

Detection and Mitigation of Organic and Inorganic Pesticide Residues on Sacred Objects at the Rochester Museum & Science Center

Prepared For

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Abstract:

Wooden ceremonial masks from the Rochester Museum and Science Center's NAGPRA inventory were selected for the investigation to determine the presence of organic and inorganic based pesticide residues. As these masks are subject to repatriation, it is important that contaminants be identified that could pose a human health risk to traditional practitioners, their family and other that may come in contact with these objects on a regular basis. The masks selected were constructed on the Tonawanda Seneca Nation reserve by their members during the Indian Arts Project (IAP) under the WPA (1935-1941). Fifty IAP masks were selected by a tribal representative for this investigation project. To accomplish the objective, a non-destructive sampling technique was developed and employed. This technique utilizes surface wipe samples to obtain a qualitative sample which was analyzed by a contract environmental laboratory for arsenic, mercury and chlorinated pesticide residues.

A condition survey was performed and all fifty masks were in good condition based on several parameters. Sampling was performed on each mask and resulted in fifty low level detections for mercury with a mean of 0.281 $\mu\text{g/wipe}$. A second batch of forty-four masks and seven turtle rattles were also sampled and resulted in similar results of fifty mercury detections with a sample mean of 0.328 $\mu\text{g/wipe}$. Background surface wipe samples within the storage vault and adjacent hallway were taken and analyzed for mercury. Three of the seven background samples had low levels of mercury with a sample mean of 0.219 $\mu\text{g/wipe}$. Four of the mercury samples from the first two batches were near or above the mitigation goal of 1.0 $\mu\text{g/wipe}$. These four masks were re-sampled and showed a decrease ranging from 21 to 72%. All four were under the mitigation goal after re-sampling. Two samples from the second batch resulted in low level arsenic detections of 1.2 and 0.64 $\mu\text{g/wipe}$. Re-sampling resulted in levels below the mitigation goal of 1.0 $\mu\text{g/wipe}$. Thus, all mercury and arsenic detections were similar to background levels found in the museum's Ethnology vault or below the mitigation goal. Of the fifty-five samples analyzed for pesticides only one sample resulted in a pesticide detection. This one sample was very low level for delta-hexachlorohexane at 0.073 $\mu\text{g/wipe}$. This detection came from a non-IAP that was included in the investigation.

Introduction:

One of the objectives of this NAGPRA grant is to determine if organic or inorganic based pesticide residues are present on sacred objects (masks) that are subject to repatriation. Should contaminants be discovered, the mitigation of these contaminants is paramount. Most of the masks chosen for this contaminant screening and mitigation project were created during the Indian Arts Project (IAP) by artists on the Tonawanda Reservation, This Project was funded by the Works Project Administration (WPA) and ran from 1935-1941.

It is important to screen objects prior to repatriation so that the traditional practitioner, their family and community members are not adversely affected by potentially harmful pesticide residues¹. The care and treatment history of many objects within the collection is incomplete. Therefore, careful screening of objects prior to repatriation is important so that experience of the Seneca Nation of Indians is not repeated².

The screening process was accomplished by use of surface wipe samples and a portable X-ray fluorescence instrument (XRF). Surface wipe samples have been used in similar investigations for screening and following the progress of mitigation with success^{3,4}. Surface wipe samples were analyzed for mercury using Cold Vapor Atomic Absorption Spectroscopy (CVAAS), arsenic samples were analyzed using Atomic Absorption Spectroscopy (AAS) and chlorinated pesticides were screened using Gas Chromatography (GC) at a contract environmental testing laboratory with New York State certification. A Bruker Tracer-III was used to perform direct analysis on the surface of the objects.

Upon completion of this investigation it will be determined if arsenic, mercury or chlorinated pesticides residues are present on the masks selected from the Rochester Museum and Science Center's NAGPRA inventory. The analysis of surface wipe samples from each mask in addition to the use of XRF will determine if gross contamination is present. No written records have been found of treatments with pesticides but these records are also incomplete.

¹ Sirois, P. J., Johnson, J. S., Shugar, A., Poulin, J., Madden, O. Pesticide Contamination, Proceedings of the Preserving Aboriginal Heritage: Technical and Traditional Approaches, Symposium 2007, Canadian Conservation Institute, Ottawa, On. 2008; pp 175-186.

² Jemison, G. P. *Collection Forum* **2001**, 17(1-2), 38-40.

³ Reuben, P. A. *Collection Forum* **2006**; 20(1-2):33-41.

⁴ Reuben, P. A. *Decontaminating Sacred Objects of the Haudenosaunee*, Proceedings of the Preserving Aboriginal Heritage: Technical and Traditional Approaches, Symposium 2007, Canadian Conservation Institute, Ottawa, On. 2008; pp 195-199.

Methodology:

Surface wipe samples were collected from the wooden masks selected. The pre-moistened Palintest dust wipes were utilized in obtaining qualitative samples from the surface of each mask. One surface wipe sample from each mask was analyzed for mercury using Cold Vapor Atomic Absorption (CVAAS), a second wipe sample was analyzed for arsenic using Atomic Absorption Spectroscopy (AAS). Analysis of the wipe samples was performed by a contract environmental laboratory with New York State certification.

Each mask was sampled on the inside (side that contacts wearer's face). As two samples were required, the sample area was equal to one-half of the total surface area of the side being sampled. A line was imagined running from the centered of the forehead to the chin of each mask. This line was used to separate the mask into a left and right sides. Thus, each side was sampled over the entire area. The left side was arbitrarily assigned to be analyzed for mercury and samples from the right side were analyzed for arsenic unless otherwise noted on the chain-of-custody forms. An estimate of surface area is approximately 0.5 square feet for each sample. Each surface to be sampled was wiped once with a serpentine motion covering the entire sample area. The wipe was then folded in upon itself and the same surface was wiped again. The wipe was folded again and used to wipe the surface for a third time. Wipe samples were then placed in properly labeled glass sample jars supplied by the contract laboratory.

For masks that were sampled for chlorinated pesticides, a third wipe sample was taken from the painted side of the mask (non-contact side). Again, a Palintest pre-moistened wipe sample was used using the same procedure as before. The only deviation was that the surface area was changed to the entire side of the mask.

A portable X-ray fluorescence instrument was used to screen 18 wooden masks for presence of arsenic, mercury and lead. The Bruker Tracer-III-V (40 KeV) was used to perform an X-ray analysis of the painted side, non-painted side and hide (if present). Each analysis was one point taken on each side and one point of the horse hair hide for 60 seconds.

Results and Discussion:

Below are several tables based on the analysis of sample from masks selected in this project or X-ray fluorescence analysis performed directly on the masks. Actual levels are contained in tables in the appendix of this report.

Table 1.) Summary of results from analysis of wipe samples taken from the first batch of 50 wooden masks.

Contaminant	Number of Objects sampled	Number of detections	Detections > 1.0 µg/wipe	Reporting Limit µg/wipe
Arsenic	50	0	0	0.5
Mercury	50	50	3	0.012
Chlorinated Pesticides	47	0	0	0.050 or 0.5

Table 2.) Summary of results from analysis of wipe samples taken from the second batch of 44 wooden masks and 7 turtle rattles.

Contaminant	Number of Objects sampled	Number of detections	Detections > 1.0 µg/wipe	Reporting Limit µg/wipe
Arsenic	51	2	1	0.5
Mercury	51	50	1	0.012
Chlorinated Pesticides	1	0	0	0.050 or 0.5

Table 3.) Summary of results from the analysis of wipe samples taken from wooden masks.

Contaminant	Number of samples	Number of detections	Detections > 1.0 µg/wipe	Reporting Limit µg/wipe
Mercury	4	4	0	0.012
Pesticides	5	1	0	0.050 or 0.5

- Notes: 1.) Four masks were re-sampled from batch 1 and 2 for mercury with detections greater than 1.0 µg/wipe.
 2.) Five non-IAP masks were sampled for chlorinated organic pesticides.

Table 4.) Summary of mercury detections in the first two batches of samples compared to the background levels.

Batch	Number of detections	Max	Min	Mean
1	50	2.4	0.024	0.281
2	50	2.0	0.032	0.328
Background	3	0.44	0.037	0.219

- Notes: 1.) All detections are reported in µg/wipe sample.
 2.) Reporting limit (RL) = 0.012 µg/wipe.
 3.) Practical Quantitative Limit (PQL) = 2.0 µg/wipe.
 4.) Four detections > 1.0 µg/wipe were removed from the batch mean.

Table 5.) Results from the analysis of wipe samples for mercury detections from batches 1 and 2.

Accession #	1st sample (µg/wipe)	Retest (µg/wipe)	% decrease
40.466.25	2.4	0.67	72
35.273.33	0.9	0.71	21
35.327.17	1.2	0.93	23
35.338.20	2	0.75	63

Table 6.) Results from elemental analysis using X-ray fluorescence on masks.

Survey of Sacred Objects using portable XRF					
Element	Painted Side (outside)	Non-painted Side (inside)	Hide	Bark	Vault wall
Lead	17	3	3	0	
Zinc	13	1	12	3	X
Iron	10	1	7	3	X
Calcium	4	0	1	2	X
Bromine	0	0	3 (?)	0	
Mercury	0	0	0	0	
Arsenic	0	0	1 (?)	0	
# of Sacred Objects	18		13	3	

- Notes: 1.) One analysis was performed per side and horsehair hide.
 2.) Bruker Tracer III used for analysis for 60 seconds per analysis.
 3.) "X" denotes presence of element was detected.
 4.) All reported results indicate presence or non-detection.
 5.) "?" denotes possible presence of element.
 6.) Ethnological Vault was sampled on the east wall.

Fifty sacred masks were selected from the RMSC's NAGPRA inventory by a tribal representative from the Tonawanda Seneca Nation for organic and inorganic based pesticide screening. Inorganic based pesticides focused on the presence of arsenic or mercury. Organic pesticides included only chlorinated pesticides such as DDT and lindane. A complete list of chlorinated pesticides is in the appendix of this report. Other organic pesticides were not included as no records were found of historic purchases.

After the objects were selected, a condition survey was completed for each object. Based on parameters of the survey, it was determined that all 50 were in good condition. These objects were visually inspected for the condition of the wood, paint and other materials used in the construction of the masks. Signs of present or past insect infestations were also included in the survey. No significant structural defects or signs of past or present insect infestations were found on the objects in the survey. Several objects were observed to have did have cracks in the wood with minor separation and were noted on the condition survey form.

Upon completion and review of the condition survey the 50 sacred objects were sampled using surface wipes. The procedure followed was as previously described in the methodology section of this report. No issues were noted during the sampling process.

The surface wipe samples were analyzed at a contract laboratory with state certification for these analytes. One sample from each sacred object was analyzed for arsenic using AAS using analytical method SW8463 6010. Each object was sampled on the non-painted side that would contact the wearer's face (inside). The sample area was equal to approximately one half of the total surface area of the inside of the mask. In this batch of samples, there were no arsenic detections above the reporting limit of 0.5µg/wipe.

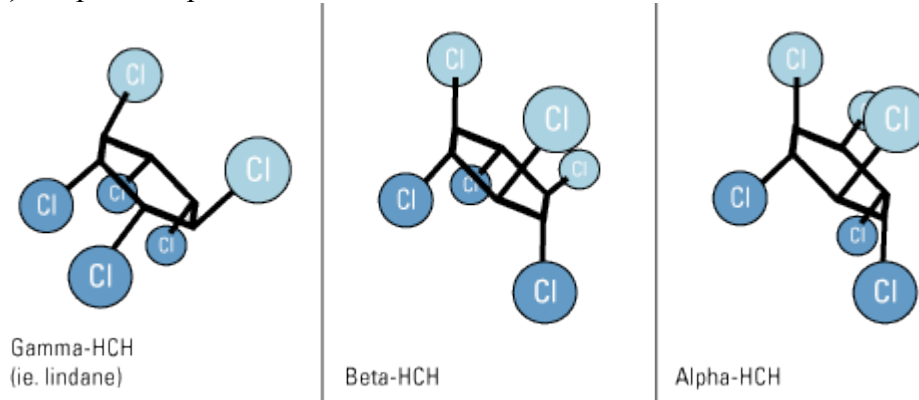
A second wipe sample from each object was taken from the non-painted inside portion of the mask. This wipe sample was analyzed for mercury by CVAAS using analytical method SW8463 7471. In this batch of 50 objects, mercury was detected in all 50 samples above the reporting limit of 0.012 µg/wipe. Three samples were near or above 1.0 µg/wipe. This threshold was used as it was established to be the mitigation goal of contaminants for this project. A mitigation goal of 1.0 µg/wipe sample was suggested by a toxicologist in a previous project with the Seneca Nation of Indians with similar sacred objects.

The third sample taken from each object was analyzed for chlorinated organic pesticides by gas chromatography (GC). The sample was taken from the painted side of the object (outside) and the sample area was equal to 100% of the surface area of the painted side. None of the 47 samples from this batch of objects had detectable levels of chlorinated organic pesticides above the reporting limit.

Based on the favorable results of this first batch of samples, it was decided to screen additional sacred objects from the RMSC's NAGPRA inventory. This batch of sacred objects consisted of 44 masks and 7 turtle rattles. The results are summarized in Table 2. For the 51 objects sampled, 2 detections for arsenic, 50 mercury detections and no chlorinated organic pesticide detections were reported by the laboratory. The single arsenic detection was marginally over the 1.0 µg/wipe threshold at 1.2µg/wipe.

The 4 mercury detections above 1.0 µg/wipe from the first two batches were re-sampled and 5 masks not associated with the Indian Arts Program were sampled for chlorinated pesticides. The results are summarized in table 3 above. Mercury was detected in all four samples at levels below the mitigation threshold of 1.0 µg/wipe. One of the five pesticide screening resulted in a positive detection for the mask identified as AE-1. The detection for the analyte listed in the laboratory report as delta-BHC. The sample value was 0.073µg/wipe and had a reporting limit of 0.050µg/wipe. Delta-BHC is the common name for the delta isomer of hexachlorocyclohexane (HCH). As seen in figure 1 below, the gamma isomer of HCH is the chlorinated organic pesticide known as Lindane. Upon review of the chromatograph and quality control parameters, it appears as this is a valid low level detection. HCH is typically a mixture of the four isomers. The ratio of these isomers was not detectable as the level was very low as further evidence of its presence.

Figure 1) Graphical representations of 3 isomers of hexachlorohexane.

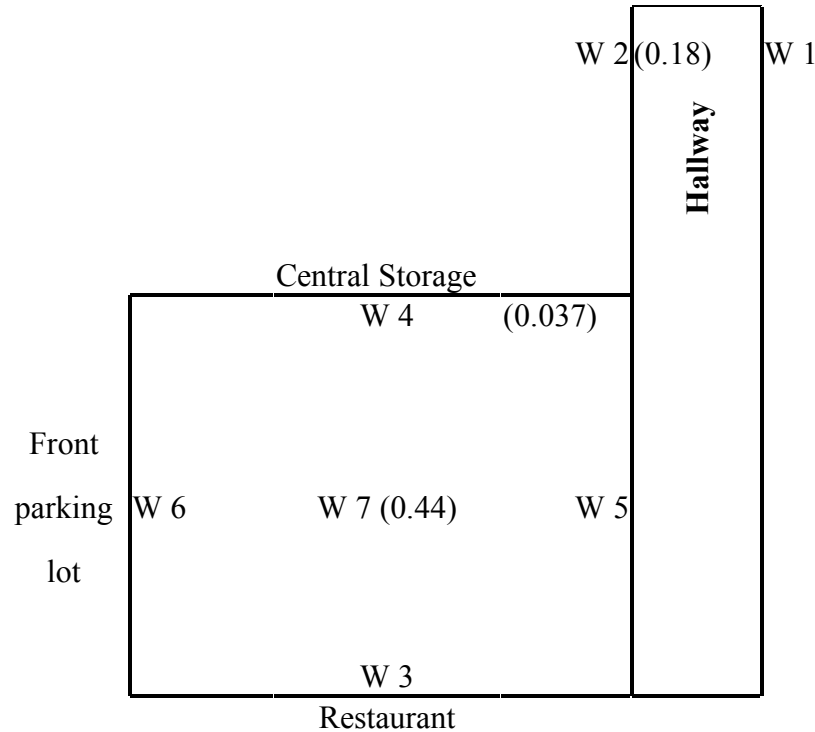


Mercury made up the majority of the contaminant detections in each batch of samples. Results from batch 1 showed 50 detections with a maximum of 2.4 $\mu\text{g/wipe}$ and minimum sample value of 0.024 $\mu\text{g/wipe}$. The second batch resulted in similar number of detection and sample values with a maximum of 2.0 $\mu\text{g/wipe}$ and a minimum sample value of 0.032 $\mu\text{g/wipe}$. The four detections above the threshold value of 1.0 $\mu\text{g/wipe}$ were removed and the mean was calculated. The corrected mean value for batch 1 was 0.281 $\mu\text{g/wipe}$ and 0.328 $\mu\text{g/wipe}$ for batch 2.

Seven background samples were taken from within the Ethnology storage vault. Mercury was detected in three of the seven samples with a reporting limit of 0.012. The sample area was approximately 0.5 square feet. This sample area was chosen to more closely compare with the sample area of the masks. The maximum value reported was 0.44 with a minimum value of 0.037 $\mu\text{g/wipe}$ and a mean of 0.219 $\mu\text{g/wipe}$. Four of the samples were reported as non-detections for mercury at a higher reporting limit of 0.020 $\mu\text{g/wipe}$. Background samples were taken from the each of the four vault walls, one from the top of the rolling shelving unit where the masks are stored and the final two were taken outside the vault down the hallway. The relative locations are illustrated in figure 2 below.

A portable X-ray fluorescence (XRF) instrument was used for the confirmation of lead based paint and signs of gross contamination associated with the preservation technique used on the horsehair attached to eighteen masks screened. Eighteen masks were selected randomly from the first two batches for this screening. High level of lead was observed on the painted side (outside) for seventeen of the eighteen masks. Three of the seventeen masks with high lead levels showed lead on the non-painted (inside). This is likely due to the transfer of lead residues from the painted side during handling. The horsehair hide was analyzed using XRF because of the difficulties in wipe sampling these surfaces. Wipe sampling would require the disassembly of the masks to obtain a representative sample.

Figure 2.) Relative locations of the background samples analyzed for mercury.



Notes: Wall samples 1-7 = W 1 -7
 Sample values are in parentheses.
 Sample W 7 is the top of the shelf where masks are stored.

A total of thirteen masks were adorned with horsehair. The method of preservation of the hide for the horsehair was suspected of containing heavy metals such as arsenic and mercury. Although the focus of the XRF screening is on the hide, hair from the hide overlapping the hide on some samples was unavoidable. Three of the masks showed high levels of lead on the hide. This may be due to the orientation of the instrument while performing the analysis in which lead may have been in the paint below the hide or the hide had traces of lead based paint. Low level of arsenic and bromine may be present on four of the hide samples. Longer duration of analysis will be needed to confirm the presence of these contaminants. No indication of gross contamination of mercury or arsenic was detected.

Recommendations:

It is recommended that each of the masks screened in this investigation be considered for repatriation. Mercury and arsenic sample values on these masks are similar to background levels or are below the mitigation goal of 1.0µg/wipe and do not appear to have been treated with inorganic based pesticides. Additional sampling is suggested for the balance of masks in this investigation not screened for chlorinated pesticides. The possible presence of bromine by XRF analysis may indicate that articles in the museum collection may have been subjected to a now historical fumigation treatment. Further investigation is suggested to determine the presence and the extent. The one pesticide detection for the isomer of lindane is also of concern to masks outside the IAP. While levels of this isomer were at trace level, it is suggested that non-IAP masks be screened for organic pesticides prior to repatriation. It is also recommended that the organic based pesticides be expanded to beyond the chlorinated in this investigation.

Conclusion:

Based on the analysis of the wipe samples, the masks in this investigation have levels of mercury comparable to the background levels found within and adjacent to the Ethnology vault. As seen in table 4, the mean for batch 1 was 0.281 and for batch 2 it was 0.328µg/wipe. These results are comparable to the mean for the background samples which had a mean equal to 0.219µg/wipe. Table 5 shows the decrease in mercury levels from the process of re-sampling. All four masks had lower levels of mercury after re-sampling. The decrease ranged from a 21% to 72% decrease, resulting in all four masks below the threshold level of 1.0 µg/wipe. One mask screened for organic pesticides resulted in the detection of an isomer of lindane, delta-BHC. This mask was a non-IAP mask was very low level marginally above the reporting limit. The two low level arsenic detections will also require further investigation to determine if they are also comparable to the background levels found in the museum.

Overall it is important to stress that all levels are very low levels but it is recommended that screening continue for organic and inorganic based pesticides. The masks from the Indian Arts Project are a unique collection in how it has been managed over years. The history of masks outside of the IAP project is not complete. It is the recommendation that each mask considered for repatriation be screened individually.

Appendix:

Table 7.) Results of the analysis of wipe samples taken from the first batch of 50 sacred objects.

Accession	Mercury	Arsenic	Pesticide
35.273.1	0.18	ND	
35.273.33	0.9	ND	x
35.273.44	0.42	ND	x
35.327.17	1.2	ND	x
35.338.14	0.23	ND	x
35.338.15	0.57	ND	x
35.338.21	0.85	ND	x
35.338.23	0.18	ND	x
36.379.14	0.24	ND	x
36.379.19	0.43	ND	x
36.379.6	0.21	ND	x
36.390.8	0.27	ND	x
36.409.6	0.24	ND	x
37.496.10	0.12	ND	x
37.496.2	0.63	ND	x
37.496.3	0.13	ND	x
37.505.1	0.086	ND	x
38.373.2	0.12	ND	x
38.373.7	0.14	ND	x
38.374.9	0.1	ND	x
38.383.29	0.23	ND	x
38.383.6	0.17	ND	x
38.385.26	0.71	ND	x
38.385.3	0.24	ND	x
38.392.10	0.63	ND	x
39.374.1	0.33	ND	x
39.374.8	0.23	ND	x
39.374.9	0.42	ND	x
39.375.3	0.14	ND	x
39.375.4	0.12	ND	x
39.376.14	0.22	ND	x
39.376.15	0.3	ND	x
39.376.18	0.39	ND	x

- Notes: 1.) All values in table are in $\mu\text{g/wipe}$.
 2.) "x" denotes the non-detection of chlorinated pesticides in table 11.
 3.) ND denotes non-detection with a reporting limit of $0.5\mu\text{g/wipe}$.

Table 7.) continued.

Accession	Mercury	Arsenic	Pesticide
39.376.19	0.22	ND	
39.376.21	0.64	ND	x
39.376.24	0.23	ND	x
39.376.27	0.17	ND	x
39.378.2	0.23	ND	x
39.389.1	0.14	ND	x
39.389.37	0.3	ND	
40.465.7	0.32	ND	x
40.466.1	0.48	ND	x
40.466.12	0.38	ND	x
40.466.22	0.19	ND	x
40.466.25	2.4	ND	x
40.466.27	0.12	ND	x
40.466.8	0.4	ND	x
40.483.7	0.18	ND	x
41.256.5	0.024	ND	x
41.256.7	0.07	ND	x

Table 8.) Results of the analysis of wipe samples taken from the second batch of 50 sacred objects.

Accession	Mercury	Arsenic	Pesticide
32.268.5	ND (RL=0.02)	ND	
35.268.10	0.036	ND	
35.268.34	0.052	ND	
35.271.11	0.09	ND	
35.271.23	0.12	ND	
35.271.30	0.032	ND	
35.271.5	0.044	ND	
35.273.23	0.23	ND	
35.273.31	0.069	ND	x
35.273.32	0.069	ND	
35.273.35	0.2	ND	
35.3.7.53	0.57	ND	
35.307.55	0.26	ND	
35.338.13	0.21	ND	
35.338.20	2.0	ND	
36.271.24	0.13	ND	
36.376.17	0.13	ND	
36.378.12	0.31	1.2	

- Notes: 1.) All values in table are in µg/wipe.
 2.) "x" denotes the non-detection of chlorinated pesticides in table 11.
 3.) ND denotes non-detection with a reporting limit of 0.5µg/wipe.
 4.) Yellow and Blue highlights denotes values above 1.0µg/wipe.

Table 8.) continued.

Accession	Mercury	Arsenic	Pesticide
36.409.13	0.24	ND	
37.307.51	0.21	ND	
37.508.52	0.33	ND	
38.373.10	0.098	ND	
38.373.6	0.81	ND	
38.374.7	0.82	ND	
38.376.2	0.35	ND	
38.377.11	0.18	ND	
38.383.3	0.083	ND	
38.383.5	0.26	ND	
38.392.12	0.95	ND	
39.374.13	0.41	ND	
39.374.2	0.21	ND	
39.374.7	0.43	ND	
39.376.12	0.64	ND	
39.376.2	0.63	ND	
39.376.23	0.64	ND	
39.376.25	0.49	0.64	
39.376.26	0.47	ND	
39.376.4	0.56	ND	
39.378.2	0.29	ND	
40.465.4	0.24	ND	
40.466.19	0.48	ND	
40.466.2	0.29	ND	
40.466.20	0.34	ND	
40.466.23	0.46	ND	
40.466.3	0.7	ND	
40.466.4	0.87	ND	
40.466.6	0.58	ND	
40.466.9	0.25	ND	
71.16.3	0.11	ND	
71.16.4	0.037	ND	
AE1332	0.06	ND	

Table 9.) Table of results from analysis of wipe sample to determine background mercury levels within the Ethnology storage vault and adjacent hallway.

Sample name	Mercury	Reporting limit	Sample Location
W1	ND	0.020	wall opposite botanicals
W2	0.18	0.012	botanical case
W3	ND	0.020	restaurant side wall of ethno vault
W4	0.037	0.012	wall on central storage side of vault
W5	ND	0.020	wall on hall side of ethno vault
W6	ND	0.020	wall on front parking lot side
W7	0.44	0.012	top of shelf above masks, center of room

Notes: 1.) All values in table are in µg/wipe.
 2.) ND denotes non-detection, actual values less than reporting limit.

Table 10.) Table of results for the analysis of wipe samples taken from non-Indian Arts Project masks sampled for chlorinated pesticide residues.

Accession	Pesticide	Reporting limit
AE 383	X	
AE 2871	X	
AE 1	0.073	0.050
AE 1689	X	
39.376.19	X	

Notes: 1.) All values in table are in µg/wipe.
 2.) "X" denotes the non-detection of chlorinated pesticides in table 11.

Table 11.) List of chlorinated pesticides included in the pesticide screen.

Pesticide list
Aldrin
alpha-BHC
beta-BHC
gamma-BHC (lindane)
delta-BHC
Chlordane
4,4'-DDD
4,4'-DDE
4,4'-DDT
Dieldrin
Endosulfan I
Endosulfan II
Endosulfan Sulfate
Endrin
Endrin Ketone
Endrin Aldehyde
Heptachlor
Heptachlor epoxide
Methoxychlor
Toxaphene