A General Overview of Pesticides, Testing, Mitigation, and Removal

Nancy Odegaard, PhD, FAIC

Conservator and Professor

Arizona State Museum

University of Arizona

Biodeterioration

The process that involves the combination of:

- An organism (the PEST)
- a food source (the MUSEUM OBJECT)
- a suitable environment (a QUIET, DARK, COMFORTABLE PLACE)

Organisms that threaten museum objects include:

People Bacteria Insects

Fungi Rodents

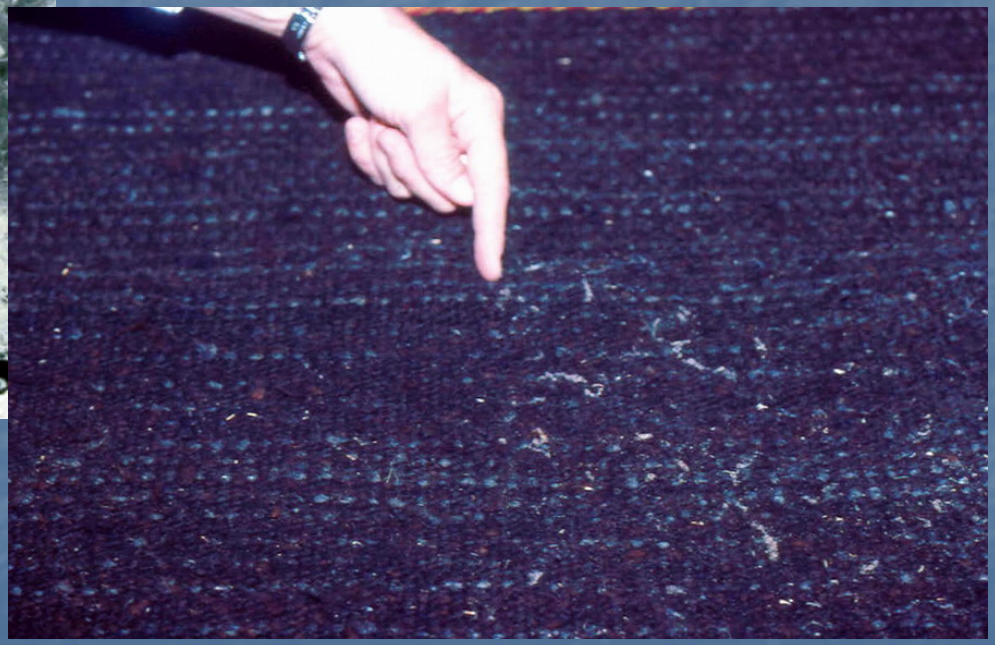
Insects of concern usually like materials such as Proteins: hair, fur, horn, quill, baleen, hoof, claw, feather, ink binders, hide glues

Insects of concern also like materials such as Cellulose and Starch: paper and sizing, paste adhesives

Unprotected Objects often become infested

Unprotected objects with no signs of infestation may have been poisoned

Insects are the most numerous, resilient, and persistent of all the agents of deterioration. Fortunately, there are relatively few species that are of concern in the museum context.



Webbing Clothes Moth

Complete Destruction by Clothes Moths

Varied Carpet Beetle

Carpet Beetle larva

Pesticides

Pesticides can be placed into categories but most are effective in more than one category:

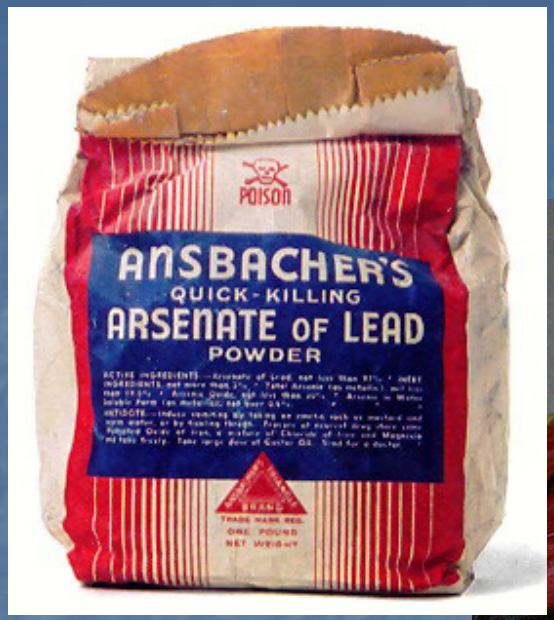
Dermal poisons penetrate the cuticle or body wall of the insect and are sometimes referred to as Contact Poisons.

Desiccants can also be used to absorb part of the outer protective was coating of the insect, causing dehydration and death.

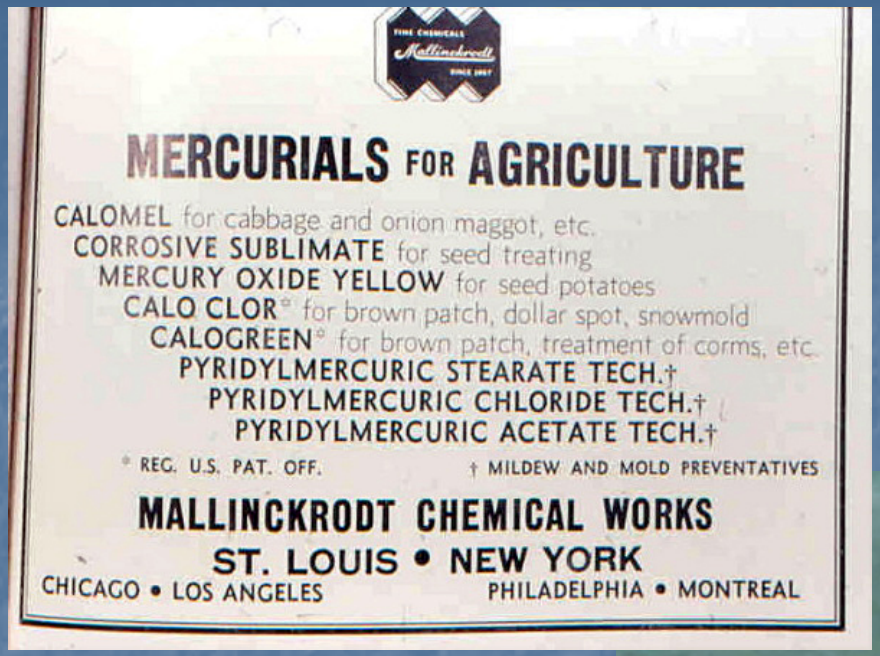
- Oral poisons enter the body through chewing and are known as Stomach Poisons.
- Inhalation poisons enter the insect through the body wall or respiratory openings and include Fumigants. Residual poisons contact the insect during or after application but require a period of time to react.

Common Pesticide Products

"Arsenic" Tag



White powder residue that tested positive for arsenic



Grey residue that tested positive for mercury

DIRECTIONS FOR USE

THIS LEAFLET CONTAINS COMPLETE DIRECTIONS FOR USE. PLEASE READ CAREFULLY AND DO NOT DISCARD UNTIL ALL PRODUCT IS USED.

FICAM® D

1% Dust Insecticide

INGREDIENT STATEMENT

ACTIVE INGREDIENT:	
2,2-dimethyl-1,3-benzodioxol-4-ol methylcarbamate†	1%
INERT INGREDIENTS:	99%
Total	100%

†Protected by U.S. Patent No. 3,736,338

EPA Reg. No. 40546-3

KEEP OUT OF REACH OF CHILDREN
CAUTION

If swallowed. Drink 1 or 2 glasses of water and induce vomiting by touching back of throat with finger or blunt object. Do not induce vomiting or give anything by mouth to an unconscious person. Get medical attention.

If inhaled. Keep patient strictly at rest and transfer to hospital immediately to get medical attention.

If on skin. Wash with soap and warm water.

If in eyes. Rinse thoroughly with clean water.

See side panel for additional precautionary statements and first aid.

FISONS®

Fisons Incorporated, Agricultural Chemicals Divison
2 Preston Court, Bedford, MA 01730

IMPORTANT: Read the entire Directions for Use and Warranty Notice before using this product.

FICAM D is a ready-for-use insecticide dust which has given effective knockdown and residual control of the pests listed.

FICAM D is for residual pest control in and on buildings and structures and their immediate surroundings and on modes of transport. Permitted areas of use include, but are not limited to: stores; warehouses; industrial buildings; houses; apartment buildings; schools; nursing homes; hospitals; restaurants; hotels; food manufacturing, processing and servicing establishments; and on vessels, rail cars, aircraft, buses, trucks and trailers.

FICAM D is intended for application with hand or power duster, or with a paint brush, or by other suitable means, to hiding and runway areas and those places where pests are found. To apply insecticide directly into cracks and crevices, use a bulbous duster or other suitable equipment. Apply lightly and uniformly to infested areas. Pay particular attention to: cracks, and crevices; service ducts; false floors and ceilings; wall voids; around electrical and telephone fittings and equipment; around water and sewer pipes; under and behind cabinets, refrigerators and sinks; around window and door frames; along baseboards; and in attics and crawl spaces. The amount to be applied will vary with the site but should usually be in the range of 1/3 to 2/3 ounces of FICAM D per square yard. Control of pests is frequently best achieved by using FICAM D in conjunction with spray treatments of FICAM W. Repeat treatments as necessary to maintain adequate control.

Cockroaches (including both non-resistant and organophosphate and organochlorine resistant strains), Ants, Crickets, Silverfish and Firebrats: Apply thoroughly to all areas where these pests crawl and hide, especially in cracks and crevices and hidden surfaces around sinks and storage areas, behind baseboards, around doors and windows, behind and under refrigerators, cabinets, sinks and stoves and in attics and crawl spaces. For ants, apply to ant trails, around doors and windows and other places where ants enter premises.

Carpenter Ants: Apply around doors and windows and other places where ants enter premises and where they crawl and hide. Also force dust into infested wood through existing openings or newly drilled small holes. When possible locate and treat nests and surrounding areas.

Brown Dog Ticks and Fleas in Buildings: Apply dust to infested areas such as pet beds and resting quarters, nearby cracks and crevices, under the edges of rugs and floor coverings, between and under cushions of upholstered furniture and other areas where these pests may be present. Old bedding of pets should be removed and replaced with clean fresh bedding after treatment. Do not treat animals or their bedding with this product.

Spiders: Apply along and behind baseboards, to window and door frames, corners, pipes, storage localities, attics, crawl spaces and other areas over which these pests may crawl.

Wasps and Bees: It is generally advisable to treat wasp and bee nests in the evening when insects are less active and have returned to the nest. Wear protective clothing if deemed necessary to avoid stings. Using hand or power duster or other suitable means, with extension tubes if necessary, thoroughly dust nest and entrance and surrounding areas where insects alight. Nests in wall voids can be located by listening with your ear against the wall. Drill a hole in the area, blow dust in, and reseal. For ground wasps, dust entrance and surrounding areas. For best results check nests carefully one or two days after treatment to ensure complete kill, then remove and destroy nest to prevent emergence of newly-hatched insects. If removal is not feasible, retreat the nest, if necessary. Do not use this product to treat overhead nests.

Sowbugs, Pillbugs, Ground Beetles, Earwigs, Millipe and Scorpions: Apply around doors and windows a where these pests may enter premises. Treat baseboar and other locations where these pests are found.

FOOD HANDLING ESTABLISHMENTS — Places ot residences in which food is held, processed, prepared

Food Areas — Application limited to spot or crack a ments only. For spot treatments, no individual spot wi square feet.

This use includes areas for receiving, storage, packin tling, wrapping, boxing), preparing, edible waste stora processing systems (mills, dairies, edible oils, syrups when food is exposed and facility is in operation are a food area.

Apply in small amounts directly into cracks and c bulbous duster or other equipment capable of appl directly into cracks and crevices between different e struction, between equipment and floors, openings lea hollow spaces in walls, equipment legs and bases wh ants, silverfish, firebrats, spiders and crickets hide. Sp also be made to areas where any of the above pests hid as baseboards, storage areas, closets, around water windows, behind and under refrigerators, cabinets, s other equipment and under drawers and similar areas.

Make applications in a manner to avoid deposits on exp introducing the material into the air. Avoid contaminati processing surfaces.

Non-Food Areas — FICAM D may be used as a crack ment or as a spot application in non-food areas. All are hide or through which insects may enter should be tre

OUTDOOR USE — Use FICAM D as a residual treatm ants, bees, brown dog ticks, centipedes, cockroaches, firebrats, fleas, ground beetles, millipedes, pillbugs, fish, sowbugs, spiders and wasps. Make a residual windows and doors, porches, screens, eaves, patios stairways and in crawl spaces and other areas where

To help prevent invasion of buildings and structures by treat a band of soil and vegetation 6 to 10 feet wide aro to the building or structure. Also treat the building foun spaces where pests are active and may find entrance. and uniformly to the band area. Pay particular attentio wasp nests in the band area. Wasp and bee nests in may be treated as noted above.

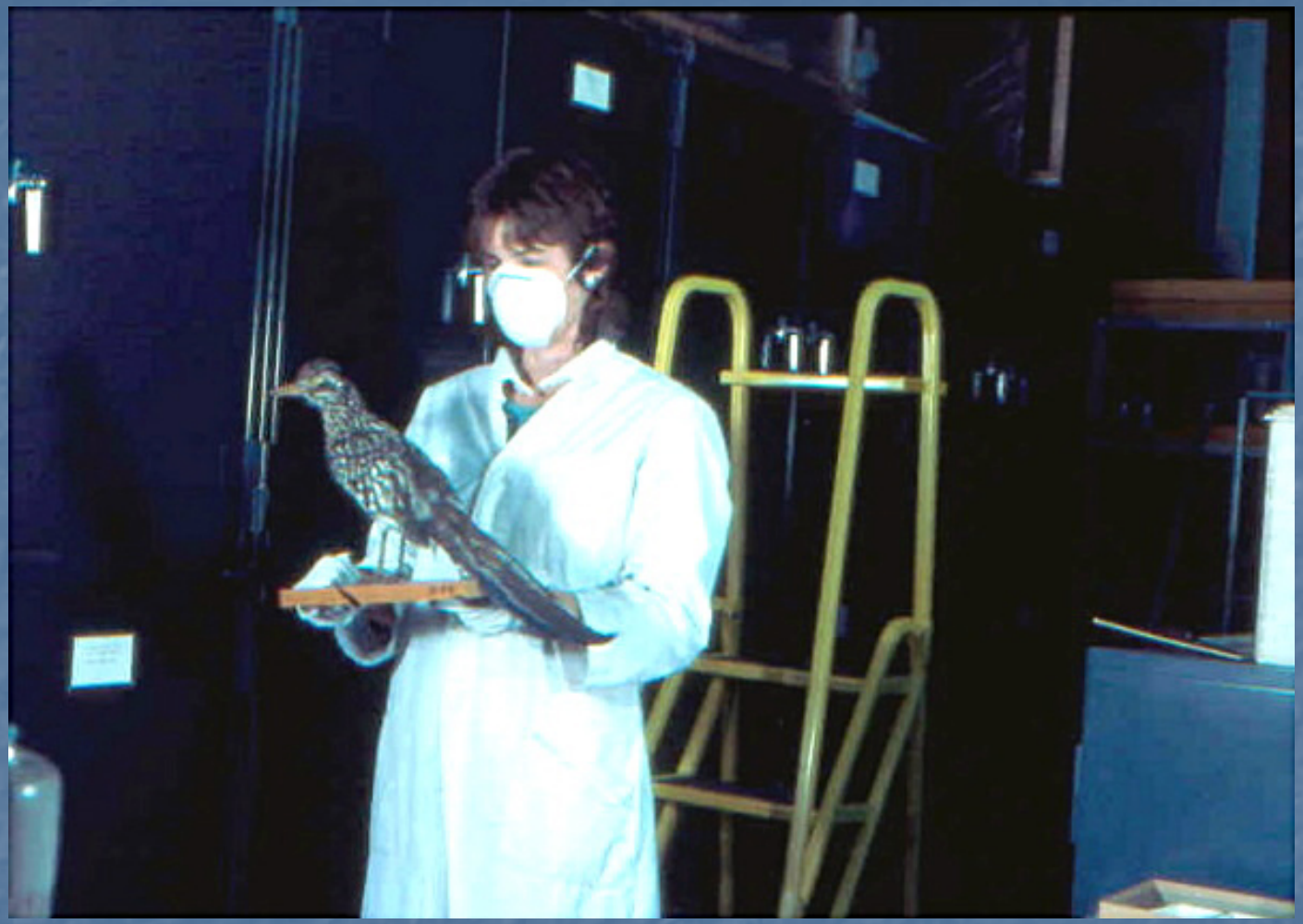
Old product instruction labels

Old containers or bags used to dispense pesticides

Current Museum Practices

- Regulatory and toxicological date is time sensitive
- Museums will have unique pesticide histories
- Donors often did not know or reveal to museums the use of pesticides on objects
- Testing techniques and refinements are ongoing
- Interpretation of testing results may vary

Remove contaminated objects from museum education programs



Wear personal protective equipment (PPE)

Creating a History

Compiling a history of museum pesticide use

Internal Information:

- Catalog cards, specimen treatment cards, loan records
- Receipts and purchase order for pesticides
- Contracts with pest control operators and exterminator companies
- Published archaeological filed notes
- Correspondence by staff members
- Monthly or annual reports done by staff

Information from existing and previous staff members:

- Interviews with present long-term and retired staff
- Interviews with pest control operator or extermination companies

Physical Evidence

- Tags, labels, marks on specimens
- Powder or crystalline residues on or around artifacts
- Well preserved Physical Evidence
- Tags but susceptible artifacts
- Persistent odors
- Old containers or bags used to hold or dispense pesticides
- Old application equipment
- Old stocks of chemicals/pesticides
- Old labels or copies of labels from containers

External Information:

- Early pest control handbooks
- Professional pest control trade magazines
- Chemistry literature
- Websites and searchable databases
- Entomology literature
- Taxidermy manuals and literature
- General museum literature
- Conservation literature
- Websites and university agricultural department databases
- Websites of government agency databases
- Websites of medical institutes toxicological databases

Isolate known or suspect objects into storage containers

NAGPRA and post museum dispositions

- Objects leave the museum they may:
- Return to cultural use and be worn
- They may be reburied in the earth
- They may be placed in caves or shelters
- They may be returned to water
- They may be burned
- They may be held in homes or cultural centers

Tribal storage

Testing

Testing for Pesticides

Protocols for spot testing pesticide residues

- Arsenic (compounds)
- Mercury (salts, vapors)
- Zinc, Copper, Lead
- Borates
- Carbamates and thiocarbamates
- Organophosphates
- Sulfur (compounds)

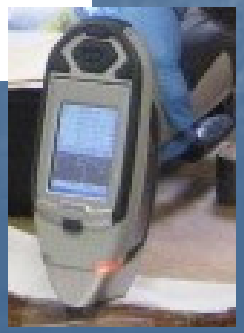
Recommendations for using Spot Tests to determine the presence of pesticides

- Wear appropriate personal protective equipment
- Read test kit or test paper instructions prior to running the test
- Use fresh reagent solutions
- Hold test papers with tweezers
- Work in well-ventilated areas
- Test samples along with known positive and negative controls
- Make written notes of procedures used and results observed
- Prepare for proper disposal of test reagents and test material
- Maintain material safety data sheets for all chemicals

XRF Instrument Advantages

- Analyzes 25 metals in materials
- Internal calibration
- Non destructive
- Portable for field use
- Downloadable data

Non Destructive XRF Testing



Bruker

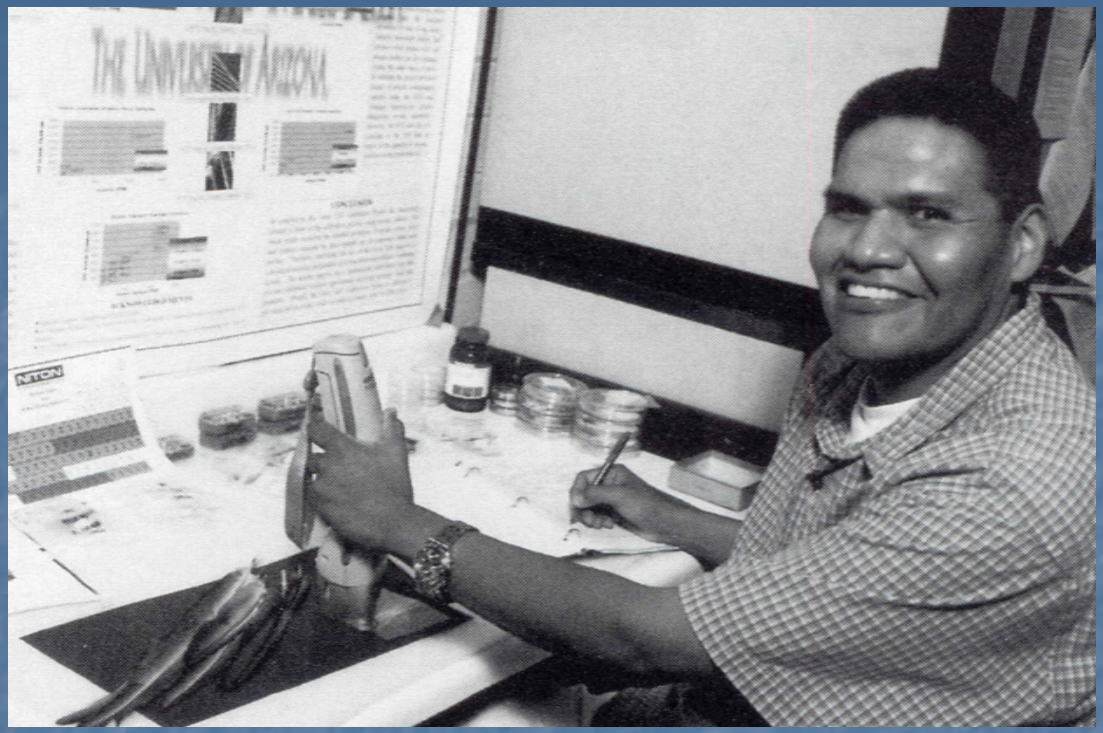
Niton

Innov-X

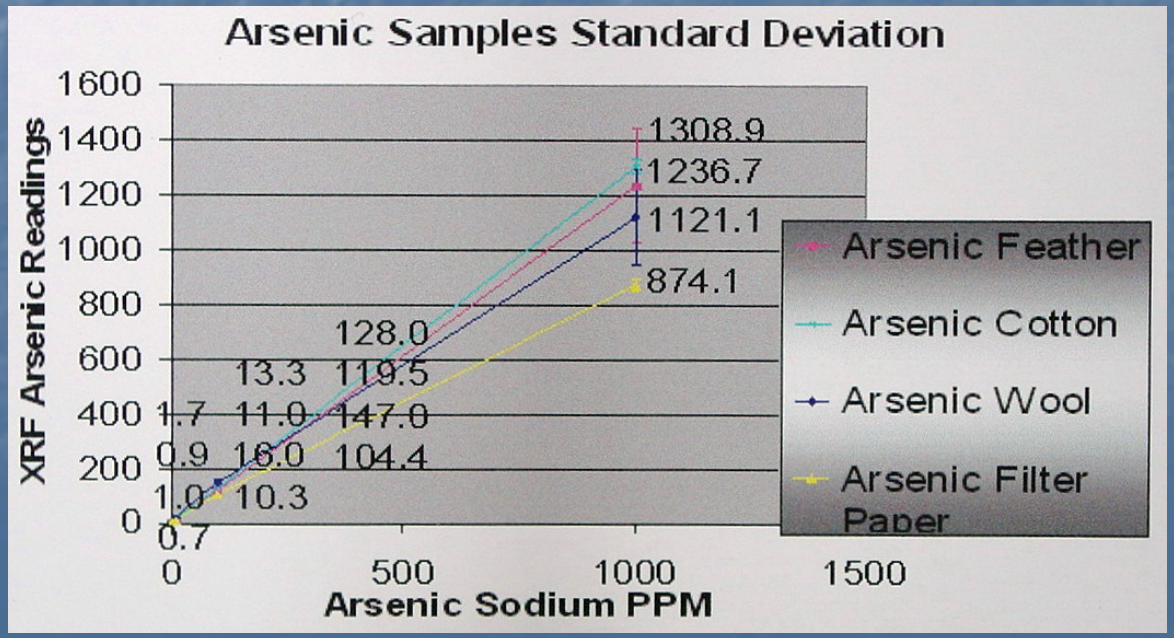
Detection Limit - Depends on the element and Analysis time

Analysis Time – Typically 30 to 90 seconds

Sample size – Approximately 1 cm by 0.5 cm



Instrument Calibration Study



Working as a team

- Some NAGPRA eligible objects have high levels of residual pesticides that pose a health risk
- NAGPRA eligible objects should be tested prior to repatriation
- Health risks of any exposure should be determined
- Personnel working with these objects should be properly trained and perhaps undergo periodic medical exposure screening
- Regulations should be enacted to ensure that individual and environmental exposures do not occur

Mitigation

<u>Mitigation:</u> efforts to diminish the effects of pesticides

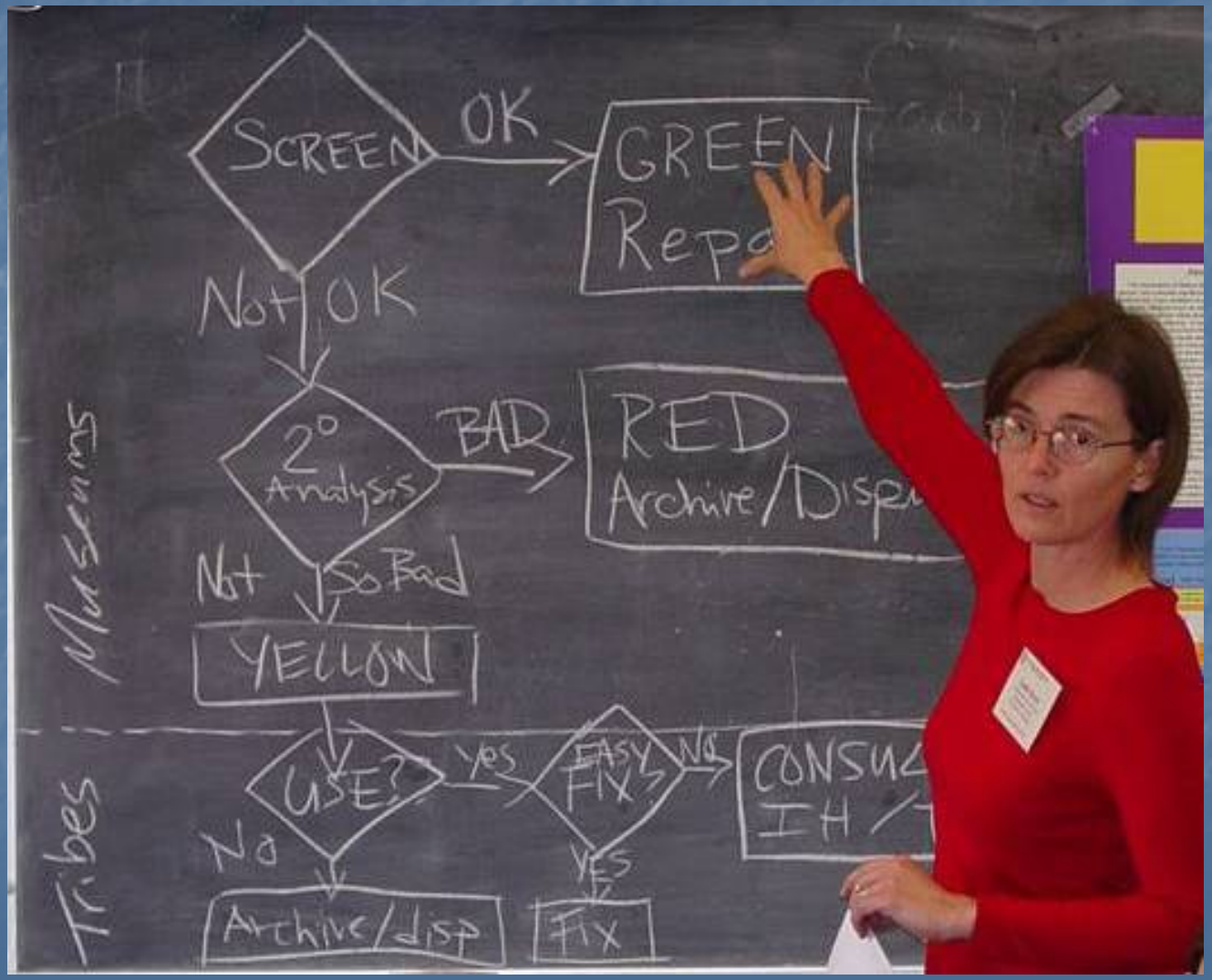
Important to any pesticide residue mediation treatment strategy are:

- The cultural appropriateness of the method if objects are considered living beings.
- The degree of pesticide residue removal necessary to achieve sufficient human detoxification may also depend on the type of cultural use that is expected
- The degree of pesticide residue removal necessary to achieve sufficient environmental detoxification may also depend on the type of physical, symbolic, or life ending use that is expected.

Risk Assessment

- **Prevention of exposure depends on**
  - Recognition
  - Risk assessment
    - Identification of hazard(s)
    - Identification of people at risk
    - Evaluation of the extent of the risks taking past history into account
    - Evaluation of existing control measures
    - Carrying out a risk rating (severity of injury x likelihood)
    - Arrangement of additional/new control measures
    - Recording of findings
    - Informing affected parties (managers, employees, contractors etc)
    - Instigate training if required
    - Monitoring and evaluation
- **Take appropriate actions**
    - Environmental
    - Personal

Recommendations for Human Health



The human heath hazards from pesticide residues are mitigated by the use of personal protective equipment and containment

Personal Protective Equipment

Eyes: goggles

Hands: gloves

Mouth: respirator

Body: lab coat or suit

Safety Guidelines

- Assume that hazardous pesticides are present.
- Wear nitrile gloves (not cotton or latex) while handling artifacts.
- Remove gloves so that hands do not touch the exterior surface.
- Discard gloves and wash hands with soap and water after handling objects, and especially before eating or smoking.
- Wear a lab coat or other protective clothing to keep dust off clothing. Remove the lab coat when out of the areas or no longer handling contaminated material. Assess the work area. If there is visible surface dust, shoe and hair coverings should also be worn.
- Keep lab coats clean so as to avoid transferring dust and dirt.
- Work with materials in a well ventilated area, ideally with a fume hood.
- Obtain medical certification to wear a mask or respirator and have an up to date fit test. Choose appropriate respirators and cartridges for the environment.
- Do not eat or drink in work areas.
- Ensure that work surfaces are well cleaned after they have been in contact with artifacts. Sponge-clean or wet-mop floors with soap and water.
- If dust has gotten onto clothing, remove clothes as soon as possible, bag and launder separately from other clothing.
- If there are concerns about exposure, consult a board certified occupational medical doctor or toxicologist.

Based on a 2000 monograph by
Monona Rossol (Conservation Scientist, Arts, Crafts, and Theater Safety)
Jane Sirois (Conservation Scientist, Canadian Conservation Institute)
http://bss.sfsu.edu/calstudies/arttest

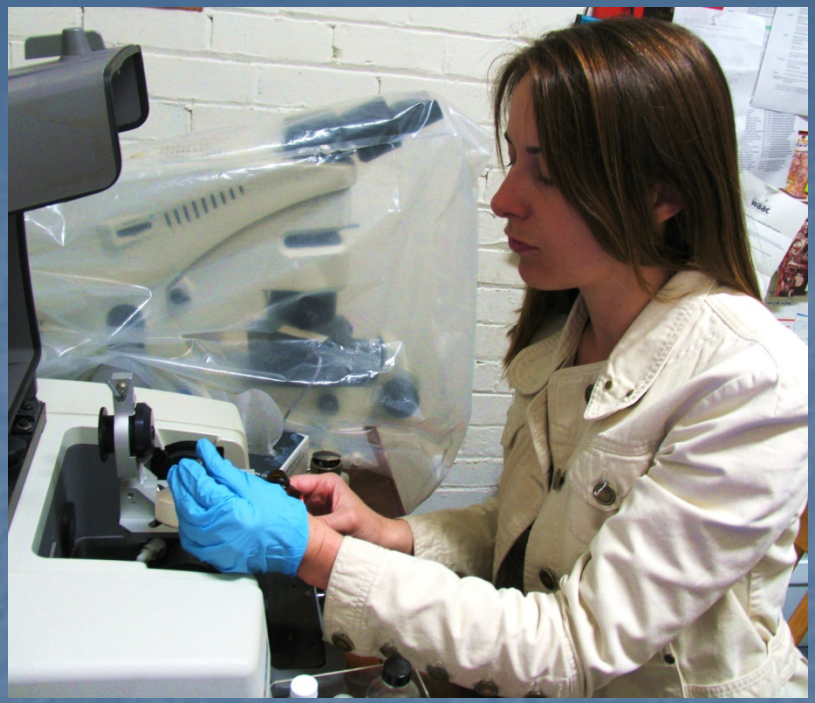
Removing Pesticides

<u>Remediation</u>: efforts to remove or counteract pesticides

Pesticide residue removal treatment considerations

- The cultural appropriateness of the method if objects are considered living beings.
- The degree of pesticide residue removal necessary to achieve sufficient human detoxification may also depend on the type of cultural use that is expected
- The degree of pesticide residue removal necessary to achieve sufficient environmental detoxification may also depend on the type of physical, symbolic, or life ending use that is expected.

Development of SERS active vapor sensors for detection of volatile museum contaminants



Odile Madden, PhD student

Pre-doc Fellow, MCI, Smithsonian

After completing pesticide identification studies with FTIR and detection studies with XRF Odile has moved her research topic to "Surface Enhanced Raman Spectroscopy".

Using a dispersive Raman Spectrometer she is preparing a sample on a roughened metal substrate that results in an amplified Raman signal. The benefits are amplification of the Raman signal above the fluorescence signal for certain fluorescent samples, and to ability to get Raman spectra for very small samples.

Gas chromatography and FTIR will be used as as supporting techniques.

Non Aqueous Mechanical Methods

- Scraping of old surfaces to re-sanctify objects. (Loma'omvaya 2001).

- Compressed Air cleaning (Glastrup 2001).

- Vacuums (Odegaard et al. 2003, Altree-Williams et al. 1993, Caldwell 1995, Lundbaek 1995).

- Absorbent activated carbon cloth used with vacuum cleaning (Piening 2001). Also tested with a fluorocarbon solvent (Kaiser 2007).

- Wiping with acetone solvent (Caldwell 1995).

Dry Cleaning by solvent emersion (Cavello et al. 2000, di Nola et al. 2002).

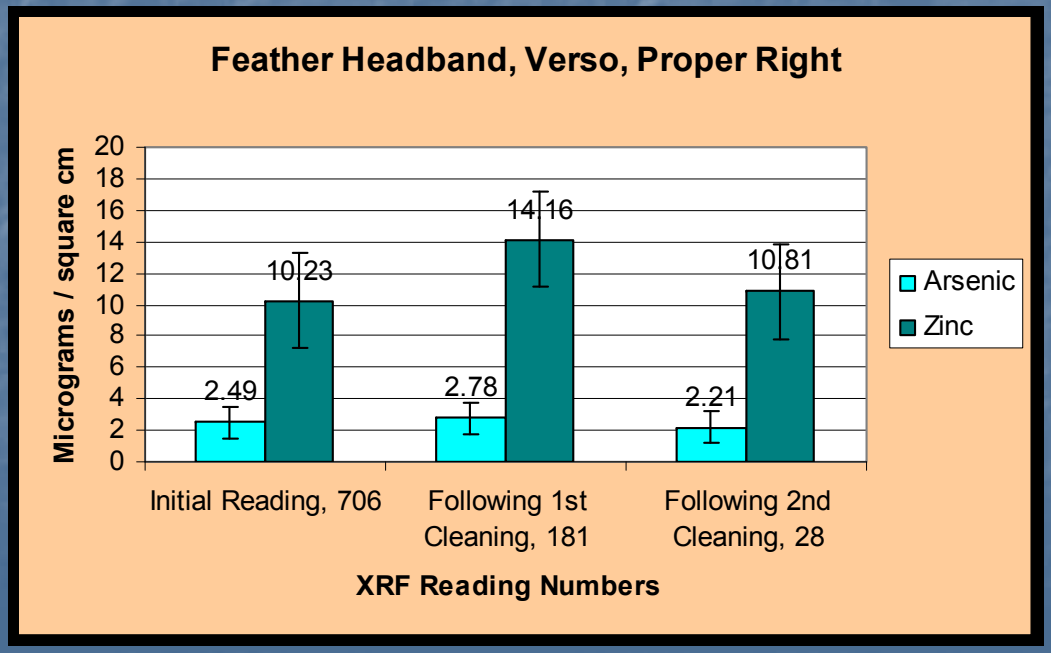
- Carbon Dioxide (Snow) for cleaning small particles (Wolbers 2000, Püschner 2002, Silverman 2006) Adapting the technique has been proposed (Unger 1998, Zimmt et al 2007).

2003

Vacuum Study RESULTS

XRF Readings:

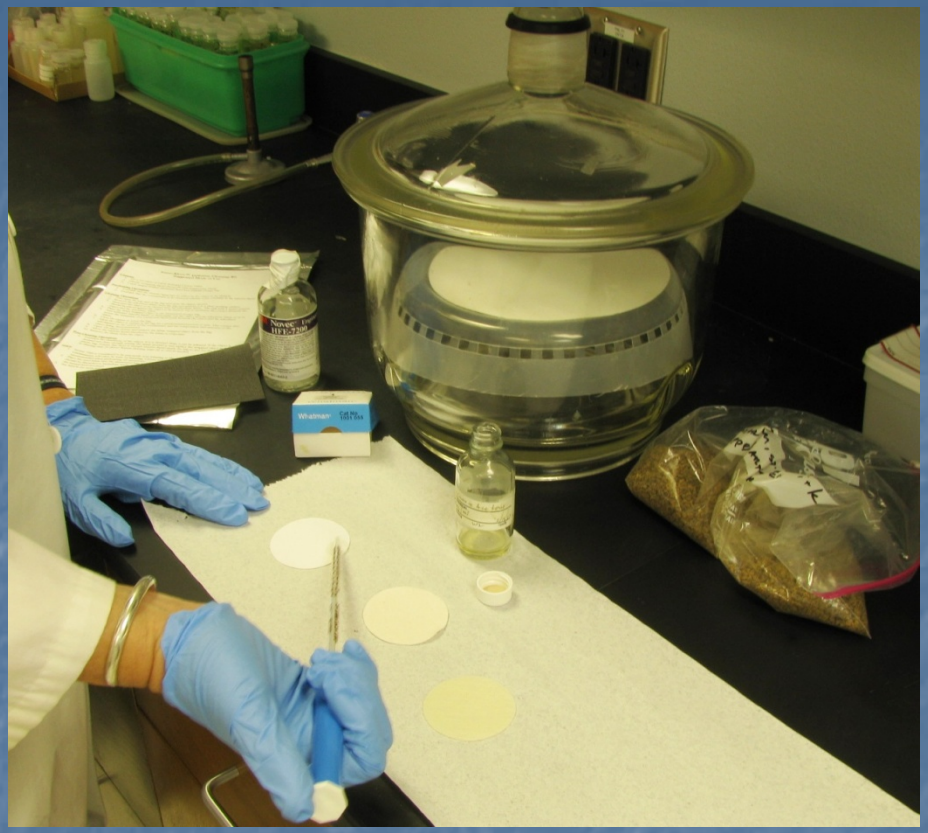
No. 706,
No. 181,
No. 28



Cheryl Podsiki, Kress Fellow

2009 Solvent Studies

In Collaboration with Dr. Robert Kaiser of Entropic Systems, Massachusetts



Activated carbon cloth is also being tested for use with a fluorocarbon based solvent (Entro-Kleen™ Diffusion Cleaning Kit) to remove organic pesticide contaminates on museum objects based on previous success in decontaminating military equipment (Kaiser 2007).

After studying the solubility of several organic pesticide residues we prepared substrate materials (paper, wool, cotton) with Diazinon pesticide residue. We propose to test the applicability of Kaiser's method as a possible pesticide removal technique for artifacts.

Aqueous Mechanical Methods

- Laundering techniques with pre-rinsing, hot water and detergents (Laughlin 1993).

- Steaming to reshape felt (Wood and Haigh 1955, Martin and Kite 2003).

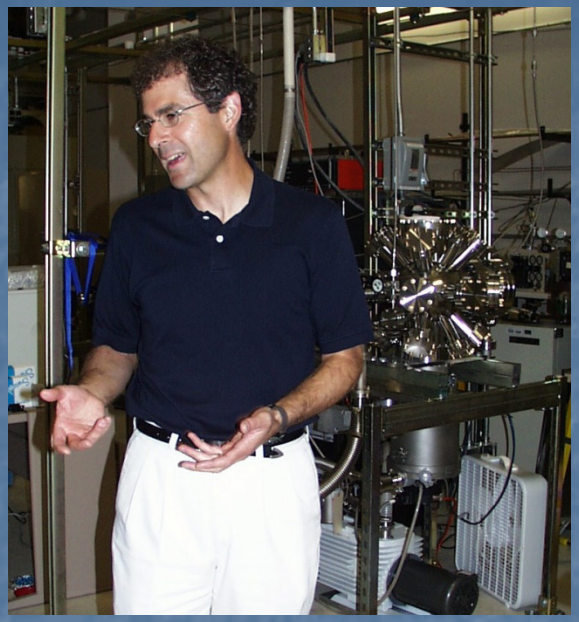
- Surface active displacement solutions (SADS) in water (Reuben 2006, 2007). Surfactants (surface active agents) from non-artifact fabrics (Park et al. 1990).

- Chelating compound, dimercaptosuccinic (DMSA) used for follow-up treatment (Hill and Reuben 2008).

- Supercritical or hypercritical carbon dioxide (Jelen et al. 2003, Von Ulmann 2003, Kang et al. 2004, Tello et al. 2005, Tello 2006, Tello and Unger 2007). $scCo_2$ studies with co-solvent for organic pesticide removal (Zimmt et al. 2007).

- Liquid carbon dioxide (Unger and Tello 2008)

2003-2005 Study Using Supercritical CO_2 to Remove Organic Pesticide Residues



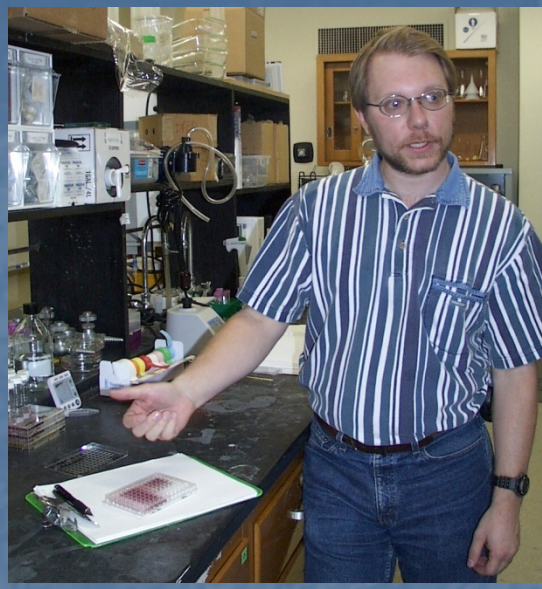
Dr. Anthony Muscat, Chemical & Environmental Engineering

Dr. Werner Zimmt, ASM and Agricultural & Biosystems Engineering

Teresa Moreno, ASM

Dr. Nancy Odegaard, ASM Materials Science & Engineering, Anthropology

Dr. Mark Riley, Agricultural and Biosystems Engineering



Support from the UA Vice President for Research

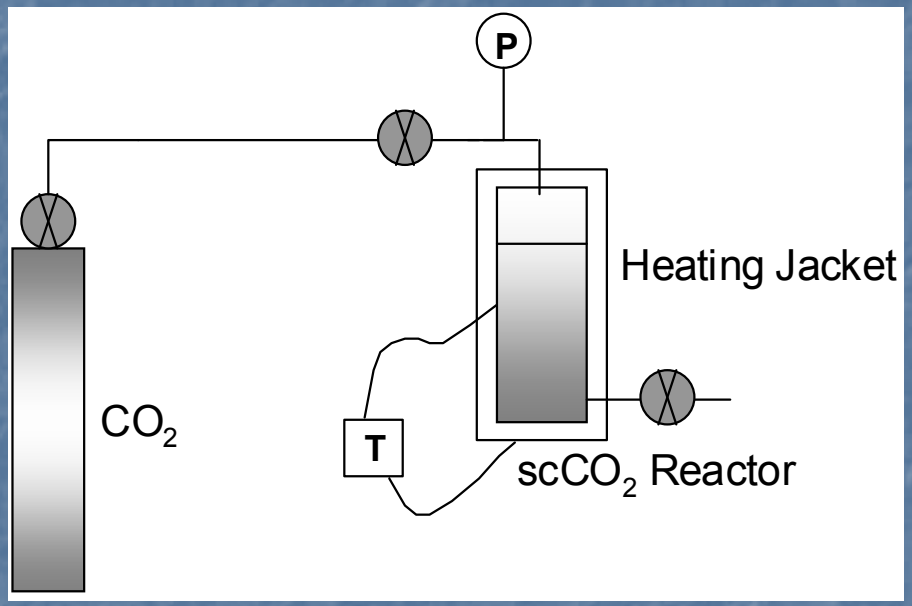
Study Procedure for Use of Supercritical CO2 to Remove Organic Pesticide Residues

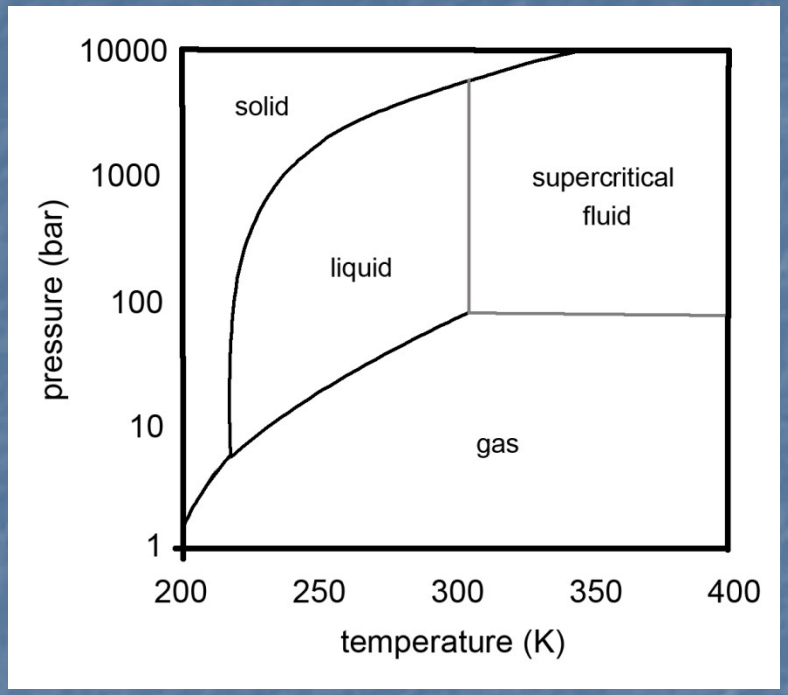
- The simulated artifacts were treated with scCO2 (temperatures of 50-60°C and pressure in the range 100-250 atm) for 2 minutes and the extent of the removal of diazinon determined. Dyed feathers were similarly extracted with scCO2 and the colors of the extracted samples compared favorably with the untreated samples.

- Detection of diazinon was performed using a unique toxicological screen based on the impact of toxins on Rat Lung Epithelial (RLE) cell cultures.

- Known quantities of diazinon solution were applied to small pieces of commercially tanned (mineral) leather.

$scCO_2$ Reactor System

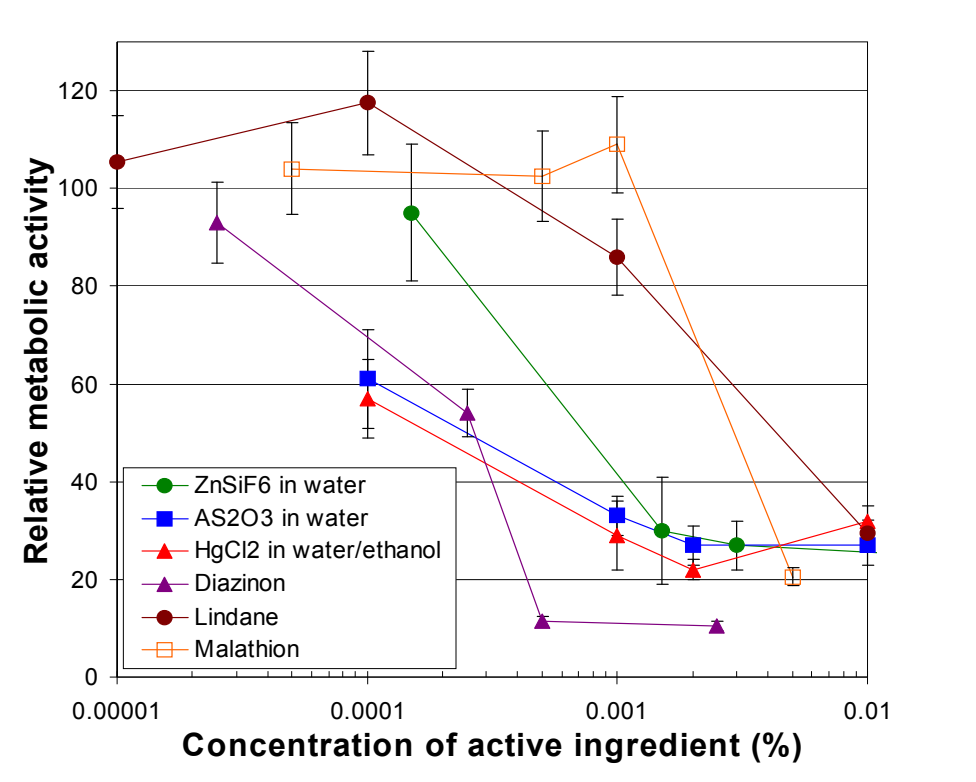




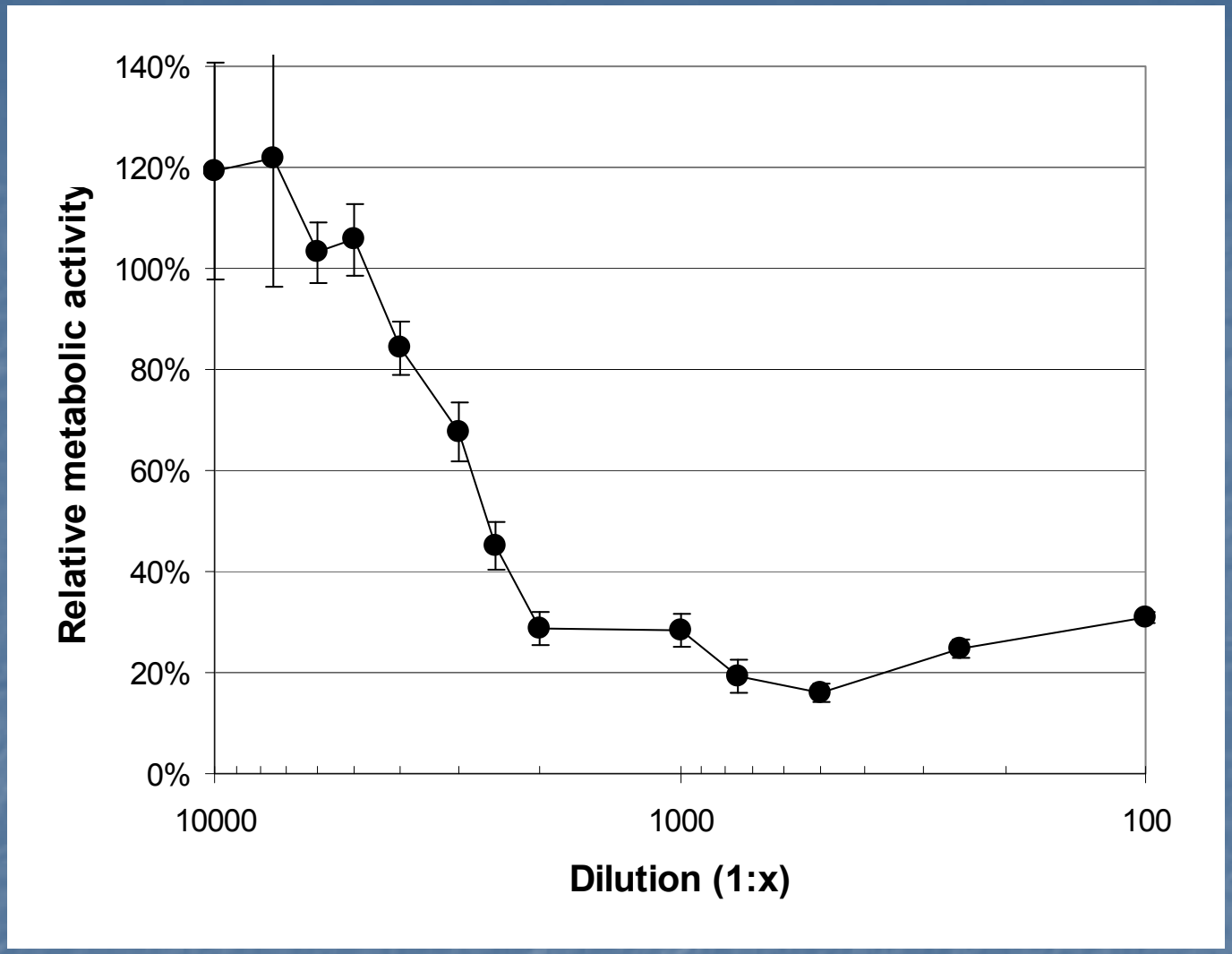
After loading, the reactor was chilled to 8°C and fed with liquid CO_2 to approximately 60 atm. The cylinder was valved off and the reactor was heated using a heating jacket and set point controller until the desired steady-state conditions were reached. After processing the fluid was exhausted through a needle valve.

Rat lung epithelial cells (RLEC) for determination of toxicity

- Results from the initial work with $scCO_2$ extraction showed that these cells will react with many different materials



Decrease in metabolism is due to presence of pesticide.
Decrease at a low concentration means pesticide has high toxicity.
Decrease that only occurs at high concentrations means low toxicity.



Effect of diazinon solution, initially at **4 mg / mL** in acetone, on RLE cell metabolic activity. The TC_{50} value is reached at a dilution of 1:2500, which represents the condition of full toxicity to which all extractions can be compared.

Effect of scCO2 on coloration of feathers

before scCO2

after scCO2

Conclusions Of Study:

- $scCO_2$ With an appropriate co-solvent, can be used to remove pesticides
- The system does not cause a change in visible appearance in the materials tested.

Further studies are justified.

- Extraction parameters (temperature, pressure, time)
- Co solvents
- Other pesticides
- Other substrate materials
- Other evaluative/analytical measurements

Chemical Alteration Methods

Dr. Timberley Roane, U Colorado-Denver, NCPTT grant collaborator

- Lugol's iodine solution to remove stains caused by mercuric chloride (Hawks and Bell 1999).

- Bacteria as a cleaning technique to remove mercuric compounds (Roane 2007). Bacteria have detoxified contaminated soils and water (Roane and Pepper 2000).

She sampled objects at ASM for bacteria. Her search yielded a species from a genus of common soil bacteria (*Arthrobacter*) that can remove about 30% of mercury contamination. *Cupriavidus metallidurans*, a bacterium isolated from zinc mine tailings that removes 60–80% of the mercury. *C. metallidurans* is also less likely to damage organic material in artifacts because it is an autotrophic bacterium that can make its own food from inorganic sources. Damage to objects has yet to be determined.

- Aqueous α-Lipoic acid solutions as a chelating agent for removal of arsenic and mercury (Cross 2007).

Peggi Cross, PhD, UA

Removal of 48.8 μg/cm² arsenic (III) from filter paper using reduced lipoic acid.

Treatme	Number of Sample	Average residual [μg/cm²]	Standar Deviati	% Arseni Remove d
Control	5	14.04	5.40	71%
Lipoic acid + alcohol	15	11.13	3.32	77%
Lipoic acid	15	5.32	1.39	89%

Percentage of mercury from various materials contaminated with mercuric chloride after one and two cleaning sequences.

Materia	Initial concentra n	1 % Removed	2 % Removed
Filter paper	1548	93	99.3
Cotton	1496	65.1	93.2
Wool	2161	8.7	36.7

Conclusions: Reduced lipoic acid solutions can be used to remove high concentrations of arsenic and mercury from sulfur containing materials and arsenic from material containing sulfur but not mercury from materials which contain sulfur.

- Arsenic and Mercury Salts can be removed from non-sulfur materials (paper, cotton) using activated lipoic acid or DI water.
- Arsenic can be removed from sulfur containing materials (wool, feathers) using activated lipoic acid or DI water solutions.
- Mercury can <u>not</u> be removed from sulfur materials (wool,feathers) using the chemicals tested.

External Energy Methods

- Microwaves to vaporize with carbon filters and suction (Tello 2006).
- Freeze-drying (Zabik and Dugan 1971).
- Ultrasonic sound waves with aeration and vaporization (Gustafsson 1993).
- Laser divestment/cleaning techniques (Asmus 2001). Additional experiments using a laser exhaust stream on wood (Jelen et al. 2005).
- Ultraviolet light from sunlight on clothing of agricultural workers (O'Rourke 2000). Pulsed ultraviolet flash lamp on painted surfaces (Asmus 2001).
- Hydrolytic and photolytic decomposition by UV light, conventional X-rays, and other sources (referenced in many journals of radiation, biochemical, analytical chemistry, and agriculture).

Conclusions

- The detection and removal of pesticide residues remains a problem for museum collections.

- Numerous factors affect the breakdown and potential removal of pesticides. There is no single solution for all pesticides or all objects.

- Most of the research currently underway includes:
  1. collaborative teamwork
  2. scientific methodology and measurements of effectiveness
  3. respect the cultural values associated with the objects.

Acknowledgements

- NCPTT Grant Program
- NAGPRA Grant Program
- Samuel H. Kress Foundation
- University of Arizona Faculty Small Grant Program
- University of Arizona Provost Award
- The Hopi Tribe
- Colleagues and students of the Arizona State Museum and Conservation Laboratory

Dept. of Chemical Engineering

Dept. of Agricultural and Biosystems Engineering

Dept. of Chemistry

Arizona Poison Center and Dept. of Medicine