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# Pesticide Mitigation in Museum Collections: Science in Conservation

Proceedings from the MCI Workshop Series

*Edited by  
A. Elena Charola and  
Robert J. Koestler*

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## ABSTRACT

Charola, A. Elena, and Robert J. Koestler, editors. *Pesticide Mitigation in Museum Collections: Science in Conservation. Proceedings from the MCI Workshop Series*. Smithsonian Contributions to Museum Conservation, number 1, vi + 72 pages, 51 figures, 15 tables, 2010. — The Smithsonian Museum Conservation Institute Workshop on Pesticide Mitigation was one of the first professional meetings dedicated to current research on removing pesticide residues from museum objects. Seven papers were presented at the workshop, and two more were added to introduce topics not focused on during the meeting but of significant importance when considering actual application of any of these methods.

The aim of the workshop was to bring together conservators, scientists, and even industry representatives to discuss the complex issues associated with pesticide removal from artifacts and to provide representative examples of the research and work being carried out at different institutions in the United States and abroad. Among the issues explored were possible methods and techniques that might become useful in the museum conservation field to reduce, mitigate, clean, or remediate undesirable pesticides on objects. The meeting also served to inform conservators and scientists in the Smithsonian Institution of the wide range of approaches that are currently being tested and that might prove useful in the future.

Topics covered in the presented papers included removal of mercury and arsenic contamination with  $\alpha$ -lipoic acid; the treatment of Haudenosaunee medicine masks with surface active displacement solutions; the possibility of using mercury-resistant bacterial communities to remediate contamination; solvent extraction through the use of special solvents such as hydrofluoroethers; carbon dioxide as a cleaning fluid either in liquid or in supercritical state; and novel cleaning techniques either through the use of additives to improve the efficiency of liquid or supercritical CO<sub>2</sub> cleaning, other gases in a supercritical state, or other techniques such as fluidized beds. The introduction of novel techniques at the workshop was encouraged in order to broaden the range of promising methods that might improve the technology of pesticide mitigation or remediation. The two supplemental papers discuss pesticide analysis on objects and safety measures that should be implemented by institutions with contaminated collections.

Cover images, from left to right: Figures 11, 2, and 9 (detail) by Tello and Unger.

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# Introduction

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The conservation of objects of cultural, historic, and artistic value is an interdisciplinary endeavor that draws from many fields—from the pure to the applied sciences, from the history of classical art to folk traditions, and from industry to arts and crafts. Problem solving in this field is complex. An example is the past use of pesticides for the protection of natural history and ethnographic objects. This action was well intentioned; however, at the time no one knew the extent of the health hazard that was being created for anyone who would have to handle these objects in the future. With today's increased knowledge about health risks, it is evident that we must “undo” previous conservation interventions. The challenge is to figure out how.

It is a difficult challenge, as complex as the objects that have been treated in the past and as vast as the list of chemicals that have been used and, in some cases, are still being used. The complexity is compounded by the variable retention rates of different materials for specific chemicals and by the fact that documentation is rarely sufficient to determine exactly how an object was treated. Questions abound: Can we determine the amount of pesticide(s) present on any given object? What is the risk for those who have to handle the object? Are there cultural sensibilities that must be considered regarding the object or the removal of the pesticide present from that object? What methods can be used to mitigate this risk? And, as we “undo” yesterday's problems, are we perhaps inadvertently creating new problems for tomorrow's museumgoers and personnel?

These were some of the considerations that prompted the Pesticide Mitigation in Museum Collections Workshop held at the Smithsonian Institution's Museum Conservation Institute on 23–24 April 2007. The papers in this volume resulted from the workshop. During the mornings of those two days, seven presentations were made, with the afternoons devoted to discussion of each day's presentations. A final discussion panel served to close the workshop.

It was the aim of the workshop to provide representative examples of the research and work being conducted at different institutions in the United States and abroad. The objective was to alert conservators and scientists in the Smithsonian Institution of the wide range of approaches that are currently being tested and that might prove useful in the future. As pointed out by Hollinger and

Hansen (this volume, p. 69), “it is unlikely that there will ever be a single method for cleaning all types of objects or materials.” Therefore, understanding the potential and the problems presented by each method will allow further development of the most promising application(s) on such sensitive materials as those found in ethnographic and natural history collections. This is the long-term objective of the workshop and the reason for this publication.

Workshop presenters were asked to submit papers reviewing the information given during their presentations; these papers constitute the bulk of those included herein. Two supplemental papers are included: (1) an introduction to the problems presented by the analysis of pesticides on objects by Odile Madden, Jessica Johnson, and Jae Anderson, and (2) a summary of the conclusions that resulted from the workshop by R. Eric Hollinger and Greta Hansen. These two overviews provide valuable perspectives on the state of the art of pesticide mitigation in museum collections.

The workshop succeeded in defining topics that need to be addressed to improve mitigation and remediation of pesticide-contaminated collections. While no endorsements for the application of any one technique were made, as much more testing needs to be performed, the workshop was a good forum for discussing advantages and disadvantages of different approaches. Bringing all this

information together and presenting it to members of the conservation field in one volume should help stimulate progress. We hope that further research will result from this workshop and that promising methodologies will be developed to safely and appropriately mitigate or remediate pesticides on museum objects.

#### ACKNOWLEDGMENTS

This publication would not have been possible without the enthusiasm and support provided by Dr. Paula T. DePriest. Many others contributed to this work also, and among them we thank, in particular, Jeff Speakman, Ann N’Gadi, Mary Ballard, and Carol Grissom from the Museum Conservation Institute (MCI), and Ginger Strader from the Smithsonian Institution Scholarly Press. Last, but not least, Beverley Smith, Francine Lewis, and Vernetta Williams from the MCI are thanked for their behind-the-scenes assistance.

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# Pesticide Remediation in Context: Toward Standardization of Detection and Risk Assessment

*Odile Madden, Jessica Johnson, and  
Jae R. Anderson*

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**ABSTRACT.** The Smithsonian Museum Conservation Institute workshop on pesticide mitigation is likely the first professional meeting dedicated entirely to current research efforts to remove pesticide residues from museum objects. However, the question of remediation is but one part of a broader field of research into pesticide residues on cultural property. Challenges of consultation and collaboration, identification and detection, risk assessment, and mitigation with regard to residues are inextricably related, and responsible and comprehensive solutions are being researched simultaneously around the world in response to these challenges. This paper attempts to contextualize the topic of remediation within the field of analytical research into pesticide residues on museum objects.

**KEYWORDS:** pesticide residues, arsenic, mercury, lead, detection, analysis, remediation, mitigation, cleaning, removal, risk assessment, museum objects.

## INTRODUCTION

When discussing the removal of pesticide residues from museum objects, often the instinctive assumption is that the pesticides present are known and that their concentrations present a hazard to human health. In fact, this is not so. Detection and quantification of pesticide residues is an ongoing topic of research, and deciding what levels of contamination present a human health risk remains under discussion. Remediation is but one part of a broader field of research into pesticide residues on cultural property. Challenges of consultation and collaboration, identification and detection, risk assessment, and mitigation are inextricably related, and responsible and comprehensive solutions are being researched simultaneously around the world in response to these challenges.

The Museum Conservation Institute (MCI) workshop on pesticide mitigation provided a forum for sharing novel methods to reduce pesticide concentrations on artifacts. As such, the tone of the presentations was more technical than cultural and focused on remediation experiments rather than detection methods or risk characterization. Group discussions between the presentations, which are not recorded in this volume, highlighted some gaps in consensus about the appropriateness of treatments and standards for detection. They also articulated

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*Paper presented at the Pesticide Mitigation in Museum Collections Workshop held at the Smithsonian's Museum Conservation Institute in April 2007 exploring possible methods and techniques that may become useful for the museum conservation field to reduce, mitigate, clean, or remediate undesirable pesticides on objects.*

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the need to consider any remediation effort within the context of mitigating risk to human health and the environment.

## BACKGROUND

In the past, museum artifacts have been treated with a range of pesticides to eradicate and prevent infestation by insects, rodents, and mold. Because many of these chemicals are hazardous to human health, it is incumbent on museums to identify those potentially hazardous items in collections and determine whether the risk posed is significant. The National Museum of Natural History (NMNH) was among the first museums in the United States to research and publish the history of pesticide use in its collections (Hawks and Williams, 1986). The results, published in “A History of Pest Control Measures in the Anthropology Collections, National Museum of Natural History, Smithsonian Institution” sounded a wake-up call to museums across the country (Goldberg, 1996). Though concern over the health risks associated with poisons used in museums has long been present, only recently did the issue of pesticide residues on cultural material and natural history specimens become a hot topic of discussion in conservation. Solutions to this problem are being sought by many museums as well as tribal groups.

A major impetus for the current wave of pesticide research in the United States is the National Museum of the American Indian Act of 1989 and the Native American Graves Protection and Repatriation Act (NAGPRA) of 1990.<sup>1</sup> According to these, museums that receive funds from the U.S. government are required to return certain Native American artifacts and human remains to the tribe of origin and inform the recipients of any known treatments that have been applied. The need to comply with this legislation, concern over potential liability, and ethical considerations have spurred research programs focused on pesticide detection and quantification as well as management of the potential health risks (Nason, 2001; Tsosie, 2001; Johnson and Henry, 2002). Concurrently, the importance of evaluating these same issues for the protection of museum workers and visitors was also recognized (Makos, 2001; Odegaard and Sadongei, 2005).

The bulk of early research focused on formulating the problem and identifying those groups with a stake in the issue. Seminal meetings were held at the Arizona State Museum in 2000, San Francisco State University in 2000, and Shepherdstown, West Virginia, in 2001. As is evident from the lists of participants in those meetings, it is now

common practice in North American museums to address pesticide questions collaboratively, with conservators, scientists, health and safety professionals, and, in the case of ethnographic collections, consultants from indigenous communities. All of them contributed expertise on this topic and brought to the table diverse priorities (Johnson and Henry, 2002), which were reflected in two issues of *Collection Forum* in 2001. Particularly for Native American material, the cultural appropriateness of testing and treatment protocols is an overriding concern, predominantly for those objects that are considered to possess a life force of their own (Sadongei, 2001; Johnson and Henry, 2002). Stakeholders now meet regularly in conferences and smaller meetings to discuss cultural ramifications as well as advances in detection and quantification of residues, risk assessment, and mitigation strategies. Some of these meetings have broad scopes, such as educational outreach to indigenous communities and conservation professionals, while others focus more narrowly on specific issues such as X-ray fluorescence spectrometry (XRF) or computerized options for health risk assessment.

## MITIGATION, REMEDIATION, AND RISK ASSESSMENT

What exactly is meant by “pesticide mitigation”? The term mitigation generally is used to describe the reduction of the risk posed by a pesticide. The risk may be to human health, the health of another species, or the environment. Mitigation can be accomplished in several ways. The pesticide can be removed from an object, which is known as remediation, or the potential for exposure can be reduced, for example by modifying the way artifacts are handled or by the use of protective clothing (Odegaard, 2001). The papers presented at MCI’s workshop on pesticide mitigation were studies in remediation. Each presentation discussed an experimental treatment designed to remove one or more pesticides from an artifact material. Most of the work was performed on experimental samples, though Reuben’s work was carried out directly on repatriated Haudenosaunee medicine masks (Reuben, this volume). As the treatments are still experimental, they might be termed more appropriately as studies in potential remediation treatments rather than mitigation. The ultimate goal of remediation experiments and of the wider field of mitigation is to reduce the risk posed by the pesticide(s).

The risk posed by a toxic substance can be described by the following equation:

$$\text{Hazard} \times \text{Exposure} = \text{Risk.}$$

The hazard is the pesticide. What is it? How much is on the artifact? How labile or mobile is it? Museums and tribal groups continue to invest heavily in sophisticated methods to answer these questions.

Exposure is more complicated to assess. One aspect has to do with the way in which pesticides are transferred from object to person or environment. How does the person interact with the contaminated artifact? What is the route of entry (ingestion, skin contact, or inhalation)? At what rate is the pesticide transferred to a person or the environment? How long will he or she be exposed and how frequently? These questions are complicated given the wide range of artifact types and ways in which museum staff, visitors, and people outside the museum interact with them.

Specific details about the person who handles the artifact are also a factor. For example, is it a 40-year-old man or a pregnant woman in her twenties? The toxicological profiles of these two populations can be very different (C. Chaisson, The LifeLine Group, personal communication).

All of these factors should be taken into consideration when assessing the risk posed by a contaminated artifact. The matrix of potential hazards, types of exposure, and diverse populations is extremely complex.

Different research groups approach risk assessment in a range of ways. Working with Health Canada, the Canadian Conservation Institute has developed a red-yellow-green warning system that correlates concentration ranges for inorganic and organic pesticides with high, moderate and low toxicity (J. Sirois, unpublished). The Arizona State Museum has collaborated with medical toxicologists at the Arizona Poison and Drug Information Center to determine total potential dose per object ranges that constitute high, moderate, and low risk (also using a red-yellow-green warning system) as well as to draft toxicological assessments of individual artifacts (Odegaard et al., 2005, 2006). More recently, the Smithsonian Institution's MCI, NMAI, and NMNH and the Canadian Conservation Institute have been exploring the potential of computer modeled risk assessment in conjunction with the U.S. Environmental Protection Agency (EPA) and The LifeLine Group, a nonprofit organization that specializes in software tools for unique public health issues related to exposure assessment and risk. For all institutions, the ultimate goal is a risk management solution that distinguishes between hazardous situations and those of little or no consequence.

It follows that to mitigate risk one can reduce or remove the hazard or lower one's exposure to that hazard. The remediation studies presented in this volume address the hazard term of the equation.

## **DETECTION AND QUANTIFICATION OF RESIDUES**

Each remediation study included in this volume employs an analytical method to identify and quantify pesticide residues. X-ray fluorescence spectrometers were used to measure arsenic and mercury at parts per million concentration directly on samples (Cross et al., this volume; Roane and Snelling, this volume). More sensitive atomic absorption methods were used on both wipes (Reuben, this volume) and digested samples (Roane and Snelling, this volume), presumably with a limit of detection on the order of parts per billion. Zimmt and Odegaard took a different approach by using a toxicological screening of rat lung epithelial cells to detect Diazinon residues (Zimmt et al., this volume). Whether analysis of artifacts or preparations of experimental samples in the laboratory are discussed, an agreed method to accurately identify and measure the amount of pesticide present is required.

The importance of detection is obvious. Although it may be known through personal recollection or archival research that a collection was treated with a pesticide, the full pesticide treatment history of specific objects is rarely known. Certain analytical methods, such as XRF spectrometry, serve to identify the presence of heavy metals on objects and their contamination levels. Detection is equally important in the laboratory when testing remediation treatments. In order to judge the degree of pesticide removal, the amount present before and after treatment must be measured.

What analytical detection methods cannot do is determine whether the contamination detected poses a human health risk. This assessment requires knowledge of the contaminant, its toxicological profile, and human judgment.

The MCI workshop on pesticide mitigation revealed two things. First, there is no standard methodology for measuring pesticide residues on artifacts or on samples prepared in the laboratory. Every study approached this problem differently, and though each showed a reduction in the amount of pesticide present after treatment, it is difficult to compare results between studies. Second, there was no consensus as to what degree of removal is sufficient or ideal. Most of the studies reported results as the amount of pesticide removed with no discussion of an appropriate

endpoint or goal. The exception was the Zimmt study that evaluated the degree of removal of the pesticide Diazinon using a biological toxicity screen of living rat lung epithelial cells (Zimmt et al., this volume). The target level of cleaning was reached when fewer than 50% of the cultured cells died from exposure to the treated samples. Toxicity bioassay tests are unique in that they indicate directly whether a substance is present in sufficient quantity to be toxic to living things. This type of testing removes the need to identify a specific pesticide (any toxic substance is measured) and avoids the risk that an instrument may not be sufficiently sensitive to detect toxins at threshold levels.

Though relative terms like percent removal demonstrate whether cleaning was efficient, they do not address the fundamental question: Is an object safe to handle? It became clear during the informal discussions at the workshop that we need to come to some consensus about target levels of pesticide residues on treated artifacts. This does not mean that we necessarily would assert that an artifact is “safe” when these levels are reached. For example, an appropriate target concentration might be tied to some accepted threshold value such as the No-Observed-Adverse-Effect level or a reference value for a given pesticide.<sup>2</sup> Nevertheless, it would provide researchers involved in remediation with a goal, so that treated artifacts are not reported unwittingly to be nontoxic and, at the other end of the spectrum, so that we do not put artifacts at risk (and waste our time and effort) in “cleaning” beyond the accepted reference levels. This is not an easy topic to reach a consensus on as there are many factors to consider, but it is an issue that needs to be addressed in the coming years.

## CHOICE OF APPROPRIATE ANALYTICAL METHODS

It is not the goal here to assert which analytical methods are most appropriate but rather to highlight some of the factors to be considered when choosing an analytical framework for pesticide analysis in the museum context. The question of which detection method is to be used depends on several factors. The first is the anticipated contaminant of interest. More than 90 different pesticide formulations are known to have been applied to museum artifacts (Pool et al., 2005), and no single technique can identify all of them.

The next distinction is the detection limit of the technique. We need to aim for methods that are appropriate to our problem. Namely, the technique should detect the highest amount of a contaminant that would not cause any

adverse health effect. For example, the fact that an instrument has a lower detection limit of 1 ppm does not mean that concentrations below 1 ppm are safe or that concentrations above 1 ppm are hazardous. At the same time, we do not need to go overboard by using the most sensitive technique available if the lowest detectable amount would not be expected to have any adverse health (or environmental) effect. In general, lower detection limits and higher precision often translate into larger price tags for analysis and usually require far longer sample preparation time.

The analytical constraints for experimentally prepared samples differ from those for actual artifacts. Experimental samples are prepared under controlled conditions such that the composition of the substrate and all applied treatments are known (and limited). It is likely that the sample can be analyzed destructively, and, for that reason, it can be analyzed directly and completely.

This is not the case for cultural artifacts. The exact composition and history of artifacts are rarely known. Artifacts are often assembled from diverse materials and may have been treated with pesticides (and other substances) an unknown number of times throughout their histories. These treatments are seldom documented. Analytical techniques for artifact analysis must be minimally destructive or nondestructive. Typically, the techniques used analyze discrete spots on the artifact (or small samples removed from the artifact) rather than the entire object. Consequently, data quality relies on testing multiple spots in order to obtain a statistically valid result. The tests should be relatively straightforward for conservators or trained and experienced technicians to execute. Finally, techniques using portable equipment have the added potential for on-site analysis and the ability to survey multiple artifacts in a relatively short amount of time.

Each technique has its own set of variables. It is imperative that researchers publish detailed, acceptable parameters so that everyone can use them. The Smithsonian Institution is making strides in this direction with respect to handheld XRF spectrometry. Researchers at NMAI, MCI, and NMNH spent 2006 and 2007 examining the variables of this analytical technique, figuring out how each variable influenced data accuracy and analytical precision, and setting up protocols that controlled for each variable as much as possible. The ultimate goal has been to standardize XRF testing protocols for pesticides across the Smithsonian Institution and make these protocols available to interested outside groups (O. Madden and J. Anderson, unpublished). It has become clear that standardization methodology depends on constraints of the analytical technique, calibration of data to standards of

known composition, and the steps by which the technique is carried out.

The factors that affect XRF data can be divided into three categories: instrumental factors, working practice, and statistical considerations. Some of these factors can be standardized in order to make XRF data more consistent across time, users, and instruments. Examples of instrumental factors include the voltage and current of the X-ray tube, duration of the measurement, and the selection of appropriate primary and secondary filters. Instrumental performance can be regulated to some extent by calibrating the instrument to standards of known composition that resemble artifact materials in terms of density, elemental composition, and thickness. For example, calibration standards for arsenic in an organic matrix that mimics cellulosic materials were prepared in collaboration with the National Institute for Standards and Technology.

Guidelines for working practices also have been proposed to limit data variability that results from multiple XRF operators. These guidelines include recommendations for setting a consistent working distance between instrument and artifact, eliminating background signal, holding the instrument still, and avoiding contamination of the instrument head. A computerized database was developed to facilitate analysis and improve the quality and statistical accuracy of data collected.

Finally, as XRF analyzes discrete spots on an artifact, statistical factors ought to be taken into consideration. All objects analyzed for pesticide residues must undergo a given number of analyses. The number of analyses is chosen to be representative of the object as a whole and be consistent with the time constraints of a typical workday. However, because artifacts often are composed of multiple materials that may have different concentrations of pesticides, artifacts are divided conceptually into one or more “zones.” A zone might be a material type such as wood, bone, or red paint. It might also be a part of the object that presents more of a handling or contact risk, such as the mouthpiece of a musical instrument and interior of a mask. For each zone within an artifact, a preset minimum number of analyses is defined. Therefore, the averaged XRF data for the artifact are presented by zone as well as for the artifact as a whole.

## **TOWARD STANDARD ANALYTICAL METHODS**

For reasons discussed above, pesticide concentration data must be accurate, reliable, and reproducible to be

useful. The numbers from one research group or museum must be consistent with those from another group if we are ever going to arrive at a universal framework for assessing the risk posed by pesticide residues on artifacts. Without consistent data, one remediation study cannot be compared to data from other studies or peer-reviewed effectively. We might benefit from the EPA Office of Pesticide Programs’ approach to this problem. Under the Food Quality Protection Act of 1996, “All pesticides distributed and sold in the United States must be registered by EPA, based on scientific data showing that they will not cause unreasonable risks to human health, workers, or the environment . . .”<sup>3</sup> Any company that distributes or sells pesticide products in the United States must provide a detailed analytical method for detecting and quantifying that pesticide in target commodities. For example, a company that sells a pesticide for spray application onto cabbage crops must provide a written analytical method to the EPA that details how the company measures the amount of pesticide in cabbages that have been sprayed with this product. These analytical methods are listed with the EPA as part of its Residual Analytical Methods program. The premise of the program is that “reliable residual analytical methods are necessary to measure the magnitude of a residue in a commodity . . .” (U.S. EPA, 2007). This situation can be compared to that of pesticides on artifacts.

In cases where experimentally prepared samples are required, it also may be beneficial to use standard substrate materials, such as those used at the Arizona State Museum for remediation tests (Reuben, this volume) and instrument calibration studies (J. Anderson, unpublished). By standardizing these points and making them available to colleagues in the field, uniform methods for detecting and quantifying pesticides can be achieved. The measured pesticide levels on artifacts will then be comparable between institutions allowing peer review of remediation studies and the ultimate goal of developing improved remediation treatments attained.

The MCI workshop on pesticide mitigation highlighted several experimental methods for pesticide removal that show promise in pesticide remediation of museum collections and repatriated objects. These remediation experiments are part of a larger body of pesticide research and should be viewed within that context. The workshop made clear some deficiencies in the current state of pesticide mitigation research. For example, in order to compare remediation strategies, standard methodologies for detection and quantification of residues are needed. Of prime importance is the definition of the target levels that treated objects should attain so as not to pose hazards to people

handling them. This could be accomplished by working with the Environmental Protection Agency, medical toxicologists, and risk assessment professionals to establish a set of risk thresholds or by linking pesticide target levels to a toxicological marker, like rat epithelial cells. It is important to remember that the aim of pesticide mitigation treatments is to make contaminated objects less hazardous to human health.

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#### NOTES

<sup>1</sup> NMAI Act of 1989 (Public Law 101-185) and NMAI Act Amendment of 1996 (Public Law 104-278).

<sup>2</sup> The EPA defines NOAEL as “The highest exposure level at which there are no biologically significant increases in the frequency or severity of adverse effect between the exposed population and its appropriate control; some effects may be produced at this level, but they are not considered adverse or precursors of adverse effects.” The reference value, an estimate of exposure that would not cause deleterious effects during one’s lifetime, may be many times lower than the NOAEL (<http://www.epa.gov/iris/gloss8.htm>, accessed 20 September 2007).

<sup>3</sup> P.L. 104-170, formerly known as H.R. 1627.

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# Aqueous $\alpha$ -Lipoic Acid Solutions for Removal of Arsenic and Mercury from Materials Used for Museum Artifacts

*Peggi S. Cross, Nancy Odegaard, and Mark R. Riley*

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**ABSTRACT.** The viability of  $\alpha$ -lipoic acid to act as a chelating agent in the removal of arsenic- and mercury-based pesticides from artifacts and museum surfaces was examined. High concentrations (50–1000+  $\mu\text{g}/\text{cm}^2$ ) of arsenic and mercury were removed from test materials such as Whatman No.1 filter paper, untreated cotton, wool, and feathers. Alpha-lipoic acid was chosen because it is a natural chemical that is ubiquitous in mammals and plants and that is deemed environmentally benign. These attributes make  $\alpha$ -lipoic acid attractive for use in removing toxic elements from sacred objects. Culturally, these objects may be considered to house sacred living beings that must be treated with the same level of care as a human being. This also applies for the safety of persons performing the treatment.

**KEYWORDS:** alpha-lipoic acid, arsenic, mercury, pesticide removal, museum objects, cleaning.

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*Paper presented at the Pesticide Mitigation in Museum Collections Workshop held at the Smithsonian's Museum Conservation Institute in April 2007 exploring possible methods and techniques that may become useful for the museum conservation field to reduce, mitigate, clean, or remediate undesirable pesticides on objects.*

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## INTRODUCTION

Lipoic acid has been shown to be effective as an agent to prevent morbidity from arsenic and mercury poisoning (Grunert, 1960). The chemical contains a carboxyl group on one end and a five-member disulfide ring that can be reduced by homolytic scission using ultraviolet light as shown in Figure 1.

Arsenic and mercury in the form of sodium arsenite, arsenous acid, and mercuric chloride were among the many pesticides that museums used. The study focused on arsenic and mercury salts for several reasons:

- They are highly persistent and toxic.
- Arsenic-based chemicals are carcinogens.
- Mercury-based chemicals are neurotoxins.
- The contamination of collections has been validated.

The level of arsenic and mercury contamination on various materials found in museum collections varies, particularly because some materials may contain these elements inherently. Table 1 presents a list of the most used materials in

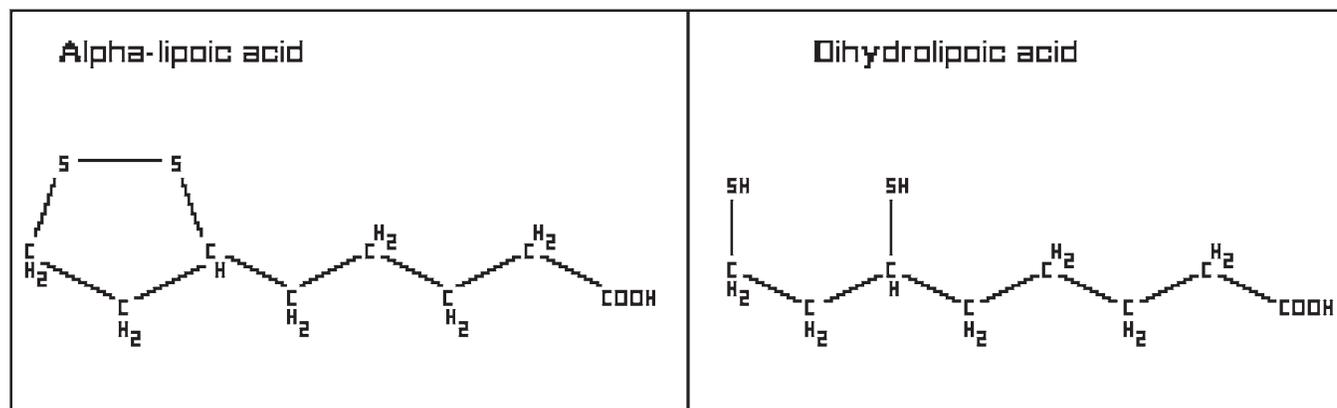


FIGURE 1. The structure of lipoic acid and reduced lipoic acid (dihydrolipoic acid).

ethnographic artifacts and their range of concentrations of arsenic and mercury.

Previous research on removal of arsenic and mercury has been limited. For example, compressed air cleaning removed 40% of arsenic residues from objects (Glastrup, 2001); soap and water washing and vacuuming techniques were used by Seneca tribal members to reduce unspecified amounts of arsenic on masks (Jemison, 2001); and vacuuming techniques were unsuccessfully used by Arizona State Museum researchers to remove arsenic from feathers (Odegaard et al., 2003).

TABLE 1. Summary of the inherent levels of arsenic and mercury found in natural materials used to make artifacts.

Material	Average level of As (ppm)	Average level of Hg (ppm)
Hair (human) <sup>a</sup>	0.04–1.04	<0.06–6.1
Hair or fur (animals) <sup>b</sup>	20 or less	20 or less
Skin <sup>c</sup>	3.5 or less	No data
Feathers <sup>d</sup>	0.05–9.16	0.01–22.3
Wood and other plant objects <sup>e</sup>	<1.0	<0.5
Soils <sup>f</sup>	0.2–40	0.01–20

<sup>a</sup> Gibson and Gage, 1982; Foo et al., 1988; Oskarsson et al., 1994; Saad and Hasani, 2001; Pesch et al., 2002; Ali and Tarafdar, 2003.

<sup>b</sup> Cumbie, 1975; Sheffy and St. Amat, 1982; Stevens et al., 1997; Evans et al., 1998; Ben-David et al., 2001; Kocar et al., 2004; Duffy et al., 2005.

<sup>c</sup> Kocar et al., 2004.

<sup>d</sup> Burger and Gochfeld, 1997; Monteiro et al., 1998; Becker et al., 2002; Veerle et al., 2004; Palma et al., 2005.

<sup>e</sup> Shacklette and Connor, 1973.

<sup>f</sup> Cadigan, 1971; Shacklette and Connor, 1973; Carey et al., 1980; Tack et al., 1997.

The sorption mechanism of arsenic and mercury salts to materials involves weak forces that can be overcome in part by immersion in distilled water and more efficiently in aqueous reduced lipoic acid solution. Both arsenic (III) and mercury will bind to the sulfur or sulfhydryl moieties of reduced lipoic acid at a kinetic rate that allows minimal exposure of the chemical to the materials being treated. The reduced lipoic acid will not leave residues on the treated materials or alter them in any way.

## METHODS

Alpha-lipoic acid (Sigma Aldrich) was dissolved in 2 M ammonium hydroxide and diluted to concentrations of 0.05–0.015 M lipoic acid in 0.04–0.2 M ammonium hydroxide. The lipoic acid was then reduced by exposing it to natural sunlight or 8 W 302 nm laboratory ultraviolet lamps in closed borosilicate test tubes. Optimum conditions were found to be 0.01 M lipoic acid in 0.07 M ammonium hydroxide with a pH range of 8.4–9.0. At this pH range, no toxic hydrogen sulfide gas was evolved during reduction, while at lower pH solutions it was evolved. Higher pH values approached the pKa of the thiol end groups decreasing the extent of reduction.

To carry out the contamination removal studies test materials were treated with arsenic or mercury in deionized water at a 1000 ppm concentration for both solutions of sodium arsenite (Na<sub>3</sub>AsO<sub>3</sub>) and mercuric chloride (HgCl<sub>2</sub>) and allowing the materials to dry prior to removal treatment. Test materials included Whatman No. 1 filter paper; Style 532 wool jersey knit fabric and Style 46001

unbleached, cotton interlock knit fabric from Test Fabrics Pittston, Pennsylvania; and wild quail feathers.

The contamination levels were measured using a 700 series Niton handheld X-ray fluorescence spectrometer (XRF) before and after treatment. The treatment sequence was developed by running a series of designed experiments using replicate samples and the statistical significance of the variables was determined until a sequence was obtained that resulted in removal to a level below the lower detection limit of the XRF ( $1 \mu\text{g}/\text{cm}^2$ , valid for both As and Hg).

## RESULTS

The test results show that the  $\alpha$ -lipoic acid must be reduced in order to react with arsenic (III) from sodium arsenite in solution. However, reaction with mercury from mercuric chloride does not require reduction for instantaneous reaction because  $\alpha$ -lipoic acid reacts directly with mercury (Brown and Edwards, 1969).

Kinetic studies were carried out in order to ascertain the rate of reaction of arsenic (III) with reduced lipoic acid and the factors that influenced that rate. It was determined that the reaction was chemically rate limited and was predominately complete in eight seconds. The presence of ambient air significantly decreased the overall extent of the reaction, particularly during rapid stirring, suggesting that oxidation of the acid was the cause. The use of a nitrogen atmosphere verified this assumption as the extent of the reaction was not affected.

Other experiments showed that reduced lipoic acid also binds to other cations such as iron, copper, nickel, cadmium, zinc, and calcium to form precipitates so that the presence of those cations on an object must be considered. Appreciable interference of the binding of arsenic (III) by the anions fluoride, chloride, sulfate, and nitrate were not evident.

Solutions of  $\alpha$ -lipoic acid were tested with and without alcohol in order to determine if an aqueous solution was as effective as an alcohol solution. The preliminary results obtained for the removal of arsenic (III) from filter paper with reduced lipoic acid, with or without alcohol, are presented in Table 2.

Further experiments were carried out to optimize the technique for the removal of arsenic from materials using a series of experimental designs. The best results, where reduced lipoic acid was capable of removing up to  $1000 \mu\text{g}/\text{cm}^2$  of arsenic or mercury from materials that contain sulfur, and mercury from materials that do not contain

**TABLE 2.** Removal of  $48.8 \mu\text{g}/\text{cm}^2$  arsenic (III) from filter paper using reduced lipoic acid. Control = two rinses with deionized water.

Treatment	Number of samples	Average residual As ( $\mu\text{g}/\text{cm}^2$ )	Standard deviation	Percent As removed
Control	5	14.04	5.40	71%
Lipoic acid + alcohol	15	11.13	3.32	77%
Lipoic acid	15	5.32	1.39	89%

sulfur, were obtained by using a sequence of steps, which included (1) prewetting the contaminated material with deionized water; (2) soaking the material in lipoic acid without stirring for 10 seconds; and (3) rinsing the material with deionized water using a serpentine pattern rinse from top to bottom. The treatment was then compared to the same sequence without the reduced lipoic acid soaking.

Tables 3 and 4 report the percentage of arsenic and mercury removed from the different materials tested in this study using the above steps in one sequence with and without the reduced lipoic acid soak step and two sequences without the reduced lipoic acid soak step. To be taken into account is that feathers are hydrophobic so that the metal salts dispersed on them from an aqueous solution do not adhere the way they do with wool, as can be seen in the amount of arsenic that remained on the feathers after treatment.

The sequence with reduced lipoic acid soak removed statistically significantly more arsenic from filter paper ( $p = 0.0005$ ) and wool ( $p < 0.0001$ ) but not from the thicker

**TABLE 3.** Percent removal of arsenic from various materials contaminated with sodium arsenite after one cleaning sequence with and without lipoic acid and two cleaning sequences without lipoic acid. The amount removed in the second cleaning is calculated with respect to the original concentration.

Contaminated material	Initial As concentration ( $\mu\text{g}/\text{cm}^2$ )	Percent As removed by treatment		
		1 cleaning (lipoic acid)	1 cleaning (water)	2 cleanings (water)
Filter paper	1484	99.4	96.5	99.8
Cotton	1224	98.9	90.8	98.0
Wool	1354	99.3	95.6	99.7
Feathers	565	Not tested	92.5	92.5

**TABLE 4.** Percent removal of mercury from various materials contaminated with mercuric chloride after one cleaning sequence with and without lipoic acid and two cleaning sequences without lipoic acid. The amount removed in the second cleaning is calculated with respect to the original concentration.

Contaminated material	Initial concentration Hg ( $\mu\text{g}/\text{cm}^2$ )	Percent Hg removed by treatment		
		1 cleaning (lipoic acid)	1 cleaning (water)	2 cleanings (water)
Filter paper	1548	>99.9	93	99.3
Cotton	1496	68.1	65.1	93.2
Wool	2161	0.0	8.7	36.7

woven cotton ( $p = 0.1135$ ). For the case of mercury removal, it clearly showed that this could be achieved only for nonsulfur containing materials, such as paper and cotton.

## CONCLUSIONS AND FUTURE RECOMMENDATIONS

Reduced lipoic acid solutions can be used to remove high concentrations of arsenic and mercury from materials that do not contain sulfur, such as paper and cotton. For sulfur-containing materials, such as wool and feathers, this method will only remove arsenic but not mercury. The treatment solutions and sequences developed show promising results for applications in decontaminating artifacts and other materials. A more comprehensive summary of the results can be found in the first author's dissertation (Cross, 2007). The next level of scientific inquiry should examine the complexities of using the aqueous solutions to promote diffusion of toxins out of more complex three-dimensional materials such as wood. It would also be useful to use  $\alpha$ -lipoic acid to develop a technique to determine whether arsenic or mercury is inherent in a material or added as a contaminant. Combining this technique with the use of an organic solvent in the initial wetting step to dislodge the contaminant from the material bringing it to the surface, such as the surface activation technique, may also prove to be effective (Reuben, 2006).

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# Solvent Cleaning of Fragile Artifacts without Mechanical Agitation

*Robert Kaiser*

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**ABSTRACT.** The removal of hazardous contaminants from fragile artifacts that cannot be treated by mechanical cleaning methods can be achieved by immersing the artifact into a solvent that dissolves the contaminant(s) of interest but is nonreactive with the artifact. By providing an adsorbent sink, such as activated carbon or an evaporative blotter, the dissolved contaminant is then removed from the solvent. Experiments were conducted in which a solvent soluble blue dye was removed from cotton gauze by placing the gauze in direct contact with an activated carbon fabric saturated with ethoxyperfluorobutane (3M's HFE-7200). With sufficient time, the dye was completely removed from the gauze without the use of mechanical agitation.

**KEYWORDS:** organic pesticides, contaminated artifacts, activated carbon fabric, hydro-fluoroethers, diffusive transfer, cleaning, removal.

## INTRODUCTION

In terms of the decontamination of organic pesticides from museum artifacts of historic and cultural value, what immediately comes to mind is that one is dealing with unique and often irreplaceable objects that are likely to be mechanically fragile. Consequently, the objects must be handled with extreme care, and if the objects are of animal or vegetable origin, they also will be likely to interact with water, which could alter and mar their appearance.

In order to remove contaminants from a substrate under industrial conditions, such as with inertial guidance instruments, time plays an important role, and it becomes necessary to introduce a high level of shear in the cleaning medium so that the contaminants can be detached by convective mass transfer. Standard ways of attaining a high level of shear are, for example, to subject the object to a high-pressure spray, to place the object in a stirred or ultrasonic bath, or to rub it with a moistened fabric. Depending on the fragility of a museum or collection artifact, any one of these treatments could result in unnecessary damage or destruction. A big difference between the treatment of museum artifacts and that of precision industrial parts is that the time available for treatment is much longer for the former, presumably weeks or months compared with seconds or minutes for the latter.

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*Paper presented at the Pesticide Mitigation in Museum Collections workshop held at the Smithsonian's Museum Conservation Institute in April 2007 exploring possible methods and techniques that may become useful for the museum conservation field to reduce, mitigate, clean, or remediate undesirable pesticides on objects.*

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Given that the allowable time for museum artifact decontamination can be fairly long, it is possible to consider the use of molecular diffusion as a means of removing contaminants. The principle is based on the molecular diffusion of a soluble contaminant through a solvent that is then transferred from the surface or pores of the object being cleaned to an adsorption blotter that traps the contaminant (see “Diffusion Cleaning Process: Diagrams”).

The molecular diffusion decontamination process uses hydrofluoroethers (HFEs) as the liquid diffusion medium for the pesticide contaminants and an activated carbon fabric as the adsorption blotter. For example, HFE-7100 (methoxyperfluorobutane,  $\text{CH}_3\text{-O-C}_4\text{F}_9$ ) and/or HFE-7200 (ethoxyperfluorobutane,  $\text{C}_2\text{H}_5\text{-O-C}_4\text{F}_9$ ), commercialized by 3M, can serve as the transfer solvents, given that they are capable of dissolving organophosphates, such as malathion, captan, or carbaryl, a class of compounds found in many pesticide formulations, because they are also compatible with a wide range of materials typically found in museum collections.

### PHYSICAL DEMONSTRATION

In order to demonstrate the viability of the diffusion cleaning concept, a simple experiment was performed. First, a gauze pad was placed in a Petri dish and small amounts of colored dyes were added to the gauze. Then a piece of activated carbon fabric was placed on top of the dyed gauze. Sufficient HFE-7200 was added to soak the stack, and weights were placed on top of the activated carbon fabric to ensure firm contact between the different fabric layers. The Petri dish was covered and placed in a sealed bag to minimize solvent loss during the course of the experiment. The sample was periodically removed from the bag for visual examination and photography and then replaced in the bag.

Two types of dyes were used in these tests: (1) a HFE-soluble dye to simulate a soluble contaminant and (2) a water soluble, HFE-insoluble dye to simulate coloring that could be present in many museum objects.

### REMOVAL OF A HFE-SOLUBLE CONTAMINANT BY DIFFUSION CLEANING

#### EXPERIMENTAL PROCEDURE

- Five, two-layer 1.75 inch (42.3 mm) diameter coupons of NU GAUZE pads (Johnson & Johnson) were each placed in a 50 mm diameter Petri dish and then contaminated with four drops of a HFE-soluble blue dye.
- The Petri dishes were labeled IV to VIII. The coupons in these dishes were then subjected to the following treatments:
  - Dish IV: 3 mL of HFE-7200 were added and the dish was covered.
  - Dishes V and VI: a 1.75 inch diameter of 50K/100 Micro activated carbon fabric coupon was placed on top of the contaminated fabric, 4 mL of HFE-7200 were added, and three 1.75 inch diameter steel washers (weighing a total of 42 grams) were placed on top of the carbon fabric layer.
  - Dishes VII and VIII: a second 1.75 inch diameter gauze coupon was placed on top of the contaminated fabric, 4 mL of HFE-7200 were added, and a steel washer was placed on top of each.
- In addition, an experiment was performed in a Petri dish labeled “0” where no HFE-7200 was added to serve as control.
- Photographs of the five coupon stacks were taken (see Figure 1).



FIGURE 1. Top view of the experimental stacks in Petri dishes.



FIGURE 2. Petri dishes in the Ziploc bag.

5. All five Petri dishes were placed in a one quart Ziploc plastic bag, as shown in Figure 2. They were allowed to stand for 116 hours (approximately 5 days).
6. Photographs were taken periodically of the contaminated fabrics.

## RESULTS

After 48 hours, the fabrics started to appear dry so that an extra 4 mL of HFE-7200 were added to samples V–VIII. The results obtained after 24, 48, and 116 hours of contact time, are illustrated by Figure 3.

## DISCUSSION

The photographs in Figure 3 clearly show that placing a contaminated fabric in contact with an activated carbon fabric in the presence of HFE-7200 results in the transfer of the contaminant from the former to the latter. The presence of HFE-7200 results in the migration of the contaminant throughout the gauze fabric, regardless of whether one is dealing with a single or two fabric coupons, an indication that relatively thick items can be treated by this process.

In the absence of a liquid diffusion medium (i.e., the HFE-7200 solvent), no transfer of the contaminant occurs

between the contaminated fabric and the activated carbon fabric, nor does the contaminant spread within the original fabric (see Figure 4).

## CONTAMINANT MIGRATION INDUCED BY EVAPORATION OF THE TRANSFER LIQUID

The diffusion cleaning exercise described above and illustrated in Figure 3 was terminated after 116 hours of contact time for purposes of convenience. The damp fabrics and the steel washers were restacked in the Petri dish base but the cover was not replaced to allow the transfer solvent, HFE-7200, to evaporate.

The samples were left undisturbed overnight and examined the next morning (Figure 5, top). As shown in Figure 5, center, the contaminant in the three fabric samples that did not have an activated carbon coupon on top (i.e., samples IV, VII, and VIII) was concentrated in the areas from which the solvent could evaporate, that is, the center hole of the washer and the rim of the gauze coupon not covered by the washer.

The contaminant also migrated vertically as shown in the case of the two layer setups, V, VI, VII, and VIII (see Figure 5, bottom). The top fabric layer of plain gauze in samples VII and VIII was much bluer than the bottom one. This is a clear indication that the transfer solvent evaporates from the top of the stack and that the contaminant migrates with it. Because of the activated carbon fabric in samples V and VI, the bottom layer was as white, if not whiter, than the ones just covered with plain gauze. The visible absence of color shows that there is less dye left on the original item with the use of activated charcoal than with a simple absorptive material.

This “evaporative cleaning” approach could be of value when undesired adsorptions occur on the activated carbon as would be the case if the transfer solvent is a mixture in which one of the solvent components may swamp the adsorptive sites. Saturation of the activated carbon would result in no further transfer of contaminant from the object being decontaminated. This could be determined by visual or instrumental examination of the contaminated object, and/or analysis of the activated carbon fabric. Further decontamination would entail replacing the used piece of activated carbon fabric with a fresh piece.<sup>1</sup>

## MATERIAL COMPATIBILITY

The purpose of this section is to present experimental data that demonstrate that the diffusion cleaning process

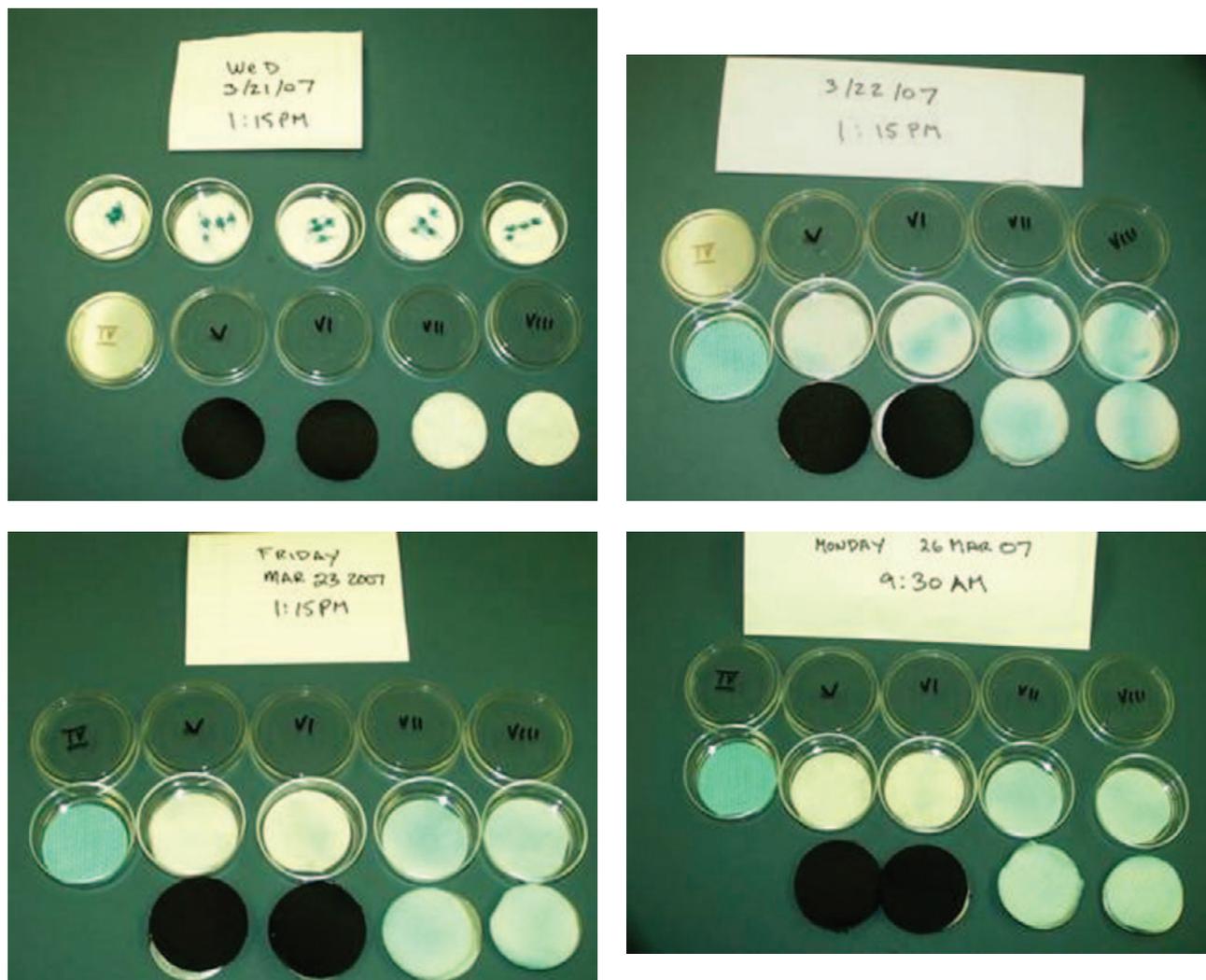


FIGURE 3. Removal of a hydrofluoroether (HFE) soluble contaminant by diffusion cleaning. Top left, at start of test just before adding HFE-7200; top right, after 24 hours of contact with HFE-7200; bottom left, after 48 hours of contact with HFE-7200; and bottom right, after 116 hours of contact with HFE-7200.

can only be applied to species that are soluble in the transfer solvent. The diffusion cleaning process is of value only if it can selectively remove unwanted contaminants from the surface or body of an object without affecting other components, such as dyes or colorants that the object may contain.

To make this point, it was decided to examine the fate of fabric coupons stained with aqueous dyes that are not soluble in HFE-7200, and subject the stained fabrics to the diffusion cleaning process described in the previous section.

#### EXPERIMENTAL PROCEDURE

1. Coupons of NU GAUZE pads (Johnson & Johnson), 1.75 inch (42.3 mm) in diameter were each placed in 50 mm diameter Petri dishes (labeled XIV and XV), and then stained with one drop each of red, green, and yellow Food Color and Egg Dye (McCormick). The poor solubility of these dyes in HFE-7200 is demonstrated by the photograph shown in Figure 6 in which one drop of each of these dyes was added to the HFE-7200 solvent in an aluminum weighing dish.



FIGURE 4. In the absence of a diffusion medium, no transfer is observed between the contaminated fabric and the activated carbon coupon. Top, at the beginning of the test; bottom, after 44 hours of contact between the contaminated fabric and the activated carbon coupon but without HFE.

2. The Petri dishes and the aluminum weighing dish were placed in an oven maintained at 105°C for four hours to remove the solvent and all volatile liquids.
3. The bottom of the weighing dish was punched out with a 1.75 inch diameter arch punch and placed in the Petri dish labeled XIII. Figure 7 depicts the three Petri dishes with the dried samples: the weighing dish and the two dyed gauze pads.
4. Five milliliters of HFE-7200 were added to each of the Petri dishes. The samples were visually examined to establish that the dyes did not dissolve or diffuse in the transfer solvent. Figure 8 shows the samples five minutes after adding the solvent.
5. A 1.75 inch diameter 50K/100 Micro activated carbon fabric coupon was placed on top of the dyed substrate,



FIGURE 5. Contaminant migration induced by evaporation of the transfer liquid overnight. Top, fabric stacks in open Petri dishes; center, view of top layer after removing steel washers; bottom, view of the second layer after removing first layer.

- both fabric and aluminum, and three 1.75 inch diameter steel washers were placed on top of the activated carbon fabric layer. The Petri dishes were covered and all three setups were placed in a one quart Ziploc plastic bag and allowed to stand for a 48 hours.
6. Photographs were taken periodically of the contaminated substrates.



FIGURE 6. Three drops of food dye, red, green, and yellow floating in HFE-7200.



FIGURE 7. The Petri dishes containing the base of the aluminum weighing dish and the stained gauzes after drying in the oven.



FIGURE 8. The same Petri dishes of Figure 7 five minutes after the addition of 5 mL of HFE-7200.

## RESULTS

The results after 24 and 48 hours are shown in Figures 9 and 10, respectively. Comparison of these photographs to those of Figures 7 and 8 demonstrate that no visual change can be observed. Testing of longer exposure times was not deemed necessary. The appearance of these samples after drying is shown in Figure 11, which can be compared to Figure 7.



FIGURE 9. Petri dishes of Figure 8 after 24 hours of contact with activated carbon fabric in the presence of transfer solvent in a sealed environment.

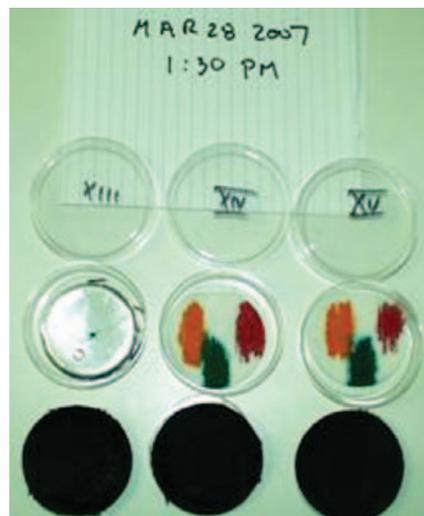


FIGURE 10. Petri dishes of Figure 8 after 48 hours of contact with activated carbon fabric.



FIGURE 11. Left, petri dishes of Figure 10 after evaporation of the solvent before dismantling the stacks. Right, view after removal of metal washers and the activated carbon fabric layer.

### CONCLUSIONS

Contaminants, such as organic pesticides, can be removed from a substrate by diffusion without any mechanical agitation. The requirements are (1) the presence of a suitable solvent that dissolves the contaminant and is compatible with the substrate being decontaminated and (2) a sink for the dissolved contaminant. This sink can be

an adsorbent material, such as activated carbon fabric, or an evaporative blotter.

#### DIFFUSION CLEANING PROCESS: DIAGRAMS

Diagrams 1–10 below sequentially illustrate the principles of how diffusion cleaning with HFE-wetted activated-carbon fabric works on porous surfaces.

Diagram 1

#### Contaminated Porous Surface

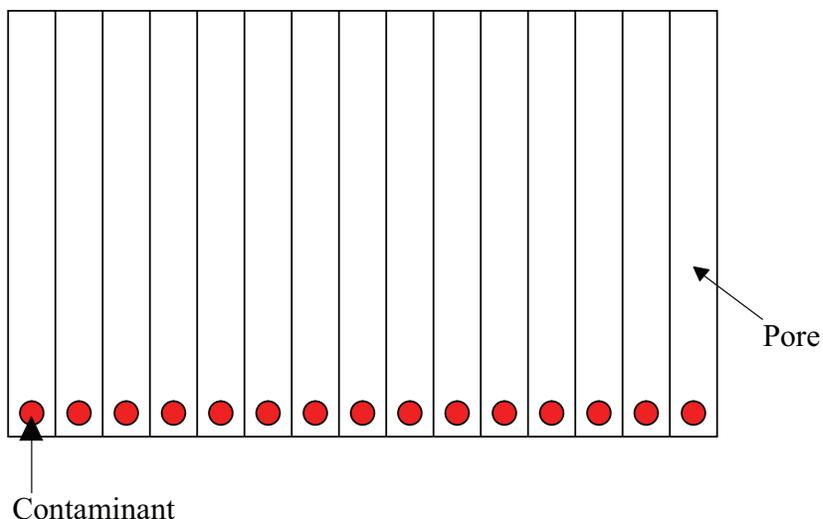


Diagram 2

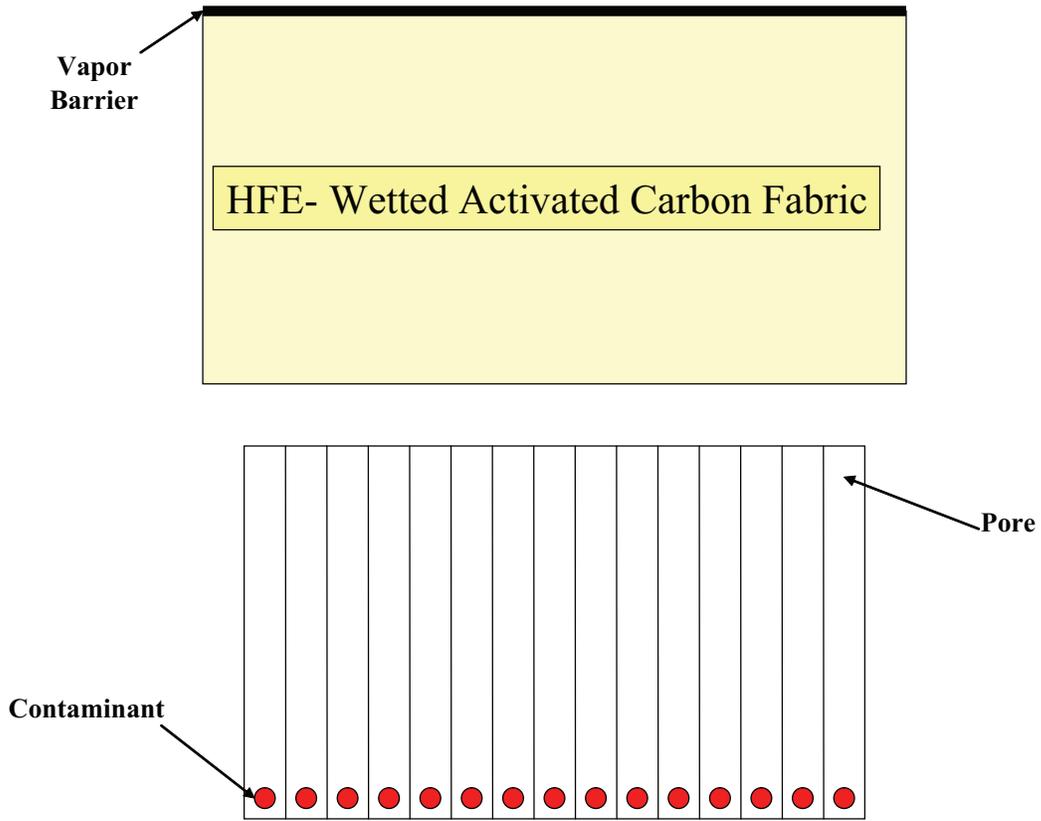


Diagram 3

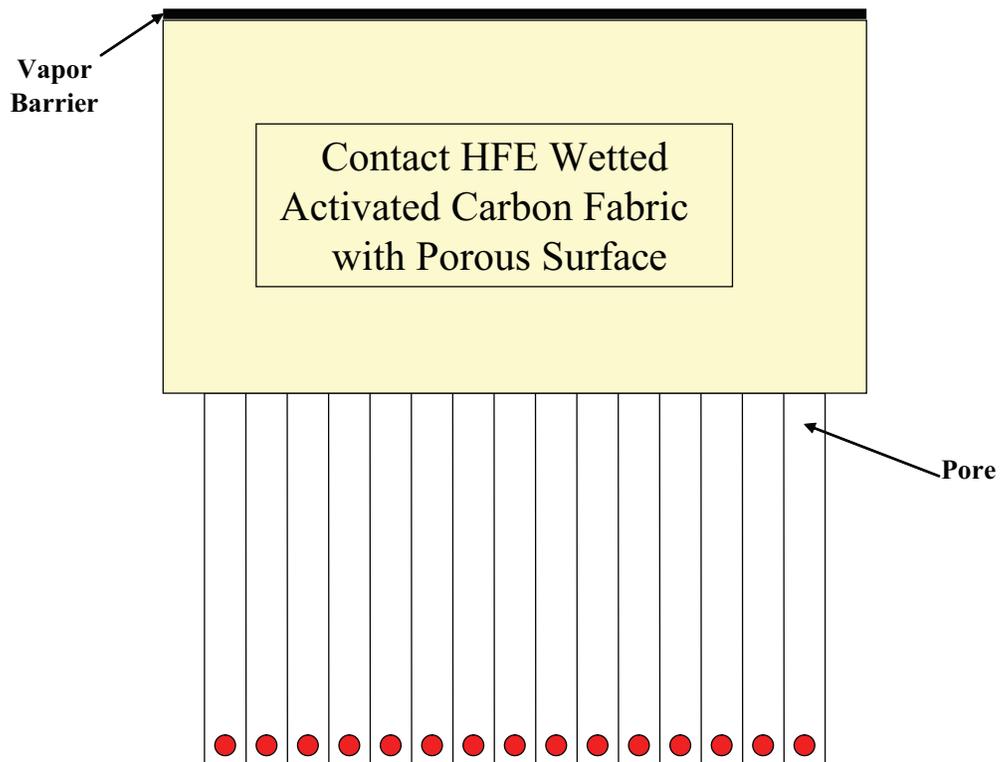


Diagram 4

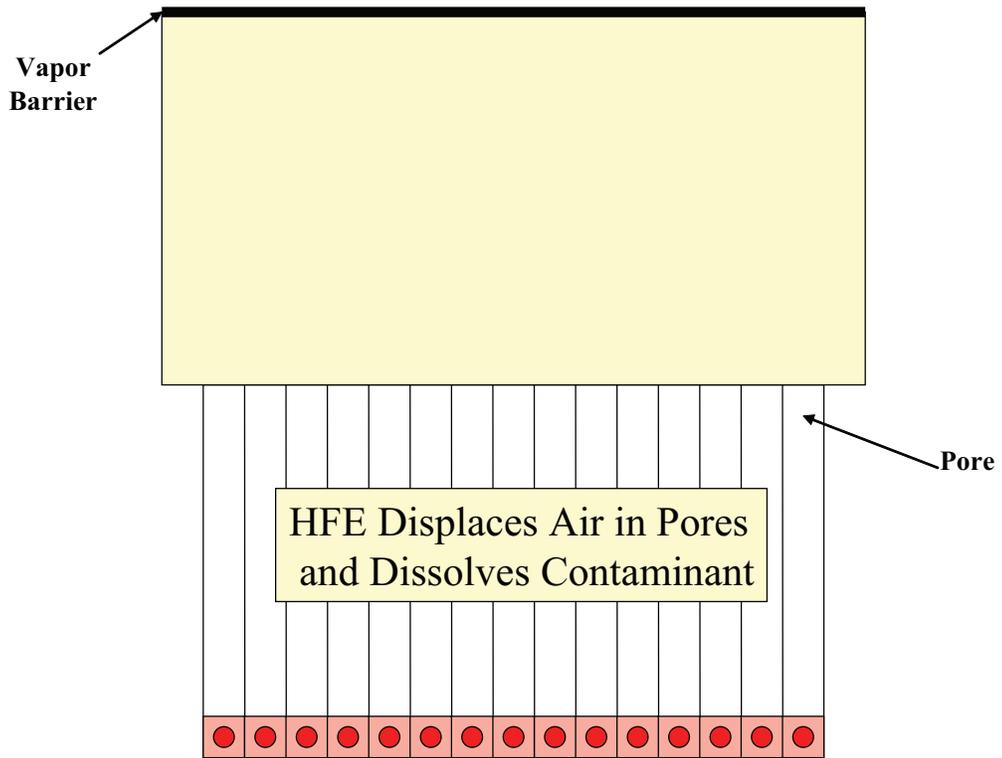


Diagram 5

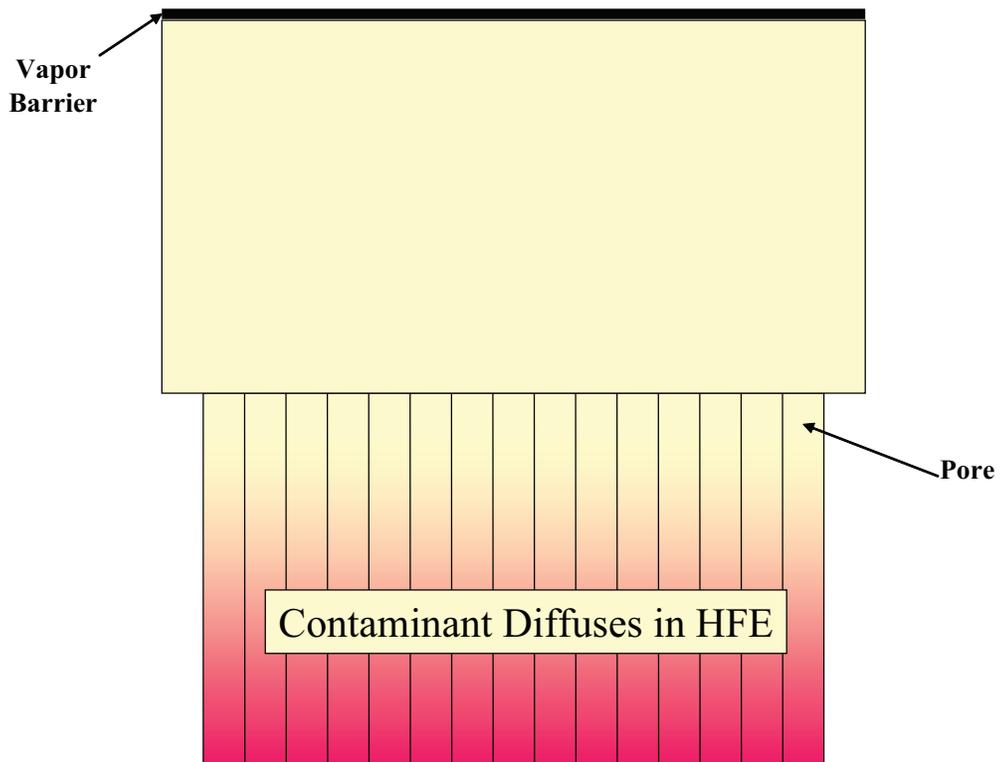


Diagram 6

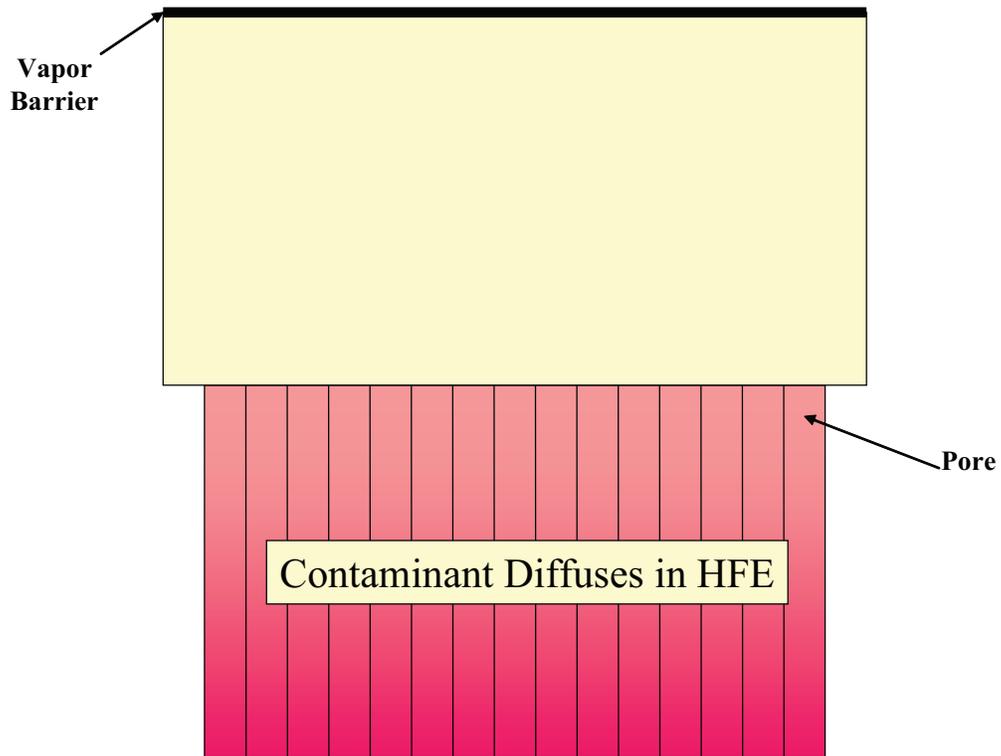


Diagram 7

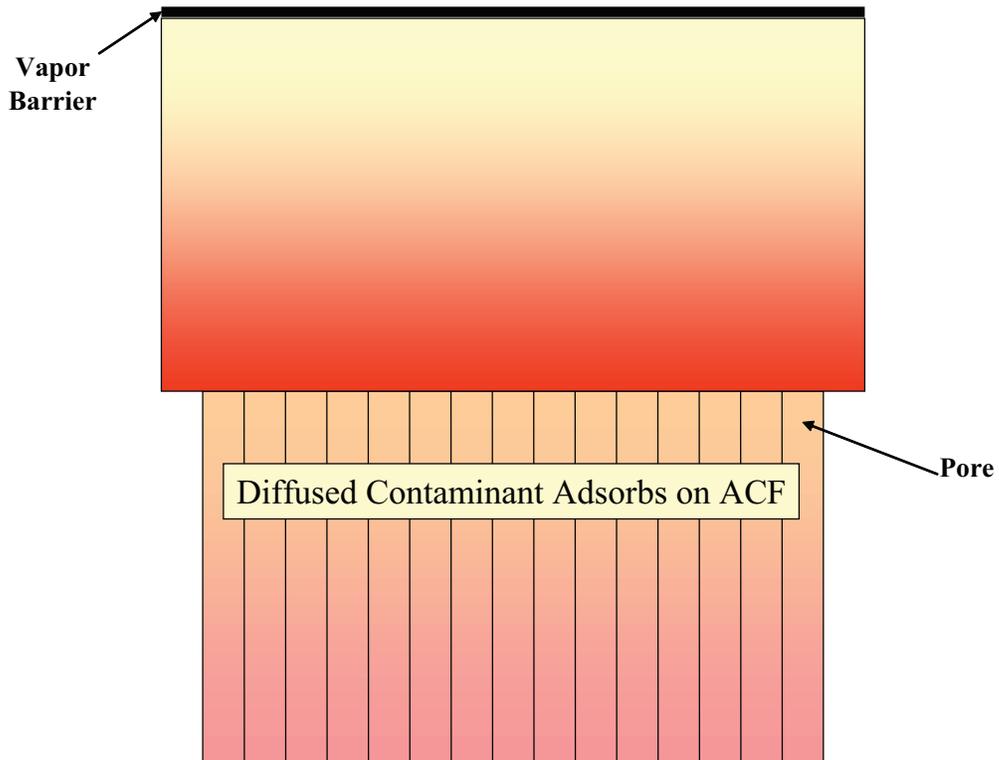


Diagram 8

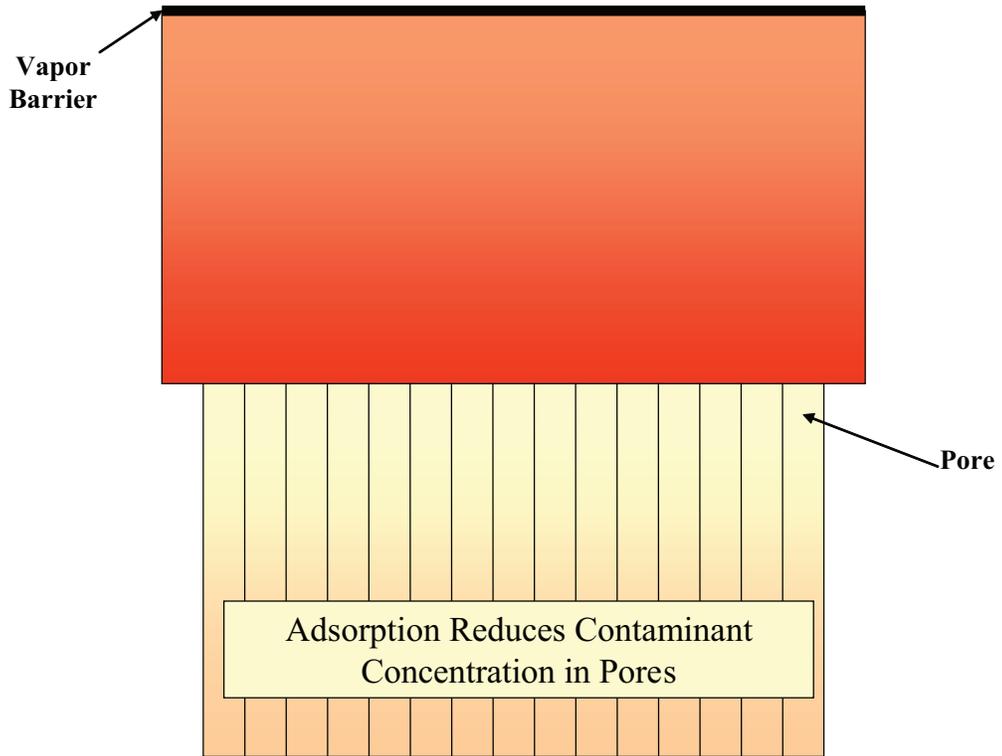


Diagram 9

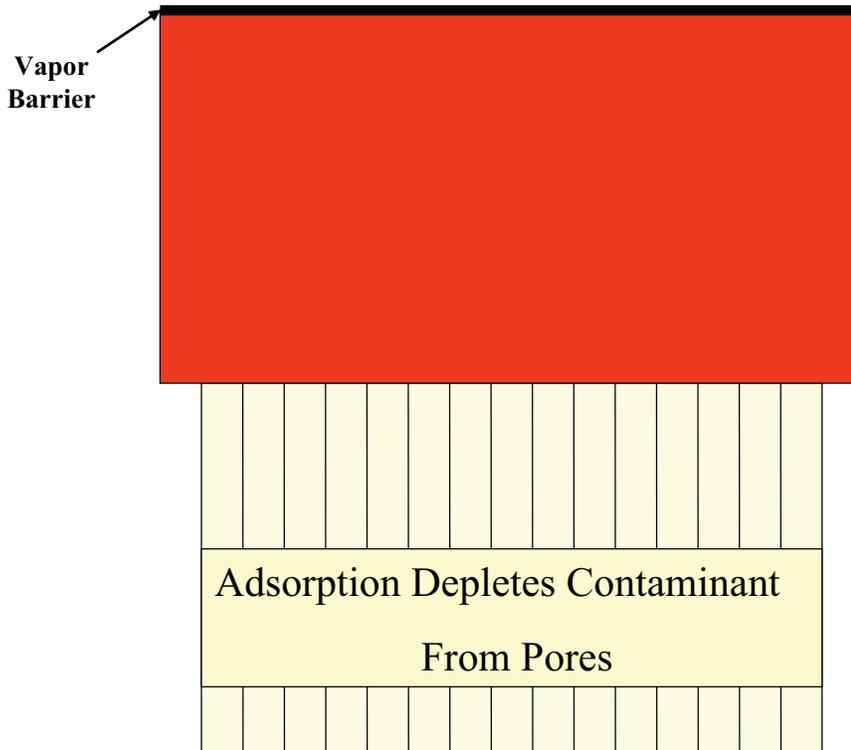
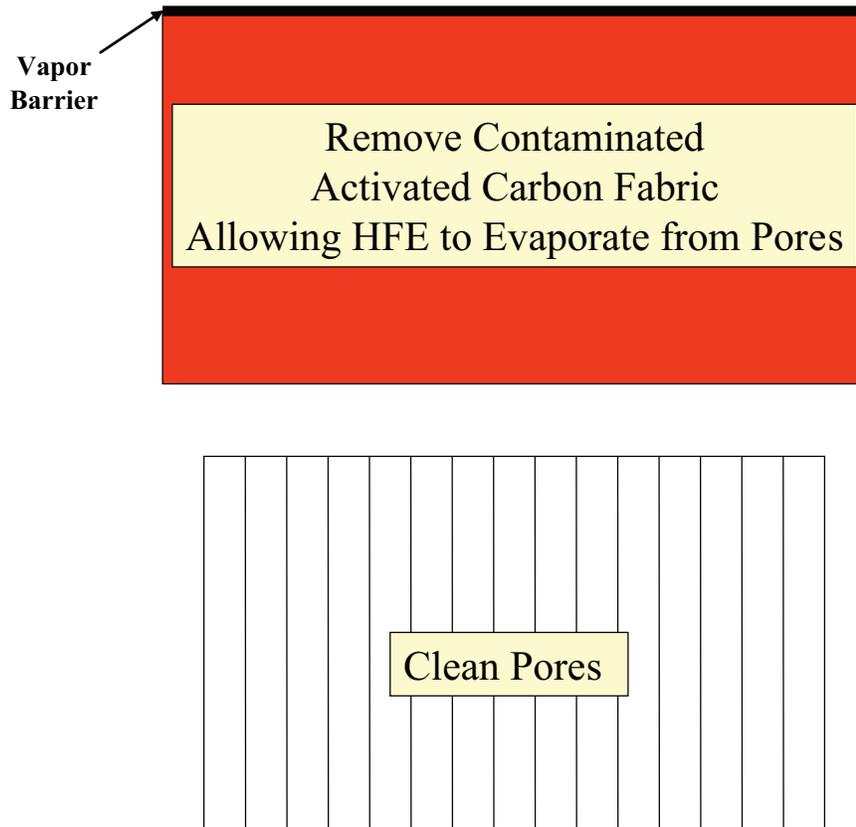


Diagram 10



**RECOMMENDATIONS**

The results presented in this paper were based only on visual observation. More rigorous work still needs to be performed. It would be useful to have scientific testing carried out to confirm the complete removal of the pesticides from the substrate and to verify that no changes take place to the water-soluble components.

**MATERIALS AND SUPPLIERS**

- HFE-7200, 3M Electronic Materials Market Division, St. Paul, Minn.
- Zorflex 50K Activated Carbon Fabric, Calgon Corp., Pittsburgh, Pa.
- Zorflex 50K/Nylon Laminate, Entropic Systems, Inc., Woburn, Mass.
- NU GAUZE Sterile Gauze Pads (Johnson & Johnson).
- Water-Soluble Food Colors (McCormick).
- Experimental Dye FC-3275 (HFE Soluble Blue Dye)—no longer commercially available (3M Electronics Materials Market Division).

**NOTE**

1. This paper made use of research and findings presented at several annual Decontamination Commodity Area Conferences from 2002 to 2006, as follows:
  - Kaiser, R. 2002. "Novel Decontamination Pads." In *DECON 2002, 4th Decontamination Commodity Area Conference, San Diego, Calif.*, CD-ROM.
  - Kaiser, R., A. Kulczyk, J. Minicucci, R. Willey, R. Spafford, and B. MacIver. 2005. "Adsorptive Wipes Using Activated Carbon Fabrics." In *DECON 2005, 6th Decontamination Commodity Area Conference, Tucson, Ariz.*, CD-ROM.
  - . 2006. "Adsorptive Wipes Using Activated Carbon Fabrics." In *DECON 2006 Science & Technology Conference, Westminster, Colo.*, CD-ROM.
  - MacIver, B., R. Spafford, and R. Kaiser. 2002. "Precision Wiping Studies in Support of Block III Decontamination Efforts." In *DECON 2002, 4th Decontamination Commodity Area Conference, San Diego, Calif.*, CD-ROM.
  - . 2004. "Portable Decontamination: Preliminary Development and Evaluation of a Decontamination Wipe System." In *DECON 2004, 5th Decontamination Commodity Area Conference, Tampa, Fla.*, CD-ROM.

# Mitigation of Surface Contaminants on Haudenosaunee Medicine Masks

*Peter A. Reuben*

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**ABSTRACT.** A novel strategy was developed for the mitigation of arsenic and mercury surface contaminants found on Haudenosaunee medicine masks. This strategy combined the replacement of specific components of the masks, the application of a surface active displacement solution (SADS), and the use of traditional cleaning methods. Initial efforts focused on the mitigation of medicine masks deemed highly contaminated with mercury; the results indicated more than 99% reduction in dislodgeable residues. The focus of this study was on the mitigation of arsenic residues after a single application of the SADS formulation as well as the removal and replacement of certain components of the masks. The results demonstrated that only trace amounts of arsenic remained and that the overall contaminant reduction was comparable with that previously obtained for mercury.

**KEYWORDS:** arsenic, mercury, Haudenosaunee medicine masks, surface active displacement solution (SADS), sodium lauryl sulfate, mitigation, cleaning, removal.

## INTRODUCTION

Since enactment of the Native American Graves Protection and Repatriation Act in 1990, the Haudenosaunee have discovered the presence of arsenic and mercury pesticide residues on some of their repatriated medicine masks (Jemison, 2001). The Haudenosaunee (People of the Longhouse) include the Tonawanda Seneca Nation, 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 Haudenosaunee Standing Committee on Burial Rules and Regulations in collaboration with the Seneca Nation's Tribal Historic Preservation Office and the Seneca-Iroquois National Museum obtained National Park Service funding in 2002 to investigate methods of detection and mitigation of arsenic and mercury pesticide residues on their historic objects. The mitigation of these residues is of great importance given that the repatriated medicine masks will be used by traditional practitioners during ceremonies, and the masks will be stored in their homes, potentially affecting their families.

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*Paper presented at the Pesticide Mitigation in Museum Collections Workshop held at the Smithsonian's Museum Conservation Institute in April 2007 exploring possible methods and techniques that may become useful for the museum conservation field to reduce, mitigate, clean, or remediate undesirable pesticides on objects.*

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With the assistance of tribal representatives, a novel multistep strategy was developed to mitigate arsenic- and mercury-based pesticide residues. This strategy includes the use of a surface active displacement solution (SADS) (Reuben, 2006) and traditional cleaning methods. Because of the cultural sensitivity of the masks, sampling and mitigation methods were limited to nondestructive techniques only. The limitations of both nondestructive techniques and limited funding led to the use of surface wipe samples that were subsequently analyzed by atomic absorption spectroscopy or cold vapor atomic absorption spectrometry at a New York State certified environmental testing laboratory (TestAmerica).

Analyses of surface wipe samples from six recently repatriated medicine masks revealed high mercury levels—levels that decreased significantly after treatment (Reuben, 2006). During that study, additional surface wipes were analyzed for arsenic, but values for arsenic were not reported. This paper reports arsenic values for the same six medicine masks before and after treatment using the SADS formulation.

## MITIGATION

Arsenic mitigation began with disassembly of the specific components of the masks, such as medicine bundles, horsehair, and headgear. The disassembly was accomplished using hand tools. Fasteners securing these items also were removed.

The SADS formulation is a multistep process that is tailored to the contaminating chemical agent and the surface from which it is to be removed. This concept has been recently used on heat exchangers and removal of microfouling films from delicate surfaces (Reuben, 2006). The first step of the SADS formulation in this study began with a 5% isopropyl alcohol solution sprayed directly onto the surface to be cleaned. This alcohol was acceptable to the traditional practitioners. The alcohol serves a potential solvent to the contaminant and provides the interfacial displacement action. The second step was a 5% aqueous solution of technical grade sodium lauryl sulfate, which emulsifies the stripped contaminant. The third step was a rinse with distilled water to minimize residues. Water is key component in the SADS concept because it carries the components of the formulation to the surface. As the water drains from the surface, it also carries the stripped and emulsified chemical contaminant. Rinsate from each step was collected and disposed of in the laboratory waste stream.

Solutions were applied using a Dynalon Quick Mist HDPE Sprayer bottle. Each solution was allowed to stand for two minutes before the next solution was applied. Soft bristled brushes were used in areas that were heavily soiled. Each cleaned mask was allowed to air dry before wipe sampling.

Surface wipe samples were obtained using premoistened Palintest dust wipes following a modified field procedure for surface wipe sampling (Brookhaven National Laboratory [BNL], 2002). The BNL procedure was modified to increase the sample area from 100 cm<sup>2</sup> to half the surface area of the exterior painted side or the unpainted interior of the mask. Sampling was carried out before and after the SADS cleaning procedure. Sampling of the medicine mask followed the general format of two wipe samples per side using a vertical centerline to separate the surface into left and right sides. The wipe sample from the left side was arbitrarily assigned to be analyzed for arsenic and the wipe sample from the right side was analyzed for mercury.

## RESULTS AND DISCUSSION

Given the unique cultural constraints and funding limitations for this project, a strategy was developed for detection and mitigation of surface contaminants on the repatriated medicine masks. Cultural constraints limited the mitigation and detection techniques to nondestructive methods only. This, in conjunction with funding limitations, led to the analysis of surface wipe samples as the primary means by which the progress of the mitigation could be documented. The objective of this project was to reduce dislodgeable arsenic and mercury contaminants (per wipe sample) to nanogram levels. This goal was suggested by a toxicologist and agreed upon by the traditional practitioners as reasonable for this project.

The mitigation strategy involved the removal of items, such as horsehair and headgear, and was performed with the approval and under the guidance of traditional practitioners. Any components removed were given to the traditional practitioners for disposal. The SADS formulation was then applied to the masks, followed by traditional cleaning methods, and finally the replacement of key components, such as horsehair by traditional practitioners.

Each of the six repatriated medicine masks in this study was screened for the presence of arsenic. To estimate the amounts of contamination, wipe samples were taken on each side of the mask. The sample area was equal to half of the surface area of the painted (exterior) or unpainted

(interior) sides of the masks. The sample area was increased from the BNL procedure to better compensate for the potential uneven distribution of surface contaminants and to improve the estimate of dislodgeable residues from the surface. The surface wipe was able to follow irregular surface contours and reach into the many ornate features of the medicine mask.

It is important to remember the qualitative nature of the surface wipe sample with respect to this study. Other sampling techniques were reviewed and considered (Reuben, 2006, and references therein). This study requires a nondestructive sampling technique to estimate dosage for the toxicologist and a method of monitoring progress during mitigation that is within funding limitations. Although the analysis of the wipe sample is quantitative, the wipe sample is qualitative in nature. Reviews of the pros and cons for sampling techniques for museum objects have been published by Sirois and Sansoucy (2001). In a previous study with different medicine masks, analysis of field duplicate wipe samples produced nearly identical results when analyzed for arsenic and mercury residues as expected. Quality assurance/quality control programs were used to assure that the results obtained were representative and defensible (BNL, 2003; P. A. Reuben, unpublished report for the Seneca Nation of Indians Tribal Historic Preservation Office: "Detection and Mitigation of Inorganic Pesticide Residues on Sacred Objects," 2005). Previous attempts reported by Reuben (2006) had shown that both distilled water and distilled water/isopropyl alcohol mixture had little effect in the reduction of arsenic residues. On the basis of these observations, wipe samples have only a minor contribution to the overall mitigation. Also, pigment transfer to the wipe sample on the painted side was not observed during the sampling event. Results for arsenic and mercury levels on both the painted and the unpainted surfaces, before and after SADS treatment, are presented in Tables 1 and 2.

Arsenic was found on painted and unpainted surfaces of the medicine masks during the initial measurement of surface wipe samples. Arsenic levels on four of the six masks were determined to be above the mitigation goal of 0.999  $\mu\text{g/wipe}$ . The same four masks also had elevated arsenic levels on the unpainted surfaces, whereas only two masks had measurable levels on the painted surface. Contamination ranged between 1,020 and 2,780  $\mu\text{g/wipe}$ . After one treatment using the SADS formulation, arsenic values decreased significantly to 0.50–0.92  $\mu\text{g/wipe}$ . The combination of removal of potentially contaminated components of the medicine masks and one application of the SADS formulation resulted in a greater than 99% removal

**TABLE 1.** Arsenic and mercury values measured on wipes of painted exterior surfaces before and after treatment with surface active displacement solution formulation. Minimum detection level (MDL) As = 0.50  $\mu\text{g/wipe}$  and MDL Hg = 0.012  $\mu\text{g/wipe}$ . Mercury data reproduced from Reuben, 2006; ND = not detected.

Object number	Arsenic ( $\mu\text{g/wipe}$ )		Mercury ( $\mu\text{g/wipe}$ )	
	Before treatment	After treatment	Before treatment	After treatment
1	<0.50	0.53	830	0.172
2	<0.50	0.52	1770	0.885
3	2720	0.65	1320	0.680
4	<0.50	0.78	1540	0.443
5	ND	ND	6860	2.38
6	1060	ND	140	0.123

**TABLE 2.** Arsenic and mercury values measured on wipes of unpainted surfaces (interior) before and after treatment with surface active displacement solution formulation. Minimum detection level (MDL) As = 0.50  $\mu\text{g/wipe}$  and MDL Hg = 0.012  $\mu\text{g/wipe}$ . Mercury data reproduced from Reuben, 2006.

Object number	Arsenic ( $\mu\text{g/wipe}$ )		Mercury ( $\mu\text{g/wipe}$ )	
	Before treatment	After treatment	Before treatment	After treatment
1	<0.50	0.56	330	0.087
2	<0.50	0.50	9160	1.495
3	1560	0.72	2120	0.088
4	1550	0.92	1470	0.093
5	1020	0.65	13200	5.06
6	2780	0.65	920	0.113

for dislodgeable arsenic residues on painted and unpainted surfaces of the masks. This is comparable with the significant reduction in mercury residues previously reported (Reuben, 2006).

## CONCLUSIONS

Six Haudenosaunee medicine masks were screened for arsenic residues. Analysis of surface wipe samples revealed high levels of arsenic on both the painted and unpainted surfaces of the medicine masks. A similar mitigation strategy was used for mercury mitigation on these masks. This included the removal of medicine bundles, horsehair, and headgear followed by a single application

of a SADS formulation. Analysis of wipe samples revealed that arsenic residues had been reduced significantly on all treated surfaces. The results from posttreatment levels of arsenic residues met the mitigation goal of 0.999 µg/wipe or less. These results are comparable with those obtained for the mitigation of high mercury levels on the same objects.

#### ACKNOWLEDGMENTS

The author thanks Kathy Mitchell of the Seneca Nation Tribal Historic Preservation Office, the Haudenosaunee Standing Committee on Burial Rules and Regulations, and Sheree Bonaparte of the Saint Regis Mohawk Tribe's Tribal Historical Preservation Office for allowing this information to be disseminated. Dr. Robert Baier of the Surface Science Center at the State University of New York at Buffalo is acknowledged for his assistance with the SADS concept. The author also thanks the Smithsonian's Museum Conservation Institute for the opportunity to participate in the Mitigation of Pesticide on Museum Collections Workshop/Symposium. This research was funded by a National Park Service NAGPRA grant 36-02-GP-324.

#### MATERIALS

Palintest Wipes are available from Palintest USA, part number PT484 (reference #505).  
Sodium lauryl sulfate (SLS) available from Fluka Chemicals part number 71730-250g [Chemical Abstract Service registry no. 151-21-3].  
Dynalon Quick Mist HDPE Sprayer bottle Fisher Scientific, part number 03-438-12A. This may be substituted by a common spray bottle.  
Isopropanol alcohol (70%) commercial grade.

#### REFERENCES

- Brookhaven National Laboratory (BNL). 2002. Surface Wipe Sampling Procedure IH75190, Revision 7, pp.1–13. Upton, N. Y.: Brookhaven National Laboratory. [http://www.bnl.gov/esh/shsd/sop/pdf/IH\\_SOPS/IH75190.pdf](http://www.bnl.gov/esh/shsd/sop/pdf/IH_SOPS/IH75190.pdf) (accessed 11 November 2003).
- . 2003. *2003 Site Environmental Report*. pp. 9.1–9.12. Upton, N. Y.: Brookhaven National Laboratory. <http://www.bnl.gov/ewms/ser/2003.asp> (accessed 6 June 2004).
- Jemison, G. P. 2001. Poisoning the Sacred. *Collection Forum*, 17(1–2):38–40.
- Reuben, P. A. 2006. Detection and Mitigation Strategies for Contaminated Nagpra Objects—The Seneca Nation's Experience. *Collection Forum*, 20(1–2):33–41.
- Sirios, P. J., and G. Sansoucy. 2001. Analysis of Museum Objects for Hazardous Pesticide Residues: A Guide to Techniques. *Collection Forum*, 17(1–2):49–66.

# Bacterial Removal of Mercury from Museum Materials: A New Remediation Technology?

*Timberley M. Roane and Lisa J. Snelling*

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**ABSTRACT.** This project investigated the removal of mercury, a nondegradable, persistent chemical, from museum materials by bacteria. Mercury-resistant bacteria have the ability to convert this element into a gaseous form. The isolation of a diverse bacterial community from mercury-treated items is reported. Two nonpathogenic bacterial isolates were capable of reducing 10 mg/L mercury concentrations. *Arthrobacter* sp. 2604 reduced the mercury associated with a gelatin medium by 30% and a paper matrix by 20% within 10 days at 28°C. *Cupriavidus metallidurans* CH34 reduced up to 50% and 60% of the mercury, respectively. Current work is focused on the optimization of conditions for bacterial mercury removal, including the nutritional requirements and appropriate environmental conditions for the remediation process.

**KEYWORDS:** mercury, bacteria, detoxification, remediation, removal, museum objects.

## INTRODUCTION

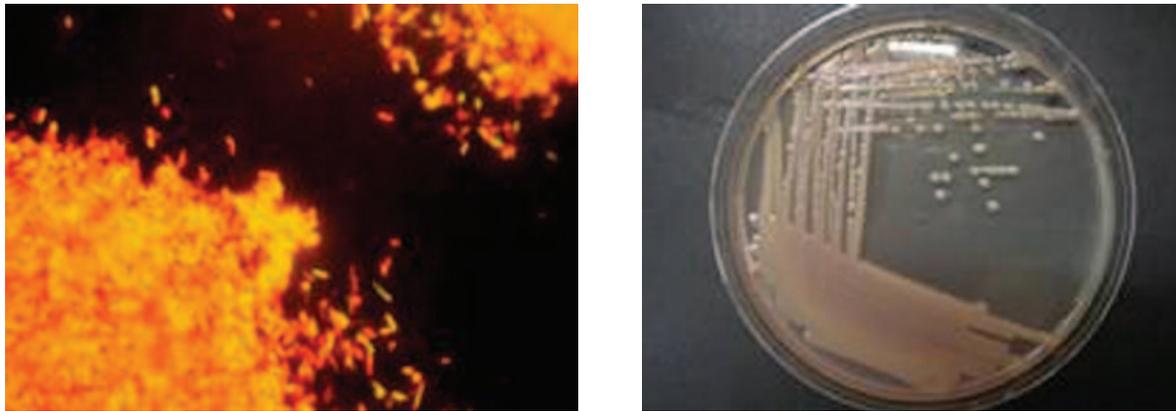
Surveys are now routinely conducted to determine the extent of mercury- and arsenic-based pesticide contamination on botanical, ethnographic, and zoological specimens in museums worldwide. In the United States and Canada, estimates suggest that as much as 80% of ethnographic and natural history specimens have been treated with metal-based pesticides (Sirois, 2001; N. Odegaard, Arizona State Museum, personal communication, 2002). Methods for mercury and arsenic mitigation of these materials are needed because of the enactment of the Native American Graves Protection and Repatriation Act (NAGPRA) in 1990 and for the safety of museum personnel. In the work discussed herein, microorganisms associated with mercury-treated artifacts were investigated as a possible treatment source for mercury removal.

Mercury has a long history of use as a pesticide. It has been used as an antimicrobial in cosmetics, as an antifungal on grain seeds, and as an antibacterial in vaccines. Mercury is currently used in batteries, etching solutions, and various other industrial processes. It is available in a variety of chemical forms—elemental mercury (Hg<sup>0</sup>), mercuric chloride (HgCl<sub>2</sub>), ethyl mercury (CH<sub>3</sub>CH<sub>2</sub>Hg<sup>+</sup>), and mercuric sulfide, also known as cinnabar (HgS)—all of which are potentially

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*Paper presented at the Pesticide Mitigation in Museum Collections Workshop held at the Smithsonian's Museum Conservation Institute in April 2007 exploring possible methods and techniques that may become useful for the museum conservation field to reduce, mitigate, clean, or remediate undesirable pesticides on objects.*

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**FIGURE 1.** Left: 1000× magnification of acridine orange-stained metal-resistant bacteria isolated from a soil. Each cell is approximately 1–2  $\mu\text{m}$  in diameter. Right: A Petri plate containing a bacterial growth medium. Bacterial growth (as colonies) is evident on the surface of the plate.

toxic. The widespread use of mercury has contributed to its prevalence in the environment where bacterial activity is one of the driving factors behind mercury's chemical transformation.

Bacteria range in size from 1 to 2  $\mu\text{m}$ , are ubiquitous in the environment, and can provide mechanisms to detoxify chemicals and reduce chemical concentrations (Figure 1).

Bacteria are ideal candidates for metal remediation studies because some have physiological means of reducing the toxicity associated with mercury (Roane and Pepper, 2001). The most widely used mechanism of mercury resistance by bacteria is the chemical reduction of mercury, i.e., the conversion of  $\text{Hg}^{2+}$  to  $\text{Hg}^0$  (Roane and Pepper, 2000; Barkay et al., 2003). The resulting elemental mercury ( $\text{Hg}^0$ ) readily volatilizes as a gas, reducing the amount of mercury associated with a contaminated medium. The gaseous mercury can be collected and properly disposed of (von Castein et al., 2002; Boheme et al., 2005).

Mercury is toxic because of its global interference with all cellular processes in macro- and microorganisms. Mercury is just as toxic to bacteria as it is to humans, interfering with enzymatic functions, protein structure, and genetic integrity. Consequently, in order for an organism to avoid the toxic effects of mercury, the organism must be able to protect all of its cellular functions and reduce its exposure to mercury. One way to achieve this is to convert mercury into a gas, which will diffuse away from the cell, thereby reducing the concentration of mercury in direct contact with the cell. The use of such mercury-resistant bacteria to treat contaminated soils and waters is being widely investigated (Daly, 2000; Okino et al., 2000;

Wagner-Dobler et al., 2000). In this study, it is hoped that the microorganisms will serve to reduce the amount of mercury associated with an object by conversion of the metal to a gaseous form without damaging the object.

The specific objectives of the work presented here were to (1) isolate mercury-resistant bacteria from the surfaces of mercury-treated museum materials and (2) evaluate the ability of the bacteria to decrease the mercury concentrations associated with different media.

## EXPERIMENTAL

### MERCURY-TREATED MUSEUM MATERIALS

Access to mercury-impacted anthropological and herbarium materials was provided by the Arizona State Museum, Tucson. As materials could not be destructively sampled, Arizona State Museum personnel used a handheld X-ray fluorescence (XRF) spectrometer (NITON XLi 700 Series Analyzer, Thermo Scientific, Billerica, Mass.) to identify objects impacted by mercury. This technique has been applied in the identification of objects containing arsenic (Seifert et al., 2000).

### COLLECTION, IDENTIFICATION, AND CHARACTERIZATION OF MERCURY-RESISTANT BACTERIA

The surfaces of museum materials were swabbed with sterile cotton applicators to collect bacteria, which were then transferred to bacterial media, brought back to the laboratory, and monitored for growth. Individual bacterial

isolates were identified using the molecular method of 16S rRNA gene sequencing (Kassab and Roane, 2006; Marchesi et al., 1998). The DNA sequencing was performed at the University of Colorado Denver Cancer Center DNA Sequencing Core Facility (Denver, Colo.). The resulting 16S rDNA sequences were analyzed with the BLAST program that is available from the National Center for Biotechnology Information (www.ncbi.com).

To examine mercury resistance, bacterial isolates were placed in varying concentrations of mercuric chloride (0–60 mg/L) and monitored for growth (Kassab and Roane, 2006; Roane and Pepper, 2000). Those isolates that did not grow in mg/L concentrations of mercury were placed in µg/L concentrations of mercury. The highest concentration of mercury an isolate grew in was recorded as the maximum mercury-resistance level.

#### REMOVAL OF MERCURY FROM DIFFERENT MEDIA BY MERCURY-RESISTANT BACTERIA

The Environmental Protection Agency (EPA) method 3051, a microwave acid digestion technique (Walter et al., 2005), was modified for the dissolution of mercury-treated materials. Subsequent quantification of mercury used a PS200II Leeman Labs Cold Vapor–Atomic Absorption Spectrometry (CV-AAS) instrument (Hudson, N.H.) for laboratory treated materials (e.g., agar and paper), which could be destructively sampled. This instrument provided a total metal quantification method for assessing the ability of bacteria to remove mercury from the entire substrate. All instrumentation necessary for mercury analysis was provided by the Shared Analytical Services Laboratory at the University of Colorado’s downtown Denver campus. Three media were examined: (1) liquid broth for the initial screening of mercury removal; (2) agar, as a representative of a permeable substrate; and (3) paper as a representative of a complex substrate.

A mercuric chloride solution was used to contaminate these substrates to achieve a final concentration of 10 mg/L mercury. Results from these initial media provide the basis for other materials in future research.

#### SUBSTRATE USAGE

As a preliminary assessment of potential material degradation, the ability of one of the mercury-resistant isolates, *Arthrobacter* sp. 2604, to degrade different organic substrates was examined. Concentrated cells were placed in each well of a commercially available 96-well GN BIOLOG plate (BIOLOG, Hayward, Calif.) for analysis. Each

well contained a different carbon substrate as supplied by the manufacturer. A color change in a given well indicated bacterial growth and substrate use (Rusznyak et al., 2008).

## RESULTS AND DISCUSSION

Several bacterial isolates were collected from mercury-treated items at the Arizona State Museum. Items sampled included several ethnographic objects, such as leather pouches and headdresses, and a Harvard cabinet housing botanical collections. The items examined had known mercury exposure—an assessment that was performed by Arizona State Museum personnel using XRF in most cases (Table 1). It should be noted that several locations on the objects were analyzed to confirm mercury presence.

The bacterial isolates obtained from the surfaces sampled represented commonly occurring bacteria. For example, *Arthrobacter*, *Bacillus*, and *Pseudomonas* spp. are readily found in soils. Five isolates, out of 20 total, were unidentifiable with the method used. These isolates may represent novel bacteria upon confirmation with additional techniques.

**TABLE 1.** Bacterial isolate identification and maximum mercury resistance levels (MRL) from mercury-treated museum objects. Here ND = not detected, although object had suffered mercury exposure according to museum personnel; (-) indicates mercury levels below detection limits <100 µg/L.

Source material	Mercury levels (µg/cm <sup>2</sup> )	Isolate identification (mercury MRL)
Leather bag	93	<i>Arthrobacter</i> sp. 2604 (50 mg/L)
Turtle fetish	ND	<i>Bacillus megaterium</i> (5 mg/L) <i>Pseudomonas</i> sp. (2 mg/L) <i>Korea rosea</i> (-) <i>Bacillus</i> sp. (-) <i>Arthrobacter</i> sp. (-) <i>Pseudomonas tolaasi</i> (-)
Spear thrower	2147	<i>Bacillus</i> sp. (10 mg/l)
Headdress 1	280	Unknown (-)
Headdress 2	1076	<i>Korea</i> sp. (-)
Moccasin	23	<i>Chelacoccus asaccharyorans</i> (-) <i>Arthrobacter</i> sp. (100 µg/L)
Harvard cabinet	300	<i>Pseudomonas synxantha</i> (1 mg/L) <i>Kaistobacter koreensis</i> (-) <i>Arthrobacter</i> sp. (100 µg/L) Unknown (-) Unknown (-) Unknown (-)
Leather pouch	ND	<i>Agrococcus jenensis</i> (-)
Red textile	370	Unknown (100 µg/L)

Interestingly, the maximum mercury resistance level (MRL) of each of the bacterial isolates did not correlate with the amount of mercury associated with the item. Isolates with high resistance were found on items with lower mercury levels (as compared to other materials). Eight of the isolates were, however, able to tolerate from 100 ppb ( $\mu\text{g/L}$ ) to 50 ppm ( $\text{mg/L}$ ) levels of mercury.

One isolate, in particular, was chosen for further analysis. *Arthrobacter* sp. 2604, isolated from a leather pouch with  $93 \mu\text{g}/\text{cm}^2$  mercury, could grow in up to 50  $\text{mg/L}$  of mercury. This extraordinary degree of resistance made this isolate an interesting candidate for use in the mercury removal studies. In addition to *Arthrobacter* sp. 2604, another bacterial isolate, *Cupriavidus metallidurans* CH34, was used as a control organism in the mercury removal studies. *Cupriavidus metallidurans* CH34 is a soil bacterium originally isolated from zinc mine tailings (Legatzki et al., 2003). This organism is resistant to zinc,

lead, cadmium, and mercury, as well as other metals, and demonstrated mercury resistance up to 10  $\text{mg/L}$  mercury.

Mercury removal from three substrates was examined. The initial screening of the isolates was carried out with broth cultures, followed by testing with agar and paper. Each substrate was amended with mercury to a concentration of 10  $\text{mg/L}$  prior to bacterial treatment. In the case of the paper, it was allowed to air dry prior to bacterial application.

Each substrate was then inoculated with  $10^7$  cells/mL of either bacterial isolate—*Arthrobacter* sp. 2604 or *C. metallidurans* CH34—and then incubated to allow for bacterial growth and mercury removal. Uninoculated controls were used to monitor abiotic loss of mercury. *Arthrobacter* sp. 2604 was able to remove 20%, 30%, and 20% of the mercury from each substrate type, i.e., broth, agar, and paper, respectively, within 10 days (Figure 2). *Cupriavidus metallidurans* CH34 was able to remove up to 40%,

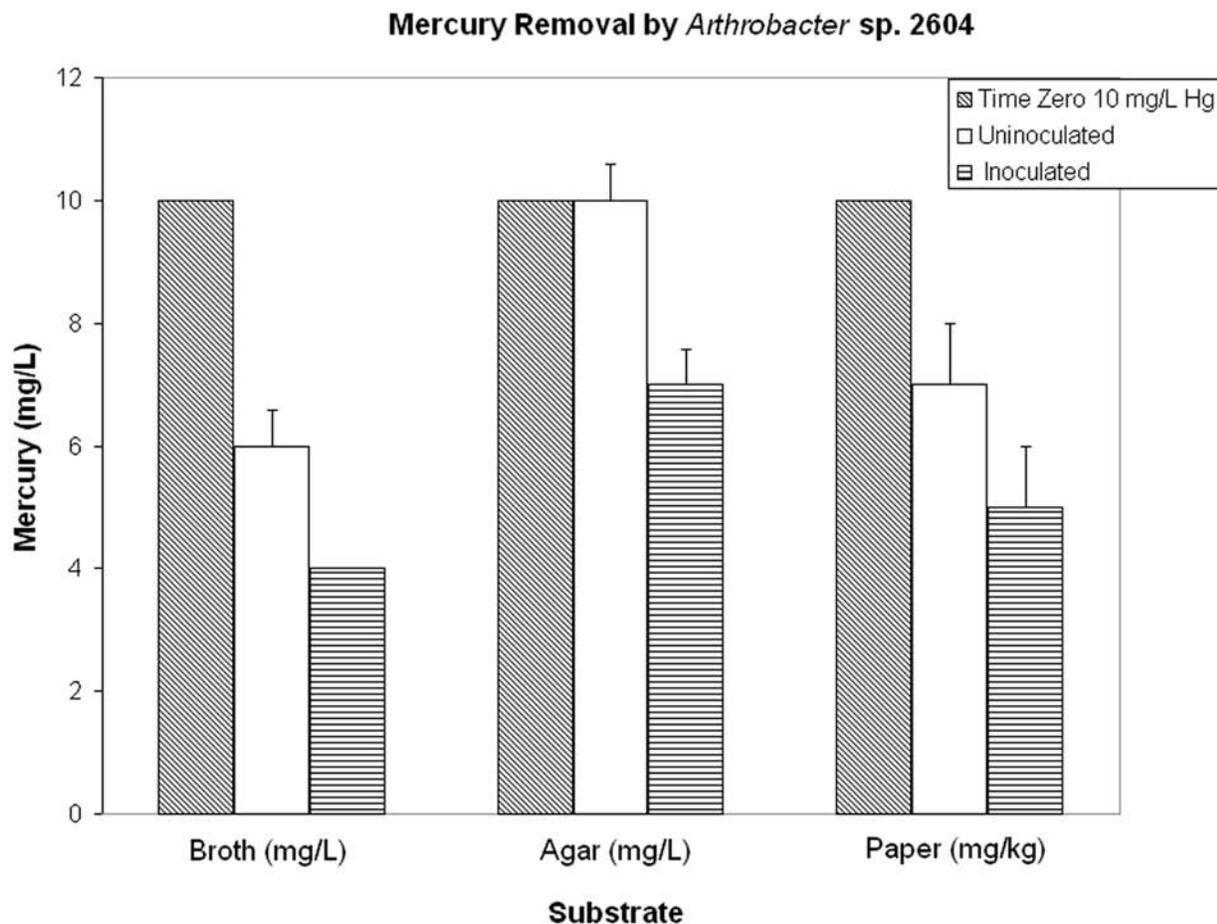
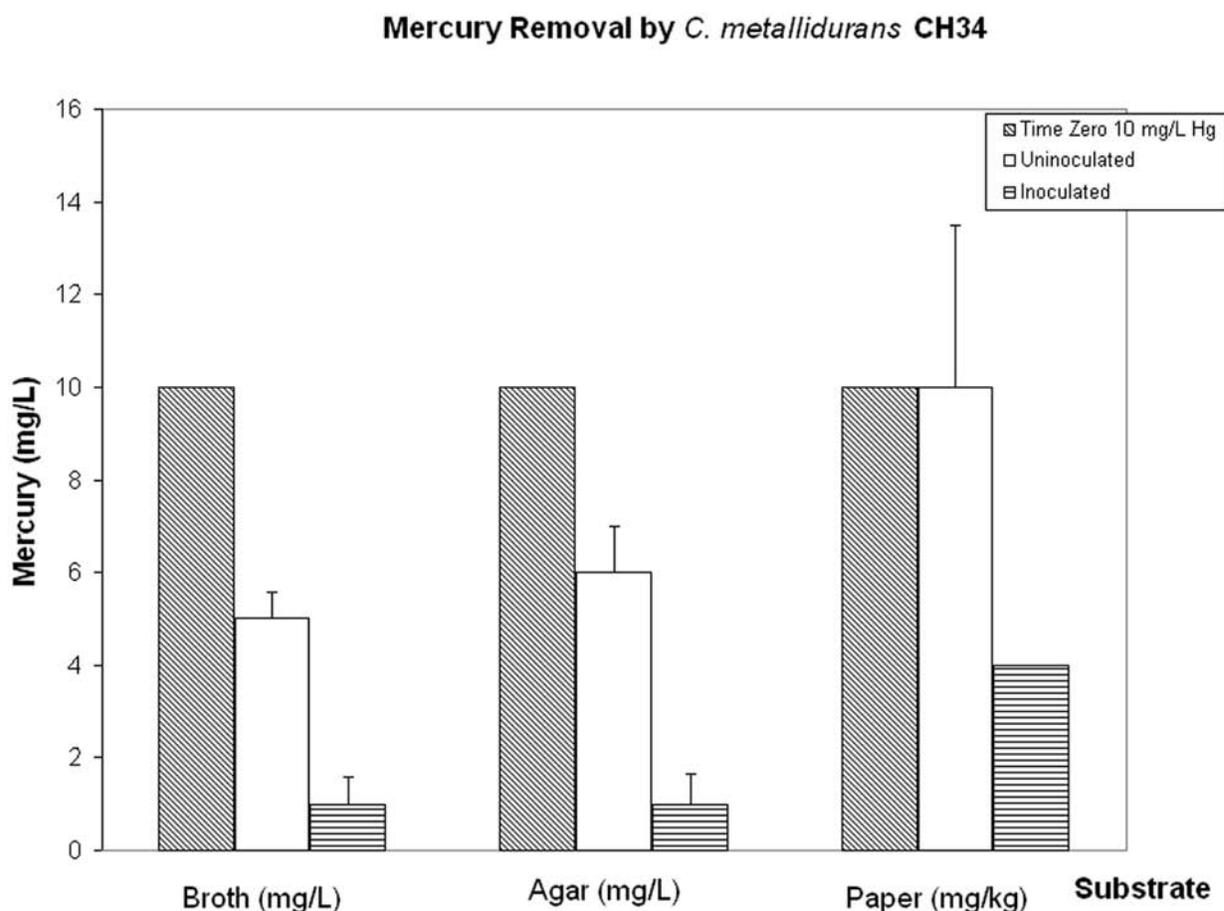


FIGURE 2. Mercury removal within 10 days by *Arthrobacter* sp. 2604 from broth, agar, and paper amended with 10  $\text{mg/L}$  of mercury. Uninoculated controls containing 10  $\text{mg/L}$  of mercury were used to assess abiotic loss of mercury. Standard error bars represent triplicate experiments.

50%, and 60% of the mercury, respectively (Figure 3). Mercury removal was measured against the uninoculated controls and so reflected actual bacterial mercury removal. Both isolates showed evidence of cell growth on each substrate within the 10 day period. Despite the porosity of the materials, both isolates removed more mercury from the solid substrates: agar and paper. This is promising given the types of museum materials requiring treatment. Additional studies will address the specific conditions needed for optimal microbial treatment and mercury removal. For example, bacterial mercury removal may be enhanced under a slightly elevated temperature or with supplied nutrients.

To begin to address the nutrients needed to sustain microbial activity, the isolate *Arthrobacter* sp. 2604 was screened for its ability to degrade various organic carbon

compounds. The BIOLOG test simultaneously monitors degradation of 95 different organic compounds. Table 2 summarizes the organic substrates *Arthrobacter* sp. 2604 preferred, such as sugars, amino acids, and organic acids. Continued analysis of organic substrate preference and resulting metabolic by-products will provide information regarding possible risks of material degradation during and after treatment. So far, *Arthrobacter* sp. 2604 shows little preference for the complex organics often associated with museum materials, e.g., cellulose, indicating a decreased risk for material influence. *Cupriavidus metallidurans* CH34, however, is capable of autotrophic metabolism, meaning it can use CO<sub>2</sub> to support its growth as opposed to organic compounds. The use of CO<sub>2</sub> should substantially decrease the risk of material changes upon bacterial treatment.



**FIGURE 3.** Mercury removal within 10 days by *Cupriavidus metallidurans* CH34 from broth, agar, and paper amended with 10 mg/L of mercury. Uninoculated controls containing 10 mg/L of mercury were used to assess abiotic loss of mercury. Standard error bars represent triplicate experiments.

TABLE 2. Substrate utilization pattern for *Arthrobacter* sp. 2604 based on the GN BIOLOG plate.

Type of substrate	Specific substrate
Sugars	$\alpha$ -D lactose
	D-galactose
	D-trehalose
	D-melibiose
Amino acids	L-alanine
	L-proline
	L-threonine
Organic compounds	Acetic acid
	Pyruvic acid methyl ester
	Quinic acid
	D-saccharic acid
	L-alanyl glycine
	Urocaric acid
	Inosine
	Propionic acid
	Bromosuccine acid
	Glucuronamide
	$\alpha$ -ketobutyric acid
	$\alpha$ -ketoglutaric acid
	$\alpha$ -ketovaleric acid
	$\beta$ -hydroxybutyric acid

## CONCLUSIONS

A diverse bacterial community was identified on the surfaces of several mercury-treated museum collections. The presence of bacteria implies a possible remediation technology given the ability of certain microorganisms to convert various mercury compounds into gaseous forms of mercury. Gaseous mercury lends itself well to collection and appropriate disposal. The preliminary work presented here demonstrates the potential use of mercury-resistant bacteria in the removal of mercury from complex surfaces. In future work, this technology will need to be examined on actual museum materials prior to widespread use. However, current work is underway addressing optimization of the process and ensuring material preservation.

## ACKNOWLEDGMENTS

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# Liquid and Supercritical Carbon Dioxide as a Cleaning and Decontamination Agent for Ethnographic Materials and Objects

*Helene Tello and Achim Unger*

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**ABSTRACT.** Health hazards posed by the application of pesticide and heavy metal treatments of museum collections are problems that must be addressed. Surface cleaning will not remove poisonous substances embedded in the matrix of items. Efforts were undertaken to find a detoxification method that would better decontaminate objects, both individually and in groups. Carbon dioxide in its liquid or supercritical state offers alternative methods for better decontamination of objects. However, a detailed knowledge about the properties of the different materials is necessary in order to prevent any possible damage to those sensitive to liquid carbon dioxide (L-CO<sub>2</sub>) or supercritical carbon dioxide (SC-CO<sub>2</sub>). Sensitive materials should be excluded from the process given that damage to the object is unacceptable from a conservation point of view.

**KEYWORDS:** liquid carbon dioxide, supercritical carbon dioxide, dry cleaning, decontamination, ethnographic artifacts, cleaning, removal.

## INTRODUCTION

In the past, ethnological objects were treated extensively with various pesticides, such as arsenic and mercury compounds, organochlorine insecticides, and other substances like naphthalene or camphor (see Figure 1) (Elert, 1994; Goldberg, 1996; Dawson, 1998; Davis and Caldararo, 2000; Hawks and Makos, 2001; Odegaard and Sadongei, 2001, 2005; Schmidt, 2001; Sirois, 2001; Johnson and Henry, 2002; Martin and Kite, 2003; Klaus et al., 2005). However, this approach resulted in considerable contamination of indoor air as the pesticides in the matrix of the treated materials would contaminate the accumulated dust on them (Krooß and Stolz, 1993; Schieweck et al., 2005, 2007; Tello, 2006). Consequently, many objects had to be removed from public exhibition. It remains difficult to safely store and exhibit such objects given that solvent cleaning techniques can reduce surface contamination but cannot remove the embedded pesticide residues from their matrix. This is illustrated in Figure 2, where white dots of dichloro diphenyl trichloroethane (DDT) (detection by thin layer chromatography, TLC) are visible on a wooden flute from the collection of the Museum of Musical Instruments in Leipzig, Germany, previously sprayed with a wood preservative.

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*Paper presented at the Pesticide Mitigation in Museum Collections Workshop held at the Smithsonian's Museum Conservation Institute in April 2007 exploring possible methods and techniques that may become useful for the museum conservation field to reduce, mitigate, clean, or remediate undesirable pesticides on objects.*

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FIGURE 1. Application of camphor to storage objects.

Current conservation solutions to deal with contaminated objects include the following:

- Packing and sealing the objects in plastic that is impermeable to pesticide vapors.
- Enclosing and wrapping the objects with active carbon tissue.
- Storing objects in cabinets with an air circulation system.
- Installing special storage areas with air circulation systems.

Current methods for removal of pesticides from works of art include the following:

- Dry surface cleaning with special vacuum cleaners using HEPA filters.

- Evaporating DDT crystals and coatings from the surface using a laser.
- Removing pesticides in a vacuum drier or using a modified Thermo-Lignum process.
- Vacuum cleaning using water with surfactants.
- Dry cleaning with hydrocarbons or liquid carbon dioxide with surfactants
- Decontamination with supercritical carbon dioxide plus modifiers/cosolvents.

The present study evaluated the use of carbon dioxide in its liquid and supercritical state for the extraction of pesticides as well as for cleaning and degreasing ethnological objects with the aim of identifying the most appropriate conditions to achieve this goal.



FIGURE 2. Dichlorodiphenyltrichloroethane (DDT) spot deposits on a flute from the Museum of Musical Instruments in Leipzig, Germany.

## CLEANING PROCEDURES

The use of traditional wet methods for cleaning objects removes dust and soiling from their surfaces but has little impact on the matrix of artifacts. However, care must be taken to ensure that the cleaning procedures used for the removal of deleterious or toxic compounds do not affect the object itself, particularly if the soiling to be removed is composed of both lipophilic and hydrophilic materials. For example, indiscriminate removal of fats, oils, and waxes from objects such as wool, leather, and fur can make them particularly frail and brittle, thus putting them at risk for handling and future cleaning interventions. In addition, some organic solvents commonly used for cleaning, such as perchloroethylene, also may affect the conservator, given that most halogenated solvents used in museum environment are carcinogenic, as well as damaging to the ozone layer, thus affecting the global environment.

To overcome this dilemma, new methods using environmentally friendly solvents that can be reused are being developed. The regeneration of the solvent also simplifies the process of elimination of the soiling and toxic burden they may have extracted during use, so that these chemicals can be handled appropriately. One such solvent is carbon dioxide. This gas is more easily obtained than the expensive organic solvents presently used. Furthermore, it can be used in a liquid phase, or in a supercritical state, it is readily recycled given that the removal of the contamination products is straightforward.

## THE CARBON DIOXIDE SYSTEM

Carbon dioxide,  $\text{CO}_2$ , is a gas at ambient temperature and pressure. Changes in temperature and pressure may turn it into a solid, a liquid, or a supercritical fluid. Figure 3 shows the phase diagram for this compound.

Solid carbon dioxide is usually referred to as “dry ice,” and in the form of particles (and even pellets), it is sprayed

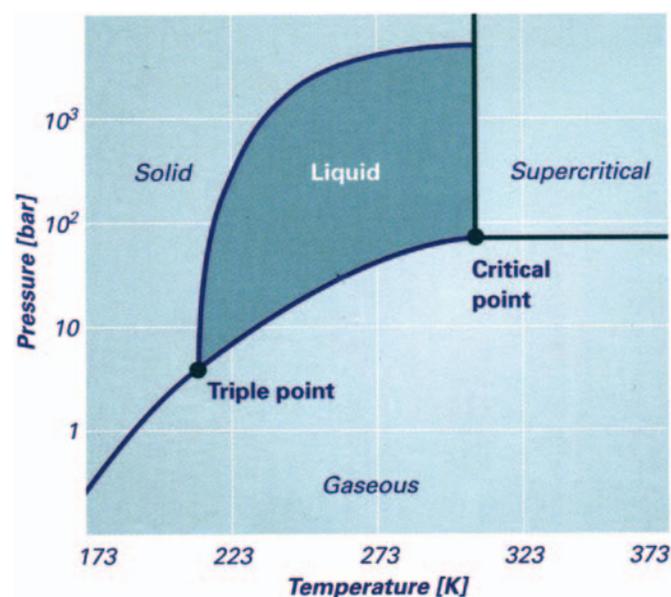


FIGURE 3. Phase diagram for  $\text{CO}_2$ .

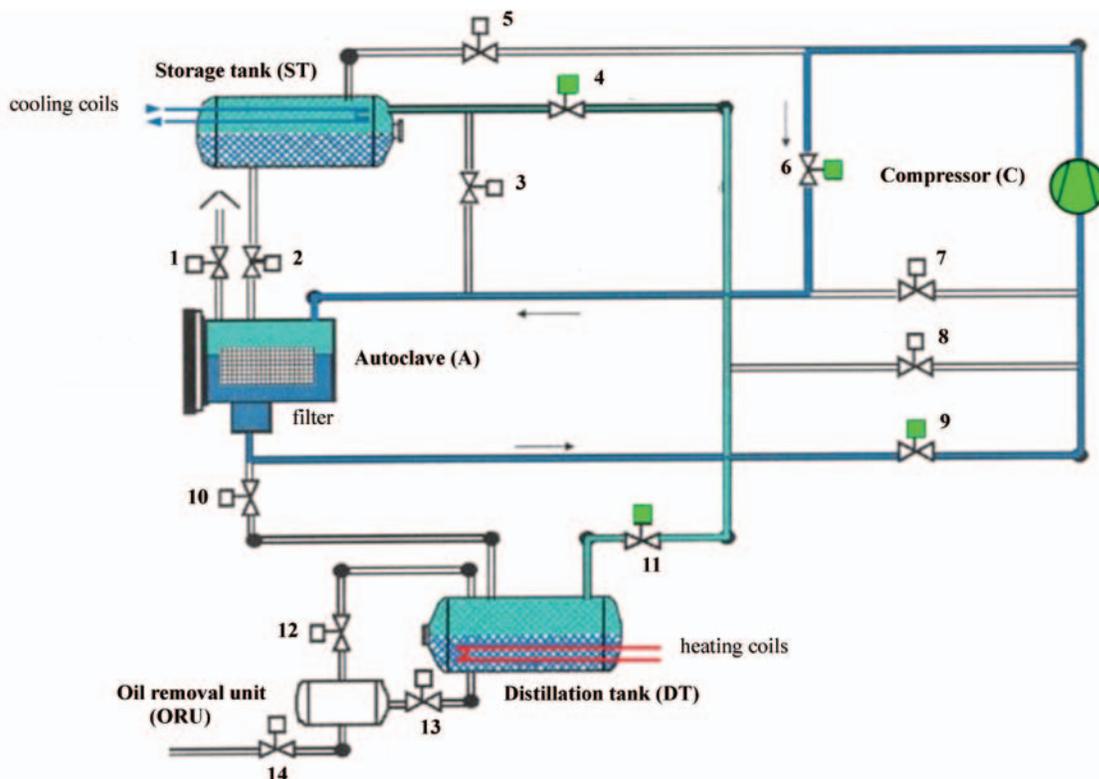
under pressure to clean relatively flat and smooth surfaces. For example, it was used to remove the paint from the interior of the Statue of Liberty and is currently used in Germany to remove wax from wooden floors because the frozen wax particles detach easily from the wood, as does paint from metal. As dry ice sublimates directly into gaseous  $\text{CO}_2$ , no residues are left.

The triple point for  $\text{CO}_2$ , where the three phases—solid, liquid, and gas—can coexist, is at approximately 5 bar (0.5 MPa, ~5 atm) and  $-57^\circ\text{C}$  (216°K). Carbon dioxide turns liquid at temperatures between  $15^\circ\text{C}$  and  $20^\circ\text{C}$  (288°K–293°K) and at 4–5 MPa pressure. The liquid is stable up to about  $31^\circ\text{C}$  (304°K) and 7.4 MPa where the critical point of  $\text{CO}_2$  lies. Above this temperature and pressure, only the supercritical fluid exists in which the physical differences between liquid and gas disappear, hence its denomination as “fluid.”

Liquid carbon dioxide ( $\text{L-CO}_2$ ) is nonpolar, but its polarity increases with increasing pressure. Therefore, it can

serve as a solvent for nonpolar molecules, such as short hydrocarbon chains, i.e., fewer than 20 carbon atoms in length, as well as for aldehydes, ketones, and ethers. Even larger molecules, such as fats, oils, and waxes can at least be partly solubilized. However, it cannot remove polar compounds that occur in the contaminating materials, and for this purpose modifiers, such as tensioactive agents, are added.

Supercritical fluid ( $\text{SC-CO}_2$ ) is being used industrially for many purposes, such as extracting caffeine from coffee beans and hop extracts from hop cones. Since the 1970s, it has been used in the cosmetic and pharmaceutical industry to extract active ingredients from plant materials. It is also used as a carrier to impregnate timber with organic fungicides (Iversen et al., 2003) and to improve consolidation of waterlogged wood with polyethylene glycol (Chaumat et al., 1999). Other uses of  $\text{SC-CO}_2$  are the decontamination of wooden objects, with and without polychromy, from pesticide residues such as DDT, Lindane, and pentachlorophenol (PCP) (Unger, 1998; Jelen et al.,



**FIGURE 4.** Flow diagram of the UniClean process with  $\text{L-CO}_2$ . Valves in the system are (1) autoclave (A) safety valve; (2) A filling valve; (3) purging valve; (4) storage tank ventilation valve; (5) gas recovery valve; (6) pressure valve; (7) gas recovery valve; (8) compressor (C) gas valve; (9) C liquid valve; (10) A draining valve; (11) distillation tank gas valve; (12) oil removal unit (ORU) gas valve; (13) ORU filling valve; (14) ORU draining valve.

2003; Unger et al., 2004). Pesticides can also be extracted from textiles using SC-CO<sub>2</sub> with the same approach (von Ulmann, 2003). The effect of SC-CO<sub>2</sub> on color retention of different paint layers on wood has been addressed by Sungmo et al. (2004).

## LIQUID CARBON DIOXIDE (L-CO<sub>2</sub>)

### METHODS

Two plants were used for the experiments reported herein. The first was the UniClean apparatus developed by the Union Engineering A/S Company in Fredericia, Denmark. This company also developed the procedure that industry uses to clean electronic accessories. The second system was the experimental plant at the wfk-Cleaning Technology Research Institute in Krefeld, Germany.

One experiment in cleaning, degreasing, and decontaminating ethnographic objects was carried out in the UniClean plant (Unger et al., 2006; Tello and Unger, 2006). Its flow diagram is schematically represented in Figure 4. The principal parts of the system are the reservoir holding the CO<sub>2</sub>, an autoclave that serves as the washing chamber, a distillation tank, the oil and fats separation tank, and a CO<sub>2</sub> compressor. Figure 5 shows the appearance of the UniClean 450 model. The objects to be cleaned are placed in a stainless steel basket in the autoclave-washing chamber (see Figure 6). When the chamber is closed, it is flooded with L-CO<sub>2</sub> that circulates through it, thus washing the objects placed in the basket. The process is carried out at 15°C–20°C and at 5–6 MPa. The time required for cleaning the objects varies from half an hour to 24 hours. When the chamber is drained, contaminated L-CO<sub>2</sub> is sent to the distillation tank where it is separated from the soiling materials by evaporation, and the extracted contaminants are collected in the separation tank.

Another experiment was carried out at the experimental plant in Krefeld, Germany, shown in Figure 7. The same temperatures and pressures were used as for the UniClean system, and the cleaning time was between half an hour and one hour. In contrast to the UniClean apparatus and procedure, the washing cylinder of the wfk plant moved slowly.

All experiments with L-CO<sub>2</sub> were performed without the addition of surfactants to determine the efficiency of the pure liquid. Although it would have been desirable to test special surfactants to improve the rate of decontamination, time constraints did not allow further tests. Surfactants are mostly used to remove polar substances, such as inorganic dirt particles, and for use on museum objects



FIGURE 5. Appearance of the UniClean 450 plant.

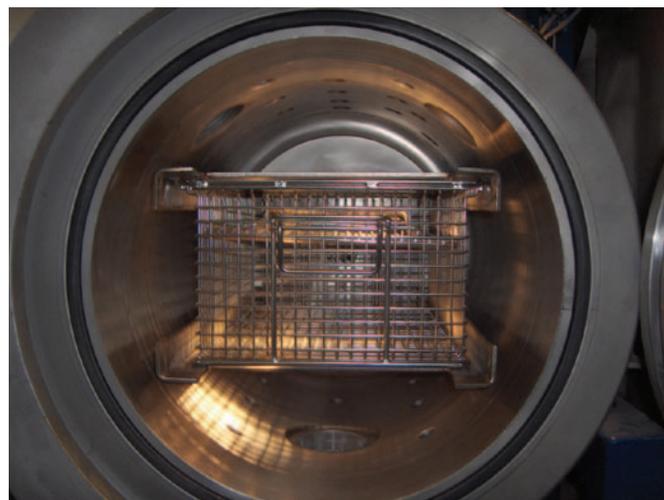


FIGURE 6. Autoclave-washing chamber with stainless steel basket.

whose composition should be well known; otherwise, their use may have a negative effect on the treated objects.

## RESULTS

Preliminary testing of the procedure was carried out on several objects as described below.

**PINEWOOD PANEL.** One half of a pinewood panel from the Green Vault of a room at the Staatliche Kunstsammlungen Dresden in Germany was used for the experiment. The panel previously had been treated with wood preservatives (“Hylotox 59” with 3.5% DDT and 0.5% Lindane and probably also with “Hylotox IP”



FIGURE 7. The experimental plant at wfk-Cleaning Technology Research Institute in Krefeld, Germany.

containing 5% PCP and 3% DDT because the presence of PCP was found on the sample). The sample clearly showed the presence of white DDT efflorescences on the dark brown background, as shown in Figure 8, top. The left half of the sample, with a weight of 184.8 g was subjected to L-CO<sub>2</sub> cleaning in the UniClean plant.

Figure 8, bottom, shows the wood panel after cleaning with L-CO<sub>2</sub>. It can be seen that the color has intensified showing the color variations of the applied tincture and the disappearance of the white DDT crystals. Table 1 presents the results of the analysis carried out before and after the treatment with L-CO<sub>2</sub>. As can be seen, there was a significant diminution of DDT and Lindane concentration. There was no significant change in the concentration for PCP; the slightly increased value can be attributed to uneven distribution of the contaminant in the sample. In spite of the positive results obtained it is to be noted that concentrations of DDT above 30 ppm and of Lindane above 100 ppm in wood remain high for these pesticides



FIGURE 8. Pinewood panel with white efflorescences of DDT on the dark brown background (top), and after cleaning with L-CO<sub>2</sub> (bottom).

(Zujest, 2003). This means that the procedure has to be repeated to reach the desired safety levels.

**EPITAPH FRAGMENT.** A second sample was an epitaph piece from the Cathedral in Zwickau, Germany. In the early twentieth century, such wooden epitaphs had been found weakened from insect attack. Consequently,

**TABLE 1.** Pesticide concentrations found on a pinewood panel before and after treatment with L-CO<sub>2</sub>. (DDT, dichloro diphenyl trichloroethane; PCP, pentachlorophenol; the dash indicates no reduction occurred.)

Treatment state	Contaminant value (ppm = mg/kg)		
	DDT	Lindane	PCP
Before	1840	186	80.9
After	204	125	81.0
% Reduction	88.9	32.8	—

they were impregnated with linseed oil, using either a cold or hot procedure. Over the years, this treatment softened the wood and the linseed oil oxidation products partly oozed out. The objective of the test was the extraction of the polymerized linseed oil and its oxidation products.

The fragment, weighing 19.3 g, was subjected to a 24 hour extraction with L-CO<sub>2</sub>. The minimal weight loss, around 1.7%, indicates that this method is not applicable for the removal of polymerized linseed oil and its decomposition products. It should be pointed out that tests on similar fragments using SC-CO<sub>2</sub> by itself, and with various

**TABLE 2.** Amount of aged linseed oil extracted by different methods (L-CO<sub>2</sub>, liquid carbon dioxide; SC-CO<sub>2</sub>, supercritical carbon dioxide; DMSO, dimethyl sulfoxide).

Method	Cosolvent	Amount extracted (%)
L-CO <sub>2</sub>	none	1.7
SC-CO <sub>2</sub>	none	1.5
SC-CO <sub>2</sub>	3% Acetone	1.8
SC-CO <sub>2</sub>	3% Methanol	2.2
SC-CO <sub>2</sub>	3% DMSO	17.6

cosolvents, were also unsuccessful (J. J. Morrell, Oregon State University, personal communication, 1997). These tests were carried out at 40°C, 4000 psi (~281 bar, 28 MPa). Table 2 compares these results. It can be seen that CO<sub>2</sub> is not effective in the removal of the aged linseed oil. Although the addition of dimethyl sulfoxide (DMSO) improved the extraction significantly, this is not a viable option of cultural heritage objects.

**GILDED LEATHER HANGING.** An eighteenth-century gilded leather hanging from the Frens Palace (see Figure 9), presumably manufactured in the Netherlands,



**FIGURE 9.** Leather hanging from the Frens Palace: left, front side, and right, back side.

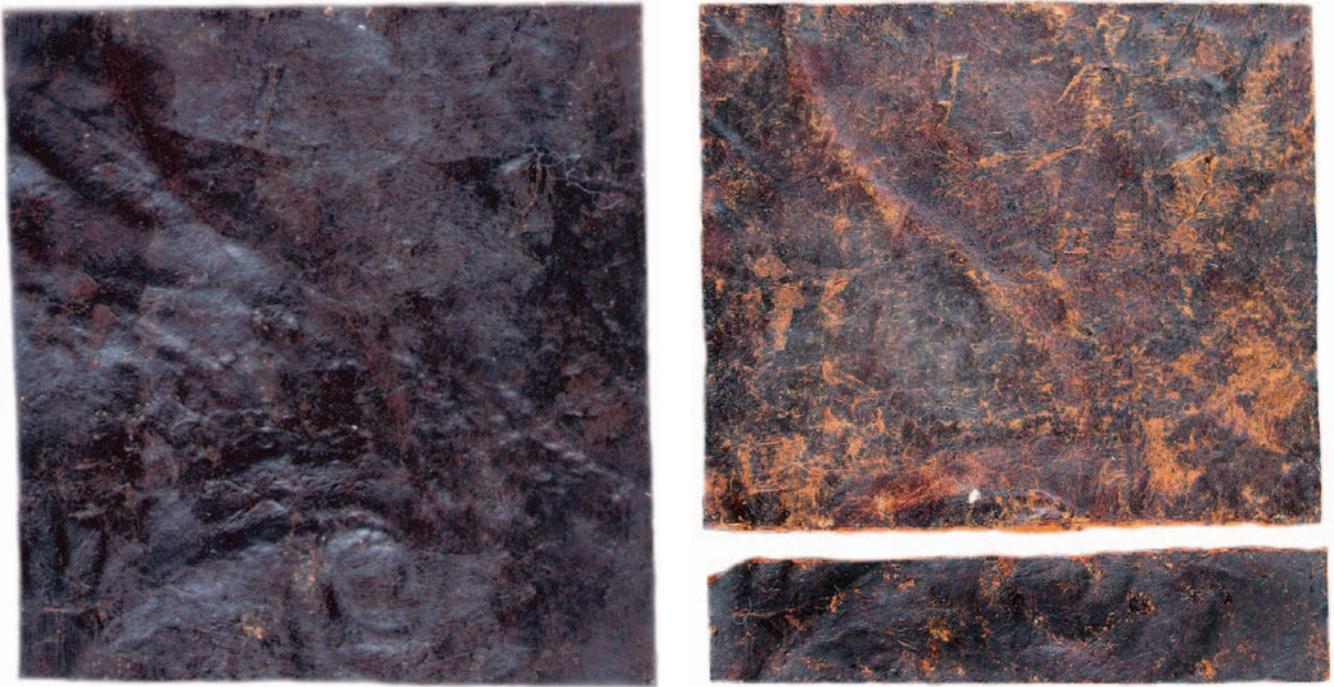


FIGURE 10. Back side of overlubricated leather hanging from the Frens Palace: left, before cleaning; right, after cleaning with L-CO<sub>2</sub>.

also was tested. The calf or kid leather had been tanned with natural tanning agents. The hanging was greased successively with a synthetic wax (Lypoderm Fat A and Lypoderm from Licker SA), Montan wax, and Vaseline to simulate the application of fat-rich products generally used in the conservation of these objects (see Figure 10, left). For instance, fat contents of about 20% by weight have been found in leather that normally would contain about 5%–6% (J. Wouters, Institut Royal du Patrimoine Artistique, Brussels, personal communication, 1998).

The cleaning improved significantly the backside of the hanging, as shown in Figure 10, right, and the grease tackiness on the front side was reduced. However, the painted layer on the front side showed an increased tendency to flake off. It was difficult to determine whether or not this negative effect was due to the treatment or merely a consequence of object handling during this procedure. Microscopic examination of the surface showed that small white opaque areas had formed on top of the painting, and these could be attributed to a partial solubilization of the beeswax, which probably was applied as a coating. No negative effects on the shrinkage temperature of the leather or its pH were observed: the shrinkage temperature

remained at 44°C, and pH remained unchanged at around 4.8–4.9.

The treated sample suffered a weight loss of about 6%, while the extraction of lipophilic materials was reduced by 15.5%, showing the effectiveness of this method for the elimination of fatty materials. One of the advantages this procedure has for leather is that entire hides can be treated at a same time, ensuring a uniform extraction. However, additional tests are necessary to optimize the parameters needed for a practical application of this treatment.

**WOOLEN BLANKET.** A Chilean Patagonia woolen blanket was yet another sample that was examined (see Figure 11). The white wool was partly dyed in red, orange, green, blue, and violet colors. The blanket showed moth holes and was darkened by soiling. The wool had a greasy feel, and the fibers appeared brittle. Some loose fibers were tested from this object (see Figure 12). Analyses showed that the object had been treated with organochlorine pesticides and that it was also contaminated with heavy metals.

After the cleaning, the woolen fibers felt softer and more elastic. The color was lighter and brighter, and microscopic observation confirmed the cleaning by the shine of



FIGURE 11. Woolen blanket from Chilean Patagonia.



FIGURE 12. Woolen fibers from the Patagonian blanket before treatment with L-CO<sub>2</sub>.

the fibers. The weight loss of the sample during cleaning was of 4.7%. The reduction of contaminant concentration is reported in Table 3. Although the amount of DDT was reduced, the low content of Lindane was not significantly affected. Also, the amounts of mercury and arsenic may be misleading because the contamination is probably not uniform across the sample. Further testing with SC-CO<sub>2</sub>

TABLE 3. Concentrations of contaminants found on woolen fibers from a Patagonian blanket before and after treatment with L-CO<sub>2</sub>; the dash indicates no reduction occurred.

Treatment state	Contaminant value (ppm = mg/kg)			
	DDT	Lindane	As	Hg
Before	66.3	1.3	4	240
After	5.9	1.1	3	290
% Reduction	91.1	15.4	25.0	—

showed that mercury levels could be reduced by 76% (Tello et al., 2005a, 2005b).

**SEAL GUT PARKA.** A piece of a translucent seal gut parka, about 37  $\mu\text{m}$  (0.037 mm) thick and about 41  $\times$  6 cm, was taken and halved, one for treatment and the other as control. The piece was very undulated and wrinkled (see Figure 13, top), and the surface was sticky and had a waxy appearance. Darker spots of waxes and grease were visible on the surface because of conservation treatments carried out in the 1960s.

Previous cleaning attempts of some areas had been carried out using a mixture of isopropanol and isooctane (1:3) and were relatively successful (Weidner, 2000). However, treatment of the entire object could not be carried out because of health concerns and the lack of adequate installation and financial support.

The cleaning procedure reduced the weight of the sample by 4.4% mainly because of inorganic soiling materials removed by the process (Unger et al., 2006). The thickness of the seal gut strip was reduced from 37 to 35  $\mu\text{m}$ , and although it still was wrinkled, it was more pliable and no longer felt tacky (see Figure 13, bottom).

## SUPERCRITICAL CARBON DIOXIDE (SC-CO<sub>2</sub>)

### METHODS

SC-CO<sub>2</sub> tests were carried out using two different units. One was a 150 mL laboratory plant (see Figure 14) for screening experiments at the Fraunhofer Institute for Environmental Safety and Energy Technology (UMSICHT) in Oberhausen, Germany. The second was the 10 L high-pressure plant of the Messer Griesheim HPE Technical Centre in Krefeld, Germany (see Figure 15) (Tello et al., 2005a).

For the extraction in the 150 mL high-pressure view cell, L-CO<sub>2</sub> was compressed to 350 bar (35 MPa,



FIGURE 13. Piece of a seal gut parka. Top, before treatment. Bottom, after treatment with L-CO<sub>2</sub>.



FIGURE 14. The 150 mL laboratory plant at the UMSICHT installation.

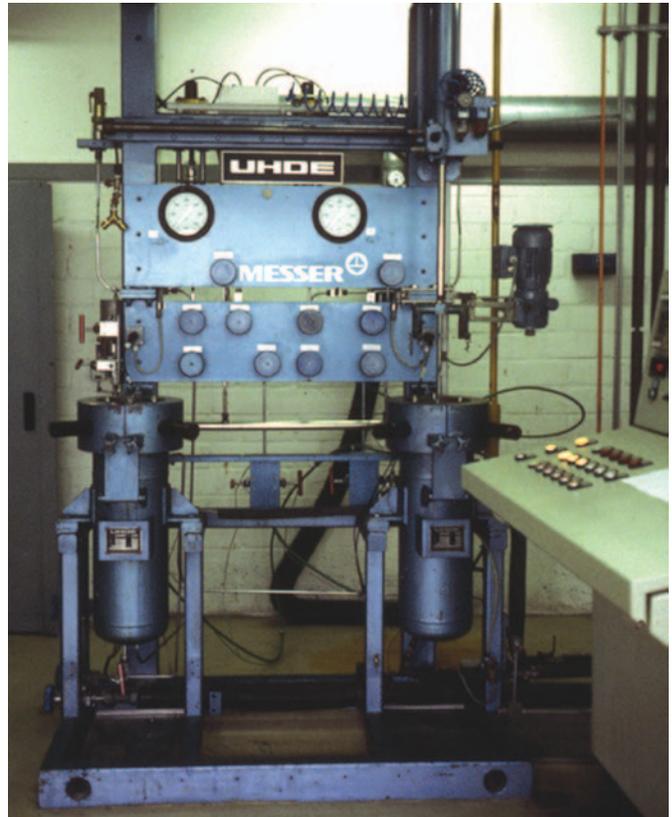


FIGURE 15. The 10 L high-pressure extraction plant at the Messer Griesheim Technical Centre.

~350 atm), using a piston pump, and heated to supercritical conditions (40°C), in a heat exchanger, before it entered the view cell containing the samples. The pressure build up lasted 15 minutes, and the time of extraction was seven hours. The pressure release lasted one hour, and the mass flow of CO<sub>2</sub> was recorded at 2 kg/h. The relatively high flow was chosen to obtain a strong decontamination effect and to prevent saturation of the CO<sub>2</sub> with the pesticides. Ethanol served as a cosolvent with and without the additional use of the chelating agent trimercaptotriazine 15 (TMT 15). Further details are given in an unpublished research report of the Fraunhofer Institute.

The high-pressure extraction plant in Figure 15 contains two 10 L extractors. For better handling of loose samples or bulk materials, a 7 L inner metal basket is used. By using one of the extractors, two experiments were carried out with the following parameters: extraction pressure, 250 bar (25 MPa, ~250 atm); extraction temperature, 40°C; extraction duration, three hours; CO<sub>2</sub> flow

rate, 20 kg/h. The 25 MPa pressure was reached within 34 minutes. The pressure release took one hour (first experiment) and two hours (second experiment).

After closing the extractor, liquid CO<sub>2</sub> was introduced from the collecting vessel. For further pressure build-up, a CO<sub>2</sub> membrane pump was used and the CO<sub>2</sub> from the collecting vessel was passed through a heat exchanger to cool it down to about 0°C to prevent cavitation due to vapor bubbles forming in a quickly moving solvent. During passage through the extractor, the CO<sub>2</sub> accumulated the soluble components from the materials. After the set extraction time had passed, the mixture was depressurized to subcritical conditions (50–60 bar, ~50–60 atm, and 25°C–30°C) by means of a valve. By reducing the pressure and/or temperature to subcritical conditions, the CO<sub>2</sub> returned to its gaseous state and the extracted materials precipitated in the 7 L separator. The gaseous CO<sub>2</sub> was again liquefied in a refrigerated condenser and collected in the collecting vessel.

To prevent the formation of L-CO<sub>2</sub> or of dry ice respectively during expansion, the density of CO<sub>2</sub> in the range between 100 and 50 bar (10–5 MPa, ~100–50 atm), was continuously changed in a linear manner. This also prevented damage to the inner structure of the materials and objects.

The conditions of the ethnographic samples were documented, examined macro- and microscopically and photographed before and after treatment. All specimens and objects were weighed. The amounts of heavy metals, DDT, Lindane, and PCP contamination on the materials also were determined before and after extraction.

## RESULTS

Preliminary testing of the procedure with SC-CO<sub>2</sub> was carried out on several samples from materials and objects of the Ethnological Museum in Berlin, Germany. The entire range of sample specimens that were tested for the extraction with SC-CO<sub>2</sub> is largely described by Tello (2006). A selection of some of these materials and objects is presented below.

**FUR, BUNDLE OF FEATHERS, AND WOOL TISSUE.** For testing in the 150 mL laboratory plant, the selected samples included a piece of fur from a small model (57 cm long, shown in Figure 16) of a fur coat from the Samojades, a feather bundle from the Amazon region, and archeological wool tissue (see Figure 17, left). Analyses showed that the different samples had been treated with inorganic (As and Hg compounds) and organic pesticides (DDT, Lindane, PCP).



FIGURE 16. Model of a fur coat from the Samojades.

Figure 17 (right) shows the samples after extraction in the high-pressure view cell of the 150 mL laboratory plant. The fur and the wool tissue showed a partial loss in weight, which was probably caused by the removal of dust, grease, water, and pesticides. The haptic examination of all samples showed no difference before and after the extraction. The sample of fur was somewhat dry, the skin appeared to be more affected than the fur hair because it was degreased considerably. The visual and microscopic examination of the wool tissue suggested a positive cleaning effect, and the brilliance of the bundle of feathers was unchanged.

Table 4 presents the contaminant content before and after treatment with SC-CO<sub>2</sub> for the fur, bundle of feathers, and wool tissue samples. As can be seen, a significant decrease in mercury and DDT concentration was achieved. Lindane was reduced to a high extent for the fur sample, but when found in low concentrations, it appeared not to be affected by the treatment. However, very



FIGURE 17. Left column, from top to bottom, samples of fur, bundle of feathers, and wool tissue before extraction. Right column, samples after extraction with SC-CO<sub>2</sub>.

**TABLE 4.** Concentrations of contaminants found on fur, feathers, and wool samples before and after treatment with SC-CO<sub>2</sub>; ND = not detected; a dash (-) indicates no reduction occurred or could be measured.

Object	Treatment state	Contaminant value (ppm = mg/kg)				
		DDT	Lindane	PCP	As	Hg
Fur	Before	358	3.9	ND	8	800
	After	8.4	0.3	0.2	19	94
	% Reduction	97.6	92.3	—	—	88.3
Feathers	Before	66.3	0.1	ND	<1	171
	After	0.3	ND	0.2	2	16
	% Reduction	99.6	—	—	—	90.6
Wool	Before	ND	ND	0.4	<1	42
	After	0.2	ND	0.3	4	10
	% Reduction	—	—	25.0	—	76.2



**FIGURE 18.** Samples of the caribou fur (top) and grass blades before extraction with SC-CO<sub>2</sub>.

low concentrations of contaminants were not influenced by the treatment.

**BLADES OF GRASS AND CARIBOU FUR.** Samples of grass blades and a piece of caribou fur were tested in the 10 L high-pressure extraction plant. The ma-

**TABLE 5.** Condition of grass blades and caribou fur before and after treatment with SC-CO<sub>2</sub> in the 10-L high-pressure extraction plant.

Characteristic	Condition before	Condition after
	<b>Grass blades (weight loss = 1.6%)</b>	
Stability	Stable	No change
Flexibility	Flexible, smooth	No change
Color	Yellowish gray	Slight lightening of color
Residues	Some soiling in the longitudinal grooves visible as small black spots	Visible cleaning effect
Surface	Regular grooves	No change
	<b>Caribou fur (weight loss = 5.3%)</b>	
Stability	Skin/fur intact and flat	No change
Flexibility	Fur is soft and elastic with firm grip; skin is flexible; edges are smooth	No change
Color	White and brown colors of hair are well distinguishable	Skin is slightly white
Residues	Skin is greasy	Skin is degreased; yellowish residues in pulp tissue
Surface	Hair is slightly wavy; structure of skin diaphragm is clearly visible, transparent	Hair is softer

terials were from Alaska and served as illustrative materials in the conservation laboratory of the Ethnological Museum in Berlin (see Figure 18). The experiment was to clarify whether or not damage of materials could be expected from this treatment. Table 5 reports the weight loss of the samples (grass blades 1.6% and caribou fur 5.3%) and the visual and haptic evaluation on the condition for these materials before and after the extraction experiment.

Visual evaluation after extraction showed a lightening effect on the grass blades that could be attributed to the removal of the small black spots that were in the grooves before extraction. Further examination by scanning electron microscopy clearly confirmed that loosely scattered and embedded dust was removed as a result of the extraction (Figure 19). Changes in tensile strength of the grass blades before and after extraction were evaluated by the measured modulus of elasticity.

The caribou fur showed slight differences in the haptic properties and residues were found in the pulp tissue of the sample (see Figure 20). These highly interesting observations lead to further analyses of the caribou fur using

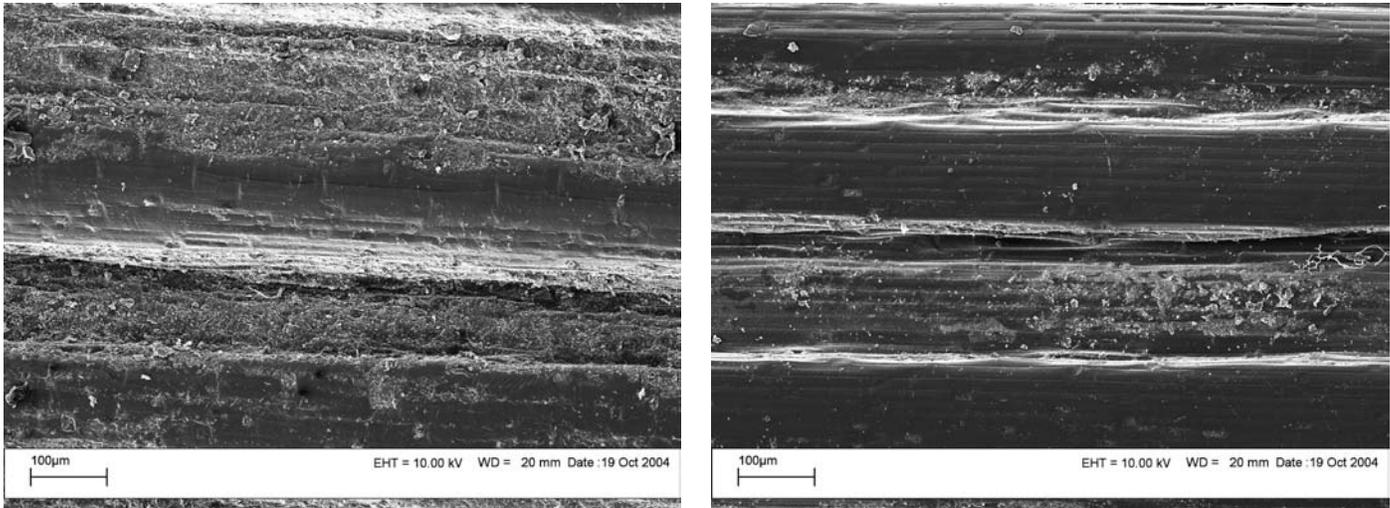


FIGURE 19. Scanning electron microscope photomicrograph of a grass blade. Left, before treatment. Right, after extraction with SC-CO<sub>2</sub>.



FIGURE 20. Residues left on the paper tissue after extraction of the caribou fur with SC-CO<sub>2</sub>.

pyrolysis gas chromatography/mass spectrometry. The results, shown in Figure 21, clearly demonstrate the noticeable impact of SC-CO<sub>2</sub> on the caribou fur. This was unexpectedly very positive because the free fatty acids from the triglycerides in the fat and their degradation products, such as aldehydes, i.e., octanal, were extracted rather than

the fat itself. And, it is well known that aldehydes will lead to cross-linking of proteins, thus inducing their hardening, which may in turn cause damage to fur.

## DISCUSSION AND CONCLUSIONS

The decontamination achieved with L-CO<sub>2</sub> for the tested pinewood panel is similar to that obtained with SC-CO<sub>2</sub> for other wooden objects. For example, DDT content was reduced by 89% with the L-CO<sub>2</sub> method, while the SC-CO<sub>2</sub> method achieved values ranging between 97% and 27%, depending on the object, with the most frequent value being around 95% (Unger, 2003). In the case of Lindane, the content was reduced only by 15% with L-CO<sub>2</sub> but ranged between 17% and 99%, with the most frequent value around 93%, for the SC-CO<sub>2</sub> method. The poor performance of L-CO<sub>2</sub> in the removal of Lindane can be attributed to the poor solubility of this pesticide in the liquid. Because of its higher polarity and hence lower solubility in CO<sub>2</sub>, PCP could not be extracted effectively with L-CO<sub>2</sub> or SC-CO<sub>2</sub>. Further experiments with addition of surfactants/modifiers need to be carried out.

Arsenic and mercury compounds were not removed to a sufficient extent with L-CO<sub>2</sub>. In the case of inorganic pesticides, further tests using chelating agents are necessary.

The effect on the decontamination rate by variation of extraction pressure and extraction temperature using L-CO<sub>2</sub> or SC-CO<sub>2</sub> could not be suitably clarified and is the subject of future research.

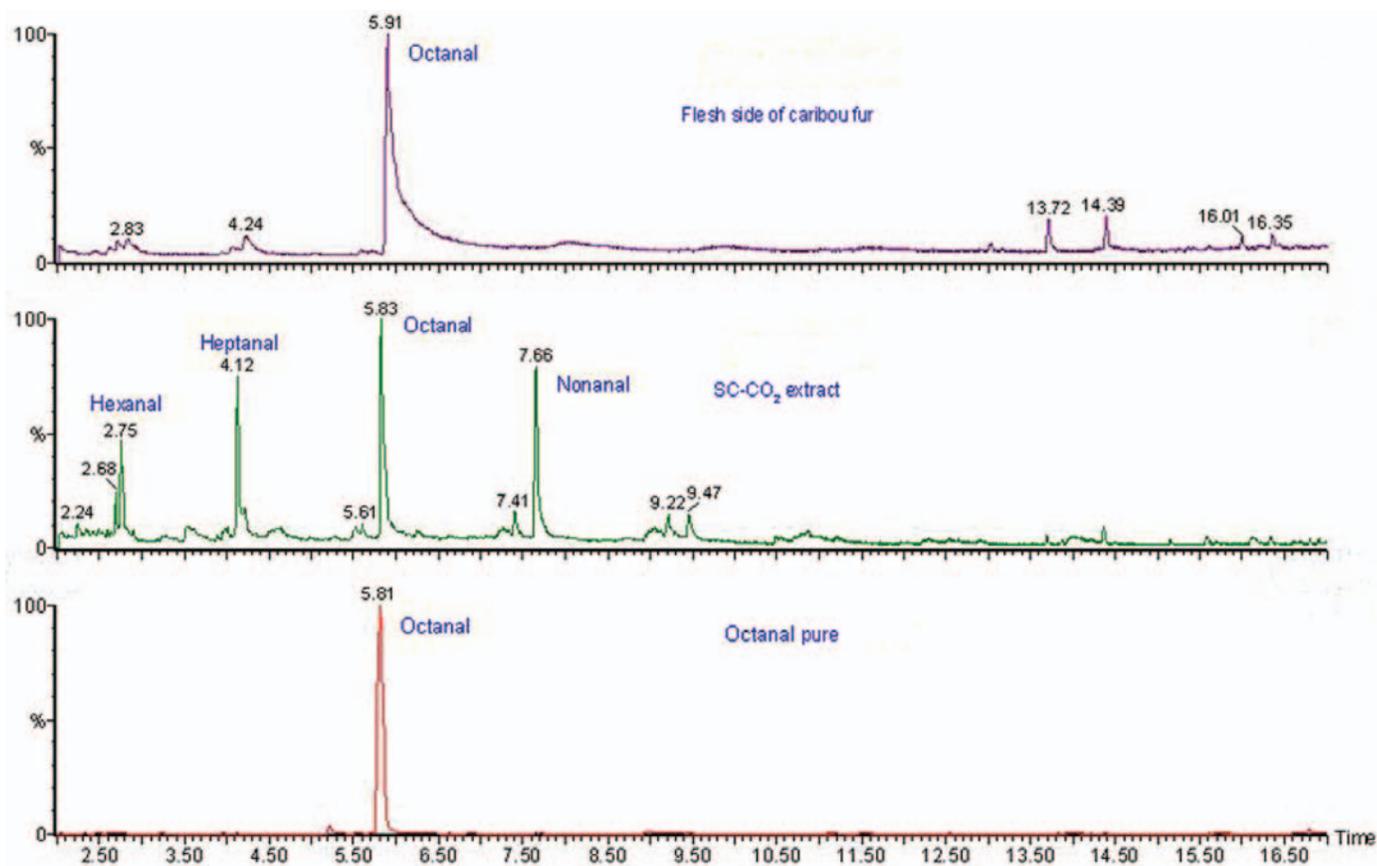


FIGURE 21. Pyrolysis–Gas Chromatography–Mass Spectrometry (Py-GC-MS) results: top graph, backside of the caribou fur; middle, SC-CO<sub>2</sub> extract found in the paper tissue; bottom, pure octanal.

Most objects did not show any marked changes in their properties during treatment with either L-CO<sub>2</sub> or SC-CO<sub>2</sub>. One exception was found in the fur samples, wherein the extent of degreasing varied, depending on the test parameters. In the case of materials with oily and fatty components, treatment with SC-CO<sub>2</sub> extracted mainly free fatty acids and the resulting degradation products from chemical aging processes of fat.

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# Pesticide Extraction Studies Using Supercritical Carbon Dioxide

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**ABSTRACT.** Because records for pesticide control procedures are often incomplete, a study was planned to determine if an unknown organic pesticide might be extracted as a residue on commonplace objects using supercritical carbon dioxide (SC-CO<sub>2</sub>). In this work, samples of chrome-tanned leather representing artifact material were treated with known quantities of a commercial Diazinon solution and, subsequently, with SC-CO<sub>2</sub> for two minutes, to determine the extent of removal of the pesticide residue. Extraction effectiveness was improved using acetone as a cosolvent. Detection of the levels of extracted Diazinon was performed by toxicological screening using rat lung epithelial cell cultures. SC-CO<sub>2</sub> may prove to be a viable solvent or cosolvent system to extract pesticides from artifacts without damaging fragile materials and without leaving a residue. A systematic study of museum materials and labeled pesticides should be carried out to define the utility of this method.

**KEYWORDS:** SC-CO<sub>2</sub>, cosolvents, pesticide removal, cleaning, Diazinon, museum objects.

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## INTRODUCTION

Often, in the past, cultural artifacts in museums were treated with a range of poisons and pesticides to prevent or retard deterioration, insects, rodents, and mold. Passage of the Native American Graves Protection and Repatriation Act (NAGPRA) in 1990 has established a mechanism for Native American groups to reclaim certain museum artifacts and return them to cultural use. In the meantime, new developments have led to the recognition and banning of many of the old poisons and pesticides. Consequently, there is an increased need to identify and report objects that pose human health risks and an increased urgency to develop methods to mitigate hazards posed through direct human contact (Odegaard and Sadongei, 2005). In May 2003, funding from the University of Arizona Vice President for Research was awarded to initiate an interdepartmental collaborative program to study pesticide removal techniques that would enable objects to return to cultural use.

Many pesticides are short lived and degrade in the environment. Others are persistent and may remain on artifacts several decades after application. Methods

to decontaminate museum objects treated with pesticides have been of critical interest to museums holding contaminated collections and to Native American tribes seeking to return these objects to cultural use. Many techniques that had been previously discussed in the museum and conservation literature include the use of high-efficiency particulate air (HEPA) filtered vacuums, compressed air, washing, ultraviolet light, chemical alteration, freeze-drying, lasers, and microbial detoxification (Odegaard, 2001). The applicability of supercritical carbon dioxide (SC-CO<sub>2</sub>) as a pesticide removal technique for museum objects has been studied (Jelen et al., 2003; von Ulmann, 2003; Kang et al., 2004; Tello et al., 2005; Tello, 2006). However, these studies address the use of unmodified SC-CO<sub>2</sub>. The purpose of the present study involved two areas of research with the following aims:

- Develop a protocol for methods that would test the use of SC-CO<sub>2</sub> for the removal of an organic pesticide from simulated artifacts.
- Assess the effectiveness of the pesticide residue removal through the use of rat lung epithelial (RLE) cell culture technique as it relates to potential human health risk.

Supercritical CO<sub>2</sub> is a solvent that has the potential to extract chemicals without leaving a residue of its own. The use of SC-CO<sub>2</sub> for removing pesticides from solid objects has several advantages over other methods. A low surface tension and viscosity allows SC-CO<sub>2</sub> to wet the surface of any object and rapidly penetrate porous materials. Releasing the system pressure causes CO<sub>2</sub> to go directly from a supercritical fluid state to a gas without becoming a liquid. An object consequently comes out dry after processing. CO<sub>2</sub> has low toxicity and is nonflammable, and as a gas it is readily separated from chemical additives and products that have much lower vapor pressures. Furthermore, this treatment may be considered acceptable by tribes because the use of SC-CO<sub>2</sub> involves minimal handling during the cleaning process, utilizes natural materials, and does not permanently introduce new products. The aim of the study was to determine if adding small quantities of a polar solvent to the SC-CO<sub>2</sub> would improve its removal of more polar pesticides. The substrate for the particular pesticide to be studied was not important; the focus was the pesticide, which had to be polar and mostly insoluble in pure SC-CO<sub>2</sub>.

Generally, low molecular weight organic compounds are soluble in SC-CO<sub>2</sub>, but high molecular weight organic compounds, especially if they are polar, are nearly

insoluble (Poltzer et al., 1993). The solubility of molecules in SC-CO<sub>2</sub> is also a function of the density of the fluid, which can be manipulated by changing the pressure and temperature (Jones et al., 2004). Testing the effectiveness of SC-CO<sub>2</sub> for the extraction of organic pesticide residues required the application of a technique to assess the concentration of the pesticide on the sample before and after cleaning. In this study, that concentration was equated to the toxicity of the pesticide in the sample before and after the pesticide removal process. Such toxicity testing was provided here by RLE cell culture analyses (Riley et al., 2003).

## MATERIALS PREPARATION AND HANDLING

To develop a protocol and evaluate the ability of SC-CO<sub>2</sub> to remove pesticides from a diverse array of museum artifacts, two types of surrogate materials (leather and feathers) were investigated. The particular leather and feather samples were selected because they were readily available. The protocol for contaminating the simulated artifact material consisted in the application of dilute pesticide solutions to 5 × 5 cm chrome-tanned leather samples that previously had been cleaned and tested for inherent toxicity (i.e., baseline reactivity) with the RLE cell culture technique. The RLE cell response is an indirect approach and was considered appropriate because of its ability to detect a wide range of pesticide toxins on artifacts with unspecified pesticide residues. Therefore, it was used as an indicator rather than traditional analytical detection methods.

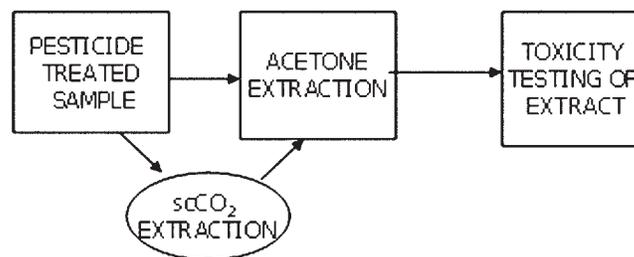
The impact of SC-CO<sub>2</sub> on brightly dyed feathers was also assessed in order to determine if the color or texture of a delicate material would be affected by the extraction process. The feathers were bought in a craft store, and digital pictures were taken before and after the extraction with SC-CO<sub>2</sub>. On the basis of visual and photographic comparison, the extraction process had no effect on the color or texture (see Figure 1). No microscopy examination was carried out for this preliminary assessment.

A broad spectrum commercial pesticide labeled "Ortho Diazinon, 25% active material" was purchased in a local garden supply store, as it was one of the few organic pesticides available. Although it was not a commonly used museum pesticide, it was considered to be suitable for the purposes of this study given its characteristics of polarity and SC-CO<sub>2</sub> solubility. It has since been withdrawn from use indoors and on lawns and gardens. Diazinon is an organophosphate, the chemical name is o,



**FIGURE 1.** Effect of supercritical carbon dioxide (SC-CO<sub>2</sub>) extraction on color and texture of three feathers: left, before extraction; right, after extraction.

o-diethyl o-(2-isopropyl-6-4-pyrimidinyl) phosphorothioate. Its use as a museum pesticide is documented by Pool et al. (2005). The product was diluted with reagent grade acetone to concentrations of 2 or 4 mg active ingredient per milliliter solution. The pesticide solution was applied slowly from a hypodermic syringe so that the leather samples were uniformly saturated. When all of the solution had been absorbed by the leather, the samples were allowed to dry while suspended in a gentle stream of ambient air. The samples were divided into two groups for pesticide removal. One set was subjected to Soxhlet acetone extraction. The other set was treated with supercritical CO<sub>2</sub> as the primary removal method, followed by the Soxhlet acetone extraction. A comparison of the two acetone extracts, made before and after the SC-CO<sub>2</sub> process, served to show what was extracted by the use of supercritical CO<sub>2</sub>. The flow of this experimental process is depicted in Figure 2.



**FIGURE 2.** Diagram of experimental flow.

The Soxhlet extractor is used to separate a contaminant of limited solubility, i.e., the pesticide, from the solvent. It consists of a distillation flask where the solvent is vaporized and goes to a reflux condenser via a side arm. The condenser drips the condensed liquid into a cylindrical chamber that contains the sample to be extracted and fills the chamber, allowing the extractable material to dissolve. A siphon on the side of this chamber allows the solvent to flow back into the distillation flask so that the system can be kept running as long as necessary. Although this Soxhlet process is not appropriate for artifacts, it did provide a rigorous and efficient means of removing the pesticide from the samples and was therefore important in evaluating the effectiveness of the SC-CO<sub>2</sub> procedure. Dilutions of these Soxhlet extracts were then introduced to RLE cells to evaluate the presence of any toxic material. Industrial grade acetone was not sufficiently pure for this process as it contained impurities that interfered with the RLE testing. The dose/response curves of the cells to the test solution provide a measure of the quantity of pesticide on the leather samples.

The experimental SC-CO<sub>2</sub> system used to process the leather samples consisted of a 200 mL stainless steel reactor fed by a liquid CO<sub>2</sub> bottle (see Figure 3). Samples were placed upright on the bottom of the reactor with the top edge leaning against the reactor wall. A disposable syringe was used to introduce 0.2 or 2 mL of acetone (analytical reagent grade) into the bottom of the reactor as far from a sample as possible to avoid direct contact. The reactor was closed, cooled to 8°C in an ice bath, and charged with liquid CO<sub>2</sub> (99.99%, Air Liquide Coleman grade) to a pressure of approximately 60 atm (6 MPa). When filled with liquid CO<sub>2</sub>, given the 200 mL volume of the reactor, the acetone concentration in the fluid was either 0.1 or 1 vol%.

The reactor was heated requiring approximately 12 minutes to cross into the supercritical CO<sub>2</sub> region, which typically occurred at 31°C and approximately 150 atm

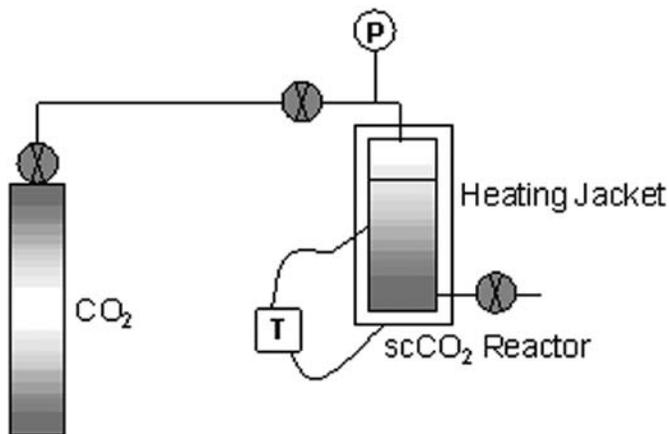


FIGURE 3. Schematic drawing of the SC-CO<sub>2</sub> reactor system. After loading, the reactor was chilled to 8°C and fed with liquid CO<sub>2</sub> to approximately 60 atm. The cylinder was closed, and the reactor was heated using a heating jacket and set point controller until the desired steady state conditions were reached. After processing, the fluid was exhausted through a needle valve.

(15 MPa), and another three minutes to reach the steady state processing temperature, in the range of 50°C–60°C, and pressure, in the range of 100–250 atm (10–25 MPa). The temperature and pressure ranges were chosen to vary the SC-CO<sub>2</sub> density from approximately 0.5 to 0.9 g/cm<sup>3</sup> based on the Peng-Robinson equation of state. The resistively-heated jacket and insulation covering the reactor allowed a temperature set point to be reached within ±5°C using a thermocouple and controller. Pressure was read using a Bourdon tube with an accuracy of ±20 psi (1.4 atm or 0.14 MPa) in the range 0–5,000 psi (340.2 atm or 34 MPa). All experiments were run as batch processes for a two minute soak time at steady state conditions. Cross-contamination was minimized by running pure SC-CO<sub>2</sub> through the system between experiments.

After processing, the reactor pressure was released quickly through a ¼ inch (6.35 mm) needle valve reaching ambient in less than 1 minute. The high mass flow rate out of the reactor was sufficient to entrain chemicals that were dissolved in the fluid during processing because no liquid residue was observed on the samples.

The extremely low viscosity and surface tension of SC-CO<sub>2</sub> makes it an ideal solvent for removal of contaminants from both exterior and interior of the object being cleaned. The organophosphate pesticide itself is a polar, slightly water-soluble material, while SC-CO<sub>2</sub> has the solvating character of *n*-hexane. Initial experiments showed that Diazinon was not sufficiently soluble in SC-CO<sub>2</sub> to

be completely removed. The addition of a cosolvent such as acetone is known to increase the solubility of slightly water-soluble contaminants (Xie et al., 2005).

#### RAT LUNG EPITHELIAL CELL CULTURE METHODS FOR TOXICITY TESTING

The lethal dosage for rats from inhaling an acute, short-term exposure of pesticide can be defined in milligrams per liter (of air) in hours. Thus, rat lung tissue was thought to be a good model to use to test the exposure to pesticides. One of the goals of this work was to use RLE-6TN (T-antigen negative) cell cultures to determine the effectiveness of the SC-CO<sub>2</sub> extraction procedure. This technique is a standard method of determining toxicity by exposing well-defined cultures to suspected toxic materials and determining the dilution of the toxins required to allow 50% of the cells to survive (LD<sub>50</sub>) (Okeson et al., 2004; Riley et al., 2005). If appropriate, this test for toxicity would obviate the need of isolating or identifying them. In this study, the RLE cells were useful for testing the protocol and the effectiveness of the SC-CO<sub>2</sub> extraction process. The tests for toxicity were conducted according to accepted protocols (Riley et al., 2003; Tello, 2006).

#### PESTICIDE REMOVAL RESULTS

To evaluate the ability of SC-CO<sub>2</sub> to remove the organophosphate pesticide from simulated artifacts without damaging their material structure or losing pigmentation, it was necessary to validate methods of extraction and the application of the RLE cell culture method for pesticide detection. Rat lung epithelial cell cultures are highly responsive to a variety of common pesticides that may have been used to treat artifacts in storage. Extracts displaying no toxicity would be expected to yield a cellular metabolic activity of 100% equal to the control (e.g., no cell damage). Decreases below this level result from cellular damage to membranes, mitochondria, or the protein components of cells and serves as a marker of toxic impact.

In initial tests, samples treated with the organophosphate pesticide and extracted with pure SC-CO<sub>2</sub> retained about 50% of the pesticide on the basis of dilution experiments. After acetone was added to the SC-CO<sub>2</sub> extraction process, no pesticide residue was detected. Some test result inconsistencies were shown to be due to the use of an industrial grade acetone, which reduced cell activity at a 1:50 dilution. Higher dilutions with industrial grade acetone showed no such decline in cell activity. The impurity from

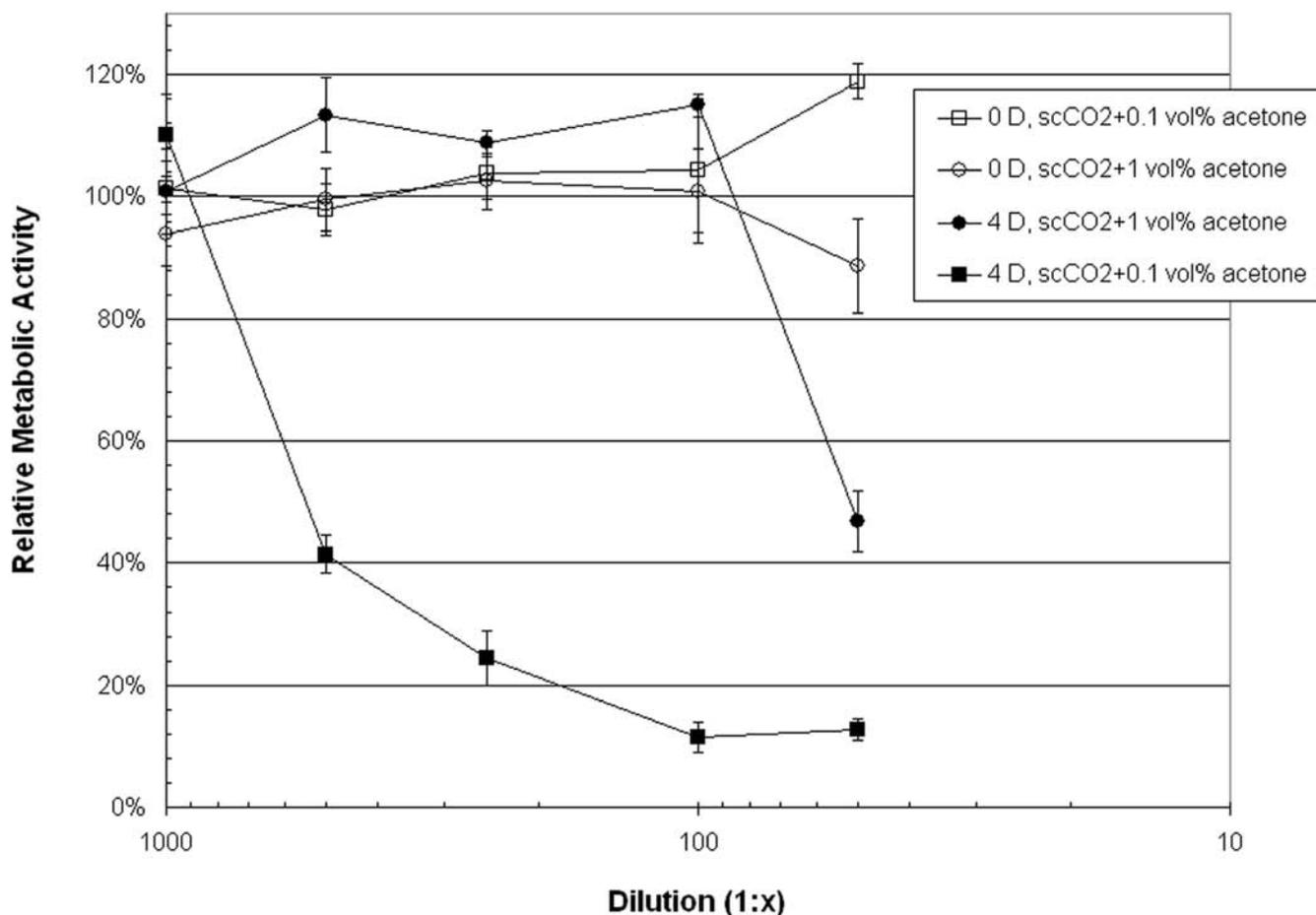


FIGURE 4. Metabolic activity of rat lung epithelial (RLE-6TN) cells exposed to extracted samples using SC-CO<sub>2</sub> and acetone as cosolvent. Samples labeled 4D were treated with 4 mg commercial formulation of the organophosphate pesticide Diazinon; samples labeled 0D were not exposed to any pesticide (0 mg) and served as controls. The decrease in metabolic activity at the 1:50 dilution ratio is most likely a consequence of impurity in the acetone used in the Soxhlet extraction but not used as a cosolvent with the SC-CO<sub>2</sub>.

the industrial grade was not identified; analytical grade acetone was used for all later experiments. These results provide an indication of the sensitivity of the test method.

Extracting samples with 1% by volume of acetone dissolved in SC-CO<sub>2</sub> maintained high cellular metabolic activity with a response similar to that obtained with unexposed controls (see Figure 4). By using the response of the initial 25% active ingredient in Figure 4 as a standard, it can be concluded that the addition of 1% by volume of acetone removed >99% of the organophosphate and the 0.1% by volume solutions removed approximately 75% of the organophosphate.

Rat lung epithelial cell cultures were exposed to several pesticide solutions at increasingly higher dilutions until their LD<sub>50</sub> was reached. The pesticides tested, apart

from the commercial organophosphate, were as follows: three inorganic compounds: arsenic trioxide (As<sub>2</sub>O<sub>3</sub>), mercury bichloride (HgCl<sub>2</sub>), and zinc fluosilicate (ZnF<sub>6</sub>Si); a chlorinated hydrocarbon: Lindane ( $\gamma$ -hexachloro cyclohexane); and another organophosphate: Malathion [2-(dimethoxyphosphinothioylthio) butanedioic acid diethyl ester]. The results are shown in Figure 5.

The commercial grade Diazinon used in this study caused similar declines in metabolic activities as As<sub>2</sub>O<sub>3</sub> and HgCl<sub>2</sub> at similar amounts of active ingredient; increasing amounts of each induced decreased cellular function in a classic dose response relationship. There is no statistical difference between the magnitudes of effects of these three pesticides. ZnSiF<sub>6</sub> is somewhat less toxic and shows a slower decline in cell function. Malathion and Lindane

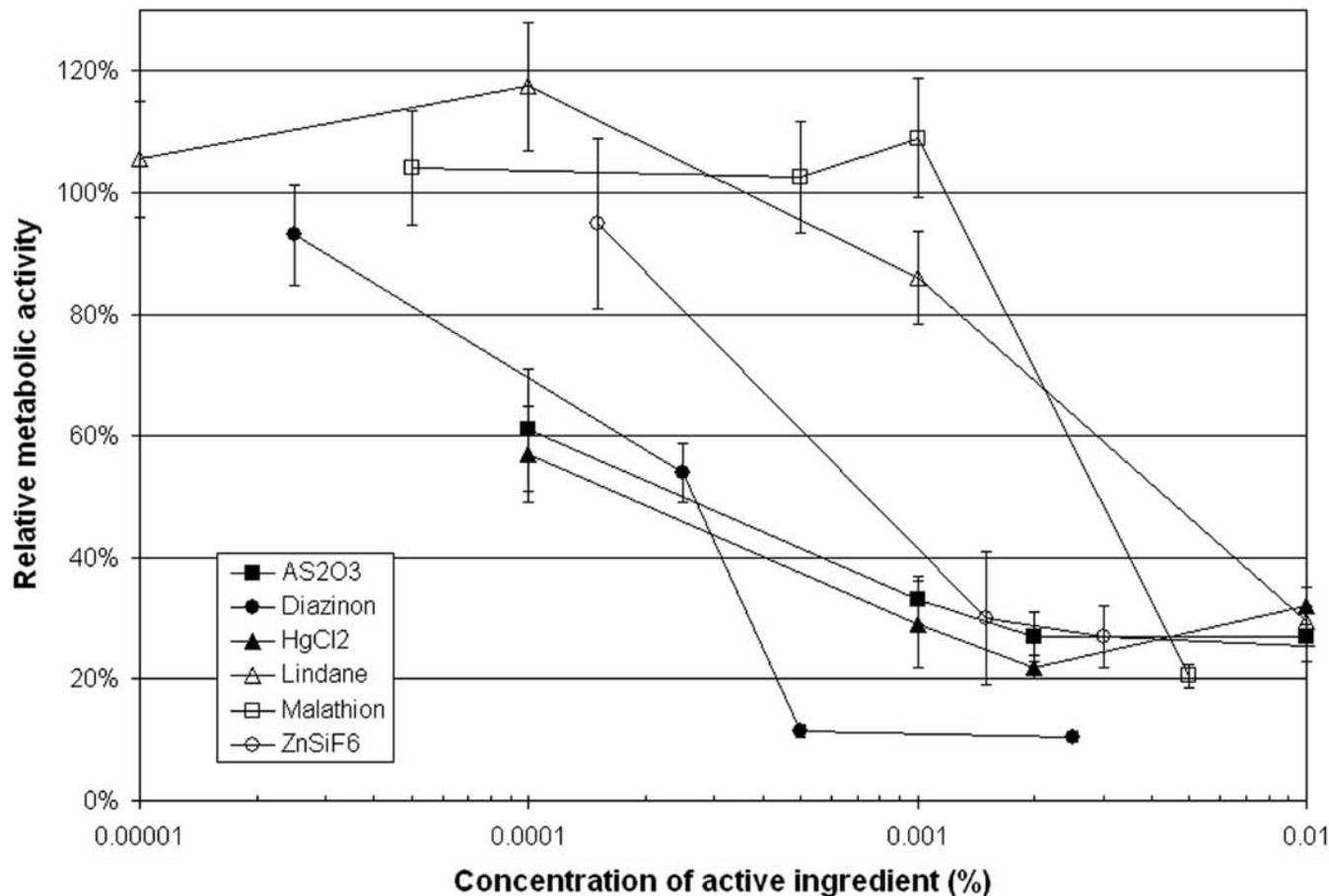


FIGURE 5. Response of RLE-6TN cells to a variety of pesticides. The decrease in metabolic activity indicates the presence of toxic effects.

show the lowest toxicity, reducing cellular function only at active ingredient concentrations of greater than 0.001%.

## CONCLUSIONS

The recognition and subsequent removal of pesticides from museum artifacts is an important issue for collections managers, conservators, researchers, and educators who use museum collections. This issue has recently become of significantly greater concern as a result of NAGPRA, which allows repatriation of artifacts and their handling during traditional cultural uses.

A goal of this work was to develop a protocol and to evaluate the utility of SC-CO<sub>2</sub> for the removal of pesticides from surrogate museum artifacts while causing minimal damage to the artifact. The work presented here provides a possible quantitative approach to assessing the

effectiveness of SC-CO<sub>2</sub> along with added cosolvents. It was found that SC-CO<sub>2</sub> alone removed only part of the organophosphate residue; however, introduction of acetone as a cosolvent significantly improved removal. For example, 1% volume to volume acetone added to SC-CO<sub>2</sub> removed more than 95% of the active ingredient in the commercial formulation tested. Overall, this approach is shown to have been successful for pesticide removal with minimal damage to leather or feathers.

A further goal was to achieve this removal without having to determine the specific pesticide present. This approach, based on the use of the RLE culture detection system, has worked very well in the tests reported here and should work well with other artifacts and pesticides. The study used a total extraction method; however, other methods of residue sampling (i.e., swabs) could also be adapted for use with the RLE cell culture detection system.

## ACKNOWLEDGMENTS

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# The Potential for Adapting Some Cleaning Methodologies to Pesticide Removal from Museum Objects

*Werner S. Zimmt, Nancy Odegaard,  
and David R. Smith*

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**ABSTRACT.** The removal of pesticide residues from museum objects is an ongoing concern. Historic information on pesticide residues and their detection, toxicity, and removal from artifacts have been the focus of numerous previous studies at the University of Arizona and elsewhere. This paper proposes four potential approaches for the removal of pesticide residues including cosolvent additives to supercritical carbon dioxide (SC-CO<sub>2</sub>), other supercritical gases, CO<sub>2</sub> snow cleaning, and fluidized bed cleaning. The aim of this paper is to point out those research areas most likely to prove fruitful in developing and adapting these techniques so as to make them safe for use on ethnographic materials.

**KEYWORDS:** supercritical gases, cosolvents to supercritical carbon dioxide, carbon dioxide snow cleaning, fluidized bed cleaning, pesticide removal, remediation.

## INTRODUCTION

Many objects in museums have been preserved with the use of pesticides based on a wide variety of chemical products to prevent their destruction by insects. A need to remove these poisons is based on the concern that their presence represents a threat to the health of museum workers, researchers, and visitors. Another important concern is the health hazard posed to Native Americans if objects are repatriated under the Native American Graves Protection and Repatriation Act or various state laws and are returned for cultural use. The applied pesticides may bond to the material, be surface deposited, or in some cases, both, depending on the chemical(s) and the application methods used. In all cases, removal is desirable, but the method to be used may differ, depending on the pesticide, the material, and the way the pesticide is attached to it.

General approaches to pesticide remediation based on methods such as washing, physical removal, chemical removal, and biological removal, in addition to object replacement and object containment has been discussed previously (Odegaard, 2001). Although it is clear that there are several possible methods for removing pesticide residues from objects, there are also numerous problems to overcome. This paper will be limited to discussing four potential approaches for the removal of pesticide residues from museum objects. These

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*Paper presented at the Pesticide Mitigation in Museum Collections Workshop held at the Smithsonian's Museum Conservation Institute in April 2007 exploring possible methods and techniques that may become useful for the museum conservation field to reduce, mitigate, clean, or remediate undesirable pesticides on objects.*

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are (1) cosolvent additives to supercritical carbon dioxide (SC-CO<sub>2</sub>); (2) other supercritical gases; (3) CO<sub>2</sub> snow cleaning; and (4) fluidized bed cleaning.

The first of these has been successfully tested by our laboratory, as described in another paper (Zimmt et al., 2010 [this volume]) and has also been reported by others. The other three suggested methods still require further work. They are merely presented as potential methods that should be investigated further, considering that no discussion of these approaches focus on the decontamination of ethnographic museum collections.

### SC-CO<sub>2</sub> AND ADDITIVE COSOLVENTS OTHER THAN ACETONE

Supercritical (or hypercritical) carbon dioxide (SC-CO<sub>2</sub>) has been shown to effectively remove organic pesticide residues from museum objects without causing additional damage (Jelen et al., 2003; von Ulmann, 2003; Kang et al., 2004; Tello et al., 2005; Tello, 2006). These studies indicated that removal of nonpolar pesticides can be accomplished with unmodified SC-CO<sub>2</sub>. Tello et al. (2005) also showed that mercury, but not arsenic, can be removed by this technique.

However, other research has shown that when the pesticide is an even mildly polar compound, the addition of small quantities (1%) of a polar cosolvent is necessary (Zimmt et al., 2010). Collaborative work at the University of Arizona among the Conservation Laboratory of the Arizona State Museum, the Department of Agricultural and Biosystems Engineering, and the Department of Chemical and Environmental Engineering has shown the ability of supercritical CO<sub>2</sub> to remove Diazinon [O,O-diethyl-O-(2-isopropyl-4-methyl-6-pyrimidinyl) phosphorothioate] from museum-like objects. It has also shown that by the addition of very small quantities of acetone, at the 1% level, the removal effectiveness can be improved significantly. Other SC-CO<sub>2</sub> studies have found the addition of 5% methanol to be highly beneficial (Tavlarides et al., 2001).

More than 90 different pesticides have been used on museum objects; however, documentation on what pesticide may have been applied to which object is largely lacking (Pool et al., 2005). On the basis of the literature of what pesticides have been used, the probability is high that many of them could be removed using a properly modified SC-CO<sub>2</sub> (Page et al., 1992). Other adjuvants may be equally or more effective. They might also allow the removal of a broad range of pesticides with a single

composition or may at least be effective in lowering their concentration. Given that CO<sub>2</sub> is a nonpolar solvent and many pesticides are somewhat polar, additives such as acetone or ethanol would greatly enhance the effectiveness of the system.

One could list a number of chemicals that might make effective additives. Generally, they should be low boiling, nonodorous, and nontoxic. Such a composition, in conjunction with the method of determining the presence of most toxins without having to identify the specific one involved, would allow museums to detoxify a large number of objects at reasonable cost. A well-designed program that includes as many different pesticides as can be collected and tested against mixtures of SC-CO<sub>2</sub> and different additives would go a long way toward this goal.

Although the use of this technique for the removal of most organic pesticides should be relatively simple, it may be more difficult to find substances that will readily remove inorganic poisons, such as lead, mercury, or arsenic. Studies have shown that even unmodified SC-CO<sub>2</sub> can reduce the amount of mercury found on an object (Tello et al., 2005). However, the possibility exists that a well-designed adjuvant that will make the metal/chelate combination soluble in SC-CO<sub>2</sub> would be very useful. Work undertaken at the University of Arizona in the Department of Chemical and Environmental Engineering has shown that trace amounts of unwanted metallic copper can be removed from computer chips by SC-CO<sub>2</sub> containing small amounts of the proper chelating agent (Xie et al., 2005). Because metal-based pesticides can be more readily identified, specific compounds for specific metals would be useful in these cases. Because objects treated by museums before the 1920s were often treated with mercury or arsenic compounds, such a process would be extremely practical.

### SUPERCRITICAL FLUIDS OTHER THAN CARBON DIOXIDE

Supercritical CO<sub>2</sub> is the most convenient and the least expensive gas that becomes supercritical in a convenient range of pressures and temperatures. Other gases, in addition to carbon dioxide, could be made supercritical in a reasonable temperature and pressure range. For some purposes, the use of other gases may provide solubility advantages over SC-CO<sub>2</sub> and even if the alternative gas is more expensive, it may provide a cost-effective solution. Table 1 lists some other gases and their critical points collected from various different sources.

**TABLE 1.** Some gases that form supercritical liquids along with their values for critical temperature ( $T_C$ ), critical pressure ( $P_C$ ), and density ( $\delta$ ).

Gas	Name	$T_C$ ( $^{\circ}\text{C}$ )	$P_C$ (atm)	$\delta$ (g/mL) at 40 MPa
$\text{CO}_2$	Carbon dioxide	31.3	72.9	0.96
$\text{N}_2\text{O}$	Nitrous oxide	36.5	72.5	0.94
$\text{NH}_3$	Ammonia	132.5	112.5	0.40
$\text{C}_2\text{H}_6$	Ethane	32.5	48.2	—
n- $\text{C}_4\text{H}_{10}$	Butane	152.0	37.5	0.50
$\text{CCl}_2\text{F}_2$	Dichloro difluoro methane	111.8	40.7	1.12
$\text{CHF}_3$	Trifluoro methane	25.9	46.9	—
$\text{BrCF}_3$	Bromo trifluoro methane	66.8	45.3	—
$\text{CH}_3\text{F}$	Fluoro methane or methyl fluoride	44.55	59.9	—
$\text{CF}_4$	Tetrafluoro methane	33.3	38.9	—
$\text{C}_2\text{F}_6$	Hexafluoro ethane, perfluoroethane, or carbon hexafluoride	19.7	29.2	—
$\text{CH}_3\text{CHF}_2$	1,1 difluoro ethane or ethylidene fluoride	30.1	43.8	—
$\text{CClF}_3$	Chloro trifluoro methane	28.8	38.2	—

It is evident that some gases listed in Table 1 would not be suitable either because the temperature required to become supercritical is too high or because they are toxic. However, nitrous oxide ( $\text{N}_2\text{O}$ ), trifluoromethane ( $\text{CHF}_3$ ), and some of the other fluorinated molecules are worth considering. Their chemical properties are substantially different from  $\text{CO}_2$ , and they may be able to solubilize a range of substances unaffected by  $\text{CO}_2$ .

Trifluoromethane and fluoromethane ( $\text{CH}_3\text{F}$ ) have some properties, such as weak acidity, that may allow them to remove metals and basic species. The chemical properties of supercritical fluids can be changed by relatively small changes in pressure (Egorov and Rabani, 2002). One of the solvents tested was trifluoromethane. Drawbacks for the use of some of these fluorinated gases include cost and environmental considerations.

Nitrous oxide ( $\text{N}_2\text{O}$ ) might be considered isoelectronic with  $\text{CO}_2$  since both have 16 valence electrons. However, the arrangement of the electrons is different and so are the chemical properties of the gases. For a start,  $\text{N}_2\text{O}$  is far more polar and so would dissolve a different range of substances. It also has relatively low toxicity. Studies have used both SC- $\text{CO}_2$  and SC- $\text{N}_2\text{O}$  to extract dioxins from sediments (Onuska and Terry, 2005). Furthermore, there are a substantial number of references on the use of SC- $\text{N}_2\text{O}$  in chromatography.

An initial literature review has found very little information on the use of other gases. Only one patent<sup>1</sup> discusses the use of gases other than SC- $\text{CO}_2$  in extracting specific ingredients from animal tissue (Kamarei, 1988), but contains no specific data. Because no reference on the use of other supercritically cooled gases for the removal of pesticides from museum collections has been found, it appears evident that further research in this area may be fruitful.

## CO<sub>2</sub> SNOW CLEANING

Solid particles of dry ice pellets or “snow” have been shown to remove dust, soot, and small particles from even the most delicate surfaces without causing scratches or other damage (Fong, 1974; Wolbers, 2000; Silverman, 2006.). In cases where the pesticide is not chemically bound to the surface of an object, this approach may constitute a safe and easy way to remove it.

When pressurized liquid  $\text{CO}_2$  is allowed to expand adiabatically into a gas, the temperature drops to the point that some of the gas solidifies into small particles, forming  $\text{CO}_2$  snow. Advantage has been taken of this effect to develop a system to remove particles and dust from a variety of surfaces (Hoenig, 2001; Young, 2003). The system consists of a source of liquid  $\text{CO}_2$  (usually in a gas cylinder) and a device that allows the required rapid expansion. The particles, because they sublime rapidly and therefore are surrounded by an envelope of gas, never come into direct contact with the surface of the object being cleaned. Because this system is dry, nonconductive, nonabrasive, non-toxic, and leaves no residue, it has found wide approval in fields like astronomy, where it can keep the delicate mirrors and lenses clean without causing scratches or other damage.

This approach would allow the removal of pesticide particles adhering to an object, even if the object does not have a smooth surface, such as fur or feathers, because the force of the gas stream moving the dry ice particles would dislodge the pesticide. Because the dry ice particles are enveloped in a blanket of gas, they would not damage the object being cleaned.

Further work needs to be carried out in a closed system so that the pesticide particles can be filtered and collected for proper disposal. The major difference between this system and the solvent cleaning procedures is that the dry ice will only remove surface contamination. However, in many cases that would be all that is required.

## FLUIDIZED BED CLEANING

Another potential solution for the removal of solid pesticides applied as powders is the use of a fluidized bed process. The fluidized bed process is a well-established technique in the chemical and oil industries for catalyzed reactions in large volume, and it has also been useful in coating applications and with odd-shaped objects (Howard, 1989). A fluidized bed is a vessel that contains finely divided powder, usually in the micrometer range size, that is levitated by a stream of air introduced through a fine screen at the bottom, so that it suspends the powder and allows it to behave like a liquid. Any object suspended in the vessel is surrounded by the powder as though it was suspended in a liquid. If a gas or liquid is moved through the suspended powder that acts as a catalyst, it will be exposed to a large amount of the surface because each particle is fully surrounded by the reactants, and consequently, the reaction rate is greatly increased. Large refineries use fluidized beds to move huge masses of catalyst powders that allow the refining and modification of petroleum fractions into gasoline, kerosene, aviation fuel, etc.

This method could be combined with standard techniques such as vacuuming because it can effectively enter into crevices of the object and adsorb the pesticide. Solid pesticides that were applied as powders can potentially be removed using a fluidized bed process.

Solid, dry materials have been used for cleaning various substrates for many years. In the 1930s a dry but gummy material was used to remove dust and grime from wall paper by rubbing over the paper and repeatedly folding the cleaner over to provide a fresh cleaning surface. Powders containing cleaning agents have been used to remove dirt as the stains are absorbed into them. The powders can be sprinkled or sprayed on rugs and upholstery, rubbed in, and then removed, usually by vacuuming. All these uses involve surface cleaning.

Over the years, some museum objects were dusted with powders to protect them from insects, mold, rodents, and other deteriorating agents. The pesticide on most of these objects is confined to their surfaces. The problem is that these are generally not smooth surfaces but have areas that are not readily cleaned, such as seams, feathers, folds, etc. One possibility might be to combine the cleaning ability of appropriate powders with the fluidized bed technique.

Fluidized beds containing powder coatings are routinely used to paint small and irregularly shaped objects because they are highly efficient and avoid losses due to overspray encountered in air spraying of objects. The equipment used for coating is the most likely candidate for

a cleaning process as envisioned here. The air velocity is just high enough to gently suspend the powder particles. There are many references to this technology, but those dealing with powder coatings are probably the most relevant.

### The possible Process I

- A powder of controlled particle size is suspended in a stream of air.
- The powder exhibits liquid-like properties.
- Penetration into the substrate occurs whenever the particle is smaller than the opening into which the air is flowing.

### The possible Process II

- A powder is selected that promotes adhesion between itself and unwanted particles on the object's surface.
- The article to be cleaned is submerged in the "liquefied" powder for a given amount of time, withdrawn, and shaken to remove as much loose powder as possible.
- The article is vacuumed to remove the remaining loose powder.
- The powder can be reused several times and is then disposed off according to extant regulations.

Fluidized beds are used in large numbers in several industries, and their engineering principles have been studied thoroughly. The internet contains thousands of references to fluidized bed technology. Many include illustrations, tables, and information. They present an interesting concept and deserve further study. Some are listed here.

### FREE PATENTS ONLINE

Vortex effect electrostatic fluidized bed coating method and apparatus (U.S.

Patent 4606928), <http://www.freepatentsonline.com/4606928.html>

Understanding Fluidized Bed Powder Coating, <http://www.pfonline.com/articles/1004qf1.html>

ArsenX<sup>TM</sup> Arsenic Removal, <http://www.purolite.com>

The Fluidized Bed Reactor Page, [http://faculty.washington.edu/finlayso/Fluidized\\_Bed/](http://faculty.washington.edu/finlayso/Fluidized_Bed/)

## CONCLUSIONS

There are numerous possible approaches to the removal of pesticide residue contaminants that have not been tested or investigated for use on cultural objects. This

brief discussion points out several directions that appear to be promising and that could be pursued in addition to the current efforts underway. It should be understood that the objective of this paper is to broaden the range of possible approaches for the removal of pesticides from museum collections not to report research already done. This was in line with the goal of the Mitigation Workshop, where it was presented orally.

## NOTE

1. Ahmad R. Kamarei, U.S. Patent No. 4749522.

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# Discussion: Mitigation of Contaminated Collections

*R. Eric Hollinger and Greta Hansen*

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**ABSTRACT.** The Smithsonian Institution's museums and research units have been working to address the challenges posed by contaminated museum collections and, to that end, organized the Pesticide Mitigation in Museum Collections Workshop to learn more about potential approaches for remediation of contaminants. The papers assembled here result from the workshop and represent experimental attempts to use a wide assortment of mitigation and remediation technologies on simulated and real cultural objects. These and other theoretical approaches hold great promise for decontamination of collections for the safety of all who work with them.

**KEYWORDS:** repatriation, mitigation, remediation, cleaning, removal, museums collections.

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*Paper presented at the Pesticide Mitigation in Museum Collections Workshop held at the Smithsonian's Museum Conservation Institute in April 2007 exploring possible methods and techniques that may become useful for the museum conservation field to reduce, mitigate, clean, or remediate undesirable pesticides on objects.*

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## INTRODUCTION

Potentially hazardous collections in museums have existed for as long as museums have been collecting. Reasons include the inherent composition of the objects as well as pest-control treatments to which they have been subjected. However, widespread recognition of the health and safety risks posed by handling these types of objects and specimens, and the need for adequate exposure controls, has been growing more recently. Over the past two decades, awareness of the problem has spread in conjunction with broadening access and use of collections and increased understanding of the potential risks to human health. Naturally, concomitant with the increased awareness of the existence of the potential hazards is the pressure to answer the question "What can be done about it"? There are many responsible safe work practices, including the use of personal protective equipment that can effectively minimize personal exposure to the health hazards posed by these agents. However, in the hierarchy of controls, permanent elimination or significant reduction of the hazard agent itself is the ultimate goal. The Smithsonian's Mitigation of Pesticides on Museum Collections Workshop and the resulting papers assembled here represent the current ability to address this important question and the hope for future advances toward tackling these problems.

## PAST SMITHSONIAN INSTITUTION EXPERIENCE

It is appropriate that the Smithsonian Institution, the world's largest museum complex, take a lead in the effort to address the problem of contaminated collections. The Smithsonian Institution, including 19 museums and galleries and the National Zoological Park, as well as research facilities, was founded in 1846 and is the oldest research and museum institution in the United States. It is today the custodian of more than 137 million objects.

Beginning with its founding collection, the Wilkes U.S. Exploring Expedition of 1843, the collections were treated with a wide range of substances from tobacco to arsenic and mercury. Research into museum records by conservators at the Anthropology Department of the National Museum of Natural History (NMNH), which houses the largest—with 125 million objects—and oldest of the Smithsonian's collections, showed that dozens of different substances have been used over the years to treat natural history collections (Goldberg, 1996; Hawks and Williams, 1996). It should be noted that early collections staff were not fully aware of the potential risks these poisons posed. However, Otis T. Mason, a Curator of Ethnology at the U.S. National Museum, described the procedures used for ethnological materials that were “sent to the poisoning department, where it is subjected to a close scrutiny. The curator has devoted much time to this subject, for it is encumbered with many difficulties, each kind of material demanding a different treatment” and he noted that one of the problems needing to be solved was “to reduce the danger to the curator and others to the lowest amount” (Mason, 1886:87–88). Even so, it seems that the need to protect collections from the attacks of insects and other pests superseded any concerns of risk to those who might come into contact with them in the future.

## REPATRIATION SPURS INCREASED INTEREST

The publication of the pesticide findings from museum records fueled wider interest in identifying potential hazards in collections and simultaneous with this an increasing concern for the problem on the part of the general public and Native American tribes in particular. This has been due in large part to the increased access to museum collections and repatriation of human remains and cultural objects from museums. Even before repatriation laws were passed, regulations for the curation of federal collections (36 Code of Federal Regulations [C.F.R.], Part 79, 1990)

required they be made accessible to Native Americans for religious purposes.

For the Smithsonian, repatriations of remains and objects began in the early 1980s before being required by law by the repatriation provisions in the 1989 National Museum of the American Indian Act (20 U.S. Code [U.S.C.], sec. 80q) and the 1996 amendments to the act. These repatriation provisions were extended to the rest of the United States by the Native American Graves Protection and Repatriation Act (NAGPRA) of 1990 (25 U.S.C., sec. 3001–3013). These statutes require museums to return remains, funerary objects, sacred objects, and objects of cultural patrimony when requested by the culturally affiliated tribe, Native Hawaiian organization, or Alaska Native Village. Although neither of these laws make mention of pesticides or other treatments, the regulations for carrying out the NAGPRA, which were promulgated in 1995, require that museums inform recipients of repatriated items of any presently known treatment of the objects “with pesticides, preservatives, or other substances that represent a potential hazard to the objects or to persons handling the objects” (43 C.F.R., 10.10 (4)e).

## PRESENT POSITION OF THE SMITHSONIAN INSTITUTION

Although the Smithsonian museums are not subject to these regulations, the NMNH and the National Museum of the American Indian (NMAI) have adopted policies of notification of treatments and have gone beyond any legal requirements by proactively testing objects for heavy metals and other substances.

Because some repatriated objects, particularly sacred objects, go back into use within their communities, it is critical that repatriation recipients be informed of any known or potential hazards that might come with the objects. Consequently, hundreds of museums across the country have notified indigenous communities through consultations or resultant repatriations that objects to which they are affiliated may have been contaminated. Some tribes have even taken to carrying out their own programs of testing for contaminants, while others have declared a moratorium on repatriations until they understand the issues more fully.

In the Repatriation Office of the NMNH we have seen the reactions of tribal representatives learning for the first time of the nature and possible extent of contamination of collections. Inevitably, after learning of potential contaminants inherent in the construction materials and the

treatment histories of the objects, as well as the efforts of the museums to test for contaminants, the representatives always ask what can be done to clean the objects or otherwise make them safer for handling. Only a few years ago we would have answered that there was no way to remove contaminants from cultural objects. Today, we can confidently reply that, as seen by the research presented in the papers gathered here, there are techniques under development that hold promise for cleaning objects of pesticides or other residues.

At the Smithsonian Institution, occupational hazard determinations and hazard communication outreach is handled by several venues. Line management supervision in each unit is responsible, under prevailing federal regulations, to “provide a safe and healthful workplace” for its employees by identifying hazards inherent to the unit’s tasks and controlling safety and health risks. The Office of Safety, Health and Environmental Management (OSHEM) assists units in evaluating those risks (through exposure sampling and biological monitoring) against established health standards and recommending appropriate controls measures, as well as providing staff training and other hazard communication, and environmental monitoring and hazardous waste determinations. The working units have also established the Smithsonian Pesticide Working Group to network on merging pesticide-artifact contamination issues, collaborate on hazard identification instrumental analyses and conservation remediation techniques, and share information on public disclosure information sanctioned by the Smithsonian Institution.

The Smithsonian Pesticides Working Group is based on the collaboration between four units of this institution. These are: the Anthropology Department of the National Museum of Natural History and the National Museum of the American Indian, the two major collecting units; the Office of Safety Health and Environmental Management (OSHEM) and the Museum Conservation Institute (MCI), which provides scientific research and analytical assistance to collecting units.

Although all of the member units have been actively identifying the presence of heavy metal or bromine-based pesticides by means of equipment such as portable X-ray fluorescence (XRF) analyzers and have utilized OSHEM for exposure monitoring, health risk assessment, and development of safe work procedures, little research or experimentation has been conducted at the Smithsonian into the actual removal (decontamination) of the pesticide hazard itself from contaminated collections. The Smithsonian Pesticides Working Group, recognizing the need to comprehensively address contaminated collections issues,

sought to explore the potentials for decontamination and collaborated with MCI to host a workshop for researchers who have experimented with mitigation or remediation. The goal was to bring together scientists who developed or applied methods and technologies for removing or otherwise reducing contaminants on museum collections and have them to present their research primarily to Smithsonian staff. With this information, the Working Group will identify and prioritize various decontamination methods and technologies for future testing. Although the primary target audience was Smithsonian staff, notices were sent to other museums, tribes, and federal agencies with interests in the topic and the final audience represented a cross section of these stakeholders. With the exception of the paper by Madden et al. (2010) and this paper, each of the papers in this volume is the written version of the presentations shared at the workshop.

## **THE WORKSHOP: PAPERS AND DISCUSSIONS**

All of the invited participants embraced the opportunity to present their research and the potentials of the mitigation approaches in which they specialized and to share their knowledge with others working to tackle similar problems. The presenters are an exceptional group of people who have dedicated considerable time, energy, and careful thought to solving the problems of chemical hazards in collections and making objects safer for handling.

The paper by Madden et al. (2010) provides an introduction to the volume and the issues by outlining some of the broader contexts in which pesticides or other contaminants should be understood in conjunction with efforts to mitigate them. The fundamental challenges of the contaminated collections problem include the detection, characterization, and quantification of the potential hazard; the assessment of the potential risks posed by that hazard; and the mitigation or remediation of the hazard.

Madden et al. (2010) rightly point out that in order to attempt to remove contaminants, it is critical to assemble information about what is actually present on the object and ideally to quantify those substances so that one can gauge the effectiveness of mitigation efforts. Many institutions, including the Smithsonian, have turned to portable XRF analyzers for their speed and nondestructive ability to detect the heavy metals lead, mercury, arsenic, and bromine. The efforts of Smithsonian researchers, as Madden et al. describe, have focused on refining the methodologies for XRF testing. These efforts have made great progress,

although there is no one Smithsonian standard protocol for XRF testing. Staff of NMAI and NMNH who conducted XRF testing of cultural objects have shared methods and information in an effort to standardize their protocols where feasible, but differences between the protocols employed at these two museums remain because of their different collection treatment histories and approaches.

At the NMNH Anthropology Department, XRF testing protocols are continually evolving with experience, improving technology, and consultation with tribal representatives, risk assessment experts within the OSHEM, XRF experts, and other museums working to develop testing protocols. Testing is carried out on all objects requested for repatriation or loaned to other institutions by systematic sampling of all surfaces, materials, and areas of handling. With an emphasis on full disclosure, all sampling data and raw spectra are provided to object recipients along with interpretations and recommendations for handling. All museums are likely to develop XRF testing procedures that are unique to their collections and goals although standardization of approaches, where practical, remains a worthy goal.

As Madden et al. (2010) and Odegaard (2001) note, most of the risk mitigation approaches explored in this volume are more accurately classified as remediation because they seek to reduce the potential hazard by removal of contaminants. The first three papers present research into chemical solution remediation techniques. The next paper by Roane and Snelling (2010) describes a novel method of bioremediation of pesticides on cultural objects. The final set of three papers addresses the use of supercritical gases such as carbon dioxide to clean objects. The last paper by Zimmt et al. (2010b) presents additional methods that may hold great potential for remediation of pesticides from cultural objects.

Cross' (2010) paper describes her research on the use of alpha lipoic acid in a solution to wash arsenic and mercury from test samples of contaminated wool, feathers, cotton, and filter paper. Her experiments showed a 93%–99.8% reduction in the metals from the feathers, cotton, and paper after two cleanings and a 99.7% reduction in arsenic from wool. Because the wool contained sulfur, the lipoic acid was only able to remove 36.7% of the mercury from the wool sample. Cross' experiments suggest great potential for remediation of heavy metals from cultural objects, and because alpha lipoic acid is a naturally occurring chemical, it is considered more appropriate for use on culturally sensitive objects by Native Americans.

Kaiser's (2010) paper presents research on decontamination of materials using a diffusion-cleaning method.

This approach employs special, engineered solvents to dissolve the targeted contaminants and blotters or adsorbent materials, such as activated carbon fabric, as sinks to capture the dissolved contaminant. Experiments were conducted using test samples of dyes on fabric to simulate a contaminated material and showed that, given sufficient time, the dyes were almost completely removed. Crucial to the success of this method is the identification of the targeted contaminant so that an efficient solvent that is harmless to the object material can be used. The method may prove particularly valuable for decontamination of materials too fragile to withstand cleaning with mechanical agitation.

Reuben's (2010) paper describes the work of the Haudenosaunee Standing Committee on Burial Rules and Regulations, the Seneca Nation's Tribal Historic Preservation Office, and the Seneca-Iroquois National Museum to mitigate contaminated Haudenosaunee medicine masks that had been repatriated from museums. The mitigation procedures employed a mixed approach that included removal and replacement of materials such as horsehair, the spray application of a surface active displacement solution consisting of sodium lauryl sulfate, and traditional physical and ritual methods of cleaning. Wipe tests had detected arsenic and mercury on the interiors and painted exteriors of the masks prior to cleaning and after treatment all of the tested surfaces showed reductions of more than 99%. The success of this method with real objects that continue to be used in ceremonies illustrates the importance of integrated approaches tailored to the needs being addressed.

The research presented by Roane and Snelling (2010), using bioremediation, demonstrates the resourcefulness being applied to the search for mitigation solutions. They harness the natural biological processes of bacteria to convert mercury compounds to a gaseous form that can be collected and removed. They have identified bacteria living on mercury-contaminated museum objects, cultured them, and then applied them to mercury contaminated broth, agar, and paper. In their experiments, one bacterial isolate was able to reduce the mercury in the test samples by as much as 30% in 10 days, while another was able to reduce levels by as much as 60%. Although a great deal of research still needs to be conducted before it is practical for treating objects, the potential of this approach is of particular interest to many Native Americans because it simply directs and encourages a natural process already at work on mercury contaminated objects.

Tello and Unger (2010) present results of their research and experimentation using liquid and supercritical carbon dioxide to clean museum objects. This technology

has been applied for some time in industrial contexts such as dry cleaning. In their experiments, five ethnographic objects or pieces of objects were subjected to treatment using liquid carbon dioxide and three samples were subjected to supercritical carbon dioxide. Pretreatment analysis of the objects had already shown the presence of various contaminants. Objects treated with liquid carbon dioxide showed marked reduction in dichloro diphenyl trichloroethane (DDT), a slight to significant decrease in Lindane, and no real change in arsenic or mercury levels. The museum samples treated with supercritical carbon dioxide showed reduction of DDT, Lindane, and mercury, but little change in the amount of pentachlorophenol (PCP) and arsenic. The majority of the test samples showed little change in the condition of the material other than becoming visually cleaner, although fur appeared to have improved by softening. The authors do note that this technique may not be appropriate for sensitive materials.

Zimmt et al. (2010a) also present experiments using supercritical carbon dioxide to remove pesticides from simulated collections materials. In their research, pieces of leather and dyed feathers were intentionally contaminated with known amounts of the organic pesticide Diazinon. The materials were then treated using supercritical carbon dioxide, which by itself only removed part of the Diazinon residue from the test materials. When small amounts of acetone were added to the supercritical carbon dioxide as a cosolvent, the process removed more than 95% of the Diazinon with no visible damage or loss of color to the materials being tested. The amounts of pesticides in this experiment were measured using a toxicological screening method of exposing the treated materials to rat lung epithelial cell cultures and watching for any decrease in cellular metabolic activity. A benefit of this method, versus the use of XRF, wipes, or other methods which detect specific targeted substances, is its ability to tell if exposure to the object is potentially harmful without knowing the contaminant.

The final paper by Zimmt et al. (2010b) continues the discussion of the research carried out by the University of Arizona and suggests additional approaches that in theory hold great promise for decontamination of museum objects. Building on their observations that cosolvents were necessary for supercritical carbon dioxide cleaning, they note that other chemicals such as ethanol might also make good cosolvents. They also explore the potential for a number of gases other than carbon dioxide to be applied in supercritical form for the cleaning of museum collections. The properties of these gases may facilitate the removal of substances that are not removed by supercritical carbon dioxide. Another potential method offered

is the application of carbon dioxide “snow” blown over the object to remove pesticides or other substances from the surface without abrasive action. Finally, the authors explore the potential of fluidized beds, a technology commonly used in industry, as cleaning technology. Fluidized beds have the potential to be adapted to treat museum objects by immersing them in powders that adhere to surface contaminants and then removing the powders by shaking and vacuuming. These methods represent the potential for innovations and adaptations of technologies to tackle the problems of contaminated collections.

## CONCLUSIONS

As our awareness of health and environmental hazards presented by pesticides and other contaminants on museum collections continues to increase, so, too, will the pressures to find ways of reducing or removing those hazards. Museum collections around the world are becoming increasingly more accessible to researchers, indigenous communities, and the public at large. As direct physical contact with collections increases, the impetus to make sure that collections are as safe as possible for handling by visitors, recipients of repatriated collections, and museum staff who come into contact with collections on a regular basis is gaining greater urgency. In the interim, it is incumbent upon museum supervisors to ensure that safe work practices with appropriate personal protective equipment, cleaning procedures, use of local ventilation, and other risk reduction measures are incorporated into all protocols. Visitors to collections need to be made aware of these issues and follow any departmental requirements for safe handling or research (such as offering protective gloves). Although the inherent toxicity hazard of these heavy metals and other pesticides may be significant, the actual health risk to the employee or object handler may be low depending on frequency and duration of contact and efficacy of work practice controls. Therefore, arranging for personal exposure monitoring and health risk assessments overseen by qualified industrial hygienists and occupational health clinicians is key to establishing perspectives on hazard and risk in any given work situation. However, the ultimate risk control is the mitigation of the hazard itself.

The papers assembled here represent some of the first steps toward developing technologies to decontaminate museum collections. These approaches represent the diversity of methods that will be necessary to deal with the broad array of materials represented by museum collections. Although it is unlikely that there will ever be a single method

for cleaning all types of objects or materials, these approaches show great promise for future applications. While some of the research presented here includes experimentation with remediation on actual cultural objects, considerably more research and experimentation is needed before most museums will be comfortable applying remediation approaches to collections on a large scale. Even then, some methods may not be culturally appropriate or may not meet requirements for conservation of particular objects requiring us to fall back to mitigating the risk through containment, personal protective measures, and handling protocols. It is likely that there will always be need for such measures, but there is also a clear need for more research into developing portable equipment for the analysis of organic pesticides, developing standards for the quantification of contamination, as well as developing experimentation into remediation of contaminated collections.

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# Appendix: Common Museum Pesticides

TABLE A.1. Organic compounds most commonly used as pesticides for museum collections.

Common name	Chemical name	Chemical formula
Camphor	<i>d</i> -2-Damphane or <i>d</i> -2 keto-1,7,7-trimethylcamphane	C <sub>10</sub> H <sub>16</sub> O
Carbolic acid	Phenol	C <sub>6</sub> H <sub>5</sub> OH
Carbon disulphide	Carbon disulphide	CS <sub>2</sub>
Carbon tetrachloride	Carbon tetrachloride	CCl <sub>4</sub>
Carboxide	Mixture of ethylene oxide and carbon dioxide (90-10%)	CH <sub>2</sub> CH <sub>2</sub> O (90%) + CO <sub>2</sub> (10%)
Chlorotene <sup>a</sup>	1,1,1 Trichloro ethane	Cl <sub>3</sub> C-CH <sub>3</sub>
Diazinon	O,O-diethyl-O-(2-isopropyl-4-methyl- 6-pyrimidinyl)phosphorothioate	[C(CH <sub>3</sub> ) <sub>2</sub> CHC <sub>4</sub> N <sub>2</sub> H(CH <sub>3</sub> )O] PS(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>
Dichlorobenzene	<i>p</i> -Dichlorobenzene or 1,4 Dichlorobenzene	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>
Dichlorvos or DDVP	2,2 Dichlorovinyl dimethyl phosphate	(CH <sub>3</sub> O) <sub>2</sub> POOCH:CCl <sub>2</sub>
Dimethyl formamide (DMF)	N, N-dimethyl formamide	HCON(CH <sub>3</sub> ) <sub>2</sub>
DD <sup>a</sup>	Mixture of 1,3 dichloropropene and 1,2 dichloropropane	ClCH:CHCH <sub>2</sub> Cl + ClCH <sub>2</sub> CHClCH <sub>3</sub>
DDT	Dichloro diphenyl trichloroethane, or more correctly 1,1,1-Trichloro-2,2-bis( <i>p</i> -chloro phenyl) ethane	( <i>p</i> ClC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> CHCl <sub>3</sub>
Dowfume G	Mixture of carbon tetrachloride, ethylene dichloride, and ethylene dibromide, or more correctly, 1,2 dichloroethane and 1,2 dibromoethane	CCl <sub>4</sub> + ClCH <sub>2</sub> CH <sub>2</sub> Cl + BrCH <sub>2</sub> CH <sub>2</sub> Br
Dowfume 75	Mixture of ethylene dichloride (1,2 dichloroethane) and carbon tetrachloride (70:30 %)	ClCH <sub>2</sub> CH <sub>2</sub> Cl (70%) + CCl <sub>4</sub> (30%)
Dowfume 85	Contains 85% ethylene dibromide (1,2 dibromoethane)	—
Ethylene dibromide or EDB <sup>a</sup>	1,2 Dibromoethane	BrCH <sub>2</sub> CH <sub>2</sub> Br
Ethylene dichloride <sup>a</sup>	1,2 Dichloroethane	ClCH <sub>2</sub> CH <sub>2</sub> Cl
Ethylene oxide <sup>a</sup>	Epoxyethane	CH <sub>2</sub> CH <sub>2</sub> O
Larvex	Contains organochlorine compounds	
Lindane or gammaxene	$\gamma$ Hexachloro cyclohexane or benzene hexachloride	C <sub>6</sub> H <sub>6</sub> Cl <sub>6</sub>

(continued)

TABLE A.1. (Continued)

Common name	Chemical name	Chemical formula
Malathion	2-(Dimethoxyphosphinothioylthio)butanedioic acid diethyl ester	$C_{10}H_{19}O_6PS_2$
Menthol	Methyl-hydroxyisopropyl-hexane	$CH_3C_6H_9(C_3H_7)OH$
Methyl bromide <sup>a</sup>	Methyl bromide	$CH_3Br$
Naphthalene <sup>a</sup>	Naphthalene	$C_{10}H_8$
Nemagon or DBCP <sup>a</sup>	1,2 Dibromo-3 chloro propane	$CH_2BrCHBrCH_2Cl$
Paradichlorobenzene or PDB <sup>a</sup>	1,4 Dichlorobenzene	$C_6H_4Cl_2$
PCP	Pentachlorophenol	$C_6OHCl_5$
Telone II <sup>a</sup>	1,3 Dichloropropene	$ClCH:CHCH_2Cl$
Thymol	5-Methyl 2-isopropyl 1-phenol or isopropyl <i>m</i> -cresol	$CH_3(C_3H_7)C_6H_3OH$
Vapam or Metam <sup>a</sup>	Sodium N-methyldithiocarbamate	$CH_3NH(S: )CSNa$
Vapona	(See Dichlorvos)	—
Vikane <sup>a</sup>	Sulfuryl fluoride	$SO_2F_2$

<sup>a</sup> Fumigant.

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