Journal of the American Institute for Conservation

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/yjac20

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JOURNAL OF THE AMERICAN INSTITUTE FOR CONSERVATION
https://doi.org/10.1080/01971360.2022.2097810

RAPID COMMUNICATION

Advances in storing and monitoring mercury-tin amalgam mirrors

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ABSTRACT
Tin-mercury amalgam mirrors are ubiquitous amongst historical collections worldwide. They present potential human health risks as they degrade, releasing liquid mercury and mercury vapor. Over the last decade, care of degrading mirrors at Winterthur Museum, Garden & Library has evolved to their present storage: removing dripping mirrors from exhibition and into a limited-access storage space. Using a Jerome Mercury sensor, various methods for storage were evaluated for the buildup of mercury vapor. Mercury vapor accumulated within a plastic bag surrounding a dripping mirror, informing an open-design tray storage solution. While these trays catch drips at the source, they are open to ambient air to allow small volumes of vapor to dissipate. Updated practices for mirror storage, monitoring, and maintenance prioritize staff safety and object preservation.

ARTICLE HISTORY
Received 30 June 2021
Accepted 28 June 2022

KEYWORDS
Mercury; amalgam mirrors; looking glasses; tin amalgam; mercury vapor; spill cleanup; safety; storage tray solution

RÉSUMÉ
Les miroirs « au mercure » (amalgame étain-mercure) sont omniprésents dans les collections historiques du monde entier. Ils présentent des risques potentiels pour la santé humaine lorsqu'ils se dégradent, libérant du mercure liquide et de la vapeur de mercure. Au cours de la dernière décennie, l'entretien des miroirs en cours de dégradation au Winterthur Museum, Garden & Library a évolué vers leur mode de stockage actuel, qui consiste à retirer des espaces d'exposition les miroirs qui suintent et à les placer dans un espace de stockage à accès limité. À l'aide d'un détecteur de mercure Jerome, différentes méthodes de stockage ont été évaluées au regard de l'accumulation de vapeur de mercure. L'accumulation de vapeur de mercure dans un sac en plastique enveloppant un miroir suintant a inspiré la conception d'un support de stockage ouvert. Bien que ces plateaux récupèrent les gouttes à la source, ils sont ouverts à l'air ambiant pour permettre à de petits volumes de vapeur de se dissiper. Ces nouvelles pratiques de stockage, de surveillance et d'entretien des miroirs donnent la priorité à la sécurité du personnel et à la préservation des objets. Traduit par Stéphanie Auffret.

RESUMO
Espelhos de amálgama de estanho-mercúrio são onipresentes entre as coleções históricas em todo o mundo. Eles apresentam riscos potenciais à saúde humana à medida que se degradam, liberando mercúrio líquido e vapor de mercúrio. Ao longo da última década, o cuidado com os espelhos degradados no *Winterthur Museum, Garden & Library* evoluiu para o armazenamento atual: removendo da exposição os espelhos que estavam "pingando" e colocando-os em um espaço de armazenamento com acesso limitado. Usando um sensor Jerome Mercury, vários métodos de armazenamento foram avaliados para o acúmulo de vapor de mercúrio. Vapor de mercúrio acumulado dentro de um saco plástico ao redor de um espelho pingando, forma uma solução que é armazenada por uma bandeja em ambiente aberto. Enquanto essas bandejas pegam gotas na fonte, elas ficam abertas ao ar ambiente para permitir que pequenos volumes de vapor se dissipem. Práticas atualizadas de armazenamento, monitoramento e manutenção de espelhos priorizam a segurança da equipe e a preservação de objetos. Traduzido por Beatriz Haspo.

RESUMEN
Los espejos de amalgama de estaño y mercurio son omnipresentes en las colecciones históricas de todo el mundo. Presentan riesgos potenciales para la salud humana a medida que se degradan y liberan mercurio líquido y vapor de mercurio. Durante la última década, el cuidado de los espejos degradados en el Winterthur Museum, Garden & Library ha evolucionado hasta su almacenamiento actual: se retiraron de la exhibición los espejos que gotean y se colocaron en un espacio de almacenamiento de acceso limitado. Usando un sensor Jerome Mercury, se evaluaron varios métodos de almacenamiento para la acumulación de vapor de mercurio. El vapor de mercurio se acumuló dentro de una bolsa de plástico que rodeaba el espejo que goteaba, informando así una solución de almacenamiento de bandeja de diseño abierto. Si bien estas

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bandejas atrapan las gotas en la fuente, están abiertas al aire del ambiente para permitir que se disipen pequeños volúmenes de vapor. Las prácticas actualizadas para el almacenamiento, monitoreo y mantenimiento de los espejos dan prioridad a la seguridad del personal y la preservación de los objetos. Traducción: Amparo Rueda.

1. Introduction

Tin-mercury amalgam mirrors can be found worldwide throughout large and small cultural heritage institutions, as well as within private collections. From the 16th through 19th centuries, a tin-mercury amalgam under glass was the primary method for manufacturing mirrored or reflective surfaces in objects, from hand-held looking glasses to carriage lanterns (Hadsund 1993; CDC 2007). Historical tin-mercury amalgam mirrors within collections present the potential for mercury liquid and vapor exposure for staff and visitors as mirrors naturally deteriorate.

Inherently unstable, tin-mercury amalgam mirrors consist of a solid and liquid phase of mercury and tin. Over time, liquid mercury migrates to the bottom of the mirror and metallic crystals corrode, producing tin oxides. This corrosion further causes the amalgam to separate, releasing more liquid mercury (Hadsund 1993). Once the liquid mercury is no longer alloyed to the tin as an amalgam, it will simply evaporate as toxic mercury vapor, exiting the mirror through openings in the frame and glass. Liquid mercury will also drip from seams between glass or the frame, falling and dispersing into areas that are extremely difficult to clean, such as cracks between floorboards or into the pile of a carpet. These drips present a potential health risk to any occupants of the space, especially if they are not aware of the active degradation and potential mercury present. Drips off-gas mercury vapor, and they may be tracked on the occupant's shoes, spreading the contamination beyond.

A known neurotoxin, mercury is considered to be one of the top ten chemicals of major health concern by the World Health Organization (WHO 2021). Nearly ninety percent of human-made mercury pollution is in the form of mercury vapor, and the primary route of human exposure to elemental mercury is through inhalation of its vapor (Kabir et al. 2017). Liquid at room temperature and standard pressure, mercury readily evaporates when exposed to air at a rate of 7 $\mu g/cm^2/hr$ at 20°C (Nriagu 1979). When inhaled, mercury vapor is absorbed across the blood–brain barrier, by as much as 80% (Cherian et al. 1978; Garetano, Gochfeld, and Stern 2006).

Mercury vapor has a density of 6.9 (relative to air, where air = 1), suggesting it will "drop" or remain close to the floor (CDC 2011); however, additional factors such as air flow and air exchange rates can affect the movement of mercury vapor in ambient conditions. Because mercury vapor is colorless and odorless, it is not possible to visualize how the vapor may disperse. While some studies have revealed that household mercury spills may emit mercury vapor at harmful levels many years into the future (CDC 1996; Carpi and Chen 2001), other studies suggest that single drops of liquid mercury will not evaporate to cause harmful vapor concentrations within indoor spaces (Hadsund 1993; Winter 2003).

Some protocols for maintaining deteriorating tin-mercury amalgam mirrors are established within the conservation and collections care community (Payne de Chavez 2010; Swan 2010; Torge et al. 2010; Koss Schrager 2013). These protocols include sealing the backs of frames with mylar, short-term half-bagging with polyethylene bags to capture drips, sealing spaces between frames and glass with felt to prevent vapor escape, utilizing absorptive materials in backings, and proper labeling of hazard descriptions directly on the objects. While these mitigation strategies exist, there is great variability in the degree of hazard management and awareness from one institution to another.

At the Winterthur Museum Garden & Library, practical mirror maintenance, awareness, and risk management have evolved over recent years in collaboration with students from the Winterthur/University of Delaware Graduate Program in Art Conservation. The focus of this work came from the need to assess and address actively degrading mirrors within Winterthur's collection. The associated tasks included: accurately identifying mirrors as mercury-tin or not, quantifying the hazard of mercury vapor emitted from three actively dripping mirrors, and using this information to assess and modify existing mirror care protocols.

2. Analyses of mirrors and existing protocols

To determine which mirrors should be more closely monitored for active tin-mercury degradation, the team used portable X-ray fluorescence spectroscopy (pXRF) to detect the presence of tin-mercury amalgam within mirrors and looking glasses (see Appendix). The presence of tin would indicate a tin-mercury amalgam was used for the reflective surface (Bright 2016). Results from this analytical survey suggested that at least 63% of the 243 mirrors at Winterthur were fabricated using tin-mercury amalgam and over a third of the analyses were inconclusive due to attenuating elements present in the glazing. All of these mirrors were deemed to be "at risk" of dripping. Only five mirrors in the collection were determined to be silvered.[1]

The mirrors on display at Winterthur hang in period rooms among dense arrangements of the Museum's decorative arts collection objects. Actively dripping mirrors sometimes drip and splatter into miniscule droplets onto the floor and surrounding objects. This makes for a time-consuming and potentially dangerous cleanup for staff. Two members of the Winterthur conservation staff use a mercury spill kit to regularly collect mercury droplets during monthly inspections (Figure 1). Staff wear nitrile gloves, disposable lab coats, and shoe covers as they make their rounds. Raking light from a flashlight is helpful for finding some droplets on the floor, but due to their small size, it is difficult to know if all droplets have been collected during clean-up. Once collected and stored in a sealed container, the captured mercury is collected for toxic chemical waste disposal by a third party.

In terms of hazard communication, Winterthur staff complete mandatory refresher training sessions to maintain their collection handling privileges. These sessions are used to update staff on handling protocols. One of the sessions covers collection hazards, which informs staff of potential health hazards, such as mercury, and instructs them to contact preventive conservation staff if cleanup is needed. Besides the refresher training, handling precautions are communicated for the "at risk" mirrors via the museum's Collections Management System[2] and the handling notes appear on the object's movement paperwork.

Given the extensive presence of the tin-mercury amalgam mirrors in the collection, the indoor air quality implications were investigated. A Jerome 431-X Mercury sensor was used to measure the concentration of mercury vapor in the vicinity of mirrors known to produce drips. This sensor is a hand-held device that provides instantaneous mercury vapor measurements from .003 to 0.999 mg/m^3 with an accuracy of +/-5% at 0.100 mg/m^3 Hg. Here, the amount of mercury was below the detection limit of the sensor. However, the reading from a drop encapsulated in a spill kit was 0.79 mg/m^3, which is above the National Institute for Occupational Safety & Health, NIOSH (0.05 mg/m^3), and the Occupational Safety and Health Administration, OSHA (0.1 mg/m^3), recommended time-weighted average exposure limits.

2.1. Evaluation of storage options

To test the efficacy of storage options for actively dripping mirrors, an experiment was devised to mitigate the risk of mercury vapor buildup. One of the dripping mirrors was stored in a small closet (volume $5m^3$) for the duration of the experiment. For the first part of the study, the mirror was hung on the wall with no enclosure, "unbagged," and following that, a

Figure 1. Mercury droplet as it forms on the seam of a looking glass (left). Preventive conservation staff clean up liquid mercury using a "Mercury Spill Control Station" kit (right). A manual vacuum gun lifts and encapsulates mercury droplets. The kit also contains a mercury sorbent, which helps to clean the vacuum reservoir by turning the mercury into a solid waste.

polyethylene sleeve with a tapered drain at its bottom was placed around the lower portion of the mirror, "bagged," to mimic a common half-bagging storage technique to collect any mercury drips (Figure 2).

Three times during this study, a Jerome 431-X Mercury sensor was used to measure mercury vapor levels in the closet. Measurements were taken approximately 2.5 cm above the floor to represent the concentration of mercury vapor in the room, and the measurements within the bag were taken approximately 7 cm from the top of the enclosure. The first measurement was at the start of the experiment after the mirror had been stored in the closet, uncovered, for one month. These readings (Figure 3) show that mercury vapor is possibly building up in the plastic sleeve compared to the room.

3. Implications for mirror storage at Winterthur

Standardizing the preventive treatment of these mirrors is challenging because solutions depend on the construction of the mirror. Sealing the seams around the back of a framed mirror is a typical alteration, and the seal keeps evaporating mercury vapor contained within the mirror/frame package. The mirrors in this case study drip from seams in the glass on the front; thus, sealing the back of the mirror to prevent vapor escape would only partially alleviate mercury contamination. Bagging or half-bagging mirrors is another common technique; however, as we demonstrated, the potential buildup of mercury vapor within the bag may create

Figure 2. The mirror is stored within a polyethylene sleeve with a tapered spout on the bottom, sealed with a binder clip. This allowed for easy opening to release liquid mercury as it collected.

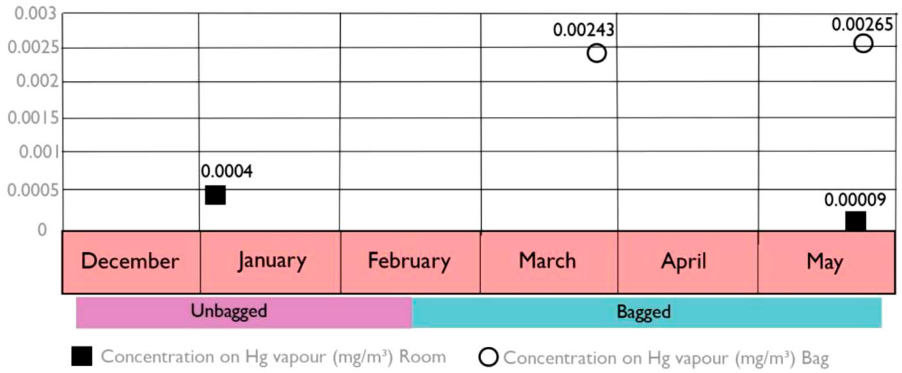

Figure 3. Mercury vapor measurements recorded by a Jerome 431-X during the duration of the study on January 11, March 25, and May 21, 2019. The surface area of the mirror per cubic meter of air is 0.1 m^2. With this taken into account, room concentrations are slightly lower than previous studies (Hadsund 1993).

an even greater hazard should the package be moved or altered.

After this investigation, all three actively dripping mirrors were moved off view and into a storage room. The primary motivation for their relocation was to prevent the hazardous drips from causing complications for preventive collections maintenance such as dusting. In the past, at least one mirror dripped onto other artifacts while on exhibition and additional mercury drips dispersed into cracks in the Museum's wooden floor, spreading mercury vapor contamination as the drips continue to evaporate. The aggregation of the three dripping mirrors in the new storage location makes their monitoring more convenient and practical and if they do continue to drip, they will not directly contaminate nearby objects. They are actively inspected by trained staff members each month who visually monitor any emergent drips and implement drip collection with a mercury spill cleanup kit.[3] None of these mirrors were bagged to avoid potential vapor buildup, nor have they been altered, such as backing with a Mylar seal or wrapping.

Since the mirrors in storage were unbagged and open to the ambient air, the environmental conditions of the room were assessed. Temperature, relative humidity, and dew point were tracked with a HOBO MX1101 unit (Figure 4). Maintaining a lower relative humidity and temperature can help slow the deterioration of the amalgam and release of mercury vapor (Hadsund 1993). The temperature and the relative humidity in the area surrounding the mirrors remained relatively constant without major fluctuations in a 24-hour period. Historical data suggests this new storage space is maintaining relative humidity 50% or lower, which is lower than that of both previous exhibition spaces and the experimental closet space. This lower relative humidity may decrease the rate of degradation and hopefully decrease incidents of liquid mercury drips.

An alternative system to bagging was needed for capturing mercury drips while minimizing the buildup of mercury vapor (Figure 5). The area where the mirrors are now isolated and stored did not have hanging racks, so an inexpensive powder coated grid system was purchased and installed on the end-caps of open shelving in the storage space. Blue board trays were fashioned to hang by S-hooks below each mirror's hanging hardware. The sides of the structure exceeded the frame depth along the two vertical sides, having a tray along the bottom for collection of mercury droplets. The tray has a depth of approximately ten cm, as it was found that mercury droplets seem to run along the mirror's surface, only scattering when making contact with the bottom member of the frame or horizontal

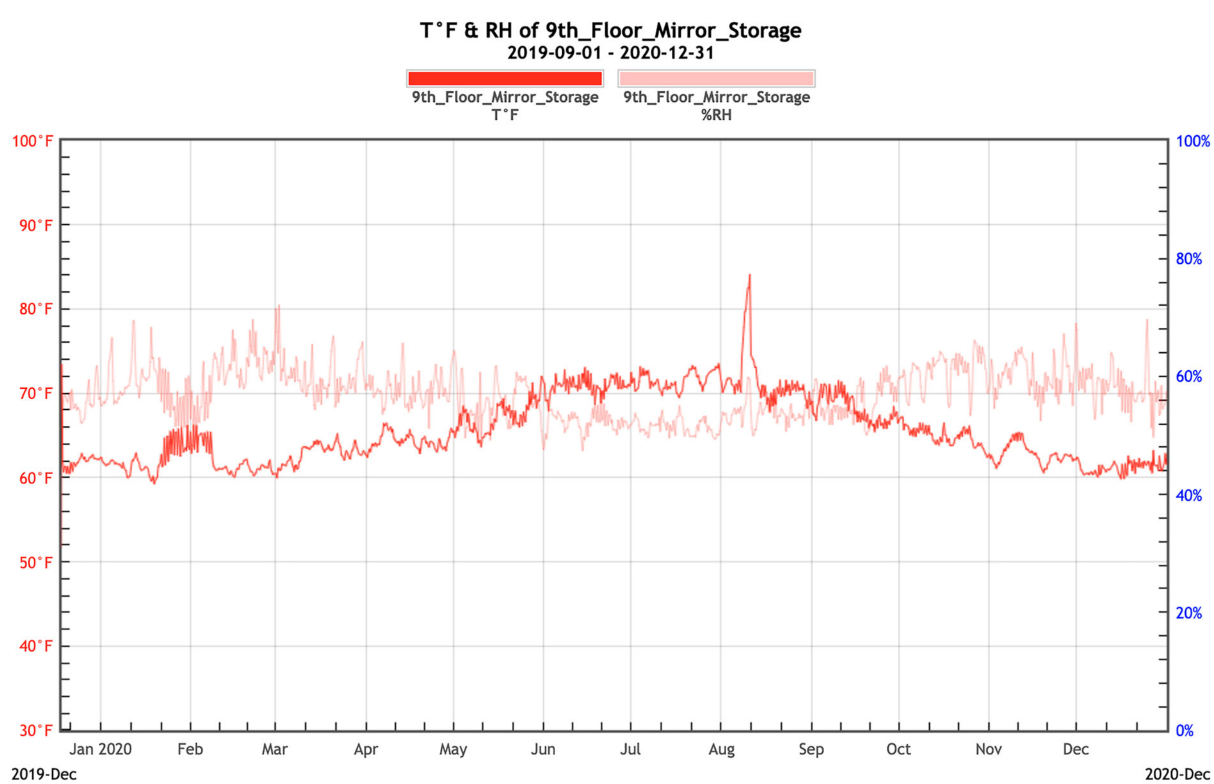

Figure 4. Environmental readings (temperature and relative humidity) of the new storage location for the three mirrors in the study over twelve months.

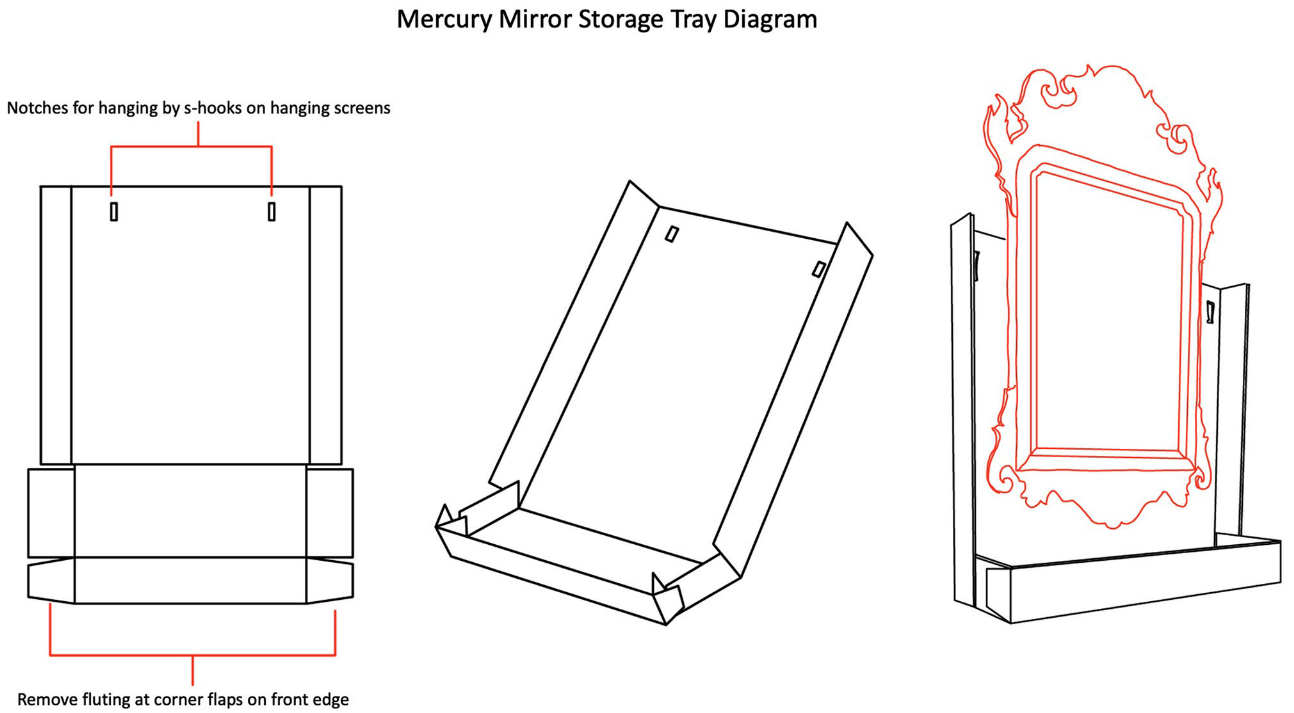

Figure 5. Storage tray construction diagram. Storage trays were constructed from acid-free blue board and were designed to hang behind the mirrors.

surfaces below. This is more evident in mirrors consisting of two panels (Figure 1). The drips from this particular mirror are along the overlapped seam of the upper panel. Mercury droplets can be found on the mirror's surface from the drip point to the bottom ledge of the frame. Other instances of mercury movement were found when mirrors were moved out of display orientation, such as laid on a table surface during routine maintenance of the display space. For this reason, it is recommended that all mirrors be handled with nitrile gloves and that they remain in display orientation at all times.

The mirror storage was assessed with a Jerome Mercury sensor, a few months after the mirrors were installed in the new storage space. Four areas were tested within close proximity to the mirrors, as well as areas of the blue board trays below the mirrors. All mercury vapor readings fell below the standards for OSHA, NIOSH, and the American Conference of Governmental Industrial Hygienists (ACGIH). In the surrounding area, no mercury was detected, whereas readings within the mirror trays were slightly higher at 0.00007 and 0.00004 mg/m^3.

4. Conclusion

The progression of mirror care and storage modifications at Winterthur are efforts to better understand the actual hazards present within the collection and to determine storage solutions that would better prioritize staff safety and object preservation. Quantitative methods were used to assess the safety of different mirror storage solutions, and ultimately moving the mirrors off exhibition and into a well-ventilated storage space was an essential step that should positively impact future preventive conservation work. Vapor monitoring over time revealed that mercury vapor could accumulate within even an open-top half-bag surrounding a mirror, although more research into this phenomenon is needed, taking into account the impacts of the room's volume, air exchange, and climate. Improvements in the environmental parameters of the new storage space, compared to the experimental closet space, may slow the deterioration of mirrors.

The new tray method, designed for actively dripping mirrors at Winterthur, may serve as a simple alternative to bagging or backing mirrors. The trays may both prevent mercury vapor buildup that occurs in bags and provide easier access for cleaning of mercury residue. The design of these trays could be improved with the use of a less absorbent lining material than the blue board, such as Mylar or a foil. They could be lined with this material to prevent drips from becoming trapped in the board, allowing for more effective drip removal during monthly spill kit cleanings. Future work would include the assessment of previous mirror exhibition spaces with a wipe test of surrounding areas, allowing for the quantitative analysis of mercury residue from prolonged dripping mirror display. Vapor levels remained low throughout this study, even after multiple mirrors were aggregated in the new storage space. This suggests that mercury vapor from mirrors, in this context, pose a very low risk to occupants within the space. Continued research and awareness of these objects will better inform future adaptations to storage and handling practices.

Sources of materials

PIG Mercury Spill Vacuum Kit
New Pig
One Pork Avenue, PO Box 304
Tipton, PA 16684, USA
Tel: 1-855-493- 4647
Email: hothogs@newpig.com
https://www.newpig.com/pig-mercury-spill-vacuum-kit/p/KIT330

Jerome 431-X Mercury sensor
Field Environmental Instructions, Inc.
301 Brushton Ave, Suite A
Pittsburgh, PA 15221 USA
Tel: 1-800-393-4009
https://www.fieldenvironmental.com/equipment-rentals/air-rentals/air-quality/gas-mercury-helium-hydrogen-analyzers/jerome-431-x-mercury-vapor-analyzer.html

HOBO MX1101
Onset
470 MacArthur Blvd.
Bourne, MA 02532 USA
Tel: 1-800-564-4377
Email: customer_service@onsetcomp.com
https://www.onsetcomp.com/applications/preservation-management
https://assets.omega.com/spec/HOBO_MX1101_Datasheet.pdf

Notes

1. In a silvered-glass mirror, the reflective surface is a thin layer of metallic silver, deposited via the reduction of a silver nitrate solution. It is usually coated to avoid oxidation.
2. Text included in Collections Management Software when tin was detected using XRF: "Analysis suggests this object may contain mercury. Nitrile gloves and disposable lab coats should be used during handling. The object should be transported in display position, e.g., hanging, as lying flat could activate mercury movement. The transport cart should be covered with polyethylene to capture any mercury droplets that fall during movement. After movement is completed, the transport cart and new installation area should be checked with the raking light of a flashlight in a low light environment to detect potential spills on surfaces below (mercury droplets appear spherical in shape and will glisten in raking light). If droplets are detected on the transport vehicle, work surface or floor below the display area, notify conservation so that the spill can be collected. Do not attempt to clean up the spill on your own and do not vacuum the contaminated area."
3. The Mercury Spill Control Station used by Winterthur Museum, Garden & Library was manufactured by Lab Safety Supply of Janesville, Wisconsin. The kit is no longer available for purchase in the United States due to a lack of SDS for the Mercury Amalgam powder supplied in the kit. A major benefit to this particular kit is the vacuum pump which is successful in capturing mercury droplets still on the object (see Figure 1) or those that have already fallen to surfaces below. Since the Lab Safety Supply Station is no longer available, the PIG Mercury Spill Vacuum Kit would be recommended. The kit comes with six vials for capturing loose mercury, so those vials are the expendable kit components that would need replacing, however it is unclear from the PIG website if replacements can be purchased.

Acknowledgements

The authors thank and ascknowledge Brandon Calitree for performing mercury measurements using the Jerome sensor, Bruno Pouliot for initiating the mirror monitoring program at Winterthur, and Kerith Koss Schrager for the valuable feedback on the content of this communication.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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Appendix

XRF Survey

The entire collection of mirrored surfaces in Winterthur's collection was analyzed to identify tin-mercury amalgam mirrors. A Bruker Tracer III was used with the following parameters: 40 kV high voltage, 9.6μA anode current, 25μm Ti/305μm Al for 30 or 60 s live time irradiation. When possible, a tripod was used to hold the instrument against the glazing. In these cases we recorded data for 60 s. Some mirrors were hard to reach. In these cases the Tracer was hand-held and reduced the live time to 30 s. Due to the large number of objects to be surveyed, only one intact spot was measured per object.

Analysis was done through the glazing either due to lack of access to the back, or risks associated with deinstalling; only once or twice was a mirrored surface accessible from the back. Measuring through the glazing has its downsides, especially if the glass is leaded. Lead attenuates XRF signal from other elements contained in the mirrored surface (fig. A-1).

The presence of mercury was rarely measured. More often than not only tin was detected (fig. A-2), which we noted as "Contains Sn which suggests the presence of Sn/Hg amalgam" in our Collections Management System. Tin K lines are higher in energy than mercury L lines and can be detected through the glass.

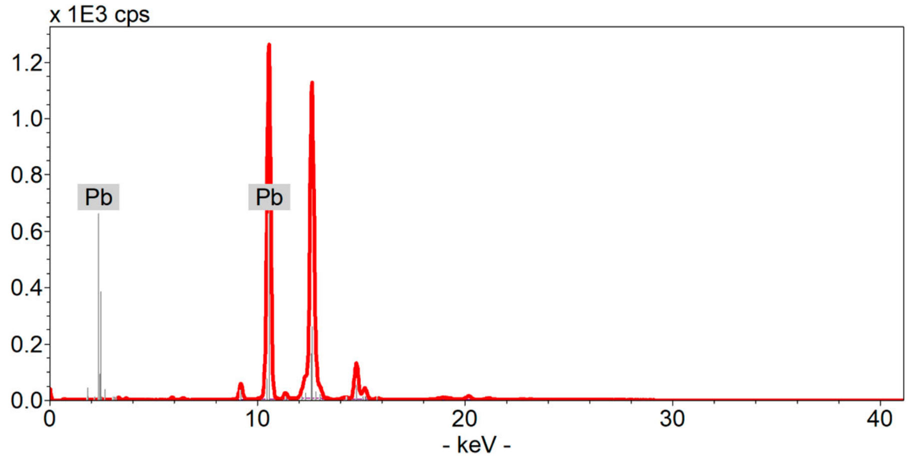

Figure A-1. XRF spectrum collected through the glazing of the mercury mirror described in this study (Figures 1 and 2) showing a leaded glass.

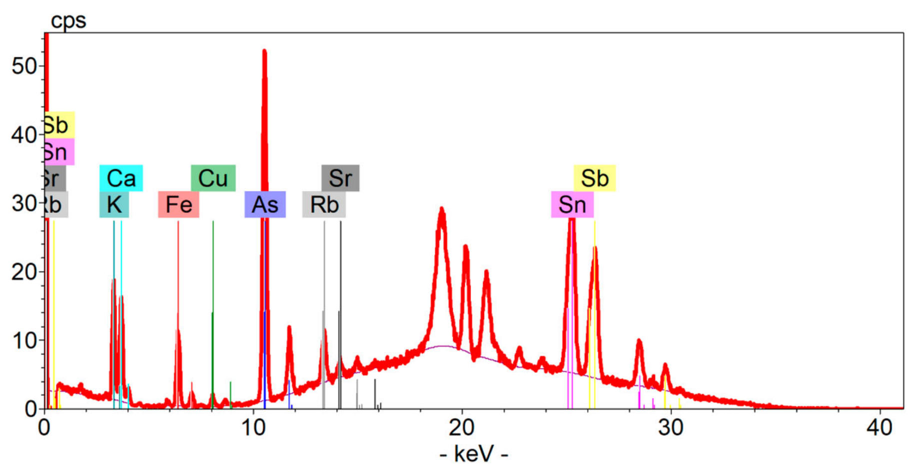

Figure A-2. XRF spectrum collected through the glazing of another actively dripping mirror in the collection. Tin is detected, but not mercury.