD of 3 mg/L for mercury *in solution,* a 50-ml extract volume, and a 10 mg sample weight, the corresponding LOD for mercury *in the sample* would be 1.5%. This suggests the use of sample masses greater than 10 mg in order to detect mercury concentrations above 1.5% in the samples. Although ICP-MS can provide much lower LODs and multi-element analysis capabilities, it requires very expensive instrumentation and hence this often precludes its use for this application. The major drawback to FAAS is the time and effort required to work up the samples. Typically, this process takes about 2 days for 25 samples; one day for digestion, filtration, and dilution; and another for instrument setup and analysis. XRF is far more efficient in terms of speed, and Sirois (2001) reported the analysis of more than 100 objects in an 8-hour time period. XRF should be the method of choice for future analysis of screening for heavy metal contamination on museum artifacts given that these instruments are portable, possess adequate sensitivity, and can be used for direct analysis of an object with results available in a timeframe on the order of a minute or less.

GC/MS appears to be the best method for identifying and quantifying the wide variety of volatile organic pesticide agents that have been employed in the past. The case studies discussed here have focused on six organic pesticides that were delineated from a prior study (Glastrup 1987). Historical data have shown that collections have been treated with other organic pesticides as well, and although

none have been tentatively identified in any published work to date, the scope of the target compounds should be expanded to include other likely substances as well as potential degradation products such as DDE. It should be noted that Solid Phase Micro-Extraction (SPME) can be used for nondestructive sampling of the headspace above an artifact. This simplifies the sample preparation versus destructive or swab based sampling (Ormsby et al. this volume), although correlating the resulting data to compute actual pesticide concentrations in the samples is difficult. Direct Sampling Mass Spectrometry represents an option for rapid screening of several pesticides within a sample. In this method, a small sample or swab is loaded onto a probe, introduced into the ion source region of a mass spectrometer, and heated to desorb the pesticides which are subsequently detected via selected ion monitoring and/or tandem mass spectrometry. This technique appears to be very promising for rapid screening of samples, and should give results in a few minutes per sample versus the typical 30–60 minute analysis times required for GC/MS.

The most important considerations in all these studies is providing data and information to Native Americans and museum professionals which can help them answer questions such as whether or not an item is contaminated, what is the extent of the contamination, what are the potential exposures and risks, and how to take appropriate measures to minimize these risks. Clearly, these case studies show significant contamination, especially with respect to mercury and DDT. One of the hardest questions to answer is evaluating the risks associated with handling or wearing the artifacts. Some work has been done to assess arsenic and mercury picked up on gloves after handling contaminated objects. Several studies have shown arsenic, mercury, and DDT in air at levels which are below appropriate workplace limits. Nevertheless, there is a need for more work in this area to more effectively answer these questions, particularly in assessing the risk from various activities, especially in light of the fact that children and elders may wear these objects during sacred dances. Finally, continued dissemination of data on contaminated collections is needed.

While several attempts have been made to secure major funding for development of new sampling and analysis methods, providing free testing of artifacts, and assessing potential exposures, these have not been successful to date. It is hoped that program managers and government funding agencies will understand that this problem affects not only Native Americans but is a public health issue that confronts a large number of museums.

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DETECTION AND MITIGATION STRATEGIES FOR CONTAMINATED NAGPRA OBJECTS—THE SENECA NATION'S EXPERIENCE

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Abstract.—Many of the sacred objects repatriated to the Iroquois people under Native American Graves Protection and Repatriation Act (NAGPRA) are contaminated with pesticides. The identity of the pesticides, amount and method of application that were applied to preserve the objects by museums and private collections are often unknown and undocumented. The focus of this study was two fold: identifying arsenic, mercury, and lead on objects repatriated to the Seneca Nation of Indians, and investigating strategies for removal of such contamination. The sampling methods used here were nondestructive and involved the use of wipe samples or direct, nondestructive analytical methods. A variety of analytical techniques, including spot tests, atomic spectroscopy, and x-ray fluorescence were used. The results showed the presence of arsenic and mercury residues. Mercury residues ranged from 140 to 6,860 μg on painted surfaces. Unpainted wood surfaces were found to have mercury residues that ranged from 330 to 13,200 μg. Initial attempts to mitigate these contaminants by vacuuming and washing showed no significant reduction, and hence a novel approach based on a surface-active displacement solution (SADS) was employed. Medicine masks highly contaminated with mercury residues showed only trace amounts of mercury residues after the first treatment with a SADS formulation.

INTRODUCTION

Since the passing of Native American Graves Protection and Repatriation Act (NAGPRA) medicine masks have been repatriated to the Seneca Nation of Indians as well as the other members of the Iroquois Confederacy (Haudenosaunee). Many of these items have been previously treated with arsenic, mercury, and other pesticide agents. The events leading up to discovery of the contamination have been previously documented (Jemison 2001).

Preliminary testing performed by the National Museum of the American Indian (NMAI) using wipe samples in 1998–1999 found the presence of arsenic and mercury on repatriated sacred medicine masks. This discovery led to a range of emotions among the Haudenosaunee and spurred numerous discussions on what to do next.

The next step for the Seneca Nation was to reanalyze those masks that previously tested positive for aresenic at NMAI. In 1999, a portion of these masks was analyzed by bench-top XRF at Mercy Hurst College and confirmed the presence of arsenic residues. Another portion of masks was evaluated by the Canadian Conservation Institute (CCI) using Radioisotope-Excited X-Ray Energy Spectrometry (REXES). Analysis by REXES confirmed the presence of arsenic and mercury. The confirmation of arsenic and now the presence of mercury were very unsettling to the community. Wipe sample analysis of the remaining portion of the masks by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) confirmed the presence of arsenic, mercury, and lead.

In 2002, the Tribal Historical Preservation Office (THPO) of the Seneca Nation

of Indians, with the support of the Seneca-Iroquois National Museum and the Haudenosaunee Standing Committee on Burial Rules and Regulations (HSCBRR), received a grant through the National Parks Service (NPS). The HSCBRR works on legislation to protect unmarked Native American burial sites in New York State and repatriation. The Standing Committee is composed of representatives from the Tonawanda Band of Senecas, Seneca Nation of Indians, Cayuga, Onondaga Nation, Mohawk Nation Council of Chiefs, the Council of Chiefs from the Six Nations Reserve at Oshweken, Ontario and Tuscarora Nation.

The purpose of this grant was to research methods for detection and mitigation of the potential human health risks associated with the pesticides that were applied to control insect infestations of NAGPRA inventories.

There were two major objectives for this research. The first was to evaluate the current condition of sacred objects subject to repatriation, including the development and use of appropriate sampling and analysis methods. The second was to identify possible methods of mitigation of contaminants for potential ceremonial use in the future. While it may not be possible to remove all pesticide residues, the goal here was to reduce them to non-detectable levels using wipe sample analysis.

Methods and Materials

Sampling

In the past, both NAGPRA inventories as well as other collections have been treated or exposed to various inorganic (i.e., arsenic trioxide, mercuric chloride, lead) and organic pesticides (i.e., naphthalene, lindane, DDT). Since this problem has come to light, documentation of the possible identities of these contaminants has continued to improve (Goldberg 1996, Hawks 2001, Palmer 2001). The types and levels of these pesticides are of great concern to curators who come in contact with collections on a daily basis and those receiving these sacred objects as they may be returned to ceremonial use.

The first consideration for this project was investigating appropriate methods of sampling and detection for arsenic and mercury based pesticides. Perhaps the most difficult aspect of this project relates to the limitations and restrictions placed on sampling. Because each mask is considered to be a living being, the sampling technique must be non-destructive. A wide range of techniques for sampling and detection has been reviewed in previous publications (Sirois 2001, Handa et al. 1999, Palmer 2001). Sampling techniques have also been developed by Occupational Safety and Health Administration (OSHA), National Institute of Occupational Safety & Health (NIOSH), US Environmental Protection Agency (EPA), and the New York State Department of Environmental Conservation (NYSDEC).

Using the assumption that dislodgeable pesticide residues are of primary interest with respect to human exposure, wipe samples were taken using a modified field procedure for surface wipe sampling (BNL 2002). Different analytical methods were used for arsenic and mercury; therefore, separate samples were needed for arsenic and mercury. Several samples were taken per mask to compensate for variations in concentration of surface contaminants. Wipe samples were also taken using Palintest pre-moistened wipes following the same procedure.

The surfaces studied were comprised of wood, hair and cornhusk. The wood

surfaces varied in texture and coating. The outsides of these masks were painted with a single layer and some had a second thin layer which could be a wash, clear coat, or lacquer. The outside texture varied from a smooth glossy surface to a rough matte texture. Sampling rougher surfaces using Palintest wipes was difficult, as the surface could easily tear the somewhat delicate wipe. The insides of the masks were generally untreated and varied in levels of smoothness that also proved equally difficult on the pre-moistened wipes. Gauze wipes proved to be more durable for sampling even the most difficult surfaces.

Analysis

The Haudenosaunee were unprepared for the then overwhelming task of what to do with the discovery of pesticide residues. As is the case with many tribes, the Seneca Nation does not maintain a laboratory for the analysis of pesticide residues. Even with an analytical facility, the methods of sampling and detection were thought to be limited to destructive or invasive sampling and analysis techniques.

Tribal custom dictates that medicine masks must be treated with the same care and respect one would show another member of the human race. Hence, the use of XRF for direct analysis of such materials is not to be taken lightly. The benefits of the direct use of XRF for screening masks were explained to the Haudenosaunee Standing Committee and the tribal representatives. They have thus far been receptive to the possible direct use of XRF on medicine masks.

One goal of this investigation was to evaluate removal efficiencies as a result of various mitigation efforts. This raised the question as to whether or not portable XRF equipment possessed the requisite sensitivity needed to detect arsenic, mercury, and lead on wipe samples taken before and after treatment of the objects. In 2004, a Niton model XL700 XRF instrument was used to perform analysis for arsenic, lead, and mercury residues using pre-moistened Palintest wipes. Wipe samples were analyzed through the assistance of the Visiting Professional Program at NMAI using the Niton's internal dust wipe analysis program and dust wipe sample holder. ICP-AES and CVAAS analyses were performed on wipe samples in order to more accurately assess removal efficiencies of arsenic and mercury.

Mitigation

A secondary objective of this project was to identify possible methods for mitigation of surface contaminants on sacred objects intended for ceremonial use. While it is understood that it may not be possible to remove all pesticide residues from contaminated objects, the goal here was to attempt to reduce the pesticide contamination below detectable levels using wipe sample analysis.

The ceremonial use of a repatriated mask means that it will come in contact with a human face. Human hands will pick up the mask and hair on the mask will come in contact with the wearer as he moves about. Body temperatures will rise and the resulting human sweat will come in contact with the surface of the mask, possibly assisting with the transfer of these residues. With this in mind, the search for a method of mitigation of these residues was of paramount importance for the tribe.

Mitigation efforts must also adhere to the same cultural limitations as the sam-

Table 1. Mitigation options and possible outcomes for medicine masks.

Mitigation option	Possible outcome
None	Exposure to surface contaminant by family members at home and traditional practitioner.
Remove wood (i.e. sanding)	Generating airborne contaminants.
Remove wood (i.e. chisel)	Some masks are too fragile from poor storage.
Repaint outside of mask	Does not remedy possible flaking of paint during use.
Remove and install new hair	Acceptable, source of new hair only difficulty.
Wash with water only	Previously attempted with no improvement.
Wash with isopropyl alcohol and water	Previously attempted with no improvement. Some color change was noticed.
Clean with synthetic skin oil	Research needed to determine effect of components on painted surfaces.
Clean with saliva	Labor intensive, no synthetic equivalent commercially available.
Dental vacuum, HEPA filter, water trap.	Previously attempted with no improvement.
Encapsulate	Process is not culturally acceptable. Unknown durability of coating.
SADS concept for cleaning	Disposal cost of waste. May not remove subsurface contaminants.
Traditional cleaning methods	May not remove surface contaminants but will aid in securing subsurface contaminants.

pling and analysis processes. Several approaches were provided to traditional practitioners as seen in Table 1. An ideal mitigation strategy would reduce surface contaminants and would prevent sub-surface contaminants from migrating to the surface. It is also important that the mitigation process does not degrade the wood, metal or paint on the mask. Photodegradation of the pesticide residues was not recommended as a mitigation option due to the potential of the breakdown products being more toxic than the parent compound (Handa et al. 1999). Furthermore, the photodegradation of lignin by ultraviolet (UV) light occurs rapidly on exposed wood surfaces (Feist 1983). Encapsulation with parylene was considered as a possible mitigation treatment. The encapsulation process is a vapor-deposition and polymerization of para-xylene or a substituted derivative. This process affords a controllable, durable plastic coating. Several encapsulated objects were examined to determine its potential as a mitigation option. The paraxylene coating was of particular interest as it was difficult to detect visually and allowed objects to remain flexible. Remembering that the masks are considered living beings, the encapsulation process would not be culturally acceptable.

Traditionally, the Haudenosaunee believe that the best way to "protect" the mask is through regular use. The mask is believed to have its own curative powers and it will "cleanse" itself. In addition, natural oils are employed to keep the wood surface clean and properly conditioned. The use of other sacred materials on the face is also believed to keep the face alive and well. Cultural sensitivity and the concerns of traditional medicines that accompany these faces make it difficult to share any more information on the handling protocols.

The best results thus far for mitigation of surface arsenic and mercury residues

were obtained with the application of the Surface-Active-Displacement Solutions (SADS). This concept was created for the cleaning of delicate surfaces. Recent application of this concept has been explored on surfaces such as heat exchangers and water-side surfaces of piping to remove micro-fouling film from micro-organisms and live plants (Baier et al. 1986). The initial use of the SADS concept was on painted metal, but may have potential for mitigating specific pesticide residues from repatriated sacred objects.

A literature review revealed that prior cleaning systems rely mainly on factors other than the surface activity of the cleaning solution, such as solvency, mechanical actions or hydrolytic components (Park et al. 1990, Campbell et al. 2000, Laughlin 1993). Caustic solutions, solvents and mechanical scrubbing are the primary means currently used for removing pesticide residues from protective equipment and work areas. This does not lend itself directly for the cleaning of delicate surfaces; hence the next step was to develop an effective displacement formulation for organic and inorganic residue coatings on solid surfaces at ambient conditions, without requiring direct solution or emulsification processes.

A SADS formulation typically consists of three major ingredients. The first is butanol or longer chain aliphatic alcohol. This provides the interfacial displacement action, and serves as a solvent for the contaminating agent. The second ingredient, a surfactant, serves two purposes: it emulsifies the stripped chemical agent in the carrier liquid and acts as a recontamination inhibitor, leaving freshly cleaned surfaces with critical surface tension. The third ingredient, water serves several functions. Since only small amounts of active ingredients are needed, water acts to carry these materials to the contaminated surface. Second, water acts as a carrier of the stripped and emulsified chemical agents. When the water drains from the surface, the chemical agent is also removed. Water also minimizes the fire and explosion hazard of the SADS mixture.

Results and Discussion

Testing in 2004 using a portable XRF at NMAI detected lead in 90% of samples, arsenic in five percent and mercury in 20% of the Palintest wipe samples. Follow up testing of these wipe samples with ICP-AES was performed for comparison showing similar results for lead but a notable increase with 20% of samples for arsenic. ICP-AES and CVAAS analysis of gauze wipe samples of these masks detected the presence of both mercury and lead in 100% of the samples. A comparison of results from these various methods can be seen in Table 2.

Given the limitations set on sampling, each method has its advantages in the screening of medicine masks for arsenic and mercury pesticide residues. The portable XRF, while not sensitive enough for detection of trace amounts of arsenic and mercury residues on wipe samples may be adequate when directly used on the surface of the masks. Both the bench top and portable XRF have the distinct advantage of rapid analysis. Analysis by ICP-AES and CVAAS are very sensitive methods and can detect metals below the sub-microgram levels; however, they require a two-week turn around time for analysis and the sample is consumed during the process.

Since first discovery of contamination in 1998, unacceptable levels of arsenic or mercury residues have been found in nearly every analysis of medicine masks

Table 2. Comparison of contaminants found using different detection methods on the same object.

Object number	Detection method/contaminant		
	ICP-AES/CVAAS	Portable XRF	Bench top XRF
7	Arsenic, Mercury, Lead	Lead	Arsenic
8	Arsenic, Mercury, Lead	Mercury	Arsenic
9	Mercury, Lead	Lead	Arsenic
10	Arsenic, Mercury, Lead	Lead	Arsenic
11	Mercury, Lead	Lead	Arsenic
12	Mercury, Lead	Mercury, Lead	Arsenic
13	Mercury, Lead	Lead	Arsenic
14	Mercury, Lead	Lead	Arsenic
15	Mercury, Lead	Lead	Arsenic
16	Mercury, Lead	Mercury	Arsenic
17	Mercury, Lead	Lead	Arsenic
18	Mercury, Lead	Lead	Arsenic
19	Arsenic, Mercury, Lead	Lead	Arsenic
20	Mercury, Lead	Mercury, Lead	Arsenic
21	Arsenic, Mercury, Lead	Lead	Arsenic
22	Arsenic, Mercury, Lead	Arsenic	Arsenic

Note: ICP-AES/CVAAS and portable XRF (Niton XL700) used same sample. Bench Top XRF was directly read on mask for Arsenic only.

repatriated to the Seneca Nation of Indians under NAGPRA. The use of wipe samples combined with ICP-AES and CVAAS has proved successful in screening for the presence and absence of arsenic, mercury, and lead residues at very low levels. Palintest pre-moistened wipes were convenient to use but were too delicate for rough surfaces. Screening for inorganic pesticide residue is made more complex by the possible uneven distribution of contaminants on the surface. As a result, comparison of results from multiple analyses of the same object via different methods may be misleading depending on the sampling location. In this project, multiple samples were taken on each side of the masks. This greatly increased the cost of the analyses but it gave greater confidence in the results.

Thus far, the analyses have focused solely on testing for arsenic, mercury, and lead. Repatriation efforts with the Peabody Museum led to a recent communication that specifies the use or probable use of organic pesticides for preservation or pest control purposes. Fifteen organic and inorganic pesticides are named in that communication and are listed in Table 3. The cost of screening for these pesticides and the amount sampled far exceeds the monetary reach of many tribes and patience of most universities. Screening techniques such as Gas Chromatography-Mass Spectrometry (GC-MS) or High Performance Liquid Chromatography (HPLC) at a certified environmental testing laboratory cost a minimum of $100 up to as much as $750 per sample for pesticide screening. A more cost-effective analytical technique is needed for screening of these organic pesticides.

Six masks were selected to validate the removal efficiency for mercury using the SADS formulation. These masks were selected based on the high levels of mercury found on the painted and unpainted surfaces of these objects. After treatment, the data provided in Tables 4 and 5 show significant reduction in mercury levels, indicating the effectiveness of this procedure for remediating this metal.

Table 3. List of chemicals used or possibly used in the Peabody Museum for preservation or pest control purposes.

Chemical/product name	Approx. dates of use
Arsenic, saturated solution with alcohol	1870s–early 20th century
Benzine/gasoline	1908–1932
Paradichlorobenzene	1932–1988, 1991
Napthalene	1930s (unconfirmed time period)
Dethol	1932 tested but no confirmed use.
C.P. Xylol	1936
Lindane	1959
DDVP	1980s
Ethylene Oxide	1980s
Sulfuryl fluoride (Vikane)	1981
Larvex	Later half of 20th century
Pyrethreum	Later half of 20th century
Thymol	Mid-1970s to mid-1980s
Expello Cedarized Moth proofer	Mid-20th century
Mercuric Chloride	No record of use but presence detected on two items.

Removal efficiency of the SADS formulation on painted surfaces ranged from 99.91% to 99.98%. The removal efficiency for unpainted surfaces showed a similar range of 99.96% to 99.99%.

Many NAGPRA inventories as well as other collections may have been directly or indirectly exposed to pesticides in the past. While this may be important to the tribe receiving NAGPRA objects, collection managers have also taken notice. Cooperation with tribes to explore detection and mitigation methods will become even more important and equally beneficial in the future. Participation in NMAI's Visiting Professional Program and cooperation from the Chicago Field Museum on the NAGPRA grant for this project are two examples of such opportunities.

The total mitigation of all contaminants may never be achieved. Even if the pesticide residues are reduced to non-detectable levels, arsenic and lead may be present in the formulation of the paint applied to the masks. Therefore, a multi-step process for mitigation on the masks will be taken. Application of the SADS concept, paint consolidants, and possible replacement of horsehair are currently

Table 4. Mercury levels found on painted surface of medicine masks determined by wipe sample analysis.

Object number	Mercury residues on painted surface of medicine masks	
	Before treatment (μg)/wipe	After treatment (μg)/wipe
1	830.00	0.172
2	1,770.00	0.885
3	1,320.00	0.680
4	1,540.00	0.443
5	6,860.00	2.38
6	140.00	0.123

Note: Wipe sample area equal to one-half of total surface area.

Table 5. Mercury levels found on wipe samples taken from unpainted surface of medicine masks.

Object number	Mercury residues on unpainted surface of medicine masks	
	Before treatment (μg)/wipe	After treatment (μg)/wipe
1	330.00	0.087
2	9,160.00	1.495
3	2,120.00	0.088
4	1,470.00	0.093
5	13,200.00	5.06
6	920.00	0.113

Note: Wipe sample area equal to one-half of total surface area.

under review as first steps. Each tribe should be made aware of possible strategies in order to decide what is most appropriate for their needs.

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USE OF HANDHELD XRF FOR THE STUDY OF PESTICIDE RESIDUES ON MUSEUM OBJECTS

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Abstract.—A handheld X-ray fluorescence spectrometer (Niton XLi-700 series) has been successfully used for detection of heavy metal based pesticide residues on museum objects. The instrument is versatile, easy to use, and economical to operate. It provides rapid, accurate analytical information without destructive sampling. Based on the greater medical risk of heavy metal residues, qualitative and quantitative analysis of these persistent but highly toxic contaminates has been the focus of studies undertaken at the University of Arizona to adapt this technology to the pesticide contamination issue as associated with museum objects.

BACKGROUND

Museum employees understand from their own experience, museum records, or literature searches that many types of institutionally held objects were treated with chemical poisons in order to "preserve" them. Most know that the destructive damage caused by insects and rodents can be devastating and may ruin objects of art, material culture, and natural science. Thus, it is understandable why pest-controlling chemicals were used in museums for a very long time.

In recent years researchers have studied and identified a wide range of pesticide chemicals that have been used with museum collections (Goldberg 1996, Hawks 2001, Odegaard et al. 2005). However, actual recorded museum histories of specimen-specific treatments are rare. This is due, in part, to the housekeeping-like nature of many of the pest control practices used from the mid-nineteenth century until the 1970s. Conservation laboratories within museums typically hold treatment records, but most museum conservation labs are less than 30 years old.

Professional museum conservators have often discussed two concerns regarding the use of chemical pesticides: 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 an ongoing and serious health hazard to individuals. More recently, conservators working with repatriation claims under the Native American Graves Protection and Repatriation Act (NAGPRA) have been asked to determine object treatment histories and this has led to renewed interest in developing an understanding of the treatment history of objects. The NAGPRA law was passed in 1990. A 1996 amendment to the law requires that the "museum official or Federal agency official must inform the recipients of repatriations of any presently known treatment of [objects] with pesticides, preservatives, or other substances that represent a potential hazard to the objects or to persons handling the objects" (Native American Graves Protection and Repatriation Act, 25 U.S.C. 3001 et seq. [Nov. 16, 1990]). This responsibility to inform tribal recipients of *any* known treatments

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that may have occurred during an object's museum history has been difficult due to the lack of museum documentation.

For the Hopi Tribe, the consequences of the NAGPRA requirement were realized in the mid 1990s. After repatriating more than 60 objects from the Peabody Museum at Harvard University to their owners on the reservation, the tribe realized that some objects had been treated with a variety of pesticides including arsenic and cyanide (Loma'omvaya 2001). The 1997 Peabody report recommended that the items not be used. This knowledge propelled the Hopi to seek further testing for all sacred objects and objects of cultural patrimony being returned to the tribe. In addition to the Peabody Museum, the Hopi worked with the Denver Museum of Natural History (Howe et al. 1999) and the Museum of New Mexico (Landry 1988), where swipe or spot tests were completed with conservation involvement. In 1998, the Hopi Tribe began the first of several projects in collaboration with the University of Arizona (Seifert et al. 2000). In addition, they have participated in virtually all the national conferences and workshops on the topic since the first workshop organized by the Arizona State Museum in 2000.

The Basic Concern

Accidental exposure to pesticides is a serious health concern. Pesticides can enter the body through (1) absorption through the skin or eyes (dermally); (2) inhalation into the lungs (by breathing); and (3) by ingestion through the mouth (orally). There is a particular concern for human health if contaminated items are returned to cultural uses, especially if these items provide contact at an individual's eyes, nose, and mouth. Determining toxicity to humans is an estimate of how poisonous a particular pesticide is when compared to another pesticide. Some pesticides are dangerous after one exposure while others are a hazard after repeated, small exposures. Most of the pesticides used in museums may be grouped as: heavy metals, volatile organic compounds, organophosphates, carbamates, organochlorines, and fumigants. Due to the greater medical risk of heavy metal residues, we have focused our studies on them. These pesticides are persistent, highly toxic to humans, difficult to detect by visual examination, and their use tends to pre-date the knowledge and experience of museum employees working today (thus, their use and application methods are not understood as well).

To assess the human health risk associated with objects containing pesticide residues, the medical toxicologists on our team needed to have an estimated quantity of pesticide present on an object in addition to the identification of the type of pesticide present. First, published medical estimates of acute oral toxic doses were consulted and interpretations were made to estimate the total object amount of a pesticide type that would assure safety in storage, handling, and use. Possible exposures through potential types of use were based on scenarios drawn from anthropological literature and tribal consultations. While is it is not clear how much exposure could occur by the scenarios and what effects could be expected, generally, it was determined that it was unlikely that enough exposure through skin absorption or inhalation would cause immediate effects (acute exposure). However, wearing a contaminated object at the face will repeatedly expose the wearer to concentrations of toxins (chronic exposure). The points of contact between the head and the object, helped by the moisture of perspiration, will result

in transfer of the toxin to the skin. Movement of the object will also generate dust that may be inhaled, absorbed or ingested.

Second, lists generated by the Environmental Protection Agency (EPA) and solid waste regulations under the Resource Conservation and Recovery Act (RCRA) were consulted to identify the threshold amount for these pesticides to be classified as hazardous wastes.

XRF Technology

For a second pesticide testing project between the University of Arizona team and the Hopi tribe in 2001, a portable XRF analyzer was used. X-ray florescence (XRF) is a highly sensitive method that detects many metals simultaneously. This type of analysis can be accomplished without removal or destruction of any part of a test object. Because of its high purchase cost, XRF was not included in the first collaborative project with the Hopi, but was available for the second through a generous loan from the Geotechnical Services Company of Tustin, CA. Using the XRF analyzer as a screening tool provided an added benefit to the testing protocol by demonstrating the presence or absence of additional heavy metals that were beyond the scope of the first project.

The XRF readings were also useful in demonstrating the utility and limitations of swipe or spot test methods. Quantitative analyses of removed dust and surface materials from items that screened positive with the XRF for arsenic, mercury, and lead were also carried out by Atomic Absorption (AA) Spectrophotometry. Here, the AA served as an essential double-check of the previously unproved methods of XRF and swipe sampling. We found good correlations between the XRF and AA methods.

XRF is an analytical technique, which is widely employed for the analysis of elemental composition in materials. The portable XRF is designed for various industrial and environmental on-site testing applications such as mining, coatings, precious metals, and powder samples. We purchased a NITON XLi 700 series unit in 2002 with partial funding from the National Center for Preservation Training and Technology (NCPTT). In our experience, we have found it useful for testing because it adjusts for the geometric effects caused by the different shapes, surface textures, thicknesses, and densities in objects (Odegaard et al. 2003). The NITON Periodic Table—X-Ray Energy Reference Chart that comes with the unit identifies the elements that can be detected by the instrument. The elements analyzed by the NITON portable XRF analyzer are dependent upon the X-ray source in the instrument. The technique has limitations in the ability to measure light elements (atomic numbers less than titanium). The instrument employed in these studies has two sources, the ^{109}Cd—cadmium and ^{241}Am—americium sources, allowing for the analysis of most elements with atomic numbers greater than titanium (atomic number 22). The levels of detection of the various elements are dependent on the element being analyzed, the matrix, and a number of experimental factors. The instrument provides an error estimate of the reading (standard deviation) allowing for an assessment of the reliability of the results. The life of the sources is controlled by the half life of the element used in the source. For example, americium has a very long half life while the cadmium source needs replacement after several years.

When an object is irradiated with a beam of X-rays, it causes the atoms of

each element present to fluoresce at characteristic wavelengths. Utilizing a spectrometer, it is possible to separate the resulting wavelengths and identify the elements present in the sample site. The amount of each element in the sample can be determined by measuring the intensity of the fluorescence. The XRF analyzer is able to determine the elemental makeup of samples of widely different sample compositions. The results screen on our NITON XLi identifies a reading number, test duration (seconds), mode line (thin or bulk sample), element column, concentration level column, confidence column (error value), and source.

Some of the advantages of using a portable XRF include: faster analysis, ease of use, a wide element range, data downloads to PCs with Windows, transportability, reduced regulatory requirements, simplified licensing, quick-swap rechargeable batteries, and it is proven for field use. Some of the limitations include varying jurisdictional licensing requirements and slowing measurements over time. NITON offers a Manufacturers Training Course that includes instrument start up, testing, maintenance guidelines, and radiation safety. In addition, the University of Arizona requires all users to complete their Radiation Safety Course. The instrument emits virtually no radiation with the shutter closed because the sources are sealed.

METHODOLOGY

In all of the contaminated pesticide residue study projects undertaken by the University of Arizona team, the sampling procedures include the following steps.

- Each object is individually examined, described, illustrated or photographed, and measured for approximate surface area. Evidence of insect damage on the object is of particular note, as objects that are contaminated with arsenic compounds rarely show this type of damage.
- Locations that could potentially provide eye-nose-mouth exposure routes for toxins are specifically identified. During the course of examination, several locations on each object are analyzed by the XRF and these test sites are recorded with a mark on the photograph or illustration to develop an understanding of distribution and concentration.
- If the initial XRF results indicate the presence of arsenic, mercury, or lead, then additional sample readings are taken to develop an understanding of distribution and concentration.

Once the sample readings of toxins are recorded, downloaded, and interpreted, an estimate of the total heavy metal amount on the object is made. We use the following formula:

$$(\text{Object Area}) \times (\text{Total amount detected} \div \text{number of readings}) = \text{total amount in g on object.}$$

When the detection of heavy metals is unevenly distributed on the object and a pattern suggestive of past exposures to naturally occurring or manufactured paint pigments is present, this is reported. For example, we have detected the presence of lead in paint with the colors white, yellow, grey, blue, green, orange, and red. Arsenic has been detected in paint with the colors white, red, and yellow. The presence of mercury in paint has been associated with the colors white, yellow, brick red, bright red, black, and green. The use of felt often indicates a reuse of

manufacturer-treated felt rather than pesticide treatment of the cultural object. When testing beaded objects high lead levels are often detected due to lead in the glass.

We propose the following danger interpretation scheme for XRF detection levels of arsenic pesticides and pigments on objects. The scheme assumes a worst-case scenario that involves multiplying the area (cm^2) of the object times the highest XRF reading (mg/cm^2) from the object for the total mg.

If the level is ≥5.0 mg; then the object is rated RED.

- "Red" objects should not be touched without personal protective equipment (PPE) and special handling protocols.
- Levels of heavy metal (consistent with pesticide treatment levels) were detected and are not associated with a pigment color or other decorative sources.
- Exposure may cause adverse effects.
- Long-term or repeated exposure or aggregate accumulation related to disposal could result in an accumulative amount that could be dangerous to the environment.
- "Red" objects should undergo further testing.
- If the object is "Red" after second analysis, the object should be labeled and archived.

Red objects are dangerous and may pose a significant health risk in their handling, storage, and use. Published estimates of acute oral doses of arsenic compounds range from one milligram to ten grams, with chronic effects occurring from exposure to as little as three to four milligrams a day.

If the reading is greater than twice the error reading and greater than five milligrams and if contamination is not in the lethal dose (LD) range, the object may be rated YELLOW.

- "Yellow" objects should be handled with caution.
- Levels of heavy metal (consistent with pesticide treatment levels) were detected and are not associated with a pigment color or other decorative sources.
- Although the amount detected is not in the LD range, repeated exposure over a long time or an unusual exposure (i.e. ingestion by a child or other concentrated accumulation) may cause adverse effects.
- Long-term or repeated exposure or aggregate accumulation related to disposal could result in an accumulative amount that could be dangerous to the environment.

If a Tribe owns the "Yellow" object, then a Tribal decision must be made. Will the object return to use? Can the residues be mitigated? If yes, the object may be cleaned or the contaminated parts may be replaced. If no, the tribe should consult with a medical toxicologist or industrial hygienist.

If the reading is less than twice the error reading, then the object is rated GREEN.

- "Green" objects may be handled normally.
- Levels of heavy metals were not detected or at levels expected in the background.
- If "Green," the object may be safely used if it is repatriated.

In summary:

Red (stop) objects are in the lethal dose (LD) range based on analysis and the quantity of toxin present.

Yellow (warning) objects are below the LD range but toxin is present and depending on use, storage, and movement the recommendations may vary.

Green (go) objects do not have detectible levels of toxin.

Current and Future Activities

Further experience with the instrument and discussions regarding the results will help clarify the advantages and limitations of the portable XRF analyzer. In our experience, a team that includes a conservator, chemist, medical toxicologist, tribal cultural preservation officer, and tribal religious representative seems to work best. All are experts that provide essential information relevant to the task of determining the human health hazard of pesticide-contaminated objects. What is truly important is that educational resources be made available to younger tribal members so that they may have the knowledge to understand the choices that must be made when dealing with pesticide contaminated cultural objects.

A working group of XRF users met in at the Arizona State Museum in January of 2004 with funding from a NAGPRA grant and decided to begin work on establishing standards of calibration amongst labs with this equipment. Recent research at the Arizona State Museum has involved calibration of the XRF analyzer to detect approximate quantities of arsenic solutions found on historically used museum artifact substrates. A Scanning Electron Microscope (SEM) was used to create images and compare the data to the XRF analysis. Our preliminary study found that the use of the NITON XRF analyzer might be considered material-independent in testing historical artifacts with these substrates containing arsenic.

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EXPOSURE OF MUSEUM STAFF TO FORMALDEHYDE DURING SOME WET SPECIMEN ACTIVITIES

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Abstract.—Biological specimens are frequently preserved for study and display by initial treatment with formaldehyde. Significant quantities of this chemical are retained in these specimens throughout the transfer to less toxic storage solvents such as alcohol, when these specimens are used for necropsy, and in some specimens which are permanently stored in formalin. Anyone working with these objects, including their transfer to other containers, is potentially exposed to both the formaldehyde as well as the current storage solvent. Exposure assessments during several operations with these materials measured the levels of exposure and found these exposures were generally below maximum recommended levels in those situations where local exhaust ventilation was used, but levels did exceed some recommended criteria where only general room ventilation was available. It is recommended that some type of local ventilation system be made available in facilities which work with wet specimens on a routine basis and that personal protective equipment such as gloves, eye protection and aprons or lab coats also be utilized to reduce exposures.

Introduction

The use of formaldehyde in the preservation of animal specimens has been a common practice for many years. This material is obtained commercially as formalin, a solution of 33% to 50% gaseous formaldehyde in water with a small amount of methanol as a stabilizer. Standard practice calls for the immersion of a specimen in a formalin solution in the field with subsequent transfer to an ethanol solution for long term storage. Such stored objects can then be used for study, display or other purposes.

The potential for exposure to formaldehyde occurs at any step in these procedures where the objects are handled, including initial immersion, transfer to another solvent, and handling during dissection or other study. While formaldehyde is ubiquitous in the environment at levels up to one part per billion by volume (ppb), maximum occupational exposure limits are established by several organizations in the U. S. to minimize irritation of the eyes and upper respiratory tract and to protect against other effects. These organizations and their respective limits are given in Table 1. The ACGIH (2002a) reports an odor threshold for formaldehyde to be as low as 50 ppb; levels from 500 to 3,000 ppb can produce lower airway and chronic pulmonary obstruction; higher concentrations can cause pulmonary edema, inflammation, pneumonia and death. Formaldehyde is connected with cancer in some animal species and is categorized as a suspected human carcinogen. For these reasons, it is recommended that the more stringent NIOSH limits be followed.

Table 1. Maximum occupational exposure limits for formaldehyde. (ACGIH 2002b, NIOSH 2003b, OSHA 2005).

Organization	Occupational exposure limit
NIOSH (National Institute for Occupational Safety and Health)	16 ppb eight-hour time weighted average 100 ppb 15 minute exposure limit
OSHA (Occupational Safety and Health Administration)	750 ppb eight hour time weighted average exposure 100 ppb 15 minute exposure limit
ACGIH (American Conference of Governmental Industrial Hygienists)	300 ppb ceiling, not to be exceeded at any time

Methods

The nature of work in most museums and conservation facilities is quite diverse, and tasks which would potentially expose workers to formaldehyde are not performed daily as might be the case in many occupations nor do these tasks necessarily require 8 hours when they are performed. While this intermittent exposure tends to lessen any toxic effects of formaldehyde, it made the evaluation of exposures more difficult since some advance notice was required for travel to the testing site and several hours of sampling during formaldehyde use were required to obtain accurate measurements. For these reasons, arrangements were made to evaluate facilities which were able to stockpile a sufficient amount of formaldehyde-associated work to occupy employees for several hours and were willing to coordinate that work with an on-site exposure assessment visit.

Three facilities participated in this study. The first was a National Park Service collections management center which was planning a large project requiring up to five employees for two or more days in the transfer, evaluation, and cataloging of several hundred specimens stored in liquid known to contain some formaldehyde. The second facility was an osteology preparation lab that had several dozen five gallon containers with whale ovaries stored in liquid also containing formaldehyde. This facility required three employees working for two days to remove, clean, inspect, tag and re-package these specimens. The third location was a college laboratory teaching comparative anatomy with sharks and cats preserved in formaldehyde. Here sample durations ranged from two to four hours rather than full shift, but preliminary testing indicated this would produce sufficient analyte for quantification. While obviously not a museum or conservation facility, the type of work done during testing here is considered similar enough for comparison of exposures.

The specimens in the college laboratory were obtained commercially from a scientific supply house that had embalmed them with a formalin solution, subsequently rinsed that solution and shipped the specimens preserved in Ward-Safe holding solution (2.76% methanol, 1.44% 1,2-propanediol, 0.68% proprietary material, and 95.01% water) (Ward's 1998). Specimens from the other two facilities had been treated with formaldehyde and subsequently rinsed and stored in ethanol. In some cases, however, collection records were incomplete and this treatment was not verifiable. Variable levels of the original formaldehyde fixative are as-

sumed to have been transferred to the final storage solution and also to have been retained in the tissue of all specimens.

Time weighted average measurements of airborne formaldehyde were collected at all three facilities from the breathing zones of workers and in selected locations in the work areas. Using NIOSH method 3500 for airborne formaldehyde, air was pulled through a treated silica gel cartridge at 1.5 liters per minute (lpm) with a battery powered sampling pump clipped to the belt of the employee (NIOSH 2003a). Samples were refrigerated until analysis by high performance liquid chromatography (HPLC) with an ultraviolet detector. Because ethanol was known to also be present in these work environments, personal exposure was evaluated by collecting ethanol samples according to NIOSH method 1400 using charcoal sorbent at 0.2 lpm with analysis by gas chromatography with flame ionization detection (NIOSH 1994).

At the college anatomy laboratory breathing zone and area samples were collected for formaldehyde as above and also by using passive monitoring devices (cat. # 526-200/201, SKC Inc., Eighty Four, PA). Passive sampling of the environment differs from the previously described "active" sampling in that no pump or mechanical device is used to move the air through the sampling device. Instead, collection of the sample is accomplished by diffusion of analyte onto sorbent material, with analysis of contaminant by the same procedure once the sample is obtained.

Another more sophisticated technique titled "video exposure monitoring" was also employed in this facility. Video exposure monitoring uses a conventional video camera to record the actions of the individuals potentially exposed to contaminant while they are being simultaneously monitored for the concentration of that contaminant in their breathing zone. A fluctuating bar can subsequently be superimposed on the video, representing the level of exposure, with periodic (e.g., one per second) updates to indicate the change in exposure resulting from various tasks. Video exposure monitoring was utilized in this anatomy lab to assist in the identification of specific actions related to high transient exposures, and that data has been presented elsewhere (Ryan et al. 2003).

Environmental measurements of formaldehyde were made during normal work operations at the facilities and using the techniques described above. The only task parameter that the workers considered unusual in some cases was the duration of the work with wet specimens since some stockpiling had occurred to have sufficient work to facilitate the testing.

During August 2003 and April 2004, 11 personal and 19 area samples were collected at the collections management center with durations ranging from 0.4 to 8.8 hours. This sampling was conducted during work with wet specimens in containers ranging in size from approximately 20 ml (0.7 fl oz) to 200 L (55 gal). These containers held a variety of animal species which were removed, inspected, treated or relabeled when necessary, and re-packaged in alcohol. Much of this work was conducted in either an exhausted or a re-circulating laboratory hood.

In April and September 2004, 14 personal samples (no area samples) were collected in the osteology preparation laboratory with durations ranging from 1.1 to 4.0 hours. During this sampling three workers were involved in opening 20 L (5 gal) containers holding specimen in liquid solution, rinsing each specimen with water, inspecting, bagging, tagging and re-packaging each in new solution not

Table 2. Summary of personal and area formaldehyde measurements, calculated over sample duration and as eight hour time weighted average. (NIOSH eight hour TWA limit is 16 ppb).

		Duration TWA (ppb)			8 hour TWA (ppb)		
	N	Mean	Median	Range	Mean	Median	Range
Collection management center, personal samples	11	20	16	5.5–44	9	9	2.0–27
Collection management center, area samples	19	19	13	0.6–140	4	2	0.1–16
Osteology Preparation Laboratory, personal samples	14	47	34	1–358	12	12	0.2–64
Comparative Anatomy Laboratory, personal samples	13	210	176	70–430	80	86	28–116
Comparative Anatomy Laboratory, area samples*	12	160	140	60–380	90	91	45–135

* Values should be considered as minimums due to overloading on some sorbent tubes.

containing formaldehyde. After initially opening the containers, most work was done in an exhausted lab hood.

In February 2001, 13 personal and 12 area samples were collected at the comparative anatomy laboratory with durations from 2.0 to 3.5 hours during the dissection and study of preserved cats and sharks by undergraduate students in a college comparative anatomy lab. Specimens were removed from a large metal storage container where they had been immersed in the solution described above, and taken to tables where the work was done. There was no local exhaust ventilation in this facility but it was observed that doors were generally opened in the afternoon lab sessions when accumulated formaldehyde levels were at their daily maxima. The amount of general exhaust ventilation and air introduced from open doors was not quantified. There were no windows in this facility.

Results

A summary of all personal and area monitoring for formaldehyde at these facilities is presented in Table 2. The mean, median and range of exposures are presented for the duration of time during which the samples were collected, and also as an 8 hour time weighted average exposure (TWA) with the assumption that un-sampled time was zero exposure.

The highest personal exposure at the collections management center was 27 ppb averaged over an eight hour work day and three of the 11 samples were above the most stringent recommended maximum of 16 ppb. None of the personal breathing zone samples was above any of the recommended 15 minute maximum exposure levels, although one area measurement of 140 ppb exceeded the 100 ppb NIOSH limit.

Three of the 14 measurements at the osteology preparation laboratory were above the NIOSH 16 ppb recommended 8 hour exposure maximum. Those measurements were 17, 20 and 64 ppb and did not exceed any of the other eight hour criteria.

All personal environmental measurements at the comparative anatomy laboratory exceeded the recommended eight hour maximum, although even here none of these measurements exceeded the legal exposure standard established by OSHA of 750 ppb.

Three ethanol samples were collected at the osteology facility with durations from 1.5 to 2.0 hours. These samples ranged from three to six ppb which corresponds to an eight hour time weighted average exposure range from 0.3 to 1.5 ppb. Monitors for volatile organic compounds including alcohols in the comparative anatomy lab showed only very low (i.e., ppb) exposures at or below the lower limit of detection for the chemicals screened. All of these samples indicate levels of exposure at least three orders of magnitude below the recommended maximum level of 1,000 ppm (1,000,000 ppb).

Conclusions and Recommendations

It must be stressed that this is a preliminary study and that additional data is required under more controlled conditions; however, the results of this preliminary work indicate:

- a high degree of variability in the duration of exposures, ranging from a few minutes to several hours per day,
- a high degree of variability in the tasks being conducted,
- a high degree of variability in the exposure measurements, both personal and area,
- a generally low level of exposure to formaldehyde, in many instances <10% of the recommended exposure maximums, and
- occasional short term exposures exceeding the recommended exposure maximums, particularly in the comparative anatomy laboratory.

Although no measures of local exhaust ventilation were made, it is noted that the formaldehyde concentrations were greater in the comparative anatomy lab where only general room ventilation was available. Good work practice dictates that local exhaust ventilation be used whenever toxic chemicals are used.

While it seems that the most consistent theme with the data is its variability, most measurements were within the levels of exposure considered acceptable based on comparison with the exposure limits presented above. These limits were developed based on available information to reflect the levels of exposure to which most workers may be exposed daily during a working lifetime without adverse health effects.

Results from the limited measurements of ethanol lead to the conclusion that this and other compounds of similar toxicity are not likely to be present in this work environment at significant concentrations.

It would be expected that during normal operations where work had not been stockpiled to allow for testing (as was done here), the duration of exposures and consequently the exposure average over time would be lower than that measured during this work. This should not, however, be considered as justification for exposures above recommended levels since, as mentioned above, formaldehyde is both a suspected human carcinogen and a sensitizing agent, capable of producing allergic reactions and sensitization following occupational and non-occupational exposures. It is recommended that some type of local ventilation system be made available in facilities which work with wet specimens on a routine basis to reduce inhalation exposure. Additionally, personal protective equipment such as safety glasses or face shields, gloves, and lab coats or aprons should be used to prevent direct skin and eye contact.

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ON THE DEVELOPMENT, CARE, AND MAINTENANCE OF COLLECTIONS OF REFERENCE AND SUBFOSSIL SEED AND PLANT MACROREMAINS

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Abstract.—This paper describes the procedures used at the Royal Alberta Museum for long-term maintenance and care of collections of reference and subfossil seeds and plant macroremains. The reference collections are used primarily as comparative material to aid in identifications of subfossil material of Late Quaternary age that is mostly derived through processing sediment from palaeoenvironmental and archaeological sites in Alberta. For the reference material, processing involves cleaning and preparing materials collected in the field. For the subfossil material, processing entails separation of plant remains from any adhering clastic or organic sediment, and concentration into size fractions. For both types of collections, the main objective is to ensure that materials do not deteriorate in long-term storage and that characteristics critical for identification are preserved. It is recommended that chemical treatments in processing and chemical preservatives are avoided if possible so that the materials can be used for further analyses, including SEM imagery and, for the subfossil material, radiocarbon dating. The techniques that have been tested and developed for the preservation of these collections at the Royal Alberta Museum may be more widely applicable to similar collections held in institutions elsewhere.

INTRODUCTION

The Quaternary Environments program at the Royal Alberta Museum maintains extensive collections of reference and subfossil seed and plant macroremains. These collections have been built up since the late 1970s, mainly as a result of various research projects in Alberta and western Canada. Research has concentrated on an understanding of postglacial landscape and environmental change. Biotic proxy indicators, such as pollen, seeds, and other plant macroremains, are fundamental to this research (see Beaudoin 1999). This paper describes the processing techniques and storage methods that have been developed and are used at the Royal Alberta Museum for these collections of seeds and plant macroremains.

The Seed and Macroremains Collection (SMRC) currently comprises 2,335 accessioned samples. In this context, "seed" is used in its broad or vernacular sense and can include fruits, nuts, nutlets, achenes, caryopses, samaras, etc. Plant macroremains includes small plant parts that can readily become incorporated in sediment and hence are often found in the subfossil record. These may comprise conifer needles, cones and cone-scales, some bracts, pods, etc. This collection is derived mostly from native Alberta plants, but there are also significant numbers of samples from weed taxa, which are often exotic. This collection is used primarily to confirm the identification of subfossil specimens. It is also used in graduate student teaching and training. As such, it is a "working" collection, and needs to be constantly accessible. The collection is documented through a card file and an electronic database, currently built in FileMaker Pro 6 (see http://www.filemaker.com).

Collections of subfossil seeds and plant macroremains arise from several types of research. Macroremains may be recovered during archaeological excavation of

specific features, such as hearths (e.g., Beaudoin et al. 1996) or privy fills from fur trade forts (e.g., Shay 1984). Macroremains may also be extracted from sediment samples from sections or cores of lake sediment as a component of palaeoenvironmental research (see Warner 1990). Samples in the collection of subfossil materials are tallied by site. At present, the majority of this collection is derived from work at the Fletcher Site (DjOw-1) in southern Alberta (Beaudoin 2000) and the Wood Bog site in northwestern Alberta (Beaudoin et al. 1996). Smaller numbers of samples are derived from around two dozen other sites, mostly in central and southern Alberta. Analysis of these materials provides information on past climate, vegetation, and landscape. In addition to these subfossil samples, about 1,300 cheek-pouch samples, consisting mostly of seeds, collected by Ord's kangaroo rats (*Dipodomys ordii*) are being analyzed as part of a joint project into kangaroo rat diets being undertaken with D. G. Gummer, Mammalogy Curator at the Museum.

Modern Reference Collection

This collection has been built up mainly by active collecting in the field. In particular, during the last five years, many samples have been gathered as part of the SCAPE (Study of Cultural Adaptations in the Canadian Prairie Ecozone) project (see Beaudoin 2003). However, about 390 samples have been obtained through the *Index Seminum* distribution of the Devonian Botanic Gardens, University of Alberta, and 1,459 samples are derived from a seed collection developed by Canada Department of Agriculture that was donated to the Botany program at the Museum in 1989 (accession number B89.51) and was transferred to the Quaternary Environments program in 1999.

Field Methods

Seed samples are collected from living specimens in the field. Generally, whole seed heads, pods etc. are collected and placed in labelled Whirlpak bags until processed in the laboratory. These bags and other products or supplies mentioned in this paper can be obtained, except where otherwise noted, from regular laboratory supply houses, such as Fisher Scientific International Ltd (http://www.fisherscientific.com/index.cfm) or VWR International (http://www.vwrcanlab.com/). While stored, fleshy fruits, berries, etc., often go soft and begin to break down. This aids in the processing later. Plant specimens are also usually collected by standard field-botany methods (see Jones and Luchsinger 1986:188–206) to confirm field identification, and are then placed in the Herbarium at the Royal Alberta Museum.

Field records include the date and place of collection (usually from map coordinates and a GPS reading), a description, usually including images, of the habitat, surrounding vegetation and landscape context, and an assessment of the degree of ripeness or maturity of the material collected. The latter observation is important because seed size does vary with ripeness and, because documentation of the sample usually includes size measurements, it is important to know if immature or unripe material was collected. Usually, ripe specimens are collected because these are likely to provide the best comparison with the subfossil material. In addition, several samples of the same taxon are collected from different regions to ensure that any geographic variation in seed size is captured in the collection.

Laboratory Processing

The main purpose of the collection is to provide comparative specimens to aid in the identification of subfossil materials. Hence, the main objective with this reference collection is to preserve hard or resistant parts of fruits, seeds, and macroremains that are likely to occur in subfossil contexts.

The main objective of processing is to detach the resistant seed from any adhering fleshy or pulpy material and dry it. Most seeds preserve well once they are dried. If seeds are not dried properly before storing, they can degrade; especially, they may become mouldy or sprout. If this happens, they are no longer useful for the reference collection and have to be destroyed. Seeds destined for planting need to be stored within defined low humidity and temperature limits (see Stein et al. 1974, Phartyal et al. 2002) and seed banks often use ultra-low temperature storage to maintain viability (Engelmann 2004). Because long-term seed viability is not a concern, drying the seeds does not affect their usefulness to the reference collection.

Processing methods depend on the type of seed material. If the seeds are surrounded by fleshy pulp, this is removed by soaking in water and gentle maceration, such as crushing with a glass rod. Gentle warming on a hotplate (not boiling!) can also aid disaggregation. In extreme cases (such as rosehips and similar fruits), more vigorous maceration (e.g., in a food processor) may be required. Pulp and other soft plant materials are then separated from the seeds, either by swirling the liquid and pouring off the supernatant or by washing through a fine screen or sieve. Many seeds will sink in water, but some float, and hence the separation process needs to be adapted to the material.

Chemical treatments are not required for processing. Tap water is usually adequate for processing and rinsing. However, because most tap water can contain soluble salts, a final rinse before drying is done with deionised or distilled water.

The seeds are then placed on plastic trays to air-dry. It is important that seeds are not "clumped" when they are set to dry but are spread out so that they dry thoroughly and do not stick together. Seeds are usually dried at room temperature. About a week of air-drying is usually adequate for most seeds. If the seeds are especially moist, they can be spread out on aluminium trays and oven-dried gently. Generally, seeds dry adequately at about 40°C overnight. Large seeds have a tendency to split and fall apart if they are dried too quickly at too high a temperature. Some large seeds, especially from cultivated plants, such as avocados, often split and break up on air-drying anyway. Other macroremains, such as needles and cones, can usually just be air-dried before storage.

Nuts are usually stored whole. Some may be broken and the nut-meat dried and the shell also preserved. Some types of nuts (e.g., hazelnuts) are quite common in archaeological contexts, and therefore examples of broken shells are useful. Some especially moist nuts (e.g., fresh acorns) may need prolonged drying otherwise they have a tendency to go mouldy.

Seeds that are not surrounded by flesh or pulp can be separated from any adhering plant material and spread on trays to dry thoroughly. These seeds do not need to be washed. Seeds in this category include many in the Asteraceae and Apiaceae families.

Seeds that occur in capsules, siliques, or pods are usually removed from them.

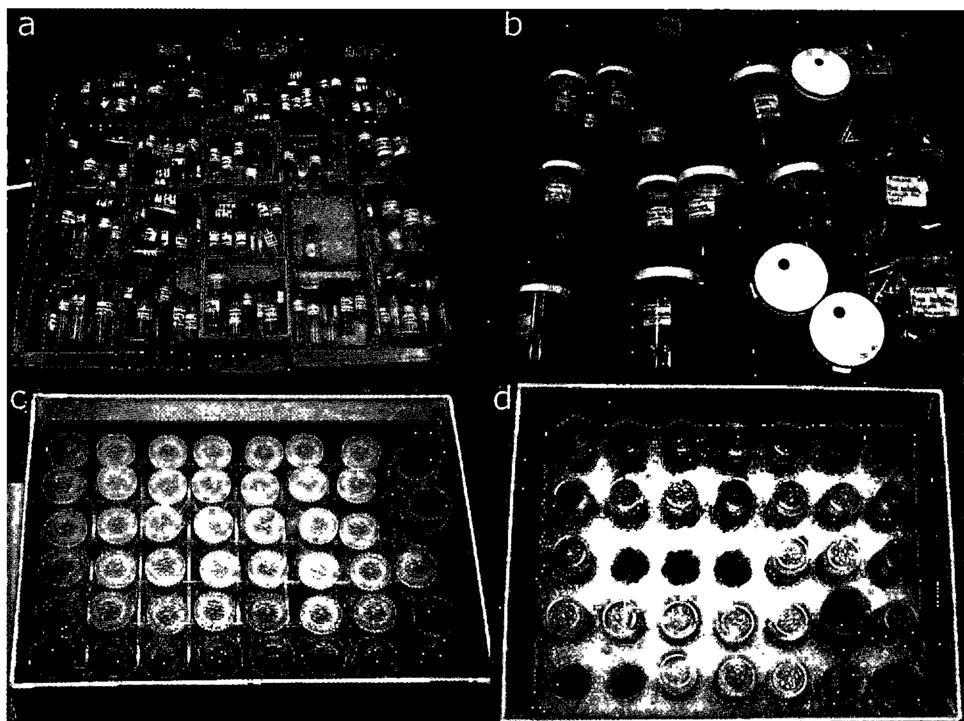

Figure 1. a: Drawer from the SMRC showing the glass vials and storage layout for the seed samples; b: Drawer from the SMRC showing the plastic vials storing larger macroremains; c: Macrofossil specimens prepared for long-term storage, with "egg-crate" grid insert; d: Macrofossil specimens prepared for long-term storage, with ethafoam insert.

However, I often keep the enclosures as part of the macrofossil collection. These rarely occur in subfossil samples, although one recent study in the Yukon did identify large numbers of siliques from Juncaginaceae (Zazula 2002). However, they are common in the cheek-pouch samples that I am currently studying. Their features and morphology can often be useful identification aids, especially in situations where the seed morphologies may be very similar between different taxa (e.g., in the Brassicaceae family).

Sample Storage

Seeds and other macroremains usually preserve well when they are dried. I generally store them in small screw-top clear glass vials (Fig. 1a). Most seeds can be stored in 1 dram vials (glass, black phenolic plastic molded screw cap, 15 mm × 45 mm) or 2 dram vials (17 mm × 60 mm) but other sizes are available. It is important that these vials are airtight so that the samples do not absorb humidity from the atmosphere. However, the vials should be easy to open. This allows the seeds to be removed and placed on Petri dishes for closer examination and comparison with subfossil material. Because the samples are handled regularly, standard glass shell vials, with a snap-cap, are not suitable, because these are not as robust and have a tendency to break if opened often.

The vials are labelled and numbered. The name and catalogue number are

written on 1″ × 0.75″ white labels, obtainable from any office supply store, with an indelible black fine-point marker. These labels are then affixed to the vials using transparent laboratory-quality polyester lab label protection tape. This tape is long lasting and chemical resistant. Regular office-quality scotch tape is inadequate, because the adhesive degrades in a few years. It is important that the tape completely covers the label, so that the label does not tear or become illegible as the vial is handled. I also number the samples on the cap tops with small round coloured coding labels, available from office supply stores. This makes it quicker and easier to find a specific vial in the cabinet drawer.

Larger macroremains can be stored in snap-cap clear plastic vials (polystyrene base, low density polyethylene cap), which can be obtained in several sizes including 4 dram, 12 dram and 16 dram (Fig. 1b). Although they are not as airtight as the screw-top glass vials, I have not found problems with specimen degradation, as long as the specimens are dry before storage.

The vials are stored flat in labelled trays, organized by plant family, in a regular Lane metal collections cabinet. Depending on the composition of the collection, trays can easily be moved to allow additional material to be added. Having several examples from different families in the same drawer allows rapid comparison of morphotypes because identifications usually are done on the basis of visual recognition. The collection from Agriculture Canada is stored in trays with clips that hold the vials in place. However, this is not as easy to use. When the samples are being used for identification, the vials are removed from the cabinet so the contents can be viewed under the microscope. This is easier to do if the vials are not clipped in place.

In the initial years of development of the collection, a few crystals of naphthalene were placed in each vial. The use of naphthalene was common practice for many Natural History collections to prevent insect infestation (see Purewal 2001). However, provided the vials are airtight and the seeds are properly dried, infestation should not be a problem, and this treatment is unnecessary. I have not used naphthalene on any of the samples added to the collection during the last eighteen years. Fortunately, only a small proportion of the collection was treated in this way. Given the known health-effects associated with naphthalene and the fact that vials need to be opened and specimens handled in the course of work, its use is definitely not recommended. Moreover, because naphthalene is volatile, seeds stored with it cannot be used for SEM imagery. This is a more serious concern for documentation of the collection.

Accessioning and Documentation

Seeds and macroremains are assigned a unique accession number. In the Quaternary Environments program, all seeds have the flag "S" and the macroremains samples are flagged "M." In the database, the seed samples can be cross-referenced with the plant specimens deposited in the Herbarium. Documentation may also involve description and measurement.

Part of the accessioning process also involves imagery. In recent years, I have used a digital camera (Nikon CoolPix 950) to record each taxon. Specimens from each sample are placed on an appropriate coloured background under a dissecting microscope. The specimens are photographed by setting up the camera on a tripod and shooting through the eyepiece of the microscope. Fortuitously, the digital

camera has a lens that is exactly the same diameter as the eyepiece of the dissecting microscope. It is a rapid, low-cost, and low-tech solution that works extremely well. The images are clear enough for documentation and identification purposes, though not generally of high-enough resolution or definition for publication; for this, SEM imagery is preferable. Alternatively, adapters may be available for some digital camera models, allowing attachment directly to the microscope and obviating the need for a tripod.

Additional Notes

Whenever possible, each seed sample consists of a minimum of 30 individual specimens and, in most cases, many more. This is so that any measurements (mean length, mean width, mean thickness, etc.) will be statistically valid. I have found the measurements derived from locally collected material often differ from published measurements of seeds (e.g., in Montgomery 1977). Therefore, I place considerable emphasis on developing size indices based on the Royal Alberta Museum's collection.

If abundant specimens are available, one or more are selected for SEM imagery. This often reveals structural or surface texture features that are not easily visible under the dissecting microscope and can help to confirm the identification of especially critical specimens from the subfossil record. These SEM images will also be incorporated into the collection's database. This imagery is, however, destructive because the specimens are affixed to stubs and gold-coated in preparation for SEM work. In future, Environmental SEM (ESEM), which does not require gold-coating, may become more widely available and be preferable (see Stokes 2003).

If abundant specimens are available, some can be deliberately degraded or altered (e.g., by charring in a muffle furnace or by soaking and warming in different chemical solutions) in order to make them more comparable to the subfossil material. These "distressed" specimens can also be stored as part of the reference collection.

Subfossil Specimens

Field Methods

Samples for palaeoenvironmental research are usually collected either from cleaned sections or from cores obtained by coring sediments in lakes or wetlands. Detailed discussions of field and coring techniques are given in Berglund (1986) and in Last and Smol (2001).

Samples taken from sections comprise 0.5–1.0 L of sediment and are placed in a labelled Whirlpak bag. Around 50–100 ml subsamples are processed in the laboratory, so 1.0 L samples ensure that enough material is available for any ancillary analyses, such as physical or chemical characterization of the sediments. Larger samples (up to 5–10 L) can be taken and placed in heavy-duty ziplock bags if specialized analysis (e.g., palaeoentomology) is anticipated. Samples are returned from the field in a field-moist condition. It is important that the samples are kept cool, to minimize biological activity and degradation. On return to the laboratory, the samples are stored in a refrigerator at 3°C or a freezer at −25°C until processed.

Cores taken from lakes and wetlands are returned to the laboratory intact for

sampling. If the cores are in intact tubes, as with a Reasoner corer (Reasoner 1986), the tubes are capped and sealed before transport. Cores obtained with a Livingstone apparatus (see Wright 1967, 1991) are wrapped in Saran wrap and aluminium foil, held in place with masking tape or duct tape, and returned to the laboratory for sampling and processing. To protect and transport these cores safely, they are placed in a purpose-built "coring box."

Samples can also be obtained during the course of archaeological investigation. Again, these are usually bulk samples, bagged in Whirlpak bags and returned to the laboratory for processing. Samples from archaeological excavations can have variable moisture content, but, especially for deeper levels, degradation is often a concern. Hence these are also stored in the refrigerator at 3°C in a field moist condition until processed.

Because archaeological excavations can yield large amounts of material, preliminary sample processing is sometimes undertaken in the field, using various types of flotation apparatuses (see Pearsall 1989). The material derived from this processing is generally air-dried in the field, bagged, and returned to the laboratory for identification.

Laboratory Processing

Seed and macroremains identification is easiest on wet material, when details of structure can be most easily seen, and the colours, if preserved, are brightest. Dried material often splits or breaks during drying, and the colours change. This degradation can make identification more difficult. Depending on the sedimentary context from which samples are obtained, the colours on subfossil material may often not be preserved. In the some situations, such as peatlands, original colours are lost or altered in the sediment. These subfossil materials may be coloured an almost uniform dark brown on recovery from the field samples.

There are three main objectives in macroremains processing. One is to separate the material of interest from any matrix or clastic sediment. The second objective is to produce concentrates by separating the material into size or density fractions. The third objective is to clean the specimens by removing adhering fine clastic material so that surface features can be seen.

Generally, seeds and macroremains are separated from adhering sediment and cleaned by wet screening, using a sieve stack to separate fractions. The procedures are outlined in Wasylikowa (1986), Warner (1990), and Birks (2001). Archaeological materials are sometimes subjected to small-scale flotation procedures in the laboratory, to reduce the amount of clastic material in the residues. One version of this procedure is described in detail by Siegfried (2002).

Macroremains can be recovered from many types of sediment, from organic-rich peats, to lake muds, to soil layers. These sedimentary settings exhibit a variety of chemical (alkaline to acidic) and physical (coarse-grained to very fine grained) characteristics. However, these Quaternary sediments are not lithified or, usually, indurated, and in most cases fall apart relatively easily during processing. Therefore, chemicals are not generally needed in this processing, water is sufficient.

Some authorities do recommend chemicals for dispersion of sediment or removal of any cementing material. For example, Wasylikowa (1986) recommends the use of sodium carbonate (Na_2CO_3) solution or potassium hydroxide solution (10% KOH solution). She also suggests the use of 5–10% HCl (hydrochloric acid

solution) on carbonate-rich sediments. Grosse-Brauckmann (1986) also recommends the use of 5% KOH solution to aid in the dispersion of peat. Birks (2001) recommends the use of 10% sodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$) solution as a disaggregant, and 10% sodium hydroxide (NaOH) solution for highly humic sediments. Note that NaOH or KOH solution and dilute HCl need careful handling, including the use of personal protective equipment and the availability of a fume hood, and require appropriate disposal of spent solutions.

Except in very rare instances, I have not found the use of chemicals necessary in materials processed from western Canada. I would recommend attempting processing without chemicals first, and only using chemical methods as a last resort. Also, if radiocarbon dating of any specimens is anticipated, chemical treatments should be avoided to prevent potential contamination and the generation of suspect dates.

Following this processing, macroremains are sorted in water under a dissecting microscope at various magnifications. Magnifications between 6.3 and 40 times are quite adequate for this work. Sorting is most efficient at lower magnification; the higher magnification is used for looking at critical features in the identification process. A cold-light (fibre optic) light source is a definite advantage. Specimens tend to dry out quickly if the microscope has an incandescent (hot) light source. A square and gridded Petri dish is used to ensure sorting is systematic. Live insect forceps (such as those supplied by Fine Science Tools, Vancouver) and very fine artist's brushes (such as 000 size) are used to pick delicate or fragile macroremains. Brushes made from hair work better for this than brushes with plastic or nylon bristles and can be obtained from art supply stores. The macroremains are sorted into small Petri dishes (e.g., Falcon brand, 50 mm × 9 mm) by morphotype. Because the lids on these dishes are tight fitting (though not air-tight), the macroremains can be kept wet until identification is complete.

Samples that are already dried (e.g., those derived by flotation of archaeological materials, or cheek-pouch samples) are sorted dry. Rewetting these materials is not advisable because delicate macroremains have a tendency to crack and fall apart. There can be considerable problems with static on plastic Petri dishes, and the dry macroremains can often be difficult to remove from the forceps or brushes. Glass Petri dishes can minimize, though not eliminate, this problem. A damp brush may be helpful to pick specimens.

Materials separated into morphotypes are often subdivided further in the identification process, as the taxonomic assignments are made. For example, a morphotype of "shield shaped" seeds can include representatives from several genera and species of Cyperaceae. In most cases, subfossil seeds can be identified to genus and often species level. Documentation may include digital photography, drawing, SEM imaging, and size measurements.

Sample Storage

Once identification is complete, specimens are transferred to tightly sealed glass vials for permanent storage. I use small straight-sided clear-glass shell vials, which have tight-fitting white plastic (polystyrene) tops, for storing macroremains. These vials are available in several sizes, including 0.5 dram (12 mm × 35 mm) and 1 dram (15 mm × 45 mm), and are sold in packs of 144. Most seeds and macro-

remains fit into these sized vials. Larger items, such as wood or bark fragments, can be stored in similar but larger vials.

Each vial contains the specimens from only one taxonomic entity. That is, after sorting and identification, the specimens are *not* recombined into one sample. Typically, anywhere between about 10 and 50 types of specimens may be taxonomically identified in any one sample. Therefore, up to 50 small vials may be required to store the specimens from any processed sample. Labelling is done in the same way as for the reference samples. However, these samples do not have an accession number, but are categorized by project name, site name (or Borden number), sample number, size fraction, and taxonomic assignment.

Samples that are sorted in water are, initially at least, stored wet in distilled water. Provided the vials are tightly sealed, I have noted no deterioration in specimens stored for several years. I monitor the vials to ensure that fungal growth has not occurred. Keeping the specimens wet may be important if it is anticipated that further identification or analytical work may be needed. Alternatively, specimens may be air-dried slowly and then transferred to vials for permanent curation. Air-dried specimens may also be stored in sealed vials. Specimens that are dried should not be rewetted before transfer to vials because this enhances their disintegration.

Several different methods are used to store the vialled macroremains. Samples from the Fletcher Site (DjOw-1) have been stored in large plastic freezer-quality ziplock bags. This allows the macroremains and the larger bone fragments, and the mineral residues, to be stored together. In the case of other sites or the kangaroo rat cheek pouch samples, where all the materials are transferred to small vials, these are stored in small cardboard boxes with specially made inserts (Fig. 1c, d).

The boxes are made from high-quality materials, and are custom-made by Four Four Four Limited, Mississauga, Ontario. I generally use boxes of 5.5″ × 4.25″ × 2″, with a tight-fitting lid (1/8″ fit on lid). They have a white paper exterior covering, which is ideal for labelling. Boxes of this size are deep enough to take the 0.5, 1, or 2 dram vials that are most common for storing macroremains. The custom-made boxes are not made from acid-free materials but, since they are not in direct contact with the specimens, this is not a problem. I have been unsuccessful in finding a cheaper alternative through shipping supply houses.

To ensure that the vials are stored in their specified order, the boxes are fitted with inserts. The smaller vials (0.5 and 1 dram vials) are held in plastic grids, cut from sheets of "egg-crate" light diffusers, made from styrene, obtainable from most large hardware stores. The grid openings are about 1.5 cm square, and the sheets are 8 mm thick. To ensure the vials do not rattle around in the boxes, the inserts are stacked two deep in the storage boxes. Up to forty-eight vials (6 rows of 8) can be stored in each box (Fig. 1c).

For larger vials, inserts can be made from 0.75″ thick ethafoam into which holes of an appropriate size are made with a drill-bit or cork-borer (Fig. 1d).

The storage boxes are labelled on the top and the front lid edge and can then be stored on shelves or on trays, as appropriate.

Additional Notes and Conservation Issues

Because plant macroremains can be in different states of degradation, their long-term curation is associated with specific challenges. The objective of curation

is to prevent further deterioration (e.g., through mechanical disintegration) or degradation (e.g., through fungal growth). Although some researchers recommend the use of a preservative for long-term curation of subfossil macroremains, I rarely use preservative with subfossil specimens and have not noted significant deterioration.

However, several preservatives are discussed in the palaeoecological literature. The most widely recommended preservative (for example, see Wasylikowa 1986) is a 1:1:1 solution of glycerol:96% ethanol:distilled water (GEW), with thymol. Glycerol impregnates the tissues and prevents shrinkage of the specimen, while alcohol acts as a fungicide. Ethanol and thymol have been used as fungicides for museum collections (Strang and Dawson 1991). Birks (2001) recommends glycerol with either formalin or thymol added as a fungicide. Warner (1990) recommends storage in 95% ethanol and glycerine in stoppered vials or just glycerine if stored in plastic boxes. He recommends adding "one or two" drops of phenol as a fungicide. Watts (1978) recommends an equal mixture of glycerol and 2% formalin. However, none of these sources provide detailed arguments in support of the use of the preservative or justify the particular formulations that they recommend.

In the past, I occasionally used the GEW mixture. For ease of handling, this solution is best made up in quantity (typically using 500 ml each of the three main components) and then dispensed from a small amber glass dropping bottle. Only a few drops of the preservative are needed in any vial. In recent years, I have not used preservative with subfossil specimens. I now prefer a more "minimalist" approach to chemical treatments, in line with current museum practice.

Moreover, the use of this preservative is associated with some significant drawbacks. Specifically, it is difficult to handle the specimens if they need to be removed from the vials for subsequent examination. Once the vial is opened and the contents are poured or washed into a Petri dish for examination, the alcohol evaporates, a process that is hastened if the microscope illumination is provided by a hot incandescent light source. Generally, good laboratory practice dictates that alcohol should not be used except in a fume hood or with good bench-top ventilation, because of safety and health concerns. Although the quantities used in this preservative are small, examining alcohol-soaked specimens can induce headaches.

Nevertheless, the use of glycerol does prevent the specimens from shrinking and cracking, as they do when drying. This may be an important concern if surface features are critical for identification, or if it is expected that the specimen might be used for display purposes or if high-quality photography is anticipated. Through time, however, especially if the vial is not well sealed, the alcohol and water may evaporate, and only the glycerol is left impregnating the specimen. This can have the effect of making the specimen "sticky" and difficult to extract from the vial. A jet of water from a wash bottle can often help remove such specimens from the vials. Alternatively, the vial may be filled with distilled water and the specimen left to soak before removal is attempted. For any such sticky specimens, handling with a fine artist's brush is recommended. The brush can be "swirled" in a Petri dish of water and the specimen usually floats off. It is more difficult to handle sticky specimens with metal forceps.

A significant drawback is that specimens that are soaked in preservative cannot

be used directly for SEM work, because the chemicals used in the preservative volatilize in the vacuum chamber, causing damage to the SEM equipment. Of the chemicals used as preservatives, glycerol and formalin are especially damaging for SEM equipment (George Braybrook pers. comm.). Specimens would need additional preparatory work if SEM imagery were required. However, glycerol is difficult to remove from specimens and removal is often incomplete (George Braybrook pers. comm.).

The major drawback to the use of preservative is the fact that specimens can then no longer be used for radiocarbon dating. The preservative is composed of carbon-containing chemicals that will become intimately associated with the specimen tissue. Even under the most rigorous pretreatment techniques, there would always be a question of contamination by these chemicals, which would render any subsequent date suspect. For this reason above all, if there is any possibility that radiocarbon dating may be required, I would recommend against the use of any preservative.

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THE EFFECT OF RELATIVE HUMIDITY ON MOLLUSC PERIOSTRACUM AND THE USE OF COATINGS TO PREVENT LOSS

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Abstract.—The periostracum is a thin layer of protein that covers the exterior surface of some mollusc shells. Although apparently insignificant, the periostracum may be important in taxonomic research and environmental monitoring. Loss of mollusc periostracum through peeling and flaking has been recorded in natural history collections and is generally attributed to desiccation of the protein. This study investigates the relative humidity conditions under which periostracal loss occurs. Gastropod (*Helix aspersa*) and bivalve (*Mytilus edulis aoteanus*) shells were exposed to a range of stable and fluctuating relative humidities to determine whether desiccation or fluctuating relative humidity cause periostracal damage. Traditional coating materials (petroleum jelly, mineral oil, and 50:50 mineral oil/white spirits) were tested to determine their effectiveness in preventing damage to the periostracum. Other properties of the coating materials were tested including gloss, dirt retention, and stability on thermal aging. Results suggest that desiccation is a more significant factor in periostracal loss than fluctuations in relative humidity. Maintaining a range of 40% to 60% relative humidity in the storage environment is recommended. Traditional coatings, however, are inappropriate for preventing periostracal loss in natural history collections because they will affect the appearance of shells and can reduce the analytical value of the specimens.

INTRODUCTION

The periostracum is a thin layer of protein that covers the outer surface of mollusc shells. Peeling and flaking of the periostracum is commonly observed in mollusc collections and can affect research value of the specimens. Periostraca may be important in taxonomic research because they can be used to identify mollusc species (Gosner 1971). Taxonomy uses increasingly sophisticated methods such as protein analysis to distinguish between species and establish the relationships between them. Periostraca have also been suggested for use in environmental monitoring, either to monitor for the presence of environmental pollutants including potassium bromide, phenols, and toluene (Hutchinson 1993, Hutchinson et al. 1993), or to determine the level of specific contaminants such as cadmium and lead (Sturesson 1978). Specimens in museum collections can be important for environmental monitoring because they provide a sample from a known time and location and can provide baseline data. "As technology develops, specimens may reveal undiscovered or potential information, the need for which may not yet even have arisen." (Pettit 1994:149).

Mollusc Shell Structure

In general mollusc shells consist of two layers of calcium carbonate crystals deposited in a matrix composed of a protein called conchiolin. Calcium carbonate is deposited in the inner, nacreous layer of the shell in the form of lamellate crystals, while in the outer or prismatic layer it is deposited in the form of vertical crystals (Barnes 1968). Overlying these two calcified layers is a thin, uncalcified conchiolin layer that is the periostracum (Hyman 1967).

Periostracum is generally described as tough, flexible, and translucent (Hunt

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1970, Saleuddin and Petit 1983). It may vary in colour from white to yellow, brown, or black (Gosner 1971) and in some cases may form hairs or other protrusions on the upper surface (Hyman 1967). It is insoluble in most solvents (Hunt 1970, Waite 1983). As some classes of molluscs do not have shells with periostraca this paper will confine itself to examining the Gastropoda (the univalves) and Pelecypoda (the bivalves), the two major molluscan classes that have periostraca. Fossil shells will not be considered as the periostracum rarely survives (Liljedahl 1994).

Periostracum Formation and Composition

Mollusc shell grows as material is gradually deposited at the edge of the shell, forming concentric ridges of shell growth (Barnes 1968). Calcium carbonate cannot form crystals in contact with seawater; the presence of a continuous protein layer (the periostracum) on the exterior of the shell provides a barrier to seawater and allows calcification of marine mollusc shells (Clark 1976). In the process of shell formation conchiolin is secreted by cells in the body wall (mantle) of the mollusc near the shell edge, in an area that is called the periostracal groove (Fig. 1). Initially a thin membrane called the pellicle is produced. As the pellicle develops and moves through the periostracal groove further layers are coated onto it. Near the shell edge these layers differentiate. The innermost layers become vacuolated and highly folded, trapping mineral ions that precipitate to form calcium carbonate crystals. These layers create slightly different 'templates' for the calcium carbonate crystals, one resulting in spherical crystals and forming the prismatic layer, and the other resulting in columnar crystals and forming the nacreous layer (Petit et al. 1979, Saleuddin and Petit 1983). Meanwhile the outermost layer of conchiolin separates slightly (Saleuddin and Petit 1983) and further develops to form the periostracum over the outer surface of the shell (Brown 1952, Petit et al. 1979, Saleuddin and Petit 1983).

The periostracum is composed of a scleroprotein (hard or structural protein) (Hunt 1970, Saleuddin and Petit 1983) that is believed to be quinone-tanned (Gregoire 1972), similar to insect exoskeletons (Hunt 1970). 'Quinone tanning' is an imprecise term describing a process in which reactive quinones form cross-links between protein molecules, producing a tough, insoluble material. It has not been proven that quinone tanning occurs in the formation of molluscan periostraca, but Waite (1983) observes that it would be possible. Small amounts of saccharide and lipid are also present in the periostracum (Gregoire 1972, Hunt 1970), forming a covalently linked protein-polysaccharide complex (Hunt 1970). The presence of pigments has also been reported (Waite 1983).

Causes of Deterioration of the Periostracum

Losses to the periostracum have been recorded periodically since the late nineteenth century (Baker 1921, Solem et al. 1981) most notably due to peeling and flaking (delamination). This has generally been attributed to changes in relative humidity (RH), particularly desiccation. It may be the cleavage from the underlying layers of the shell during formation as noted above that makes the periostracum susceptible to delamination. The problem is particularly pronounced in thin, poorly calcified shells with thick periostraca such as *Paryphanta* sp. where the shell itself may be broken apart as the periostracum cracks and cups (I. Loch

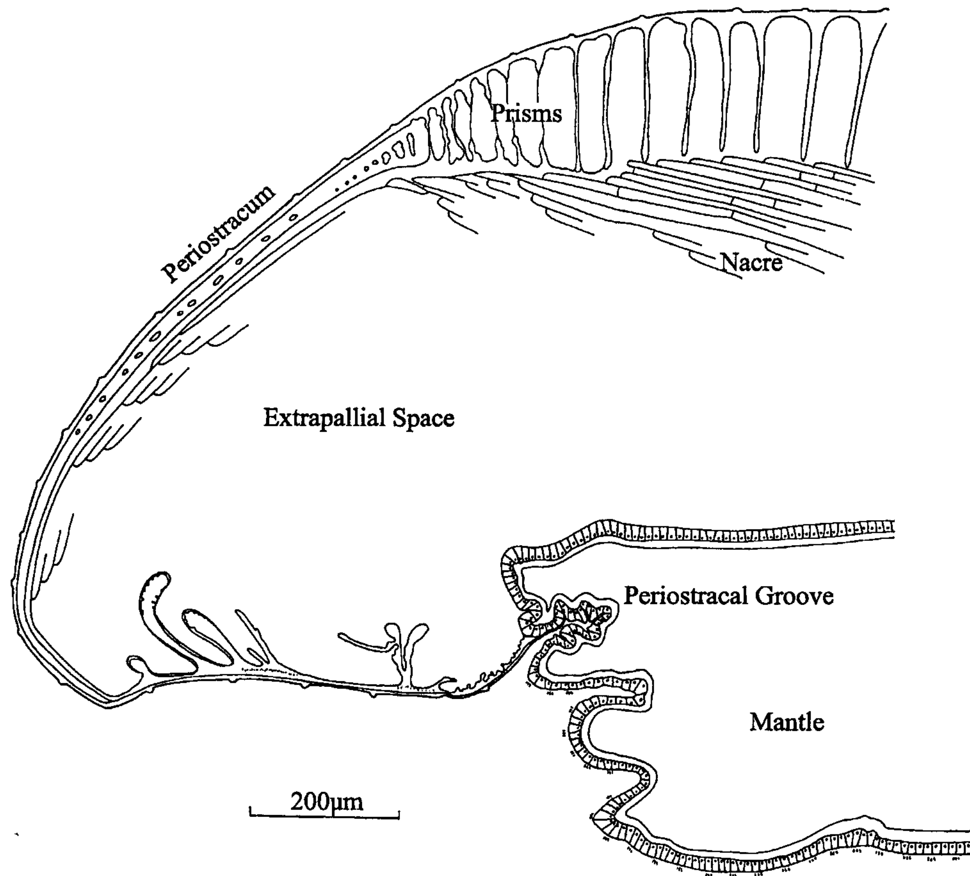

Figure 1. Cross-section of shell showing periostracum formation (after Saleuddin and Petit 1983: 212).

pers. comm., D. McMichael pers. comm.). Results from an unpublished survey conducted by the author suggested that periostracal loss is a current problem for malacological collections in many institutions in Australia and Hawaii, and reinforced the link between damage and uncontrolled RH conditions.

Hygroscopic materials (including most organic materials) will absorb or release water as the RH around them changes. As materials absorb moisture they tend to swell, while as they lose moisture they tend to shrink (Thomson 1986). Sorbed water exists in two forms in proteins—as free water or bound water (Paude 1974). Water is either attached directly (usually by hydrogen bonding) to a hydrophilic group on the protein as bound water, or is more loosely attached to existing layers of sorbed water (Paude 1974), as free water. Free water is easily lost as the material dries (Florian 1984). Free water bulks out materials, so loss results in shrinkage.

Below a certain critical RH, loss of free water could result in enough shrinkage of the periostracum against the rigid calcified matrix to cause it to simply peel off. Proteins generally sorb water rapidly at low relative humidities, slowing to

more gradual sorption at around 10–30% RH (Kuntz and Kauzman 1974). It is unknown how much water the periostracum can sorb, but it seems likely to be a relatively small amount. Florian (1984) notes that absorption of water is inhibited by strong crosslinks such as those found in periostracum.

Alternatively, fluctuations in RH could cause periostraca to delaminate. When a layer of hygroscopic material is bonded to a less hygroscopic material, stresses are caused by RH change as one material swells or shrinks more than the other. These stresses can build up over cycles of swelling and shrinking, causing cracking, cupping and peeling of the surface layer (Berger and Russell 1986). In mollusc shells, the proteinaceous periostracum is usually quite thin, and could be expected to expand and contract relatively readily with changes in RH, while the conchiolin in the matrix is held relatively rigid by the deposits of calcium carbonate and so is unlikely to be able to expand or deform significantly. Even with small changes in RH, significant cumulative stresses could be built up by repeated cycles of RH change.

Prevention Methods: RH Control and Coatings

Control of RH has been suggested as a means of preventing periostracal loss (C. Hawks pers. comm., Buttler and Child 1996) although suitable RH conditions have not been established. Buttler and Child (1996) suggest that fluctuations in RH are the cause of damage to mollusc shells, while Hawks (pers. comm.) maintains that periostracal loss only occurs at low relative humidities. Only general recommendations for RH control in natural history collections exist. The Museums and Galleries Commission recommends 18°C and 50% RH for storage of "air dried zoological" specimens, but also note that "little research has so far been done on the appropriate humidity levels in which to keep different types of biological specimens" (Museums and Galleries Commission 1992:44, 52).

Applying a protective coating to the shell has also been suggested as a means of preventing periostracal damage. Coatings that are suggested in the literature include linseed oil (Byne 1906), mineral oil (baby oil) (Knudsen 1966), Parylene (Grattan and Morris 1991), Vaseline (petroleum jelly) (Baker 1921, Wagstaffe and Fidler 1955), and a mixture of 50:50 baby oil and white spirits (Coleman 1976). Coatings are problematic for natural history specimens, however, because application of coatings can alter the specimen, potentially changing its colour, obscuring fine morphological features and interfering with future analysis.

In addition, the effectiveness of coatings in preventing periostracal loss has not been proven. Hawks (pers. comm.) conducted experiments in 1987–1988 to test the effectiveness of coatings in preventing periostracal loss. She found that consolidation with paraffin or microcrystalline wax did not prevent losses on *Quadrula* shells (bivalves from the family *Unionidae*) moved from 55% RH to 10–12% RH and held there for six days, although microcrystalline wax did result in some reduction in the level of damage that occurred.

However, despite these objections, coatings are still used on shells in natural history collections. Respondents to the author's unpublished survey reported the use of varnish, 50:50 mineral oil/white spirits, and Vaseline as coating materials. Some further investigation of traditional coatings therefore seemed warranted.

The ideal coating material would be effective at preventing periostracal loss, and would be colourless, transparent, non-glossy, inert, a good water vapour bar-

rier, easily applied in a thin coating, non-toxic to the user, and would dry to a non-sticky finish. Neither linseed oil nor Parylene appear to meet these conditions. Linseed oil is a drying oil that undergoes oxidative crosslinking as it dries, polymerising to a tough, insoluble film (Windholz 1983). It can yellow badly, particularly if oxidation has taken place in the dark (Horie 1987, Windholz 1983). Parylene is a synthetic polymer, poly(para-xylylene) that is applied as a monomer vapour that polymerises on the surface of the object forming a very thin, conformal coating (Humphrey 1984) that could form a good vapour barrier. However Grattan and Morris (1991) note that bivalve shells closed up slightly during coating "presumably in response to moisture loss." Parylene has also been shown to yellow on accelerated light aging (Halvorson and Kerr 1994). In addition, Parylene is insoluble in almost every chemical and once applied "should be regarded as irreversible on most if not all organic substrates" (Humphrey 1984). Both linseed oil and Parylene were rejected for further investigation.

Coatings that appear more promising are petroleum jelly and mineral oil. Petroleum jelly, also known as paraffin jelly (Windholz 1983) or Vaseline, is a derivative of petroleum oil (Wall 1972). It is a colloidal mixture of solid and liquid hydrocarbons (Windholz 1983). It is insoluble in water and alcohols, but soluble in chloroform and a few other solvents (Windholz 1983). The manufacturers describe it as inert and the pH as neutral (Lever Rexona pers. comm.). Mineral oil, also known as paraffin oil, liquid paraffin or liquid petrolatum, is a fraction of liquid petroleum, and consists entirely of alkanes (saturated hydrocarbons) (Hendrickson et al. 1970, Windholz 1983). It is colourless and its solubility is similar to petroleum jelly (Windholz 1983). Johnson and Johnson manufacture baby oil, which consists of mineral oil with a small percentage of perfume. They describe the pH of baby oil as neutral (pers. comm.). Problems with dirt pick up have been observed with both petroleum jelly and mineral oil. (Horie 1987, C. Hawks pers. comm.). However, given their other promising qualities, and the fact that there appears to be little information on either material in the conservation literature, it was felt that both warranted further investigation.

In this study experiments were conducted to evaluate the relative humidity conditions that cause damage to the periostracum. Mollusc shells were exposed to a range of stable and fluctuating relative humidities to determine whether desiccation or fluctuating RH causes periostracal damage. In addition traditional coatings were tested to compare the effectiveness of petroleum jelly and mineral oil in preventing periostracal loss under fluctuating RH and to determine other properties such as gloss, dirt retention, and stability on thermal aging.

Methods and Materials

Preparation of Samples

The species chosen for experimentation were a gastropod, *Helix aspersa* (the common English garden snail) and a bivalve *Mytilus edulis aoteanus* (the New Zealand black mussel). Live snails were collected from home gardens in Canberra. Specimens of similar size and with periostraca as intact as possible were chosen. No shells with perfectly intact periostraca were found. The shells were prepared by the commonly used method of live boiling in water and removing the mollusc body from the shell with forceps (Baker 1921, Knudsen 1966, Wagstaffe and

Fidler 1955). After rinsing, the *Helix aspersa* shells were allowed to air dry and then stored in sealed containers with Artsorb conditioned to 50% RH. Water remaining in the shell whorls initially caused the RH to rise to 100%, so the Artsorb was replaced several times with fresh Artsorb conditioned to 50% RH. RH at the start of experimentation was 60%.

Live *Mytilus edulis* specimens were purchased from a supermarket in a single batch. It is not known how they were prepared for sale, although it seems probable that this included mechanical cleaning as there were losses to the periostracum over the umbo on all shells. The *Mytilus edulis* shells were prepared in the same manner as the *Helix aspersa* shells. To avoid incidental damage to the periostraca the two valves remained physically attached by the hinge ligament, although their condition was assessed separately.

Relative Humidity

To determine whether damage is caused by desiccation or RH fluctuations two sets of experiments were carried out. In the first, shells were subjected to constant RH of various levels, while in the second, shells were subjected to relative humidity fluctuations. Conditions of stable RH were created in sealed 2.5 L glass desiccators using 8 g of conditioned Artsorb. The jars were sealed with white petroleum jelly and the RH in each monitored with a dial hygrometer. The hygrometers were calibrated at the beginning of the experiment, and at ambient RH the reading of the hygrometers varied by ±2%. At the start of experimentation the measured RH in each desiccator varied from the nominal value by ±1%. Separate desiccators for 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, and 90% RH were set up.

For the constant RH experiments a set of shells was placed in each of the nine desiccators for 14 days. To minimize the shock of change from the initial RH (60%) all the shells were first placed in the 60% RH desiccator and then each day subsets moved progressively to each of the other relative humidities. The experiment was repeated twice, first using sets of five *Helix aspersa* shells, and then using sets of two *Mytilus edulis* shells. The two valves of each Mytilus edulis shell were assessed separately, giving a total of four valves per set.

In the second set of experiments fresh shells of the same number and type were subjected to the following cyclic changes of RH: 50% ±10%, 50% ±20%, 50% ±30% and 50% ±40%. Fluctuating RH conditions were created by manually moving the sets of shells from the desiccator conditioned to 50% RH to the upper limit of the cycle at 9 am; back to 50% RH at 12 pm; to the lower limit of the cycle at 3 pm and back to 50% RH at 6 pm. These cycles were repeated for fourteen days.

Assessing Periostracal Damage

It was originally intended that damage to the periostracum would be assessed using the Australian Standard method 1580.481.1.0 for assessing peeling and flaking of paint films. In this method samples are compared visually to diagrammatic standards under standard viewing conditions, and the degree of damage is assigned a number from 0–5 according to the percent area that is damaged, or which diagrammatic standard it most closely resembles. However this method proved to be inappropriate for assessing the very minor damage that occurred, as it was too

subjective and the 0–5 scale was too coarse. In addition, accurate assessment was hindered by the fact that most shells exhibited some damage prior to the start of the experimentation. Despite modifications to attempt to address these problems, the Australian Standard method was eventually abandoned during the experiments and replaced with a simple YES/NO assessment of whether noticeable peeling of the shells was observed (YES) or not (NO). *Mytilus edulis* shells were assessed using this criteria both before and after exposure to constant RH conditions, however, the experiments had already been carried out for *Mytilus edulis* shells exposed to fluctuating RH, and for *Helix aspersa* exposed to both fluctuating and constant RH. These shells were re-examined for peeling after exposure and anecdotal descriptions were recorded, rather than a YES/NO peeling/no peeling choice.

Coating Materials

A series of experiments was carried out to test three different coatings for effectiveness in preventing periostracal loss, stability under thermal aging, gloss, effect on the appearance of the shell at 100× magnification, and resistance to dirt pick-up. The coatings tested were petroleum jelly, mineral oil, and a 50:50 mix of mineral oil/white spirits. The petroleum jelly used was produced by Lever Rexona under the brand name Vaseline. The mineral oil used was Johnson and Johnson's baby oil, as this was considered to be the most readily available source for natural history collections. Both were purchased from a local retailer at the start of the experiments. To ensure consistency all the samples for each test were prepared from the same bottle or jar.

Effectiveness of Coatings.—Sets of five *Helix aspersa* shells were each coated with a) petroleum jelly; b) 50:50 mineral oil/white spirits; and c) mineral oil. The coatings were applied in the way in which they are most likely to be in natural history collections—using an artist's paintbrush for the mineral oil and 50:50 mineral oil/white spirits, and with a fingertip for the petroleum jelly. The coated shells were exposed to 14 days cyclic RH change and then assessed according to Australian Standard 1580.481.1.0 as described in above.

Thermal Aging.—Thermal aging is based on the principle that heating speeds up the reactions that will occur at ambient temperature. The general rule is that increasing the temperature by 10°C will double the reaction rate (Blackshaw and Ward 1983). However, increases in temperature tend to exaggerate the effect of deterioration reactions with high activation energies. The activation energies for deterioration reactions of Vaseline and mineral oil were not known. Therefore a "compromise" regime of 70°C for 28 days as suggested by Blackshaw and Ward (1983) was chosen with the aim of achieving a result closer to the effect of natural aging.

Change in yellowing was chosen as the means of measuring deterioration of the materials due to thermal aging. Yellowing is frequently examined for this purpose because the autooxidation products of some organic molecules form yellow chromophores (de la Rie 1988).

Triplicate samples of the coating materials were prepared. As well, two control materials were included to give baseline data: Paraloid B72, a material known to be stable to aging (Horie 1987), and polyvinyl alcohol, a material which is known to yellow rapidly (Feller and Wilt 1990). Control samples of the acrylic resin

Paraloid B72 were acquired from a batch purchased from a conservation supplier within the last six months. Polyvinyl alcohol samples were acquired from a batch that was several years old.

The test method was adapted from a method commonly used to test resins (see Blackshaw and Ward 1983, Horton-James et al. 1991). The materials could not be tested in the usual form of cast films. Instead, 20 ml samples were poured into petri dishes to form thin layers. The petroleum jelly was heated to 70°C to allow pouring. The materials dissolved in solvent (50:50 mineral oil/white spirits, Paraloid B72 and polyvinyl alcohol) were made up in 50% solutions and the solvent allowed to evaporate for one week prior to commencing thermal aging. The petri dishes were then covered with glass plates to prevent loss by evaporation and placed in a thermostatically controlled oven at 70°C for 28 days.

Colour measurements were taken for each material before and after thermal aging using a Hitachi U-3200 double beam UV-VIS spectrophotometer. Ten percent solutions were made up using one gram of each sample. The mineral oil and 50:50 mineral oil and white spirits were diluted with white spirits, the petroleum jelly in chloroform, the polyvinyl alcohol in distilled water, and the Paraloid B72 in acetone. It was necessary to filter the cloudy petroleum jelly sample using Whatman glass fibre paper to obtain a clear fluid for testing. Spectra were run from 300–750 nm.

Gloss Measuring.—Gloss measuring was carried out according to Australian Standard 1580.602.2.1995. Gloss could not be measured directly on the shell due to problems caused by curvature of the shell. Instead coatings were applied using a doctor blade or draw-down bar to glass plates that had been painted black on the reverse. The 30 μm recess was used instead of the 120 μm recess recommended in the standard to avoid producing a thick pool of mineral oil.

A second set of glass plates was prepared applying the coatings by hand in the manner in which they would be used in natural history collections, using even strokes in a uniform direction. Sets of three plates were prepared using each coating. Gloss measurements were taken at 60° geometry using a Novogloss glossmeter. Two measurements were taken from each sample plate. The plates coated with 50:50 mineral oil/white spirits were set aside for 15 minutes prior to gloss measuring to allow the white spirits to evaporate as 15 minutes was observed to be sufficient time for a sample 30 μm film of white spirits to evaporate. Gloss measurements for other coatings were taken immediately.

Appearance of the Shell.—To investigate how application of the coatings affects the appearance of shells, photomicrographs were taken of a shell from each species before coating, while coated, and after removal of the coating. The same location was photographed each time. Coatings were applied in the manner most likely to be found in natural history collections, as described above, and removed by repeated swabbing with white spirits. Photomicrographs were taken using an Olympus microscope at 100× magnification with raking light. Scanning electron microscopy (SEM) could not be used for this test as the mineral oil would volatilize and cause damage to the SEM equipment.

Dirt Retention.—The tendency for coatings to attract dirt and dust was assessed by a method adapted from Australian Standard 1580.491.1.3.1991. The coatings were applied to glass plates painted black on the reverse. Coatings were applied in the manner likely to be found in natural history collections. The coated plates

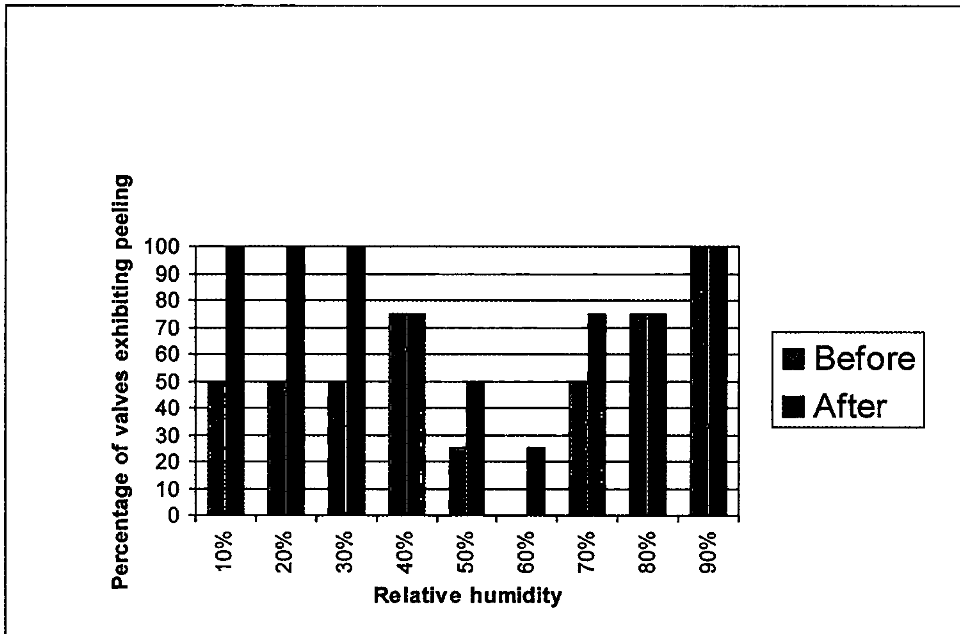

Figure 2. Comparison of peeling of bivalve shells (*Mytilus edulis)* before and after exposure to different levels of constant relative humidity (RH) for 14 days.

were exposed to a dusty domestic environment for seven weeks. The standard requires that samples are swabbed under running water prior to assessment. This would have disturbed the coatings being tested, so instead loose dust was blown off using a photographic blower brush.

The samples were assessed visually and rated according to the scale given in the standard:

0—no dirt collection
1—slight dirt collection
2—moderate dirt collection
3—considerable dirt collection
4—large amount of dirt collected
5—completely obscured by dirt

Results and Discussion

Relative Humidity

100% of the *Mytilus edulis* shells exposed to constant relative humidities of 30% or less for fourteen days showed distinct peeling of the periostracum around the edges of the valves (Fig. 2). Some had exhibited peeling prior to the experiment; however 50% of the valves originally showed no peeling before the experiment but showed obvious peeling after exposure to 10%, 20% and 30% RH. As this occurred consistently on half the valves, it can be concluded that constant

exposure to RH of 30% or less will cause damage to *Mytilus edulis* periostraca. This peeling was largely along the edge of the shell, and mainly concentrated in the upper area, adjacent to the umbo. This damage was largely associated with curling of a 3–4 mm wide area of the periostracum that overhangs the calcified edge of the *Mytilus edulis* shell. Some peeling and cracking also occurred around the edges of areas of existing periostracal damage on the upper surface of the shell.

At constant RH levels of 50%, 60%, and 70% fewer valves showed peeling; a change from no peeling to peeling only occurred on 25% of these valves. Moreover, compared to the type of peeling observed below 30% RH, this peeling was quite minor. In addition, as this only affected one valve in each case, it could be attributed to variations between individual shells and not strictly to the RH level.

The *Mytilus edulis* shells that had already been exposed to constant RH, and the *Helix aspersa* that had already been exposed to both constant and fluctuating RH were re-examined for peeling. No comparable peeling was found on any of these shells. Only two *Helix aspersa* shells were observed to have incurred any visible peeling, one that was exposed to fluctuating RH of 50% ± 40% and one exposed to 50% ± 20%. In both cases the periostracum was initially slightly damaged and peeling, and only the additional peeling was due to the experimental RH regime.

Some *Mytilus edulis* shells exposed to all levels of fluctuating RH except 50% ± 10% showed some very minor peeling around edges of shells, associated with damaged areas, and around the edges of particularly distinct growth rings. However this peeling was much less pronounced than that observed on the shells held at constant RH, and cannot necessarily be attributed to the experimental RH regime, as peeling was not assessed prior to the experiment. Therefore it can reasonably be concluded that noticeably more peeling (in terms of number of valves involved and extent of damage) occurred when *Mytilus edulis* were exposed to constant levels of low RH, than had occurred in the other experiments. These results suggest that fluctuations in RH are less important than desiccation in causing periostracal damage.

However, fluctuations in relative humidity cannot be ruled out as a cause of damage on the basis of these results. As noted, some minor peeling that may be attributable to the experimental RH regime was visible on the *Mytilus edulis* shells exposed to fluctuating RH. In addition, fourteen days is a relatively short exposure time. While it is probably sufficient time for significant desiccation to occur, it may be too short for significant stress to be caused by changes in RH, which typically causes damage over a long period of time. Much more significant damage may occur with small RH changes over a much longer period of time. The degree of fluctuation was also relatively small. The greatest single change in RH was 40%, and this was only held for three hours at a time. More extreme and prolonged daily fluctuations are possible, and could cause more damage.

The results do suggest that protecting mollusc shells from prolonged exposure to low RH is likely to be an important means of preserving periostraca. This could be achieved by the use of air conditioning in storage and display areas. Alternatively, Hawks (pers. comm.) suggests the use of airtight glass containers with glass or "very pure polyethylene" closures, or containers made of Mylar (polyethylene terephthalate) as a means of creating stable RH conditions. Buttler

and Child (1996) suggest that "microclimates" can be created for individual specimens by placing them in airtight polyethylene boxes with conditioned silica gel.

The most interesting aspect of these results is the difference between the damage found on *Mytilus edulis* and *Helix aspersa* shells. Damage was clearly greater on the *Mytilus edulis* shells, despite exposure to identical RH regimes. This appears to suggest that the effect of RH varies between species and this warrants further investigation.

Coatings

Effectiveness of coatings.—No damage was observed on either coated or uncoated *Helix aspersa* shells after exposure to fluctuating RH. Because of the previously noted limitations of the Australian Standard method, no conclusions can be drawn about the effectiveness of coatings in preventing periostracal loss. More useful results would have been obtained if the experiment was repeated using *Mytilus edulis* shells exposed to constant low RH, and assessed using the YES/NO peeling/no peeling method. Unfortunately this was not possible due to time constraints. However, it was observed that when coated the shells appeared significantly less damaged than they had been initially. This visual effect may be a factor in the popularity of coatings for shells.

Thermal aging.—Initially the petroleum jelly and mineral oil samples, and the Paraloid B72 formed clear, colourless solutions. The polyvinyl alcohol control appeared slightly yellow to the naked eye. After thermal aging, the petroleum jelly, mineral oil and Paraloid B72 samples again appeared clear and colourless. In contrast the polyvinyl alcohol had become visibly yellowed. This was reflected in a visual examination of the UV-VIS spectra (300–750 nm) from samples before and after aging. Data from absorbance at 380 nm was then analysed more closely. 380 nm is frequently chosen as the wavelength for analysis of yellowing (Down 1986, Lafontaine 1979) as it is on the edge of the visible spectrum, very close to the ultraviolet spectrum. Measurements at this wavelength are therefore very sensitive to shifts in absorption peaks from the ultraviolet to the visible spectrum, which indicate an increase in yellowness. The results at 380 nm were quantified by measuring the height of the plotted line and converting this to a percent absorbance using the scale given on the traces.

Paraloid B72, baby oil and 50:50 mineral oil/white spirits all show only a very small change in absorbance at 380 nm, while the polyvinyl alcohol sample shows a significantly greater change (Fig. 3). These results clearly indicate that all of these coating materials are extremely stable to thermal aging, with a level of stability similar to that of Paraloid B72. This could be expected from the chemical structure of mineral oil: it consists mostly of saturated hydrocarbons, which are highly unreactive, undergoing reactions only in combustion conditions (Zumdahl 1993). Petroleum jelly also contains olefins, which are slightly more reactive as they are unsaturated and contain double bonds (Zumdahl 1993). Two of the petroleum jelly samples showed a surprising fall in absorbance at 380 nm (Fig. 3). The reason for this is unclear, but may be due to experimental error while filtering the samples. However, petroleum jelly does not appear to yellow noticeably. The samples were clear and colourless to the naked eye following aging, and the third sample showed only a minor increase in absorbance, comparable to the mineral oil samples.

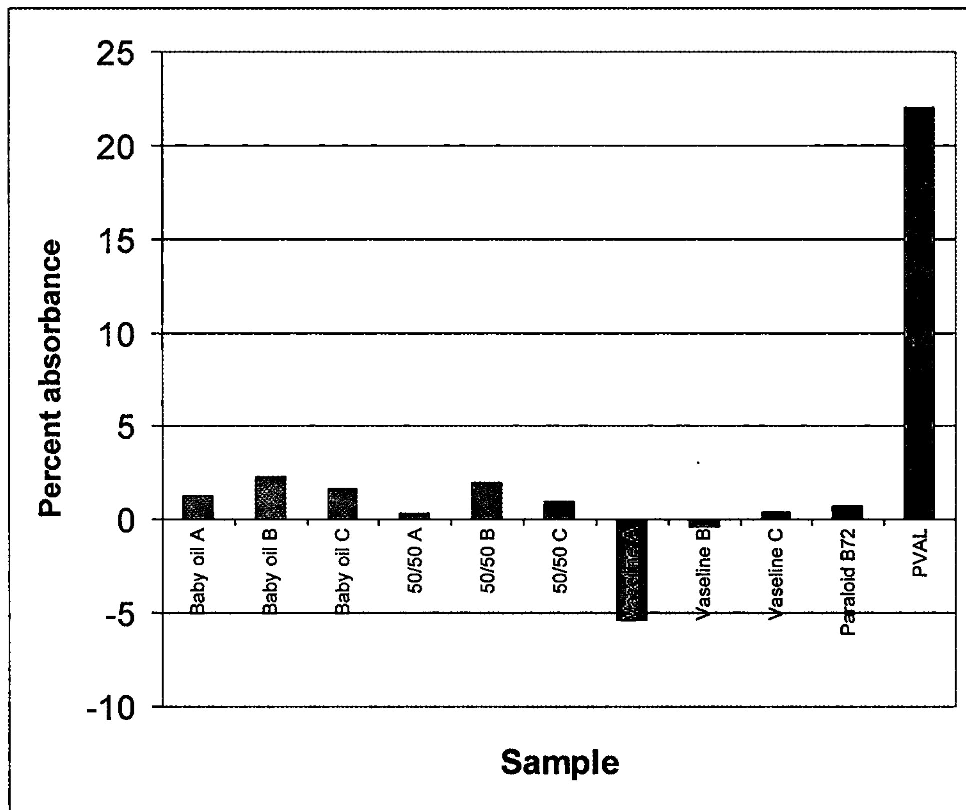

Figure 3. Change in percent absorbance (= yellowing) of thermally aged coating samples: mineral oil, 50:50 mineral oil/mineral spirits, and petroleum jelly, and two controls, Paraloid B72 and polyvinyl alcohol (PVAL).

Gloss measuring.—Striations formed in petroleum jelly films applied with the block applicator produced large variations in the gloss measurements. These results were therefore disregarded. Instead the results obtained from the films applied by hand were considered. The gloss measurements of all coatings applied by hand were very similar. The mean gloss measurement for all coatings fell between 72.5 and 84.3 gloss units. This corresponds to a gloss finish as defined for Australian and NZ paint standards. Visual examination of coated shells also showed a richer, darker, glossy, wet appearance. As treatments that alter the appearance of the specimen are generally undesirable the gloss of all the coatings must be considered undesirable.

Appearance of the shell.—Comparison of 100× photomicrographs of coated and uncoated shells showed that all the coatings obscured some of the fine surface detail of the shell. In particular, it could be seen that some damage was obscured. Surprisingly, swabbing with white spirits appeared to remove all of the coatings adequately for visual purposes. Comparison of the photomicrographs of uncoated shells with those where the coating had been applied and then removed showed very little difference. However, coatings may pose more of a problem for ex-

amination under higher magnification, or where shells have a heavily textured periostracum. Note that to the naked eye the shells remained slightly glossy after removal of the coatings, indicating that some coating residue remained.

Complete removal of coatings in the future is unlikely to be achievable. For example, Horie (1983) observed that repeated solvent cleaning could not remove 100% of a resin applied to a glass slide, although that resin was completely soluble. In addition, although conchiolin is extremely insoluble, there does not appear to be any research into the effects of solvents on the saccharides and lipids that are associated with the protein. It seems possible that these components could be extracted by use of solvents on the periostracum.

Dirt retention.—Some dust was retained by all the plates, including the uncoated control, as the samples were unable to be washed. However, it is clear that all the coated samples retained significantly more dust than the control. All the coated samples were rated as '3' (considerable dirt collection) while the control was rated '1' (slight dirt collection). There was very little discernable difference between the different coating materials. Very little dust could be blown off the coated samples by the blower brush. The coatings appeared to retain all the dust that fell on them. Dirt pick up must therefore be considered a problem for all three coatings.

Conclusion

Clear damage occurred to *Mytilus edulis* shells when RH conditions were held constant at 30% RH or below for 14 days. This corroborates standard recommendations for storage of natural history specimens at RH conditions between 40% and 60% RH. RH conditions below 60% are recommended to guard against mould growth. Comparable damage did not occur to *Mytilus edulis* or *Helix aspersa* shells held for 14 days in conditions of RH which fluctuated daily as much as 50% ± 40%. This suggests that desiccation is a more significant factor in periostracal loss than fluctuations in RH.

Fluctuations in RH cannot be ruled out as a cause of damage, however, as some minor damage appears to have occurred after fourteen days exposure and longer or more extreme exposure may cause greater damage. The two species responded very differently to the same RH conditions. The reasons for this cannot be concluded from this study.

Little variation was found between the three coating materials that were tested. Petroleum jelly, mineral oil, and 50:50 mineral oil/white spirits all appear to have very good stability in accelerated aging tests. Information from the manufacturers indicates that the pH of all three is acceptable for use on shells. If removed by swabbing with white spirits the coatings do not appear to affect visual examination of surface structure under magnifications up to 100×. Nonetheless, application of these coatings does affect the appearance of the shells: they are glossy, and darken and saturate the colour of the periostracum. All the coatings tested rapidly pick up and retain dust and dirt. In addition, applying coatings will reduce the analytical value of the specimens, and periostracal analysis is becoming increasingly important for monitoring environmental conditions. Use of solvents to remove the coating may leach out some of the soluble components of the periostracum (lipids and saccharides), and may alter the material unacceptably. Application of

coatings therefore cannot be considered an appropriate means of preventing periostracal loss in natural history collections.

The effectiveness of using a coating to prevent damage to the periostracum could not be concluded from this study. Instead it appears that protecting mollusc shells from conditions of low RH may be an effective means of conserving mollusc periostraca. This can be achieved by air conditioning or by creating controlled microenvironments for individual specimens.

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THE FUTURE OF COLLECTIONS: AN APPROACH TO COLLECTIONS MANAGEMENT TRAINING FOR DEVELOPING COUNTRIES

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Abstract.—Natural history collections in Latin America are growing, and the rates of collection use are increasing. In response to the need for professional collections care training in Latin America, we developed a comprehensive workshop to provide on-site training. The workshop uses a combination of lectures, readings, and hands-on activities to teach participants how to better manage collections and identify archivally sound materials. The workshop is structured around a conceptual model for teaching the theoretical bases of collections management that integrates preventive conservation with concepts of order and collection growth, and includes the history of collections, emphasis on the quality of the storage environment, and collection assessment. The workshops have identified several new areas for collections care research. The model can be successfully applied to other developing regions outside of Latin America.

Resumen.—Las colecciones de historia natural de América Latina están creciendo, y la tasa de su uso también esta creciendo. Por lo tanto la necesidad de oportunidades para capacitación profesional del cuidado de las colecciones en América Latina, desarrollamos un taller completo para proveer capacitación en sitio. El taller es una combinación de presentaciones, lecturas, y actividades para enseñar a los participantes como manejar mejor las colecciones e identificar materiales archivables. El taller esta estructurado sobre un modelo conceptual para enseñar las bases teoréticas del manejo de colecciones que integra conservación preventiva con los conceptos de orden y crecimiento de las colecciones, e incluye la historia de las colecciones, un énfasis en la cualidad del ambiente de almacenamiento, y la evaluación de las colecciones. Los talleres han identificado algunas áreas nuevas para la investigación del cuidado de las colecciones. Nuestro modelo puede ser aplicado con éxito en las regiones en desarrollo fuera de América Latina.

INTRODUCTION

A survey published in 1992 revealed that there are at least 6,500 museums and other institutions with natural history collections worldwide (Howie 1992). Estimates of the total number of specimens in natural history collections vary from 1.5 to 2.0 billion (Howie 1986) to 2 to 3 billion (Krishtalka and Humphrey 2000), with an estimated rate of growth of approximately 50 million specimens per year (Howie 1986). Of these 1.5 to 3.0 billion specimens, very few are housed in institutions in Latin American collections—in fact, there are more natural history museums in the United States (1176) than in all of Latin America combined (326) (Mares 1992), even though the biodiversity of Latin America (which includes 40% of known plant and animal species) is much higher than that of the United States (UNEP 2005). Worldwide, the ratio of natural history collection care workers to specimens is about 1:200,000 (Howie 1992).

Recently, a combination of factors has increased the need for natural history collections care and management training in Latin America. These factors include:

- A decline in collecting activities by non-national collectors.

- A decline in the exchange of specimens with non-national collections (due to restrictions on the shipment of hazardous materials).
- Growth of national collections in Latin America.
- An increase in the use of national collections.

A Decline in Collecting Activities by Non-national Collectors

In 1798, King Carlos V of Spain granted Alexander von Humboldt permission to make the first extensive scientific collections in Spanish America (Helferich 2004). Although six scientific missions had previously been allowed in the Spanish colonies, Humboldt was the first individual scientist to receive a permit for extensive collecting in Latin America. During the next 300 years, the pattern of scientific collecting in Latin America followed that established by Humboldt—collectors from Europe and the United States traveled to Latin America, conducted field work, and took most of the specimens back to their home museums. Duplicate specimens were rarely left in country, nor were other forms of assistance usually provided to the Latin American museums (Herrera-MacBryde 1986). This pattern began to change in the 1990s, as it became increasingly difficult for foreigners to obtain permission to export scientific specimens from most Latin American countries (Duellman 1999), and the cost of collecting increased while the resources available to support it declined. As a result, fewer specimens are being exported to European and North American museums.

A Decline in the Exchange of Specimens with Non-national Collections

The enforcement of new regulations governing the shipping of hazardous materials (including biological specimens) has severely limited the formerly free exchange of museum specimens between Europe, North America, and Latin America. Although the regulations make some provisions for the exchange of specimens, hazardous material shipping costs have skyrocketed (within the last two years, shipping costs have more than quadrupled for international shipments of most biological specimens).

Growth of National Collections in Latin America

The growth of national collections has been stimulated by (1) an increase in the number of nationals trained in systematics; (2) the decrease in the number of non-national collectors; and (3) the difficulties facing Latin American scientists in accessing specimens in European and North American institutions, including the cost of shipping specimens and lack of funds for visits to non-national collections. As an index of collection growth, five major journals were surveyed. The results of this survey (Table 1) reveal that between 1980 and 1984, 54% more holotypes and paratypes of newly described Latin American amphibians, birds, and reptiles were deposited in museums in Canada, the United States, and Europe than in Latin American museums; however, between 2000 and 2004, 59% more types were deposited in Latin American museums than in museums in Canada, the United States, or Europe.

An Increase in the Use of National Collections

The number of Latin American scientists, particularly systematists, has increased significantly during the last 20 years (National Science Board 2000). More

Table 1. Comparison of deposition of holotype and paratype specimens of amphibians, birds, and reptiles described from Latin America in five major journals (*The Auk, Copeia, Herpetologica, Journal of Herpetology,* and *Wilson Bulletin*).

Five-year period	Number of new taxa named from Latin America	Holotype and paratype specimens deposited in Latin American collections (number/percent)	Holotype and paratype specimens deposited in US, Canadian, and European collections (number/percent)
1980–1984	48	254/31%	553/69%
2000–2004	127	1325/71%	538/29%

systematists means increased use of research collections in Latin America, which has created a need for more individuals trained in natural history collection care and management.

Collections Care Training Opportunities in Latin America

Formal training for museum professionals is not widely available in Latin America; training opportunities specifically for natural history collections care and management are particularly scarce. The few opportunities for professional training in care and management of natural history collections in Latin America have included occasional workshops that differ significantly in content from the workshop described below.

Formal training of museum professionals began in the United States in 1908 at the Pennsylvania Museum's School of Industrial Art and at the Museum of Natural History of the State University of Iowa in 1911 (Cushman 1984, Glaser 1987). The first museum professional training programs in Latin America were offered in Argentina and Brazil in 1922 (Rego Novaes 1986, Singleton 1983). Over the next 50 years, the rate of growth of museum studies programs was slow. The number of museum studies training programs in North America increased greatly in the late 1970s and early 1980s, but remained small in Latin America (Simmons in press). Comparative data on the number of museum studies programs in the United States and Canada is available (Simmons in press, Williams and Genoways 2004). These data show that few North American programs offer specialized training in the care and management of natural history collections; none of the Latin American programs provide such training. Although the need for training in natural history collections care and management has been recognized for some time and a curriculum was suggested to meet this need (Duckworth et al. 1993, National Institute for the Conservation of Cultural Property 1991), the curriculum has only been implemented piecemeal in the United States (Williams and Genoways 2004). One of us (JES) was a participant in the 1987 Collections Care Pilot Training Program and the National Institute of Conservation's "Conservation and Preservation of Natural Science Collections Project" that led to the development of the recommended curriculum; these experiences informed the structure of the workshops described below.

Materials and Methods

Well-managed museum collections better serve the public and the scientific community. In response to the need for specialized training in the care and man-

Table 2. Workshop venues and formats (all workshops were presented in Spanish except as noted).

Year	Format	Location	Number of partici-pants
1998	5 days	Instituto de Investigaciones de Recursos Biológicos Alexander von Humboldt, Villa de Leiva, Colombia	15
1998	5 days	Museo de Zoología, Pontificia Universidad Católica del Ecuador, Quito, Ecuador	13
2000	5 days	Instituto de Investigaciones de Recursos Biológicos Alexander von Humboldt, Villa de Leiva, Colombia	18
2001	0.5 day	Parque Zoológico Nacional de El Salvador, San Salvador, El Salvador	30
2002	5.5 days with guest speakers	Instituto de Investigaciones de Recursos Biológicos Alexander von Humboldt, Villa de Leiva, Colombia	25
2002	3 days with emphasis on fluid collections	Universidad Autónoma de México, Ciudad de México, México	19
2004	5 days	Universidad Nacional Mayor de San Marcos, Lima, Peru	29
2004	5 days	Part of Museografía para Personal de Museos Peruanos, Museo de Arte Precolombino, Cuzco, Peru	31
2004	5 days, presented in English	Chulalongkorn University, Bangkok, Thailand	33
2005	5 days	Museo de Zoología, Pontificia Universidad Católica del Ecuador, Quito, Ecuador	16

agement of natural history collections in Latin America, we developed a workshop that is presented on-site in institutions with natural history collections. A combination of lectures, readings, group activities, and hands-on experiences are used in the workshop to teach collection care and management concepts (Simmons and Muñoz-Saba 1999). Since 1998, we have presented the workshop at several venues and in different formats (Table 2). The workshop is designed to address several factors that make it difficult to provide collections care and management training in Latin America. These factors include:

- The scarcity of collections care information in Spanish or Portuguese.
- The lack of professional collections care positions in Latin American museums.
- The unavailability of affordable archival supplies.
- The relative lack of funding to support collections in most Latin American countries.

The Scarcity of Collections Care Literature in Spanish or Portuguese

We have compiled a reading list of Spanish and English resources on collections care that is tailored to fit the needs of each group of workshop participants. In general, the most successful combination of readings consists of approximately 300–400 pages. Because the workshop is designed for individuals with at least an undergraduate degree in science, we have found that the majority of the par-

ticipants are accustomed to reading technical literature in English, even if they do not speak English. Since 1998, the amount of literature available in Spanish has increased from approximately 10% to more than 50% of the readings.

The Lack of Professional Collections Care Positions in Latin American Museums

Perhaps the biggest reason that professional training in natural history collections care is not available in Latin America is that until recently, there were very few opportunities for collections care professionals. In North America, the collections care profession has grown dramatically since the mid-1970s (Simmons 1993), but this growth did not have a Latin American counterpart. The majority of the workshop participants have been researchers with collections care responsibilities, collections care technicians with limited professional training, or biology graduate students. Participants have had responsibility for a wide range of collections, from small teaching collections to large research collections.

The Unavailability of Affordable Archival Supplies

Archival supplies for collections are not available in most developing countries. In countries where archival materials are available, their cost is usually beyond the resources of natural history museums. For this reason, the workshop teaches participants how to test local materials to evaluate which are the most suitable for use in collections care.

The Relative Lack of Funding to Support Natural History Collections

The workshop teaches participants how to implement low-cost and no-cost solutions to collections problems. For example, an emphasis is placed on improving the quality of the collection storage environment as the most cost-effective way of improving collections care.

Workshop Structure

We have experimented with different lengths for the workshop, ranging from a single half-day session to more than five days (Table 2). Based on the evaluations provided by workshop participants and our post-workshop analyses, we have concluded that a workshop of approximately 40–50 hours over five days is the best compromise between the amount of information to be presented and the amount of time that participants can afford to be away from their regular work while still maintaining a productive learning environment. The workshop structure presumes that most participants will have a limited knowledge of collections care concepts (e.g., order and entropy, preventive conservation, integrated pest management), limited access to archival materials, and that the climatic conditions of the participants home institutions may vary from the dry air of the high mountains to the extreme humidity of the rain forest.

The participants are encouraged to develop Latin American standards and solutions to collection problems, rather than to import standards and solutions from Europe or North America.

At the conclusion of each workshop, the participants were asked to provide either a written or an oral critique of the information presented, the format, ac-

tivities, readings, workshop venue, and interactions with other participants. These evaluations are used to adjust and fine-tune the workshop on an on-going basis.

The Theory of Collections Management

The participant evaluations from the first workshop (in 1998) revealed a major weakness—the lack of a coherent, comprehensive theoretical framework for collections management that integrated preventive conservation principles with collection acquisition and use—the need for a theoretical framework is particularly important in the context of the intense learning experience provided by the five days of the workshop. This weakness was resolved with the development of a conceptual model for teaching the theoretical bases of collections management (Simmons and Muñoz-Saba 2003). Traditionally, collections management has been concerned primarily with establishing and maintaining a system of order in a collection, but this concept is both simplistic and limited. Our model is based on a new concept of collection order combined with collection growth and the principles of conservation. Set theory (Levy 2004) is used to analyze collection order, disorder, growth, and loss, combined with the principles of preventive conservation (Rose and Hawks 1995), particularly the theory of enclosures and environmental stability (Michalski 1994b). In our conceptual model, each specimen or object in a collection (= each element of a set) is assigned a position in a three-dimensional array, where order or disorder are plotted on the x-axis, growth or loss are plotted on the y-axis, and preservation or deterioration is plotted on the z-axis. The resulting cluster of the points p(x, y, z) provides a mathematical description and a visual representation of the collections status. Furthermore, the position and shape of the cluster of points (the collection elements) can be used to make predictive statements about the management of the collection.

Workshop Content

Preventive conservation.—Preventive conservation refers to caring for specimens in ways that prolong their useful life. The concept of preventive conservation was not widely applied to natural history collections until the early 1980s (Hawks 1990). Preventive conservation emphasizes the quality of the collections storage environment and responses to the agents of deterioration—direct physical forces; thieves, vandals, and curatorial neglect; fire; water; pests; contaminates; radiation; incorrect temperature; and incorrect relative humidity (Michalski 1994a, Rose and Hawks 1995, Waller 1995). Preventive conservation also emphasizes the importance of reducing fluctuations in temperature and relative humidity to provide a stable storage environment, with set points determined by the local climate and museum architecture; and the advantages of like-with-like collections storage. Using the theoretical framework, participants quickly comprehend the relationships between preventive conservation, collection growth, and systems of collection order.

The history of natural history collections and specimen preparation.—Many procedures and techniques used in specimen preparation and collections care are not based on the principles of preventive conservation, but are traditional practices that may actually shorten the useful life of the specimens. The first step in improving natural history collections management is to understand the history of specimen preparation and collection care in order to determine how changes

Table 3. Categories of specimens by type of material.

Group	Category
Group 1. Dry Specimens	1. Animals and plants, whole organisms or parts (includes eggs, larvae, frozen parts or entire specimens, SEM stubs, etc.)
	2. Bones and teeth
	3. Invertebrate shells and exoskeletons
	4. Fossils, rocks, and minerals
Group 2. Wet Specimens	5. Animals and plants, whole organisms or parts
	6. Histological preparations, whole animals, plants, or parts
	7. Fossils, rocks, and minerals
Group 3. Documentation	8. Paper-based records
	9. Film and tape based records
	10. Electronic records (databases)
	11. Casts
	12. Other media

should be made. Collection history is divided into six broad periods based on Whitehead (1970, 1971), and is presented with particular attention to how specimens have been prepared and preserved; changes in how collections have been used; and how collection development has been affected by the evolution of scientific enquiry (e.g., the progression from the typological species concept of Aristotle to cladistic species concepts).

Care and management of natural history specimens based on specimen composition.—Traditionally natural history collections have been separated along taxonomic lines (e.g., ornithology, ichthyology, paleobotany). Given the importance of the storage environment, the limited resources available to most museums, and the advantages to economy of scale resource allocation, the workshop addresses collection care by composition rather than by systematic discipline (Table 3). Using the theoretical framework, the participants can evaluate the impact of resource allocation based on specimen composition in terms of overall collection management efforts.

Materials and materials testing.—Because archivally sound materials are either not available or are prohibitively expensive in most developing countries, the workshop teaches simple tests that can be used to evaluate locally available materials (see *Laboratory Exercises* below).

Collections management.—The workshop teaches the importance of documenting all collection care and management activities; the use of policies to guide collection growth and use; and application of integrated pest management (monitoring, evaluation, and the application of non-chemical control measures). Professional ethical standards are discussed, with particular attention to the code of ethics of the International Committee on Museums (ICOM) and issues specific to natural history collections (e.g., destructive sampling).

Collection assessments.—To emphasize how the collections management theoretical framework can be applied to any museum collection, the workshop participants perform a critical assessment of the collections of the host institution. The assessment is based on the Collection Health Index (McGinley 1993, Williams et al. 1996) and the Museum Assessment Program of the American Asso-

Table 4. Laboratory exercises.

Type of exercise	Activity	Purpose
Practical laboratory exercises	Tests for volatile acids	Use of simple tests to identify materials that may produce volatile acids. Tests include the Oddy test; use of pH indicator strips and glycerin solutions; testing plastic films for the presence of plasticizers; the Beilstein test for chlorides in plastics.
	Ink and paper tests	Tests of ink and paper combinations for long-term stability; including lightfastness, solvent resistant, use of a pH testing pen, ink smear test, and the tape lift test.
	Testing fluid preservatives	How to make a simple gravimetric device to test concentration of fluid preservatives; how to make formaldehyde test strips; how to evaluate the evaporation potential of jar seals.
	Radiation detection	The use of photographic film to detect radiation produced by geological and paleontological specimens.
	Environmental monitoring	How to use a visible light meter, ultraviolet radiation meter, psychrometer, and relative humidity detectors.
Conceptual laboratory exercises	Preservation of chicken eggs	To observe the effects of fixatives and preservatives on biological membranes.
	Can crushing	To observe the force of atmospheric pressure on container closures.
	Surface tension	To observe the evaporative potential of fluids of differing surface tensions.
	Use of UV and visible radiation meters	Participants learn about the relationships between infrared, visible light, ultraviolet radiation, radiation intensity, and flux.
	Light damage slide rule	Participants learn the concept of reducing light exposure to prolong specimen life.

ciation of Museums (Topping 2002). The participants work in groups that are arranged to ensure that no participant will be looking at preparations they are familiar with (e.g., the botanists may assess fish in alcohol, the entomologists look at fossils, the herpetologists evaluate dry bird skins). This exercise allows the participants to apply their newly acquired knowledge and forces them to think more critically as they must work outside their area of systematic expertise. In addition, the host institution receives suggestions for improvements to collections care.

Laboratory Exercises

Hands-on activities include both practical instruction and conceptual exercises designed to help the participants grasp overall preservation concepts. The laboratory exercises are summarized in Table 4.

Group Exercises

The workshop is structured to promote in-class discussions, particularly regarding such topics as ethics and the use of collections. To promote the interchange of ideas, laboratory exercises are carried out in small groups. One in-class group exercise is designed to bring together diverse viewpoints on a common problem—planning a collections storage space that meets certain restrictions.

Guest Speakers

Some workshops have included guest speakers addressing such topics as database applications, collecting laws, and the use of collection assessments.

The Learning Environment

The intensity of the workshop learning experience has advantages and disadvantages. Participants are able to focus intensely on the subject matter for several days, but also may suffer some degree of burnout. To minimize the impact of this burnout, a variety of learning experiences is provided (lectures, discussions, readings, hands-on laboratory opportunities, and small-group projects) as well as opportunities to address particular problems at the participant's home institutions.

Discussion

In most Latin American natural history museums, collection care and management is the responsibility of either technicians who have little formal training or individuals trained for research and teaching. There are very few positions equivalent to the collections managers in the United States and Canadian institutions. The combination of research professionals, students, and technicians together in a single workshop presented a novel learning environment for many of the participants, but the evaluations indicated that the workshop concepts were understood and well-received.

Follow-up communication with many workshop participants indicates that they are applying the theoretical framework and other workshop concepts to their collection care and management activities. Furthermore, the workshops in Colombia were a factor in the formation of the Asociación Colombiana de Colecciones Zoológicas (Simmons and Muñoz-Saba 2000, 2002). It is anticipated that as the workshop information is further distributed, it will lead to the formation of national level organizations of museum collections care professionals, and that in turn, such organizations will contribute to the growth of collections care literature in Spanish. For example, a book has recently been published based on the collection care and management workshops (Simmons and Muñoz-Saba 2005), and one of us (YMS) has been offering a regular undergraduate course at the Universidad Nacional de Colombia since 2003 on the care and conservation of natural history collections.

The emphasis in the workshop on testing of local materials has led to the identification of several areas where future research may lead to improvements in collections care. These areas for future research include:

- The use of local herbal preparations for pest control.
- Museum design based on indigenous architecture that is better suited to local climates (e.g., Daniel et al. 2000).

- Re-structuring of collections management systems based on like-with-like storage (as opposed to discipline-based storage arrays).

Conclusions

Based on analysis of the workshop evaluations, we have determined that the five-day format for the workshop is more successful than the shorter versions. However, sections of the workshop can be fit in well with other museum topics, as was demonstrated in the Cuzco workshop (Table 2) for which the sections on preventive conservation, collection management, and integrated pest management were adapted for a week-long general museology workshop.

The workshop has also been presented in a developing country outside of Latin America (in Thailand in 2004). The workshop concepts and activities translated well, largely because natural history museums in southeast Asia face problems very similar to those in Latin America.

The best long-term solution for museums in Latin America and other developing regions is to offer natural history collections care and management training in the context of graduate programs in museum studies, similar to the programs advocated by Williams and Genoways (2004), Simmons (in press), and Williams and Simmons (in press). Workshops based on the principles described above fill an important training role in the short term, and will continue to be an important means for training working professionals to better care for and manage natural history collections for the future (Cato et al. 1996).

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The idea for a collections care and management training program for Latin America was first proposed in 1987 by Antonio Salas. The first workshop was made possible thanks to the generous support of the Instituto Alexander von Humboldt in Colombia. The idea of writing a book based on the workshops was suggested in 2000 by Cristián Samper, then director of the Instituto de Investigación de Recursos Biológicos Alexander von Humboldt. David S. McLeod assisted with the workshop in Thailand. Numerous colleagues have made suggestions over the years that have greatly improved the workshops. A special appreciation goes to the workshop participants for their enthusiasm and energy.

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COLOMBIAN HERBARIA

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Abstract.—Decree 309/2000 establishes the legal guidelines for scientific investigation of biological diversity in Colombia and Resolution 1115/2000 determines the procedure to continue for registering biological collections with the Humboldt Institute. In Colombia there are 59 herbaria: 57 registered, 33 associated with the Colombian Association of Herbaria (ACH), and 24 cited in Index Herbariorum. Overall, 39% are national in character, 59% are regional, and 2% are local. The La Salle University Herbarium, founded in 1912, is the oldest collection. The main herbarium is the Colombian National Herbarium (COL), with 500,000 specimens.

Resumen.—El decreto 309 de 2000 reglamenta la investigación científica sobre diversidad biológica y la resolución 1115 de 2000 determina el procedimiento a seguir para registrar las colecciones biológicas ante el Instituto Humboldt. En Colombia hay 59 herbarios, 57 registrados, 33 asociados a la Asociación Colombiana de Herbarios (ACH) y 24 adscritos al Index Herbariorum. El 39% de los herbarios tienen un carácter nacional, el 59% regional y el 2% local. El herbario Colección Universidad de La Salle, es el más antiguo y se fundó en 1912. El principal herbario es el Herbario Nacional Colombiano (COL) con 500,000 especimenes.

INTRODUCTION

Article 51 of the Natural Resources Code of Colombia (1974) regulates natural resources rights and use; Article 258 outlines norms for botanical gardens, zoos, natural history collections, and museums. Additional laws enacted after 1974 concerning national parks, wildlife, hydrobiological resources, and wild flora (1977, 1978) have been implemented to regulate the registration of natural history collections, unique specimens, and biological collecting. The National Political Constitution of 1991 encourages scientific research and the conservation of natural resources and the environment; additional legal norms have since been established with the creation of the National System for Science and Technology, the National Program of Environmental Sciences and Habitat, the reorganization of COLCIENCIAS (1990–1993), and the creation of the National Science and Technology Council (Sistema Nacional Ambiental 1997). Decree 309 of 25 February 2000 (Ministerio del Medio Ambiente 2000a) further regulates the scientific investigation of biological diversity. Chapter III, in particular Article 12, addresses biological collections, defining a "biological collection" as "a set of cataloged biological specimens that is maintained and organized taxonomically." With this basis, the Ministry of the Environment issued Resolution 1115 of 01 November 2000 (Ministerio del Medio Ambiente 2000b) to establish procedural norms for registering biological collections intended for scientific research, emphasizing that "any person or organization possessing a biological collection is required to register it." Article 7 outlines the functions of registered biological collections; among these are informing scientific investigations and other studies which re-

Collection Forum 2006; 20(1–2):95–107

quire the cataloging, maintenance, and taxonomic organization of legally-obtained specimens, and serving as a reference for the identification of specimens in environmental and biodiversity research.

With the databasing of biological collections and the publication and updating of the information regarding these collections, it will be possible to: (1) quantify how much of the country's biodiversity is represented in Colombian herbaria; (2) establish what groups and biogeographic regions are represented; (3) identify priorities with reference to endemic groups, endangered groups, and groups of ecological and/or economic interest; (4) quantify how many and which type specimens are found in which national collections; and (5) characterize groups of special interest for each herbarium. Moreover, these collections are a center of documentation for past and present biodiversity, with historical information not only at the species level, but also spatiotemporal landscape changes. On the basis of the information collected in the registration process, the Alexander von Humboldt Institute and the Colombian Association of Herbaria (ACH) undertook an analysis of the status of Colombian herbaria. The objective of this review of herbaria is to focus both human and economic resources on current strengths and weaknesses in order to contribute to the National Inventory of the Floristic Biodiversity of Colombia.

Methods

Analyses were conducted of information provided about the herbaria registered with the Alexander von Humboldt Institute (http://www.humboldt.org.co/colecciones) and those cited in the Index Herbariorum (http://sciweb.nybg.org/science2/IndexHerbariorum.asp), consulted in March 2005. This information was sent to the Asociación Colombiana de Herbarios (ACH) for verification.

Discussion

There are 59 herbaria in Colombia belonging to 45 institutions in 28 cities located throughout the country. As of March 2005, 57 (97%) of these herbaria were registered with the Alexander von Humboldt Institute; 33 (56%) were members of the Colombian Association of Herbaria; and 24 (41%) were cited in Index Herbariorum (http://www.nybg.org/science207.156.243.8/emu/ih/herbarium_list.php, consulted 28 March 2005) (Appendix 1).

There are approximately 1,442,735 specimens in Colombian herbaria, of which 1,059,469 (73%) are cataloged and 383,266 (27%) not yet available for use (Appendix 2). Of these 59 herbaria, 39% are national in scope, 59% are regional, and 2% are local. The regional herbaria are: Andean (73%), Caribbean (10%), Amazonian (8%), Chocoan and all regions (5%), and Orinocoan (2%) (Appendix 3). Local herbaria are restricted to a municipality.

The general objective of the regional herbaria is to preserve a comprehensive and representative sample of plant species of a biogeographic region. Far from competing with the national herbaria, these institutions complement them and contribute significantly to the National Biodiversity Inventory. Thirty-five of the regional herbaria are associated with public or private universities.

Nevertheless, there is considerable duplication of effort among Colombian herbaria. In Bogotá, for example, there are ten herbaria, eight of which are associated with universities, and are national in character. In Medellín there are six herbaria;

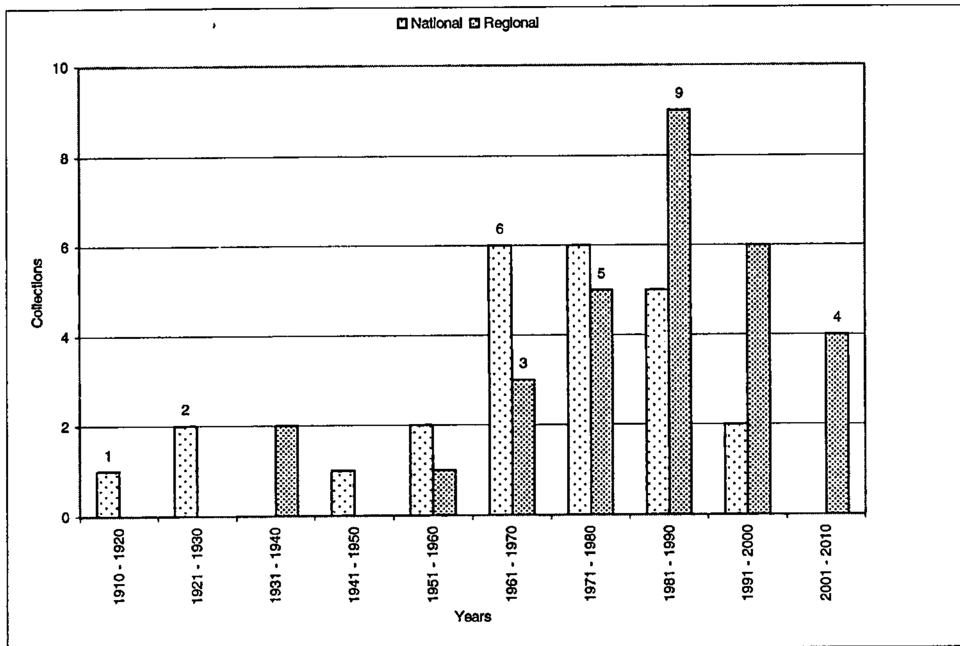

Figure 1. Date of founding of Colombian Herbaria.

five of these are associated with universities (four are part of the National University of Colombia) and six are national in character (Appendix 3).

The Museo de La Salle herbarium (MLS), created in 1912, was the first Colombian herbarium. The first regional herbaria were the Museo de Historia Natural Universidad del Cauca (MHN-UC) and the Herbario Universidad del Cauca (CAUP), founded in 1936. The 1960s through the 1990s was the period of the flowering of national herbaria; regional herbaria arose mostly in the 1980s and 2000s (Forero 1977, http://www.humboldt.org.co/colecciones/araneus.humboldt.org.co/colecciones/index.html consulted 29 March 2005) (Fig. 1, Appendix 2).

The largest Colombian herbarium is the Herbario Nacional Colombiano (COL) of the Instituto de Ciencias Naturales of the Universidad Nacional de Colombia; founded in 1929, it has 500,000 cataloged specimens. Next in size is the Herbario Universidad de Antioquia (HUA), with 650,000 specimens from throughout the country. At the regional level, the most important herbaria are the Herbario Amazonico Colombiano (COAH), with 50,000 specimens, and the University of Nariño Herbarium (PSO), with 42,000 specimens (Appendix 2). Information is databased in 43 (75%) of the Colombian herbaria and available to the public in 47 (84%).

Information from the registration forms is insufficient to assess the curatorial status of the herbaria; however, some generalizations can be made. Basic curatorial processes (inclusion of new labeled material in the collection, mounting of specimens, pest control, basic identification, cataloging, databasing, and filing each mounted specimen in its appropriate place) are very slow. In general, the herbaria have basic facilities: housing, furniture, computers, etc. All the herbaria have a maintenance system of some sort, although not necessarily optimal. The great

majority do not have explicitly defined protocols or policies for management and use, nor for loans, exchanges, or deposition of material. Not all collections have appropriately-trained staff (curators, botanists). Some herbaria are "managed" by undergraduate students or technicians.

Recommendations

With the results of this survey, as well as information regarding the character and number of specimens in each collection, it is possible to establish which herbaria are in need of the greatest investment (both economically and in terms of personnel) to achieve an adequate level of curation. The regional collections are especially important in this context, so that the regional national resource authorities will know what specimens are available and their state of curation.

The process of databasing these herbaria is not a task just for each institution, but a collective priority, because the entire scientific community and the general public will benefit. As Llorente et al. (1999) point out, herbaria are not used exclusively by taxonomists; their usefulness extends to other fields which benefit from their collections and to decision makers who can use them as analytical tools.

Planning is needed for focusing human and economic resources on the care, management, and conservation of biological collections; trained staff is necessary for herbaria to function well. Determining the Collection Health Index (CHI; Spanish acronym = ISC) (McGinley 1990, 1992, Williams et al. 1996, Fernández et al. 2005) for each herbarium, and thereby quantifying what material is available and what state it is in, will facilitate proposing action plans for the future.

Determining (1) how many herbaria there are in the country and what the fundamental objectives are of each one (teaching, research, exhibition); (2) their geographical scope (local, regional, national); (3) their lines of work (e.g., morphology, physiology, taxonomy, systematics, evolution, ecology); (4) their curatorial state; and (5) what information is deposited in each will contribute to the objectives outlined in the Action Plan for Colombian Biodiversity 21st Century (Instituto de Investigación de Recursos Biológicos Alexander von Humboldt 1998), as well as the Systematic Agenda for the 21st Century (Forero et al. 1999) and the Strategy for Plant Conservation (Instituto de Investigación de Recursos Biológicos Alexander von Humboldt 2001). These documents concur in recommending the strengthening of herbarium collections, the databasing of the specimens deposited in each, and in making this primary and secondary information available to the scientific community and/or the general public as critical elements for determining the current status of Colombian flora, for generating the knowledge necessary for its conservation, and for contributing to the National Biodiversity Inventory.

Plant conservation strategies in general and for particular groups must be based on the taxonomic information available in herbaria and their associated libraries. The Registry of Biological Collections, headed by the Alexander von Humboldt Institute, is providing the base for continued coordinated work by (1) strengthening herbaria through institutional recognition, (2) databasing Colombian herbaria, and (3) proposing strategies for the conservation of the Colombian flora based on making information accessible about what material resides in herbaria, exchanges of material among herbaria, and communication among specialists.

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Appendix 1. List of Colombian herbaria, March 2005.

Acronym	Herbarium	Organization	City	Registry	ACH	Index Herbarium
AFP	Herbario Álvaro Fernández Pérez	Fundación Universitaria de Popayán	Popayán	015	X	
ANDES	Herbario Museo de Historia Natural Universidad de los Andes	Universidad de los Andes	Bogotá		X	
AP-UNM	Arboretum y Palmetum Universidad Nacional sede Medellín	Universidad Nacional de Colombia	Medellín	122		
BOG	Museo de la Salle	Universidad de la Salle	Bogotá	133	X	X
CAUP	Herbario Universidad del Cauca	Universidad del Cauca	Popayán	155	X	X
CDMB	Herbario Jardín Botánico Eloy Valenzuela	Corporación Autónoma Regional para la Defensa de la Meseta de Bucaramanga (CDMB)	Floridablanca	029	X	
CHOCO	Herbario Chocó	Universidad Tecnológica del Chocó (DLC)	Quibdó	023	X	X
CIAT	Herbario CIAT	Centro Internacional de Agricultura Tropical (CIAT)	Cali	020	X	
CMVB-UCO	Material Vegetal Unidad de Biotecnología	Universidad Católica de Oriente	Río Negro	074		
COAH	Herbario Amazónico Colombiano	Instituto Amazónico de Investigaciones Científicas (SINCHI)	Bogotá	001	X	X
COL	Herbario Nacional Colombiano	Instituto de Ciencias Naturales	Bogotá	006	X	X
CRQCNEBG	Herbario de Bambusoideas del Centro Nacional para el Estudio del Bambú–Guadua	Centro Nacional para el Estudio de Bambú–Guadúa	Montería	150		
CUVC	Herbario CUVC	Universidad del Valle	Cali	034	X	X
CVGBR	Colección Viva Germán Botero de los Ríos	Fundación Jardín Botánico Guillermo Piñeres	Turbaco	126	X	
DUGAND	Herbario Armando Dugand Gnecco	Universidad del Atlántico	Barranquilla	083	X	
FAUC	Herbario Universidad de Caldas	Universidad de Caldas	Manizales	028	X	X
FMB	Herbario Federico Medem	Instituto de Investigación de Recursos Biológicos Alexander von Humboldt	Villa de Leyva	004	X	X
HECASA	Herbario Catatumbo-Sarare	Universidad de Pamplona	Pamplona	018	X	
HPUJ	Herbario Pontificia Universidad Javeriana	Pontificia Universidad Javeriana	Bogotá	011	X	X

Appendix 1. Continued.

Acronym	Herbarium	Organization	City	Registry	ACH	Index Herbarium
HR-C	Herbario de Referencia de CORANTIOQUIA	Corporación Autónoma Regional del Centro de Antioquia–Corantioquia	Medellín	117		
HUA	Herbario Universidad de Antioquia	Universidad de Antioquia	Medellín	027	X	X
HUC	Herbario Universidad de Córdoba	Universidad de Córdoba	Montería	022	X	X
HUQ	Herbario Universidad del Quindio	Universidad del Quindío	Armenia	010	X	X
HVc	Herbario Vittoriano	Fundación Ciencia, Ecología, Arte e Historia Fundación CEAH	Bogotá	013		
ICA	Herbario Nacional de Malezas	Corporación Colombiana de Investigación Agropecuaria Corpoica	Mosquera	014		X
JAUM	Jardín Botánico Joaquín Antonio Uribe	Fundación Jardín Botánico Joaquín Antonio Uribe	Medellín	033	X	X
JAUM-JB	Jardín Botánico Joaquín Antonio Uribe	Fundación Jardín Botánico Joaquín Antonio Uribe	Medellín	120		
JBAVH	Jardín Botánico Alejandro von Humboldt	Universidad del Tolima	Ibagué	112		
JBB	Jardín Botánico José Celestino Mutis	Jardín Botánico José Celestino Mutis	Bogotá	130	X	
JBC	Jardín Botánico de Cali	Fundación Jardín Botánico de Cali	Cali	111		
JBEV-CDMB	Colección de Plantas Vivas Jardín Botánico Eloy Valenzuela	Corporación Autónoma Regional para la Defensa de la Meseta de Bucaramanga (CDMB)	Floridablanca	103		
JBGP	Colección de Herbario María Jiménez de Piñeres	Fundación Jardín Botánico Guillermo Piñeres	Cartagena	069		X
JBJCM-H	Herbario Jardín Botánico José Celestino Mutis	Jardín Botánico José Celestino Mutis	Bogotá	021		
JBJMC	Jardín Botánico Juan María Céspedes	Instituto para la Investigación y Preservación del Patrimonio Cultural y Natural del Valle de Cauca (INCIVA)	Tuluá	106		
JB-Medicinales-CEA	Jardín Botánico de Plantas Medicinales del CEA	Corpoamazonia	Mocoa	151		
JBP	Jardín Botánico de Popayán	Fundación Universitaria de Popayán	Popayán	137		
JBQ	Jardín Botánico del Quindío	Fundación Jardín Botánico del Quindío	Calarcá	136		
JBUC	Jardín Botánico Universidad de Caldas	Universidad de Caldas	Manizales	105		

Appendix 1. Continued.

Acronym	Herbarium	Organization	City	Registry	ACH	Index Herbarium
JB-UTP	Jardín Botánico de la Universidad Tecnológica de Pereira	Universidad Tecnológica de Pereira	Pereira	139		
JEBVL	Villa Ludovica	Fundación Jardín Etnobotánico Villa Ludovica	Santa Marta	132		
JSJ	Colección de Flora Material Vivo y Herbario	Corporación Botánico San Jorge	Ibagué	113		
LLANOS	Herbario de la Orinoquía Colombiana	Universidad de los Llanos	Villavicencio	017	X	
MEDEL	Herbario Gabriel Gutiérrez Villegas	Universidad Nacional de Colombia	Medellín	016	X	X
MHN-UC	Museo de Historia Natural Universidad del Cauca	Universidad del Cauca	Popayán	044		
MMUNM	Museo Micológico	Universidad Nacional de Colombia	Medellín	007		
PSO	Herbario Universidad de Nariño	Universidad de Nariño	Pasto	040	X	X
SURCO	Herbario Universidad Surcolombiana	Universidad Surcolombiana	Neiva	024	X	
TOLI	Herbario TOLI	Universidad del Tolima	Ibagué	019	X	X
TULV	Herbario TULV–Jardín Botánico Juan María Céspedes	Instituto para la Investigación y Preservación del Patrimonio Cultural y Natural del Valle del Cauca (INCIVA)	Tuluá	072	X	X
UDBC	Herbario Forestal Universidad Distrital Francisco José de Caldas	Universidad Distrital Francisco José de Caldas	Bogotá	025	X	X
UDCA	Colección Biológica UDCA	Corporación Universitaria de Ciencias Aplicadas y Ambientales (UDCA)	Bogotá	051		
UIS	Herbario UIS	Universidad Industrial de Santander (UIS)	Bucaramanga	030	X	X
UMNG-H	Herbario de Botánica Económica Universidad Militar Nueva Granada	Universidad Militar Nueva Granada	Bogotá	141		
UPTC	Herbario UPTC	Universidad Pedagógica y Tecnológica de Colombia	Tunja	026	X	X
UTMC	Herbario Universidad del Magdalena	Universidad del Magdalena	Santa Marta	032	X	X
UV-mico	Hongos, Univalle	Universidad del Valle	Cali	114		
VALLE	Herbario José Cuatrecasas Arumi	Universidad Nacional de Colombia	Palmira	031	X	X
X-UNCM	Xiloteca	Universidad Nacional de Colombia	Medellín	123		
	Herbario Universidad de la Amazonia	Universidad de la Amazonia	Florencia		X	
	59	45	28	57	33	24

Appendix 2. Status of specimens in Colombian Herbaria, March 2005.

Acronym	Herbarium	Date Founded	Vascular plants: Specimens cataloged	Vascular plants: Specimens not cataloged	Non-vascular plants: Specimens cataloged	Non-vascular plants: Specimens not cataloged
AFP	Herbario Álvaro Fernández Pérez	1995	6,355	1,200	215	50
ANDES	Herbario Museo de Historia Natural Universidad de los Andes	2004				
AP-UNM	Arboretum y Palmetum Universidad Nacional sede Medellín	S.F.				
BOG	Museo de La Salle	1912	12,990	2,000	328	
CAUP	Herbario Universidad del Cauca	1936	9,902	8,000	2,048	2,300
CDMB	Herbario Jardín Botánico Eloy Valenzuela	1990	1,140		335	
CHOCO	Herbario Chocó	1980	10,026	9,000	40	660
CIAT	Herbario CIAT	1978	14,166	1,000		
CMVB-UCO	Material Vegetal Unidad de Biotecnología	1990	51			
COAH	Herbario Amazónico Colombiano	1983	38,794	8,000	2,788	100
COL	Herbario Nacional Colombiano	1929	410,865	182,000	49,360	30,000
CRQCNEBG	Herbario de Bambusoideas del Centro Nacional para el Estudio del Bambú–Guadua	1998	51			
CUVC	Herbario CUVC	1965	30,500	15,000	300 bag	100 bag
CVGBR	Colección Viva Germán Botero de los Ríos	1978	2,740	7,000		
DUGAND	Herbario Armando Dugand Gnecco	1995	600	1,200	10	
FAUC	Herbario Universidad de Caldas	1952	17,686	91	28	1
FMB	Herbario Federico Medem	1969	26,244	47%		650
HECASA	Herbario Catatumbo-Sarare	1990	1,400	300		50
HMJP	Colección de Herbario María Jiménez de Piñeres	1978	12,680	14,000		
HPUJ	Herbario Pontificia Universidad Javeriana	1986	2,497	9,000		
HR-C	Herbario de Referencia de CORANTIOQUIA	1999	2,400			
HUA	Herbario Universidad de Antioquia	1969	122,000	10,000	11,000	500
HUC	Herbario Universidad de Córdoba	1976	4,227	228		

Appendix 2. Continued.

Acronym	Herbarium	Date Founded	Vascular plants: Specimens cataloged	Vascular plants: Specimens not cataloged	Non-vascular plants: Specimens cataloged	Non-vascular plants: Specimens not cataloged
HUQ	Herbario Universidad del Quindío	1985	22,000		1,500	
HVc	Herbario Vittoriano	2000	160			165
ICA	Herbario Nacional de Malezas	1971	625	85		
JAUM	Jardín Botánico Joaquín Antonio Uribe	1973	35,438	20,000		2,000
JAUM-JB	Jardín Botánico Joaquín Antonio Uribe	1969	2,500	10,000		
JBAVH	Jardín Botánico Alejandro von Humboldt	1969	567	50		35
JBB	Jardín Botánico José Celestino Mutis	1955	8,404	3,027		
JBC	Jardín Botánico de Cali	2001	537	430		
JBEV-CDMB	Colección de Plantas Vivas Jardín Botánico Eloy Valenzuela	1990	2,200	383		
JBJCM-H	Herbario Jardín Botánico José Celestino Mutis	1955	3,468	50		
JBJMC	Jardín Botánico Juan María Céspedes	1966	456	1,000		
JB-Medicinales-CEA	Jardín Botánico de Plantas Medicinales del CEA	1990	514			
JBP	Jardín Botánico de Popayán	1997	1,006	8		
JBQ	Jardín Botánico del Quindío	1979	834		25	
JBUC	Jardín Botánico Universidad de Caldas	1991	1,000		50	
JB-UTP	Jardín Botánico de la Universidad Tecnológica de Pereira	1983	877	35		45
JEBVL	Villa Ludovica	2000		120		
JSJ	Colección de Flora Material Vivo y Herbario	1991	763			
LLANOS	Herbario de la Orinoquía Colombiana	1990	6,926	76	2	
MEDEL	Herbario Gabriel Gutiérrez Villegas	1927	42,000	2,000	552	120
MHN-UC	Museo de Historia Natural Universidad del Cauca	1936	3,100	6,200	1,400	600
MMUNM	Museo Micológico	1987			910	390
PSO	Herbario Universidad de Nariño	1962	25,300	2,500	11,200	3,300

Appendix 2. Continued.

Acronym	Herbarium	Date Founded	Vascular plants		Non-vascular plants	
			Specimens cataloged	Specimens not cataloged	Specimens cataloged	Specimens not cataloged
SURCO	Herbario Universidad Surcolombiana	1986	3,400	17%	200	7%
TOLI	Herbario TOLI	1978	6,623	385	1,222	720
TULV	Herbario TULV–Jardín Botñico Juan María Céspedes	1983	14,700	3,000		
UDBC	Herbario Forestal Universidad Distrital Francisco José de Caldas	1973	12,600	3,750		
UDCA	Colección Biológica UDCA	1990	2,234	339		
UIS	Herbario UIS	1978	9,986	1,347	127	76
UMNG-H	Herbario de Botánica Económica Universidad Militar Nueva Granada	2001	400	100		
UPTC-H	Herbario UPTC	1970	8,576	15,000	588	300
UTMC	Herbario Universidad del Magdalena	1963	9,000	3,000	600	300
UV-mico	Hongos, Univalle	1970			1,750 sheets	90 sheets
VALLE	Herbario José Cuatrecasas Arumi	1943	18,527	5%	74	
X-UNCM	Xiloteca	1975	2,832			
	Herbario Universidad de la Amazonia	2004				
Total	59		974,867	340,904	84,602	42,632

Appendix 3. Distribution of Colombian herbaria, March 2005. (Character: L = Local; R = Regional; N = National. Biogeographical region: A = All, Am = Amazon; An = Andean; Ca = Caribbean; Ch = Chocoan; O = Orinocoan)

City	Number of herbaria	Number of botanical gardens	University affiliated		Character			Biogeographical region					
			Number	University	L	R	N	A	Am	An	Ca	Ch	Or
Armenia	1	0	1	Universidad del Quindío		1				1			
Barranquilla	1	0	1	Universidad del Atlántico			1				1		
Bogotá	10	1	8	Corporación Universitaria de Ciencias Aplicadas y Ambientales, UDCA	1	3	7		2	9			
				Pontificia Universidad Javeriana									
				Universidad de la Salle									
				Universidad de los Andes									
				Universidad Distrital Francisco José de Caldas									
				Universidad Nacional de Colombia									
				Universidad Militar Nueva Granada									
Bucaramanga	1	0	1	Universidad Industrial de Santander (UIS)		1				1			
Calarcá	1	0	0			1				1			
Cali	3	1	2	Universidad del Valle		1	2			3			
Floridablanca	1	1	0			2				2			
Ibagué	3	0	2	Universidad del Tolima		2	1			3			
Manizales	1	1	2	Universidad de Caldas		2				2			
Medellín	6	2	5	Universidad de Antioquia		1	6			8			
				Universidad Nacional de Colombia									
Mocoa	1	0	0			1			1				
Montería	2	0	1	Universidad de Córdoba		1	1				2		
Mosquera	1	0	0				1			1			
Neiva	1	0	1	Universidad Surcolombiana		1				1			
Palmira	1	0	1	Universidad Nacional de Colombia			1			1			
Pamplona	1	0	1	Universidad de Pamplona		1				1			
Pasto	1	0	1	Universidad de Nariño		1				1	1		
Pereira	0	1	1	Universidad Tecnológica de Pereira		1				1			
Popayán	3	1	4	Fundación Universitaria de Popayán		3	1	1		3			
				Universidad del Cauca									

Appendix 3. Continued.

City	Number of herbaria	Number of botanical gardens	University affiliated		Character				Biogeographical region				
			Number	University	L	R	N	A	Am	An	Ca	Ch	Or
Quibdó	1	0	1	Universidad Tecnológica del Chocó		1						1	
Río Negro	1	0	1	Universidad Católica de Oriente			1	1					
Santa Marta	1	1	1	Universidad del Magdalena		2					2		
Tuluá	1	1	0			2				2			
Tunja	1	0	1	Universidad Pedagógica y Tecnológica de Colombia		1				1			
Turbaco	1	1	0			2						2	
Villa de Leyva	1	0	0				1	1					
Villavicencio	1	0	1	Universidad de los Llanos		1							1
	50	11	40		1	35	23	3	5	43	6	3	1

USING CAPILLARITY FOR DETERMINING AND MAINTAINING A POLYMER CONSOLIDANT CONCENTRATION AFTER SOLUTION PREPARATION

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Abstract.—The use of consolidants to stabilize and strengthen fragile fossil material plays an important role in the preparation and conservation of palaeontological specimens. Polymers such as polyvinyl acetate, dissolved in acetone or ethanol solvents, are widely used as consolidants because of their versatility and long-term stability. The concentration of dissolved polymer can be high (35% by weight) producing a thick solution useful as archival glue, or low (<5% by weight) to provide a thin solution that can penetrate dense cortical bone. Additionally, there is often an optimal concentration that provides maximum penetration of consolidant into the object being conserved. The optimal concentration can be within a narrow range and vary from specimen to specimen, therefore determining and maintaining consolidant concentration is important. A method based on the capillary action of fluids is used to quantify and monitor the polymer concentrations of consolidant working solutions. The procedure is quick, inexpensive, and requires no specialized equipment. Regular assessment of working solution concentrations can increase quality and consistency of artefact conservation.

INTRODUCTION

The use of Poly-vinyl acetate (Vinac, B-15) polymer, dissolved in a solvent such as ethanol or acetone is commonly advocated as an effective archival consolidant for strengthening fossil specimens (Doyle 1987, May et al. 1994, Shelton and Johnson 1995). Studies examining the bond strength and drying time of polymer adhesives (Wenz et al. 1996, Wenz et al. 1995) found that *adhesive* effectiveness was maximized at specific concentrations that varied for each polymer (e.g., 45% for Vinac-B15) and that optimal concentrations also varied with the size of the bone elements being re-attached. Similarly, polymers used as *consolidants* will be most effective when liquid solutions maximize both the penetration *depth* and the *amount* of polymer delivered into the object, and each of these factors will vary depending upon the porosity and material characteristics of the objects being conserved.

Polymers are typically purchased in dry (bead, pellet) form and dissolved into a solvent to form a *stock solution* for use in the conservation lab. The stock solution is then easily diluted to produce the desired concentration of working solution. Consolidant concentrations used in palaeontology conservation typically range from 2–15% (by weight).

Of course, care should be taken to ensure solvents are compatible with the artefacts to be conserved; acetone and ETOH can dissolve organic and some inorganic molecules. Solvents can also react over time to degrade the containers used to store stock and working solutions. Most supply catalogues provide a listing of bottle types and the reactivity with various solvents. Polypropylene (PPP) bottles are useful because of their resistance to both acetone and ethanol.

Aside from the compatibility of the solvent with the containers and material being conserved, the evaporation rate of the solvent is an important factor in

consolidant effectiveness. Evaporation rates vary for each solvent. A solvent that evaporates quickly will reduce polymer linkage (drying) time, resulting in a shallow penetration depth. Consolidant penetration depth also decreases with increasing polymer concentration, as viscous consolidants are unable to flow as well into the small pores of the object. A consolidant can stabilize and strengthen an object by filling pores and cracks and can protect artefact surfaces from environmental conditions. Complete consolidation of an object is improved by maximizing both consolidant penetration depth and the amount of polymer delivered into the object.

The method described below uses a liquid's capillarity, which varies directly with viscosity, to indirectly determine and monitor the polymer concentration of a working solution that has an unknown concentration due to solvent evaporation. Measuring the capillarity of a series of known solvent/binder solutions develops a calibration. The calibration is then used to estimate binder concentration in monitored working solutions.

METHODS

Mixing Stock Solutions and Preparing Baseline Samples

To begin, it is necessary to record with permanent pen or paint, the weight of containers (empty, with lids) on the bottom of all bottles. The weight of the bottle will be required throughout this process for calculating the solution weight contained in the bottle. Fill an empty container halfway with solvent, leaving sufficient space for the addition of polymer. Determine the weight of solvent by measuring the total weight and subtracting the bottle weight. To make a stock solution, measure the required amount of polymer for your target concentration (suggest 30–50% of solvent weight) into a dry dish. Slowly add a small portion of the polymer to the solvent, shaking periodically until polymer is dissolved. A stirrer and spin bar may also be used to promote polymer dissolution. Repeatedly adding small amounts of polymer will prevent clumps of polymer from forming at the bottom of the solution. Only an amount of stock solution that can be used within a few months should be mixed at one time. To provide a safe working environment, all bottles should include a label with a list of all the materials contained in the solution, as well as safety symbols associated with the elements, the concentration of the solution, and mixing date.

Once a stock solution has been prepared, it can be used to mix several different concentrations of working solution. Again the solutions are prepared based on weight measures of solvent and polymer. Into an empty bottle (with empty weight permanently marked on bottom) add some stock solution, leaving enough room for additional solvent, and then calculate *stock weight* (= total − bottle weight). Determine the amount of new solvent to add by the following formula:

$$\text{Solvent to add (weight)} = ((\text{Stock }\% \times \text{Stock Weight})/\text{New }\%) - \text{Stock Weight}$$

To produce a series of baseline measures, use the above procedure to mix a range of known working solution concentrations. The stock solution (e.g., 35%) and pure solvent (0%) are the two endpoints in the range. A good baseline can be constructed by mixing five solutions equally spanning the stock to pure solvent range. Other concentrations can be mixed and added to the baseline if there are specific endpoints of interest.

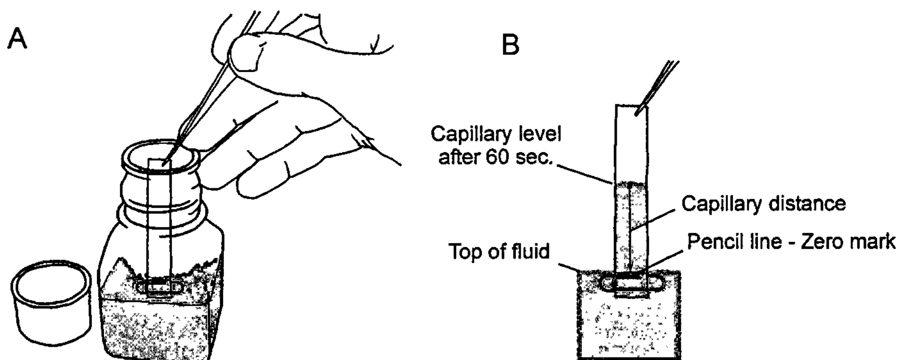

Figure 1. Measuring the distance of capillary flow for a consolidant working solution. Tweezers are used to hold a strip of filter paper inside the bottle (A). After sixty seconds, the strip is removed and the top of the capillary level is quickly marked with another pencil line (B). The distance between the lower zero line and the top capillary level represents the capillary distance.

Measuring Capillarity

This system of concentration monitoring is based on capillarity, the tendency of a solution to travel up a porous material (piece of filter paper) by capillary action. A thick (viscous) liquid will have a lower capillarity than a thin (low viscosity) liquid, or in other words, a thin liquid can travel further up a piece of paper than a thick liquid.

Strips of filter paper are used to measure the capillary height a liquid can travel in one minute. Test strips approximately five centimetres long and one centimetre wide have proven effective, but longer strips may be required depending upon the type of bottle used in your facility. Large (#4) cone coffee filters can be located in any grocery store, are inexpensive, flat, and can be cut easily to produce excellent test strips. The same type (and supplier) of filter paper should be used consistently to maintain reliable results.

Once a number of identical test strips have been created, attach a small paper clip to the end of a test strip and draw a pencil line just above the paper clip (Fig. 1A). The pencil line will be placed at the top of the fluid being measured and represent zero capillarity. The paper clip acts as a weight to keep the paper clip from floating. Tweezers are needed to hold onto the top of the test strip as it is inserted into the bottle. Insert the paper clip and test strip (up to the "zero" pencil line) into the solution. It is important to keep the test strip above the fluid line within the empty portion of the bottle in order to prevent excessive evaporation of solvent as the fluid travels up the filter paper. Immediately upon the test strip entering the solution, start a timer. Hold the test strip motionless for sixty seconds, then remove the strip from the bottle and quickly mark a second pencil line at the highest point the solution traveled on the test strip. The distance between the lower and upper pencil mark represents the capillary height reached after one minute (Fig. 1B).

Measuring Baseline Samples

Using the method described above, measure the capillary height three times for each baseline solution, calculate the average height for each solution and plot

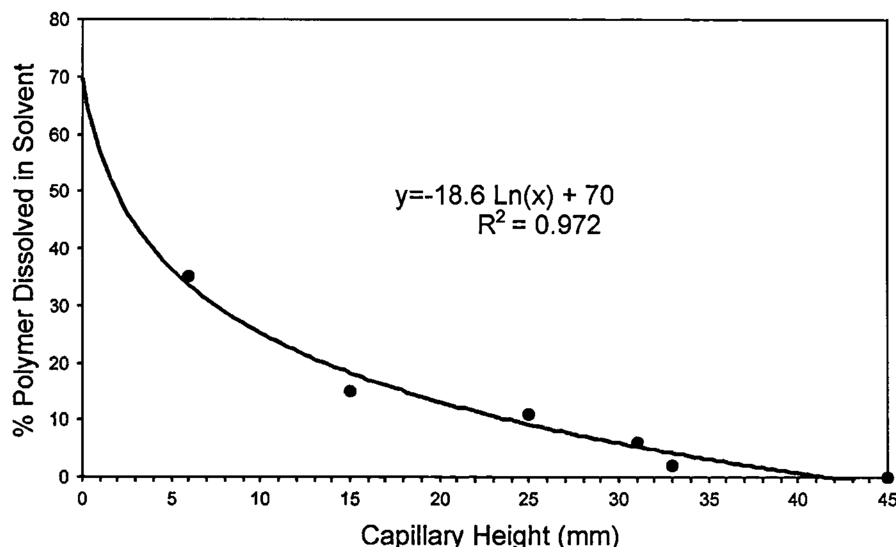

Figure 2. Plot illustrating relationship between the polymer concentration and capillary height attained after one minute. Each point represents the average measured capillary height (after 60 seconds) for each known polymer concentration in the baseline series.

these values against polymer concentration (Fig. 2). The graph and formula that results from evaluating the baseline solutions can then be used to measure and monitor consolidant concentration of the test polymer dissolved in the test solvent. Capillary height decreases exponentially with increasing polymer concentration.

Measuring Concentrations of Working Solutions

While conservators are treating objects with consolidants, bottles of working solutions are open and exposed to the air. Solvents can quickly evaporate when the solutions are open, causing the relative polymer concentration to increase. Personal experience suggests a consolidant working solution used for only two weeks in a palaeontology laboratory will have a substantially higher polymer concentration than when it was originally mixed. The concentration of an unknown solution can be determined by measuring the capillary height of the (unknown concentration) solution and comparing this height with the formula or plot generated from the baseline samples. With this concentration estimate, the amount of solvent required to return the consolidant to optimal concentration can be calculated with the formula mentioned above; the estimated solution concentration replacing the "stock" concentration in the formula.

Conclusion

Each bone/artefact to be conserved benefits from the application of an optimal concentration of consolidant, allowing for maximum penetration and pore filling capacity, therefore the optimal concentration should be determined for each specimen. Pre-measured viscosities of consolidant can be used to determine the most effective working concentration, and this easy and inexpensive monitoring system can then be used to ensure the working solutions used during specimen conservation remain at optimal levels.

As polymer concentrations of working solutions increase quickly in lab settings, weekly of biweekly monitoring of the consolidant concentration is warranted. The above method takes the guess work out of determining if a consolidant is "thick enough" or "too thin," allowing the concentration of polymer to be carefully controlled within narrow limits.

Acknowledgments

The methods presented in this paper were developed during the preparation of dinosaur specimens that are the focus of the author's dissertation research. Therefore the Nova Scotia Museum, Fundy Geological Museum (FGM), NSERC and the Jurassic Foundation are acknowledged as providing financial resources related to this project. Also, the lab staff at the FGM, particularly Katherine Goodwin and Patricia Boland, provided helpful assistance with the early trials of the method.

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Associate Editor: Paula T. Work

BOOK REVIEWS

THE CONSERVATION OF FUR, FEATHER AND SKIN, 2002, Margot M. Wright, ed. (*Conservators of Ethnographic Artefacts Series No.3,* Archetype Publications, London, England, 92 pp. plus introductory material.) This book is the edited postprints of a seminar held by the Conservators of Ethnographic Artefacts at the Museum of London. It is the third in a series about the conservation of ethnographic objects published by Archetype Publications Ltd. While by no means comprehensive, this somewhat eclectic publication provides an interesting and useful synopsis of ethnographic object conservation treatments and concerns to practicing conservators. The research presented about fabrication technology, cultural context, and methods and ethics of display should prove interesting to curators and ethnographers as well as the interested, general, lay public.

An introduction to the types of tannages used on ethnographic leather. This first paper provides a classic overview of the types of tannages found in ethnographic object collections and gives a brief assessment of their abilities to prevent decay in the presence of moisture and heat and retain the property of the resulting type of leather with repeated wetting and drying. While the coverage is quick and by no means comprehensive, the non-conservation trained reader may find it to be a clear and useful synopsis of the various methods of tanning traditionally described in the literature until the late 1900s.

The conservation of Plains Indian shirts at the National Museum of the American Indian, Smithsonian Institution. The next paper is largely treatment related and describes a multidisciplinary conservation approach to dealing with a large collection of Plains Indian hide shirts. The entire project is described in great detail. Rationale for selection of materials used in treatment is explained. Explicit diagrams of how adhesives were tested and selected, how mends were made, etc. are given. Many will find this tips and techniques type of approach highly useful. Among the techniques are further refinements of a technique of mending quillwork with Paraloid B72 film that was developed by Ann Krahn and David Grattan at the Canadian Conservation Institute in the early 1980s. Of perhaps greater interest to me was the discussion about spit cleaning having been abandoned upon the exhibit curator's request because of ethical considerations. He felt that spit cleaning was equivalent to spitting on an object.

A brief summary of laser experimentation undertaken on parchment at the Conservation Centre, National Museums and Galleries on Merseyside (NMGM), Liverpool. The third entry reviews the initial results of cleaning parchment with lasers as compared to more traditional methods.

The conservation of a turtleshell mask from the Torres Strait Islands, and, *Love a duck: the conservation of feathered skins.* Chapters Four and Five represent traditional conservation report papers. The turtleshell paper in particular is highly interesting due to the rarity of such an object in ethnographic collections. Both discuss cultural context and history of use, as well as structure, fabrication technologies, current conditions and treatments. Materials used in treatment are given, as well as brief details on methods of conservation. These two papers should prove useful references both to conservators dealing with objects made of such materials and ethnographic researchers.

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Cleaning of feathers from the Ethnological Museum, Berlin, and, *Colourful feathers: Multidisciplinary investigation of the Amazonian featherwork from the ethnographic collection at the National Museums and Galleries on Merseyside (NMGM)—initial results.* To varying degrees, both Chapters Six and Seven address the cleaning of feathers and their light sensitivity. Chapter Six has a concise review concerning feather structure and deterioration, and, the efficacy of various wet and dry cleaning methods. While these summaries add to our compendium of theoretical knowledge, they do not address the question of how to clean fragile feathers that cannot be moved or removed from an object, a problem acknowledged by the authors. Chapter 7 is a report on the progress to date a long-term project started in 2000 on the fading rates and laser cleaning of Amazonian featherwork. Interim results are not surprising, but they do provide a scientific basis for common assumptions held about the sensitivity of the brightly colored feathers to light. I look forward to hearing about the rest of the study.

Fur will fly: exhibiting controversy. The eighth paper, written by a curator is stimulating but has little to do with conservation. Rather it focuses on the exhibition, preparation and presentation of a controversial topic, the use of fur in Western fashion.

Caring for fur at the Museum of London. The conservation of fur costumes is summarized in the final chapter; the stress is on the need for preventive conservation. Synopses are made of proper storage and care, and causes of deterioration. The paper is rambling discussion, rather than a comprehensive conservation overview

I found this series of papers disappointing for several reasons. First, the quality of the papers is highly variable, ranging from rambling, classroom-like discussions to polished presentations of professional stature. Second, the coverage of the different materials (furs, feathers, skins) is not the same, ranging from brief discussion of preventive conservation approaches (fur) to in-depth descriptions of treatments (hide shirts). Third, the publication is diluted by the fact that various materials are covered. It differs from the previous two publications in the series that focus solely on one type of material (beadwork and barkcloth respectively). However, as part of a series on ethnographic conservation, the publication serves to build the much-needed published information on ethnographic conservation.—*Madeleine W. Fang, Phoebe Hearst Museum/UC, 103 Kroeber Hall, Berkeley, California 94720-3712, USA*

OLD POISONS, NEW PROBLEMS: A MUSEUM RESOURCE FOR MANAGING CONTAMINATED CULTURAL MATERIALS, 2005, Nancy Odegaard, Alyce Sadongei and Associates. (AltaMira Press, Walnut Creek, CA, 126 pp). This book is intended first and foremost for those working with cultural materials of the American Indian; however there is an overlap into more general social history, ethnography and natural history.

The book uses US legislation throughout, regarding the use and restrictions of certain pesticides, so those living outside of the US, will have to check their own country's health and safety legislation. Native American Graves Protection and Repatriation Act (NAGPRA) requires that some previously detained cultural materials, should now be returned to the tribes. This book covers the issues of managing contaminated cultural materials and repatriating these materials safely.

There have been many complications arising through repatriation including the issues of handling such culturally sensitive material, and of course the fact that these collections have been repeatedly poisoned as part of museum policy to prevent the biodeterioration of the objects. These items, upon return are not only accepted back into the tribes' ownership but they are engaged in rituals and ceremonies. Due to the possible contamination of the objects, the risks of handling, wearing of the items or burying them can affect the health of the individuals involved and that of the environment.

Chapter 1 concentrates on the law governing the change in ownership of such materials and clarifies the responsibility of both the tribal representative and the museum curator, regarding the issue of contaminated material. It shows how NAGPRA has succeeded in encouraging selected tribal representatives to sit on the review committee, fully understanding the consequences of taking back ownership of their lost heritage now poisoned by museum procedures. This work is presented as a case study for the remainder of the chapter.

Chapter 2 highlights the history of pesticides, the identification of the main pests through comprehensive diagrams, the damage they cause, present day insect pest management techniques with a small section on some of the pesticides used. There are various tables covering the pests targeted, the synonyms of 91 pesticides, their dates of use and restrictions, half lives and environmental persistence. There are tables relating to legislation and the pesticides names and classifications. This chapter contains a great deal of information, which may account for the number of errors. Nomenclature, generic names and chemical formulae are lacking or incorrect. Often the information is misleading and sometimes common names are used with no corresponding scientific name and so the interpretation could be ambiguous. The text mentions that *inorganic* compounds such as Naphthalene ($C_{10}H_8$), Tar Camphor ($C_{10}H_8$) and Paradichlorobenzene($C_6H_4Cl_2$) were also used; these should have been listed with Thymol ($C_{10}H_{14}O$) as the *organic* volatile fumes. There were very many discrepancies within this chapter and caution should be taken when referring to the scientific information provided.

Chapter 3 is a case study of how the Arizona State Museum compiled a technical report on their collections and produced a complete history of its own pesticide use with the corresponding production of four databases. The chapter gives a full description of how to prepare for repatriation and gives an example of a completed form. Sensible advice is given throughout including recommending that occupational hygienists be employed to oversee the assessment and decon-

tamination of artefacts and that it is not left to conservators or curators to assess the medical hazards of the contaminant. It is clearly stressed that no decontamination treatment should be attempted without prior consent of the tribal representative.

Chapter 4 deals initially with the most common elements or compounds expected to be present on the collections. Each section highlights a compound or element that is the active ingredient within a particular pesticide and gives synonyms and trade names.

There is a small amount of information relating to each species and then a recommended method of identification, for example a specific spot test. The chapter then further expands on the health and safety issues relating to such experimentation and goes into detail on how to carry out each test for: arsenic, mercury, copper, lead, zinc, borates, carbamates, organophosphates, and sulphates. The chapter concludes by discussing how to carry out more advanced sensitive analysis and recommends the instrumentation required to do so.

An important point that is not clearly stressed is that it is imperative when taking a sample for analysis to have a good idea of what it is you are looking for. XRF and ICP are good all round methods of showing what is in the sample, but AAS, HPLC and to some extent GC-MS are much more specific. For AAS analysis the element under scrutiny can only be detected when the correct reference bulb has been fitted. In all cases standards must be made up before quantitative data can be acquired.

Chapter 5 covers more of the scientific data relevant to this subject and again several errors were found in regard to inorganic mercury and within Table 5.1 where some of the conversion formulae were incorrect. Table 5.2 is a noteworthy piece of work and must have taken some time to complete, it will be invaluable to all working with contaminated collections.

This book has provided a vast amount of very useful practical advice and should form a good basic point of reference to some of the main queries surrounding the problems of working with contaminated materials. As a cautionary note it may be worth checking the technical and scientific details. This having been said, few other books have been this ambitious in putting together such relevant information into one source. Keeping abreast of pesticide regulations and occupational health data is extremely important, especially in the profession of conservation.—*Victoria Purewal, National Museum Wales, Cathays Park, Cardiff CF10 3NP, UK.*

Reviewers

SPNHC is grateful to the following people who reviewed manuscripts for Collection Forum:

C. Ahearn, C. Cook, M. Costello, D. Erwin, J.-M. Gagnon, D. Grattan, J. Johnson, Cathleen King, L. Klise, R. MacCulloch, E. Merritt, E. Moffatt, N. Odegaard, P. Palmer, C. Podsikj, V. Purewal, R. Rabeler, C. Ramotnik, J. Simmons, J. Sirois, J. Waddington, R. Waller, S. Williams, P. Work.

Museum Collection Resources Display Available for Loan

The Resources Subcommittee of the Conservation Committee (SPNHC) maintains two displays of supplies and materials used by many museums for the storage and preservation of natural history collections. Examples of items included in the displays are: materials used in the construction of storage containers and specimen supports; equipment for monitoring storage environments (e.g., humidity, temperature, air quality, insects); and a variety of containers for the storage of collections and documentation. Some of the products are discipline-specific (e.g., pH-neutral glassine for interleaving between herbarium sheets) but most can be used in multidisciplinary collections (e.g., Ethafoam™ for lining shelves and drawers; Tyvek™ tape for box and tray construction). The displays are available for loan to interested parties for meetings, conferences, and other museum-related activities. Shipping costs to and from the requested venues are the responsibility of the borrower. There is no loan fee but SPNHC invites borrowers to make a voluntary contribution to cover the costs of routine maintenance. For additional information, or to borrow a display, contact:

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Instructions to Authors

Articles for Collection Forum are six to 30 pages double-spaced (approximately 7500 words including abstract and literature cited), plus figures and tables. They may include original contributions to the literature or significant review articles dealing with the development and preservation of natural history collections. Contributions may include, but are not restricted to, reports of research and methodologies for the collection, preparation, conservation, storage, and documentation of specimens, and discussion of some philosophical, theoretical, and historical aspects of natural history collection management. Case studies that serve to document or augment a philosophy, methodology, or research activity will be considered, but general descriptions of a specific collection or institution are not accepted.

Manuscripts should be submitted digitally in Microsoft Word or WordPerfect, IBM format. All parts of the manuscript must be double spaced to letter (8 ½ × 11 inch; 21.6 × 27.9 cm) or A4 paper size with at least one inch (2.5 cm) margins on all sides. Each page of the manuscript should be numbered. Do not hyphenate words at the right-hand margin. Each table and figure should be on a separate page. Each table and figure should be in a separate file unless they are .doc files. The ratio of tables plus figures to text pages should generally not exceed 1:2.

On the first page indicate only the name, email address, telephone, and mailing address for the author to whom correspondence and proofs should be addressed. The second page then includes only the title of the article, names of the authors, affiliations and addresses of authors, and the abstract. Begin the text on the third page.

The preferred language for manuscripts is English, but a summary in another language can precede the literature cited, if appropriate. Manuscripts written in other languages may be considered at the discretion of the Managing Editor if the language uses the Roman alphabet, an English summary is provided, and reviewers are available for the language in question.

Abstract. An abstract summarizing in concrete terms the methods, findings, and implications discussed in the paper must accompany each article. The abstract should be completely self-explanatory and should not exceed 200 words.

Style and Abbreviations. Symbols, units, and nomenclature should conform to international usage. Cite all references in the text by the author and date, in parentheses. For example, (Deer et al. 1992, Fraser and Freihofer 1971, Mahoney 1973, Taylor 1967) would be an acceptable citation. Footnotes are not accepted in the text.

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Brokerhof, A.W., R. Morton, and H.J. Banks. 1993. Time-mortality relationships for different species and development stages of clothes moths (Lepidoptera: Tineidae), exposed to cold. Journal of Stored Products Research 29(3):277-282.

Jones, E.M. and R.D. Owen. 1987. Fluid preservation of specimens. Pp. 51-64 in *Mammal Collection Management* (H.H. Genoways, C. Jones, and O.L. Rossolimo, eds.). Texas Tech University Press, Lubbock, Texas. 219 pp.

Thomson, G. 1986. *The Museum Environment*, 2nd ed. Butterworth's, London, England. 293 pp.

For references to Internet sites, the format is:

ICOM International Committee for the Training of Personnel. 2000. ICOM Curricula Guidelines for Museum Professional Training. http://museumstudies.si.edu/ICOM-ICTOP (15 July 2002).

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Tables. Tables should not repeat data contained in the text. Each table should be numbered with Arabic numerals, include a short legend, and be referred to in the text. Column headings and descriptive matter in tables should be brief. Vertical rules should not be used. Tables should be placed, one to a page, after the references.

Figures. Figures should not repeat data contained in the text, and must be of professional quality, because they will not be redrawn by the editorial staff. They may include line drawings, graphs, or black and white photographs. Colour images will be printed as black and white. Photographs should be cropped to show only essential features. Each figure should be numbered with Arabic numerals and referred to in the text. Captions for figures should be provided on a separate page at the end of the manuscript. Magnification scale, if used, should be indicated in the figure by a scale bar, not in the caption alone. Figures must be produced at a scale that will reduce clearly to a maximum page width of five inches (12.5 cm) or 8 inches (20 cm) in landscape orientation (portrait orientation is preferred). Please consult the Allen Press specifications for digital art.

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