Health and Safety

Mercury, The Other Heavy Metal

In the past, this column has devoted a lot of space to lead. It is arguably the heavy metal that potentially more conservators come into contact with than any other. This column will be devoted to the other heavy metal, mercury.

Mercury is one of the most interesting elements in all creation: the only metal that is a liquid at room temperature; a liquid of remarkable density (d=13.5); an excellent conductor of electricity; able to amalgamate with many other metals; surprisingly noble (it can be found in its elemental form in nature); and an amazing toxin.

When we think of mercury poisoning, most of us recall Lewis Carroll's "A Mad Tea Party" from *Alice's Adventures in Wonderland*:

"There was a table set out under a tree in front of the house, and the March Hare and the Hatter were having tea…"

And the Hatter was mad, because, as I imagine you all know, hatters were exposed to mercury. The most credible mechanism of hatters' exposure to mercury can be found at: www.hgtech.com/Information/MadHatter.htm. To wit...

The popular top hat of the time were made from beaver fur, but cheaper ones used furs such as rabbit instead. A complicated set of processes was needed to turn the fur into a finished hat. With the cheaper sorts of fur, one step was to brush a solution of mercurous nitrate on to the fur to roughen the fibres and make them mat more easily, a process called carroting because it made the fur turn orange. Beaver fur had natural serrated edges that made this unnecessary, one reason why it was preferred, but the cost and scarcity of beaver meant that other furs had to be used.

Whatever the source of the fur, the fibres were then shaved off the skin and turned into felt; this was later immersed in a boiling acid solution to thicken and harden it. The acid treatment decomposed the mercurous nitrate to elemental mercury. Finishing processes included steaming the hat to shape and ironing it. In all these steps, hatters working in poorly ventilated workshops would breathe in mercury vapor.

The website article goes on to say that mercurous nitrate was banned in 1941 in the US, noting also that the "the ravages of mercurialism among hatters had been known and tolerated in the United States" for nearly a century before the ban.

Conservators potentially come into contact with mercury in quite a few ways. It has been used as an insecticide in collections for years (generally mercuric chloride) to treat taxidermy and botanical specimens as well as a fixative for biological specimens. Decorative arts collections may contain elemental mercury and mercury amalgams in the silvering of historic mirrors. It is in the pigment vermilion (cinnabar). It can be found in mineralogical collections. It could still be present in historic felts like those ersatz beaver felt top hats. History collections (as well as your attic or basement) can have industrial materials like dry-cell batteries, switches, historic medicines, etc which are mercury bearing.

These occupational exposures are in addition to the daily exposure from mercury in the environment. Add to that possible contact with dental amalgam, broken fluorescent light tubes, broken switches in auto trunks, thermostats and thermometers, and, of course, seafood.

This column was suggested by Dr. Chandra Reedy who passed on this cautionary story. You know those testing ovens found in almost every conservation lab. They usually measure about 3' x 2' x 2', are almost always set to 100° C, and are used for artificial aging and Oddy testing. You've seen them, they usually have a thermometer poking out of the top of the oven. (Oh, did I mention that another one of mercury's remarkable properties is that it doesn't wet glass and has a remarkably linear coefficient of expansion making it just right for use in thermometers and manometers?)

A colleague of Chandra's was heating samples in the lab oven. Unbeknownst to her, the thermometer cracked, and the mercury spilled out into the oven. After she opened the oven door and stood there for a while adjusting her samples, she noticed the globs of mercury all over the bottom. She had the presence of mind to shut the door, but by then had already breathed in the mercury vapors that had permeated the oven.

Although a subsequent blood test indicated her mercury levels were not dangerously elevated, she nonetheless had significant symptoms indicative of mercury poisoning for about six months after the incident. (It was also an ordeal to decontaminate the oven, as it had to be moved outside and left open until the safety officer found no detectable mercury levels. Fortunately there was a space available that was away from human activity.)

Chandra wrote that this story reminded her that she has seen lab ovens in a number of conservation labs with what appeared to be mercury thermometers poking out of the top.

There are three broad classes of mercury toxins: organic and inorganic which includes both elemental and mercury salts. Elemental mercury is just mercury, also called quicksilver. Inorganic salts include mercuric chloride and the mercurous nitrate that our hatter friends were so mad about. Organic forms include methylmercury, Thimerosal, and dimethyl mercury. As a rule, organic mercury is the most toxic.

Some of you will probably remember the story of chemistry Professor Karen E. Wetterhahn at Dartmouth College. She died from exposure to dimethylmercury. In August of 1996, she spilled between one and a few drops of the compound on her latex gloves. She died in June of 1997 in spite of treatment for mercury poisoning.

Inorganic mercury can be converted into organic mercury via some biological processes. In the environment, industrial mercury waste released into the air (the largest single source is coal fired power plants) settles into river and ocean sludges where bacteria convert it into methylmercury. The low levels of methylmercury released into the environment by the bacteria bioaccumulate as big fish eat little fish. Towards the top of the food chain, the levels of methylmercury can increase to dangerous levels.

In 2001, the FDA (US Food and Drug Administration) issued a consumer advisory for pregnant women stating in part: "Nearly all fish contain trace amounts of methylmercury, which are not harmful to humans. However, long-lived, larger fish that feed on other fish accumulate the highest levels of methylmercury and pose the greatest risk to people who eat them regularly. You can protect your unborn child by not eating these large fish that can contain high levels of methylmercury: shark, swordfish, king mackerel, and tilefish."

They further recommended that: "While it is true that the primary danger from methylmercury in fish is to the developing nervous system of the unborn child, it is prudent for nursing mothers and young children not to eat these fish as well."

In response to the FDA advisory, the Environmental Working Group and the US Public Interest Research Group released "Brain Food: What Women Should Know About Mercury Contamination in Fish," contending that the recommendations do not go far enough to protect women and children from mercury contamination. (A pdf of the full report can be found at: http://www.pirg.org/toxics/reports/brainfood/brainfoodreport.pdf.)

The report recommends that the list of fish to be avoided during pregnancy be expanded to include: tuna steaks, sea bass, oysters (Gulf of Mexico), marlin, halibut, pike, walleye, white croaker, and largemouth bass as well as the four listed by the FDA. Further it recommends that consumption of: canned tuna, mahi mahi, blue mussels, eastern oyster, cod, pollock, salmon from the Great Lakes, blue crab from the Gulf of Mexico, channel catfish (wild), and lake whitefish be restricted to one meal per month. Lastly, they state that it is safe for pregnant women to eat the following fish: trout (farmed), catfish (farmed), shrimp, fish sticks, flounder, salmon (wild Pacific), croaker. blue crab (mid Atlantic), and haddock. (Personally, I find it something of a culinary insult to include fish sticks in the same sentence with wild Pacific salmon.)

Organic mercury salts are also used as preservatives in a wide variety of products. Now banned, it used to be mixed with marine paint to create antifouling paint (barnacles and such wouldn't grow on the hull). Fans of bad 1980's television might remember that one character on "Dynasty" induced psychosis in his brother by painting his office with marine antifouling paint.

Staggeringly, organic mercury (Thimerosal) is still used as a preservative in some over the counter medications and, most alarmingly, in some vaccines. While its use in vaccines in the third world may be justifiable on the basis of lack of refrigeration and reducing the per dose cost, it is shocking that in the first world, where refrigeration is ubiquitous, that vaccine manufacturers can't package all vaccines in single dose units that don't require a preservative.

So, organic mercury is very, very bad. Elemental (or metallic) mercury is more vexing. Not unlike the metal itself, it is very difficult to grasp fully anything about mercury. The more you try, the harder it is to pick up all the disparate pieces.

Since mercury has an appreciable vapor pressure, mercury vapor poses the greatest risk and is far more challenging to control. Mercury vapor passes through the lungs with great ease. About 74% of the mercury vapor present in a breath of contaminated air passes into the body through the lungs. (Alcohol in the air or blood reduces this percentage.) Mercury vapors are not well absorbed through the skin although elemental mercury can enter the body through direct skin contact.

Once in the body, elemental mercury gets past the blood-brain barrier and through the placenta, a trick which inorganic mercury salts cannot manage. In the body, the mercury can be oxidized to the mercuric ion (Hg^{++}) by hydrogen peroxide-catalase (an enzyme that protects cells from damage by hydrogen peroxide). Also in the body, the mercuric ion can be reduced to elemental mercury by a number of biological pathways. Thus the mercury can be recycled through the body changing from dissolved vapor to salt and back to dissolved vapor. One of the implications of this is that testing for mercury in urine and blood samples can be remarkably variable.

The ACGIH (American Conference of Governmental Industrial Hygienists) has published a BEI (Biological Exposure Index) for mercury. Mercury can be measured in the blood or urine. It can take up to 20 hours after exposure for increased mercury levels to show in blood. The half life of mercury in the blood is about 85 hours so blood test are only valid during a short window after a single exposure. Mercury collects in the tissue of the kidneys. This causes a latency in the elimination of mercury. It takes 4 to 6 months of continuous occupational exposure before mercury levels in urine correlate with exposure.

Mercury accumulates in the gray matter of the brain, the kidneys, and liver. The classical signs and symptoms of inorganic mercury poisoning include: tremors, emotional instability and irritability, peripheral neuropathy, gingivitis, stomatosis, erethism, ocular and vision changes, hearing loss, and renal impairment. Inhalation of high mercury vapor concentrations for relatively brief periods of time can cause pneumonitis, bronchitis, chest pain, dyspnea, cough, stomatitis, gingivitis, salivation, and diarrhea.

A developing fetus is particularly sensitive to mercury – remember the fish? Children are highly susceptible to mercury and cases of mercury poisonings in the home are both disturbing and indicative of the need to prevent contamination of the home from workplace exposure. A 23 month old toddler suffered mercury poisoning from a broken carton of fluorescent light tubes. The carton was broken in a shed adjacent to the nursery. The glass and mercury were removed but the children continued to play in the area. 5 months after the tubes were broken, symptoms manifested.

Mercury is used in amalgam based tooth fillings. The major source of temporarily increased levels of inorganic mercury in blood and urine is fresh dental amalgams. Small amounts of mercury vapor are given off by dental fillings. Whether or not this low, ongoing exposure is harmful is a matter of ongoing debate. Mercury deaths have arisen from exposure in a residence from home smelting of dental amalgam in an attempt to recover the silver.

The most alarming and uncontrolled exposure to mercury in the museum is from collection items that have been treated with mercuric chloride. This would include taxidermy specimens, some ethnographic materials, herbaria collections, and the like. Recent research has been done by Catharine Hawks, Kathyryn Makos, and coworkers.

The C/Kathys are both exoffico members of the AIC Health and Safety committee. At the most recent AIC H&S committee meeting, Cathy Hawks described their research program and their results which they are writing up as you read this. While the formal papers are being prepared, I've been told I can spill some of the beans and dangle a few shiny baubles to get everyone's attention.

The most exciting aspect of their research is that they've taken a commercially available product and developed a test-strip indicator that is exquisitely sensitive to mercury vapor. It is so sensitive that exhaling on the test strip will give a positive reaction if you have amalgam fillings in your mouth. (Machines costing tens of thousands of dollars can barely do that.) For the details, you will have to wait for them to publish. (So nudge them forward by sending them encouraging emails.)

Furthermore, I've developed a theory about what I think is happening with mercuric chloride treated materials. The choice of opening with a quote from Lewis Carroll is more subtle than you might realize. Carroll was an early photographer. Photography is based on silver chloride's reaction to light and forming metallic silver (which is developed into an image). I think much the same thing happens with mercury. A bold leap forward or a foolish conjecture? You decide.

Many of the clues came from my long discussions with Cathy. One clue was that they had found mercury was being released into the air from the collection items they were studying. Their testing couldn't determine the form of the mercury with absolute certainty, but it's a good bet it is elemental mercury. In fact, they found that opening a cabinet of herbarium specimens could expose the curator to a dangerously high level of mercury.

By measuring the mercury concentrations in the cabinet, the air exchange rates in the storage area, and factoring in the current TLV-TWA (0.025 mg/m^3), they were able to come up with a protocol for safely opening the cabinets. Now, the curator goes into storage, quickly opens the cabinet of interest, and promptly leaves the nearby area for a proscribed amount of time. In that time, the climate control system will have diluted the initial high mercury concentration to safe levels. Then they can work with the collection items safely.

Another bit of evidence: Cathy said that they had observed that paper in the inner pages in plant specimen folders (where the floral matter had been treated with mercuric chloride) were free of discoloration. The edges of the pages of some folders, however, had developed dark stains. Many of the folders with discolored edges were known to have been stored in glass-fronted cabinets. They suspected that either light or external contaminants were the cause of the darkening.

They tested mercuric chloride on Whatman filter paper alone and in the presence of ionized sulfur contaminants. They found that mercuric chloride alone formed the stains on exposure to short wave UV light and that the darkening reverted when removed from the radiation. (They also found that the presence of sulfur prior to light exposure lead to the formation of a permanent stain.) Hmmm.

Another factor to consider. Remember that vermilion can turn from red to black with light exposure. (The change is not chemical. The hexagonal mercuric sulfide, red cinnabar, somehow changes to cubic mercuric sulfide, black metacinnabar.)

The chemistry literature I had at hand didn't mention anything about light interacting with mercuric chloride. I spoke with some chemist friends, exchanged emails with the H&S committee, and checked the web. And, with the correct search term, "photoreduction," supplied by a chemist friend of a chemist friend, I found the missing link.

Inorganic chemists don't seem know about mercuric chloride's interaction with light… but environmental scientists do! The research was sponsored by the EPA (US Environmental Protection Agency) and is published on their website: "Final Report: Light Induced Mercury Volatilization from Substrate: Mechanisms Responsible and In Situ Occurrence" by Mae Sexauer Gustin at the Environmental and Resource Sciences Department, University of Nevada-Reno <es.epa.gov/ncer/final/grants/96/airchem/gustin.html>.

Dr. Gustin's research found that mercury vapor was always being released from mercuric chloride but the level didn't change with exposure to light. Cinnabar did release mercury in response to light exposure. But, and here's the good part, mercuric chloride does release mercury in response to light if it is mixed with organic matter or iron oxide.

So, I'll bet a dozen Krispy Kremes that this is what happens: When a specimen is treated with mercuric chloride, the substrate absorbs light and transfers the energy to the mercuric chloride which promptly is locally reduced to metallic mercury. The metallic mercury migrates into the crystalline structure of the mercuric chloride where it forms a reservoir from which elemental mercury vapor is slowly released into the environment.

The consequences of this scenario, Krispy Kremes aside, is that mercury release from collection objects that have been treated with mercury salts is ongoing – something that is also supported by the C/Kathys and coworkers' research. Short of removing all traces of mercuric chloride, we can never beat the problem. So the solution is to move to scavenging.

My suggestion is to co-opt an idea that came out of the GCI's research on organic acids in display cases. Some years ago, the Getty demonstrated the efficacy of using a small fan to draw air into a display case through a respirator cartridge designed to remove organic acids. I would think the same idea would be well suited for the mercury problem. Depending on how efficient mercury vapor cartridges are at removing the contaminant, one could probably place one of Cathy's indicator strips on the down-wind side and have a monitor that would signal when the cartridge was spent.

I don't think passive scavengers will be as effective because they will not protect specimens in the same case from cross contamination, but they should be tested, too. The metal sponges that are used for mercury spill clean-up are a possibility. Cathy said they successfully used Pacific Silver Cloth as a mercury vapor scavenger during their research. I suspect microchamber and other zeolite based products and activated charcoal will not be particularly effective at sequestering mercury vapor.

Clearly there's much work to be done on the subject.

I would like to express my deepest thanks and gratitude to Cathy Hawks and Kathy Makos for their work and contributions to this paper. I also thank Dr. Duane Chartier, Dr. John McNally, Dr. Chandra Reedy, and Tania Collas for thought provoking discussions on the subject.

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Duct tape, anyone?