Reduction of Mercury Emission from Historical Tin-Mercury Mirrors

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Problem

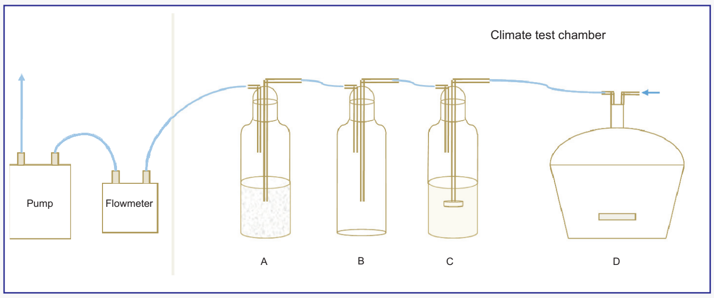
Tin-mercury mirrors were made by coating glass with tin amalgam. Nowadays many of the ancient mirrors are partially damaged, the image quality is compromised and the material integrity of the mirror threatened. The amalgam layer is often destroyed and restoration has become necessary. Restorers have to follow strict safety precautions while handling amalgam mirrors because of possible mercury emissions and corrosion of the amalgam during which elemental mercury accumulates near the mirror frame in droplets and is emitted into the air. In an R&D project the quantity of the mercury emissions from historical mirrors was examined and a technique to decrease these emissions was developed.

Merseburger Spiegelkabinett 1712-1715
(Merseburger Hall of Mirrors)
Kunstgewerbemuseum Berlin

Measuring emissions from mercury mirrors

Several original mercury mirrors of different origins and historically accurate "modern" tin amalgam mirrors /1/ were available as sample material. Historical and "modern" tin amalgam mirrors of 10 x 10 cm^2 were used as test items. The tests took place in desiccators under accelerated conditions in a climate test chamber at 40 °C and a relative humidity of 50 %. Mercury emitted by the mirror was enriched in a 33 % nitric acid solution. The mercury enrichment set-up is shown below. The air was saturated with mercury emissions from the mirror sample placed in the closed desiccator over 24 hours. The desiccator (D) was connected to a gas wash-bottle (C) fitted with a frit and filled with 100 ml of 33 % nitric acid. Next were two gas wash-bottles, one empty, acting as overflow protection (B), and a second filled with sodium hydroxide and activated charcoal filter (A). The air was fed from gas wash-bottle (A) through the flow controller and the gas meter to the pump and finally out through the exhaust. The throughput of the pump was approx. 6 L/minute. The gas flow was adjusted to 0.45 L/min (27 L/h).

The mercury concentration in the absorption solutions was determined using cold vapor atomic fluorescence spectrometry (spectrometer “mercur”, Analytik Jena, Germany). Ionogenic mercury from the solution was reduced to elemental mercury (Hg^0) using tin(II)chloride and then stripped from the solution with argon. The gas flow was continuously dried and – if necessary, after enriching the Hg^0 at a gold collector and subsequent thermal desorption – transported to the measuring cell (fluorescence cuvette) of the spectrometer. This is where the excitation of the element-specific fluorescence radiation takes place by means of a high-energy low-pressure mercury lamp, and where the intensity of the radiation emitted at a resonance wavelength of 253.7 nm is measured. The detected signal is directly proportional to the mercury concentration in the analysed sample.



Schematic of the mercury enrichment set-up

Mercury emissions from "modern" tin amalgam mirrors were lower than the emissions from historical mirrors by a factor of approximately 10 under the selected test conditions. It is assumed that damage from aging processes and the associated corrosion of the tin amalgam layer leads to an increased release of mercury from the mirror /2/.

Mercury-Emissions reduction

Various ideas exist for decreasing mercury emissions from historical and "modern" tin amalgam mirrors. Enclosing the back of the mirror with a layer impermeable to mercury vapor is one possibility. Another is to bind mercury vapor with adsorbing materials.

The suitability and effectiveness of different adsorbents such as iodized activated carbon, Mercurisorb® and gold sputter-coated paper were tested.

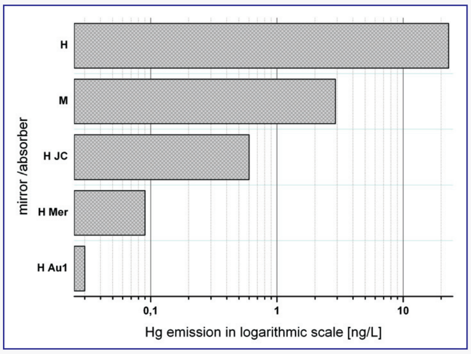
Tests results for mercury emissions from "modern" and historical tin amalgam mirrors with and without adsorbing materials. Results from cold vapor atomic fluorescence spectrometry (CV-AFS)

Test	Mirror	Enrich [h]	Pump [h]	Flow rate [L/h]	Hg concentration in 100ml HNO_3 [ng]	Hg concentration per liter of air pumped [ng/L]
M	16	24.00	5.00	28.0	406,8	2.9
H	H1	24.00	5.00	30.60	3510.0	22.9
H JC	H1	24.00	5.00	31.4	96.6	0.6
H Mer	H1	24.00	5.00	31	13.9	0.09
H Au 1	H1	24.00	5.00	25.4	2.7	0.02
M Au1a	16	24.00	5.00	29.1	4.5	0.03

M: modern, H: historical, Au: gold adsorber, JC: iodized activated carbon, Mer: Mercurisorb®

Results

Modern and historical mercury mirrors are distinguished by different mercury emission. The obtained measurement results indicate a deterioration of the amalgam layer of the mirrors under environmental conditions. The best way to reduce the emission rate of mercury into the environment is to use gold sputtered paper as adsorption material that is affixed to the back side of the mirror. A model mirror was produced as a sample for practical application in restoration practice.



Logarithmic presentation of the analytical results for the emission of mercury from historical (H) and "modern" (M) tin amalgam mirrors and the effects of iodized activated carbon (JC), Mercurisorb® (Mer) and gold sputter-coated paper (Au) as adsorbing agents.

Restoration of mercury mirror; binding mercury vapor with gold sputtered paper on the back side

1: tin amalgam mirror in a historic frame, 2: acid-free Tyvek® fabric, 3: gold sputtered paper, 4: acid-free Tyvek® fabric, 5: back board

/1/ Gerhard Glaser *„Das Grüne Gewölbe im Schloss zu Dresden“* Dresden: E.A. Seemann Verlag 2006, pp. 144-149
/2/ Per Hadsund, *"The tin-mercury mirror: its manufacturing technique and deterioration processes"* Studies in conservation, v.38, no.1, 1993, pp. 3-16

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