Measuring mercury emissions from cinnabar lacquer objects

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This paper presents the results of a study on mercury emissions from Asian lacquer objects containing the red pigment cinnabar, also known as vermilion, which is mercury (II) sulfide. Initial tests for mercury vapor emission from a variety of lacquer objects were carried out using mercury-indicating powder, while more accurate measurements were made with a mercury vapor meter. The emissions were compared to American Occupational Safety and Health Administration (OSHA) guidelines. The results revealed that cinnabar lacquer objects emitted a small amount of mercury vapor, that this could accumulate in enclosed spaces, and that under certain conditions, objects and storage containers housed near cinnabar lacquers may become contaminated. Recommended methods and guidelines for storing, treating, and handling cinnabar lacquers are provided.

Keywords: Cinnabar, Handling, Health risk, Lacquer, Mercury, Storage, Vermilion

Introduction

Usually, the role of conservators is to protect works of art from people, but there are times when it is necessary to protect people from work of art. This paper presents the results of a study of mercury emissions from Asian cinnabar lacquer objects (Strahan & Tsukada, 2014). It begins with a brief definition of cinnabar and its use in Asian lacquer before reviewing test methods and the results. Finally, general guidelines are provided for the handling, exhibition, storage and transport of cinnabar lacquer objects that minimize exposure to mercury vapor.

Metallic mercury, or quicksilver, is easily extracted from its principal ore cinnabar — known also as cinnabarite or mercury (II) sulfide — a dense red mineral that is widely distributed globally. Mercury can be obtained from cinnabar by heating the sulfide ore in a current of air. Oxygen combines with sulfur to form sulfur dioxide while metallic mercury is liberated at a temperature above its boiling point (357°C); the resulting mercury vapor is then condensed to the liquid phase. Mercury is a liquid at room temperature and begins to vaporize at or near 13°C. The higher the ambient temperature, the more vapor is released in a given time. For example, the vapor pressure of mercury will double when the temperature increases from 18 to 26°C (Singer & Nowak 1981). It has long been known that mercury ore deposits give off mercury vapor; indeed, detecting the vapor is one method used to locate ore sources (McCarthy, 1972).

Mercury is a metal with many uses; it readily alloys with copper, silver, nickel, gold, and zinc to form amalgams. It has been used in a variety of instruments and applications, e.g. for thermometers, barometers, thermostats, pressure gauges, clock pendula, and fluorescent lamps, and in dental fillings, women’s make-up, and medicines (Hawks et al., 2010, p. 67). An amalgam of mercury and gold has been used for gilding copper alloy objects since ancient times. The amalgam was applied to the object’s surface, which was then heated, driving off much of the mercury to leave a gold layer that is burnished to a glossy finish.

However, mercury vapor and inorganic mercury compounds pose a threat to human health; in particular, the central nervous system is very sensitive to mercury (Hawks et al., 2010, pp. 338–9). Mercury compounds vary in toxicity and can enter the body by absorption through the skin or inhalation of vapor or dust. Body heat can often be sufficient to cause some mercury to vaporize and the resulting gas can be absorbed through the skin or inhaled.

Because many industries used mercury, it became a common waste product and there is much literature on the health and safety issues that surround it. These
include descriptions of methods to detect and measure mercury vapor emissions, either chemically or instrumentally, as well as methods recommended for cleaning up mercury spills.¹

**Mercury in the conservation literature**

In the conservation literature studies of mercury emission have focused on historic tin-amalgam mirrors, felted fur hats, mineral collections and the use of mercury (II) chloride as a pesticide for anthropological and natural history collections. Thus far, mercury vapor emission from cinnabar in lacquer objects has not been investigated.

From the fifteenth to nineteenth century mercury was used to manufacture mirrors by applying a tin-mercury amalgam to a sheet of glass to produce a bright, reflective surface. Over time tin-amalgam mirrors can develop mercury drips that may collect along the bottom edge of the mirror, polluting the air and even dripping onto the floor (Hadsund, 1993, p. 3; Torge et al., 2010, p. 156).

The early eighteenth century saw the introduction of the ‘carroting’ technique of making felted fur hats, which entailed the application of a solution of mercury salts in nitric acid to pelts to facilitate the felting process (the solution dissolved some of the keratin scales on the fur, making them interlock more easily during the felting process). However, when steam was applied later in the felting process, mercury fumes were released into the air. When inhaled by the hatters, this mercury vapor had a detrimental effect, causing the serious damage to their nervous systems that lay behind the use of the term ‘mad hatter’ (Martin & Kite, 2003).

Along with arsenic, mercury (II) chloride was used as a pesticide on anthropological and herbarium collections in museums from the eighteenth century until the early 1980s (Oyarzun et al., 2007, p. 346). It was usually sprayed or applied as a powder over the surface of the objects. Although it very successfully prevented infestation by pests, it has more recently been recognized as a hazard to museum staff and researchers (Hawks et al., 2004, pp. 783–4).

**Mercury in Asian lacquer**

Paintings and art objects, for the most part, contain only a small amount of mercury (II) sulfide in the form of the pigment cinnabar/vermilion. Much of it is bound in a medium and does not, therefore, present a substantial health hazard (Nöller, 2015, pp. 79–80). However, carved red Asian lacquers contain a significant amount of cinnabar/vermilion (the names cinnabar and vermilion are often used interchangeably, partly because it can be very difficult to distinguish between them visually or microscopically.

There are three types of red mercury (II) sulfide pigment. The oldest is the mineral cinnabar, ground to produce the eponymous pigment. Because it comes from the unrefined mineral, it often contains inclusions and matrix minerals such as quartz, gypsum, calcite, dolomite, fluorite, barite, pyrite, marcasite, stibnite, or chalcedony (Gettens et al., 1993, p. 160). The other two pigment types are synthetic forms of mercury (II) sulfide, both known as vermilion, that are prepared by the so-called dry or wet processes.

Dry process vermilion is made by heating a mixture of mercury and sulfur in an iron pan until it forms a black amorphous mass of mercury (II) sulfide. The black mass is pulverized then slowly heated in earthenware retorts until, at temperatures over 580°C it sublimes. The mercury vapor thus produced condenses on the cooler interior surfaces of the pots as red crystalline mercury (II) sulfide (α-HgS). The red material is treated with a strong alkali to remove any free sulfur, then washed and ground. The change from black to red is merely the result of a rearrangement of the crystalline structure. This product is very pure, with fewer contaminants, which makes it brighter and more highly valued than powdered cinnabar. The dry process was developed during the Han dynasty and a late seventeenth-century Chinese treatise describes the preparation of vermilion using this same method. Its preparation by this method continues in contemporary China (Gettens et al., 1993). The presence of impurities or differences in particle size have been used to differentiate the dry process vermilion from natural cinnabar, although this method is not infallible, due to different grinding methods or the presence of contaminants in processed vermilion (Nöller, 2015, pp. 79–80).

The other synthetic form of vermilion is made by the wet process. Black mercury (II) sulfide is heated in a solution of ammonium or potassium sulfide, yielding a fine, uniformly sized product typical of a chemically precipitated material. The wet process for making vermilion was developed in Europe in the seventeenth century and there is no evidence that it was used in Asia prior to the nineteenth century (Gettens et al., 1993, pp. 160–3).

Cinnabar has been used since ancient times in both the east and west. It was found as a pigment on a painted bowl at least as early as 6000 BC in China (Wang & Wang, 1999). Besides its use for grave ablutions and as a pigment, it was used in traditional medicines where it was thought to prolong life, heal fractures and generally help to maintain good health. Mercury pills have been consumed since the Han period in the belief that they confer immortality and

¹See, for example, [www.cdc.gov/niosh/](http://www.cdc.gov/niosh/) and [www.osha.gov](http://www.osha.gov).
Cinnabar pills are still taken in some parts of China today (Liu et al., 2008). There is speculation that the tomb of the first Chinese emperor (Qin Shih Huang Di) contained rivers of mercury and elevated levels of mercury have been detected in the region of the unexcavated tomb (Duan, 2007; Higham, 2009, p. 274).

Lacquer pigmented with cinnabar can be applied as a single painted design layer or built up in dozens of layers, which are often then carved. During the Song dynasty (ninth to twelfth century AD) lacquer artists developed carved lacquers to such an extent that a new form of lacquer art was created (Fig. 1). Lacquer layers were built up into a coating of considerable thickness, then grooves of various depths were cut into the lacquer to produce elaborate designs. The cross-section in Fig. 2, from a large lacquer screen, has more than 40 layers. With some modifications, the use of the technique continues today, although cinnabar is rarely used in lacquer objects and has normally been replaced with cheaper colorants, usually dyes.

**Testing for the emission of mercury vapor from objects**

**Testing with mercury indicator powder**

The Metropolitan Museum of Art has a collection of 132 carved red Asian lacquers (approximately 90% Chinese and 10% Japanese), providing a large study group. Initial tests for mercury vapor were carried out with a commercially available mercury-indicating powder (Mercury Indicator Powder from J.T. Baker), which contains sulfur, silicon dioxide and copper (I) iodide. It should be noted that this product must not be used near metal objects as it can corrode certain materials.

![Figure 1](image1.png)  An example of a Chinese carved cinnabar lacquer. Dish with birds and hollyhock, (2011.120.1) China, fourteenth century. Diam. 12 3/4 in. (32.4 cm). The Metropolitan Museum of Art, gift of Florence and Herbert Irving, in honor of James C.Y. Watt, 2011. Photograph Studio, The Metropolitan Museum of Art.

![Figure 2](image2.png)  Cross-section of Chinese cinnabar lacquer screen magnified at 50× revealing nearly 40 layers of lacquer. (1971.74 g), Qing dynasty, dated 1777, The Metropolitan Museum of Art. Photo by Suzie Shaw.
metals (Craig & Andersen, 1995). Free mercury reacts with copper (I) iodide, causing a color change from cream to pink-orange and finally to gray, depending on the amount of mercury present. The method has been shown to be extremely sensitive, with a change in color observed in response to mercury concentrations of less than 1 μg m\(^{-3}\). (Hawks et al., 2004, p. 786) This is well below the exposure limit of 0.1 mg m\(^{-3}\) (100 μg m\(^{-3}\)) for an eight-hour time weighted average (TWA) set by the American Occupational Safety and Health Administration (OSHA) and the limit of 0.025 mg m\(^{-3}\) (25 μg m\(^{-3}\)) for an eight-hour TWA recommended by the American Conference of Governmental Industrial Hygienists (ACGIH).

Initially eight objects were tested. The mercury indicator powder was mixed with deionized water, applied to glass microscope slides and dried in air. Once prepared, the glass slide was placed inside a sealed plastic bag with an object and a second slide was placed outside the bag as a control. The indicator slides were examined after the recommended two-week exposure period and in every case the test was positive for the presence of mercury inside the bag and no change was seen in the control slide. The mercury indicator powder changed from cream to pinkish-orange, although there were variations in the extent of color change among the objects tested, as can be seen by comparing the slides shown in Figs. 3, 4 and 5.

**Figure 3** Cinnabar ore with mercury-indicating powder slide inside a bag with control slide on the outside of the bag after two weeks. Photo by Donna Strahan.

**Figure 4** Carved cinnabar Hu vessel in storage cabinet with indicating powder after four months. (13.100.139), China, late 18th to early 19th c., John Stewart Kennedy Fund, 1913, The Metropolitan Museum of Art. Photo by Donna Strahan.

**Figure 5** Vermilion (left) and cinnabar (right) pigments tested positive for mercury vapor; compare these slides to the control slide (top).

Testing with a mercury vapor analyzer
In some instances, for example the large vessel shown in Fig. 4, it was clear that considerable mercury vapor had been emitted after four months, turning the indicator powder dark gray. It seemed possible that the
indicating powder was acting as a scavenger, removing mercury from the enclosed atmosphere, which might lead to further emission from the object. To obtain an accurate reading and quantify the emissions, a Jerome 431-X mercury vapor analyzer with a data logger and probe was rented. The meter draws a given volume of air into the instrument and measures its mercury content, providing a reading in micrograms per cubic meter (μg m\(^{-3}\)). The Jerome meter can detect mercury vapor concentrations in the range 3–999 μg m\(^{-3}\) (0.003–0.999 mg m\(^{-3}\)), with an accuracy of ±5% at 100 μg m\(^{-3}\) and a response time of 13 seconds per reading.

Prior to renting the meter, 37 lacquer objects and four powdered pigments were selected for the test. The selection included both Japanese and Chinese objects, from various periods, but of roughly similar size. Each lacquer object was placed in a plastic bag matched approximately to its size and left sealed for 30 days. After a baseline reading of ambient air in the test area had been made, the probe of the Jerome meter was inserted into each bag to record the amount of emissions within (Fig. 6). Three readings were taken for each bag, cleaning the probe thoroughly between measurements.

The average of the three readings made for each object was graphed and compared directly to the tighter ACGIH eight-hour TWA guidelines; the results of these tests are presented in Fig. 7. Nearly every lacquer object emitted a small amount of mercury, well below the ACGIH and OSHA recommended exposure limits. One object, an eighteenth-century brush holder (object 5 in Fig. 7), emitted substantially more mercury, for reasons not currently understood. While the tests results provide evidence that mercury is being emitted by cinnabar lacquer objects, the many variables, such as object shape, time period, condition and whether cinnabar or vermilion was used, make it difficult to detect trends in the amount of mercury liberated.

Potential accumulation of mercury vapor in storage cabinets

The positive mercury vapor emission results, in combination with the age of some of the objects tested suggested that emission of mercury vapor from cinnabar lacquer objects may occur over an extended period. In storage, there are frequently many objects enclosed within cabinets and drawers that are seldom opened. Unless the saturated vapor pressure of mercury is reached in these enclosed spaces, cinnabar will constantly emit elemental mercury vapor into the surrounding air, allowing it to accumulate until the cabinet is next opened, when it might constitute a hazard to museum staff. Therefore, having determined that individual objects were emitting mercury vapor, four test slides of indicator powder were placed in separate storage drawers and shelves. All four tested positive for mercury. In the case of the large vessel in storage (shown in Fig. 5) sufficient mercury had been emitted over four months to turn the indicator powder dark gray. Measurements were also taken from the lacquer storage cabinets using the Jerome meter. Since mercury vapor is heavier than air it will accumulate at the bottom of a closed cabinet over time. Sets of measurements made at the tops, centers and bottoms of cabinets used to store lacquer gave inconclusive results; extremely low mercury levels, in the range 0.59–3 μg m\(^{-3}\), were measured in nearly all the cabinets. Unfortunately, it was only discovered after the measurements were made that the cabinets had all been opened on the morning of the test, dissipating the accumulated mercury vapor.

The minute amount of mercury emitted from a single object is not considered a problem, but when large numbers of cinnabar lacquer objects are stored...
or exhibited together in closed containers, the emissions may build up and become a more serious concern. Furthermore, mercury vapor can contami

nate other objects housed in the same cabinet or exhibition case. If they are in the same closed environment for a long period of time, they may absorb enough mercury to pose a health hazard in their own right. For example, in tests of herbaria specimens, airborne concentrations of up to 700 μg m⁻³ of mercury were found in storage cabinets, well above the OSHA recommendations. The mercury was readily absorbed by the wooden cabinets and could be released from these surfaces long after the removal of contaminated specimens (Oyarzun et al., 2007, p. 349).

Discussion

Although the tests established that no individual object was emitting mercury vapor at a level that exceeded OHSA or ACGIH exposure limits, nearly every object tested emitted some vapor. The variation in color of the indicator slides implies a difference in the amount of mercury emitted (Hawks et al., 2004, p. 786). These difference may be a result of:

1. The total amount of cinnabar present in an object. Carved objects with multiple cinnabar lacquer layers contain much more cinnabar than uncarved lacquers and might therefore emit more mercury.

2. Whether the object incorporates natural cinnabar or synthetic vermilion. A single visual test of equal amounts of dry pigment using the indicator powder showed greater emission of mercury from cinnabar than synthetic vermilion.

3. Deterioration of the lacquer matrix in which the cinnabar is bound may allow more mercury vapor to be emitted. Carved red lacquers use a large proportion of cinnabar in their multiple layers to produce the beautiful, opaque red color. The pigment is bound in the lacquer resin in the same manner that mineral pigments are bound in oil in an easel painting. However, over the centuries the surfaces of many lacquer objects have degraded and are worn from improper handling and excess light exposure, leaving the pigment exposed at the surface. The mechanism by which elemental mercury is emitted from cinnabar or vermilion is not entirely clear. It may be present as free elemental mercury, in which case its release would cease once all the free mercury has evaporated. However, the detection of continued mercury emission from red lacquer objects of considerable age implies that another source of elemental mercury, presumably as a result of the dissociation of mercuric sulfide to yield elemental mercury.

Mineral cinnabar ore is associated with the emission of mercury vapors (McCarthy, 1972). Vermilion synthesized by the dry process can also contain elemental mercury. This mercury can condense alongside the red vermilion crystals on the walls of the reaction vessel used in the dry process. The mercury derives either from unreacted mercury in the black, amorphous mercury (II) sulfide or from thermal decomposition of this latter material to gaseous mercury and sulfur, which can occur at the temperatures used in the dry process ((Leckey & Nulf, 1994). Vermilion synthesized by the wet process probably contains less elemental mercury as most of the recipes cited in the literature contain no steps that involve the reduction of the mercury (II) ion to elemental mercury (Nöller, 2015). This hypothesis is supported by the results reported above that indicated greater mercury vapor release from cinnabar pigment than synthetic vermilion (although the authors are not absolutely certain whether the synthetic vermilion used for the test was produced by the dry or wet process, suspecting the latter because it is more common).

Mercury (II) sulfide is generally considered a relatively stable compound, but darkening or blackening of cinnabar or vermilion by light exposure is a well-known phenomenon. Previously this discoloration was considered as the conversion of cinnabar/vermilion (α-HgS) into metacinnabar (β-HgS). More recent studies proposed a reaction path caused by the presence of chlorine and/or other impurities in the pigment, or from the environment, after the detection of elemental mercury, mercury chlorides and other mercury salts on deteriorated areas of paintings (Keune & Boon, 2005; Anaf et al., 2013). This elemental mercury might contribute to emissions from the pigment. In a geochemical context, off-gassing is considered to be the result of oxidation and weathering of mercury-containing ores, including cinnabar (Schlüter, 2000). The reaction is slow, even in oxidative environments in the soil, so it is unlikely to contribute greatly to the emission of mercury from lacquer objects stored in museum environments (Lollar, 2005, p. 161). More research would be needed to understand these various degradation phenomena fully.

Guidelines

It is not possible to stop mercury emissions from cinnabar lacquer objects, but an awareness of the hazard will allow precautions to be taken. The most common routes of exposure for elemental mercury are inhalation and absorption through the skin.

Guidelines for handling, storing, exhibiting, and traveling:

1. When handling cinnabar lacquer objects, wear rubber, nitrile or latex gloves to prevent skin exposure and discard these gloves after a single use. Conservators working with objects should work in a well ventilated location.

2. Mercury absorbents can be placed in cabinets, storage boxes, transit crates, and exhibition cases.
Adsortbents include activated carbon (not iodized activated charcoal as the iodine may corrode metal parts on objects), Mercurisorb® (amalgamation powder) or other mercury absorption kits, and gold-coated paper.

3. Store lacquers in individually closed plastic bags; open these bags in a well ventilated area. Replace the bag when the object is returned to storage after it has been exhibited (Torge et al., 2010). Objects emitting a high amount of mercury vapor can be sealed in Marvelseal® or Corrosion Intercept® bags.

4. Provide air exchange in storage cabinets and use unsealed/breathable exhibition cases to prevent vapor build up. Ideally storage cabinets should be located in well ventilated areas with sufficient space between rows to allow for adequate air circulation.

5. Label cabinets where excessive mercury vapor concentrations have been detected, so that anyone opening them is aware of the hazard.

Those responsible for the care of cinnabar lacquer collections may wish to use an indicating powder or a meter to determine whether further steps are necessary. It has been known for some time that Asian lacquer objects need to be protected from the damaging effects of excess light, as well as avoiding dust and fingerprints (Webb, 2000, pp. 54–56), but it is also clear that we may need to protect ourselves from some lacquer objects.

Materials and suppliers

Note that certain products mentioned below require careful handling, storage and disposal. In all cases the suppliers’ instructions and local or national health and safety regulations should be followed.

Corrosion Intercept® storage enclosures: Engineered Materials Inc., 113 McHenry Rd #179, Buffalo Grove, IL 60089, USA. www.staticintercept.com.

Jerome 431-X gold film mercury vapor analyzer: Arizona Instrument LLC, 1912 West 4th Street, Tempe, AZ 85281, USA. www.azic.com.

Mercury Indicator Powder (product code 4509): J.T. Baker Chemical Co., 3477 Corporate Parkway, Suite 200, Center Valley, PA 18034, USA.

Mercurisorb® amalgamation powder: Sigma-Aldrich, 3050 Spruce Street, Saint Louis, MO 63103, USA. www.sigmaaldrich.com.

Marvelseal® bags: University Products Inc., PO Box 101, 517 Main Street, Holyoke, MA 01041, USA. Email: custserv@universityproducts.com.

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