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ORIGINAL ARTICLE

Investigations on fire-gilding

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Abstract

Fire-gilding is a historic technique for the application of golden layers on a number of different base materials utilizing a gold amalgam. This technique leaves a significant amount of Hg in the golden layer, giving archeometrists a reliable indicator to identify fire-gildings. Recent findings on presumably fire-gilded objects have shown in several cases significantly lower Hg content than previously studied objects. This prompted a synchrotron-based X-ray fluorescence investigation into the Hg distribution along the material–gilding interface, as well as a series of measurements regarding the Hg content development in fire-gilded samples during artificial aging. This work presents findings on laboratory-prepared fire-gildings, indicating an Hg enrichment at the interface of fire-gilded silver samples. Notably, such an enrichment is missing in fire-gilded copper samples. Further, it is confirmed that fire-gilded layers typically do not undercut an Hg bulk content of 5%. In this light, it seems improbable that ancient samples that contain <5% Hg are fire-gilded. The results presented in this study might lead to a non-destructive method to identify the Hg enrichment at the interface. This might be obtained by a combination of different non-destructive measurements and might also work unambiguously in samples in which the gold top layer is altered.

KEYWORDS

archeometry, artificial aging, artificial samples, BESSY, depth profile, fire-gilding, gilding, gold, identification, mercury, X-ray fluorescence analysis

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INTRODUCTION

Fire-gilding is an ancient technique for the gilding of objects utilizing mercury (Hg). The oldest source commonly cited for a historical description of the fire-gilding process is Pliny the Elder (Bostock & Riley 1855), although it is debated whether his description actually refers to another method using Hg as an adhesive for gold (Au) leaves (Vittori, 1979). However, in this paper the term always refers to the process today most commonly described by the name fire-gilding: the application of a gold amalgam (a mixture of Au and Hg) to a surface and the subsequent evaporation of the Hg by heating until an obvious color transition to dull gold occurs. This method obviously was the dominant gilding method in the Mediterranean by the 3rd century CE and had been established in the two centuries before (Lins & Oddy, 1975).

To fire-gild an object, Au is first dissolved in a surplus of Hg, yielding a viscous liquid. A thin layer of this liquid is easily applied to the surface of an object, for example using a brush, yielding a dull silvery color. By heating, the largest part of the Hg is subsequently evaporated and there remains a gold layer, still containing traces of Hg. The color change occurs abruptly at a certain point when a phase transition to the ζ phase (Au_3Hg) occurs (Okamoto & Massalski, 1989). This transition is easily identified with the naked eye. A further heating rather deteriorates the color (see Anheuser, 1999; Kuhn, 2007; Margreiter, 2016), so it is very reasonable to assume that in historic times the heating was stopped more or less immediately after the color transition. Identification of Hg in the golden layer allows for a relatively straightforward identification of fire-gildings with instrumental analysis, as it is the only historical technique that incorporates Hg into the golden layer. A more thorough overview of the historical development of the various gilding methods is given elsewhere (e.g., Darque-Ceretti & Aucouturier, 2013; Lins & Oddy, 1975; Oddy, 1991).

Besides the purely academic interest for the history of science, the unambiguous identification of fire-gildings is strongly connected with questions concerning our cultural heritage: Knowledge of the gilding techniques used on a particular object as well as the exact composition of the gold layer might be crucial in deciding about conservation and preservation issues. This relevance is also the reason why there have been broad examinations of archeological objects (see below).

Instrumental analysis has so far been performed on many archeological objects that have been attributed to fire-gildings (e.g., Becker et al., 1996; Drews, 1984; Faßbender et al., 1997; Gunter & Jett, 1992; Lang, 1997; Lechtman, 1971; Lins & Oddy, 1975; Mango & Bennett, 1994; Meyers, 1981; Sobottka-Braun, 1997; Spiering & Eggert, 1991). The Hg content in these golden layers varies widely, starting at around 8% but commonly reaching 20% and above. Various authors later have shown that these results follow directly from the fact that fire-gildings consist of gold amalgam in the α - and ζ -phase (Anheuser, 1997, 1999).

The extensive works of Anheuser (1997, 1999) on historical samples as well as samples prepared under laboratory conditions (Kuhn, 2007; Margreiter, 2016), give valuable insight into the chemical and physical processes during the gilding process. One of the most important aspects is the discussion of the temperatures necessary for fire-gilding. Anheuser found that the color change from the grey/silver to yellow/gold appears at around 260°C and is easily identified by eye. These experiments were performed by heating the samples for a longer time to a certain temperature.

Anheuser identified fire-gilding as a non-equilibrium process. The Hg content of the sample therefore largely depends on the heating time and layer thickness, rather than the precise temperature. This supports the assumption that the goldsmith (lacking an exact thermometer in historical times) would likely stop the heating process more or less immediately after the color

change, so that up to 25% of Hg remained in the gold layer. This view is further supported by the observation that longer heating times and higher temperatures increase the likelihood of visually destroying the golden layer, either by promoting diffusion into the upper layer of the object or by oxidizing the surface of the base material, both resulting in an uneven faded-out or burned look of the object (Kuhn, 2007). Hence an Hg content of <5% is seen by several authors (Fütting, 2010; Wolters, 2006) as a chemical–physical limit that is not underrun by historical fire-gildings.

MOTIVATION

Our research was prompted by a serial examination of gilded silver objects in the Antikensammlung Berlin (Collection of Classical Greek and Roman Antiquities, National Museums of Berlin) by Niemeyer (2018), as presented in Figure 1. All objects originate from the Mediterranean region; the ages of the objects cover the range from the 7th century BCE to the 7th century CE, with emphasis on the 1st century CE, the timespan when fire-gilding is commonly assumed to be established. A complete list of the samples is given in Supplement 1 (Supporting Information). These measurements were performed using synchrotron-based X-ray fluorescence (SR-XRF). With this method, both Au and Hg can be easily distinguished, and Hg might be quantified besides a surplus of Au down to a relative content of about 0.1% (see Figure 1).

The data are consistent with the common understanding that, until the 1st century BCE, fire-gilding was not known in the Mediterranean region. All Hg contents of this period are consistently below 0.5%. As argued by Lins and Oddy (1975), such small impurities and contaminations are reasonable to expect since Hg was well known in ancient times even before being used in gilding, so it might have been present in workshops at that time. The data seemingly correspond to the gradual introduction of Hg into the gilding process in the first century CE, showing clear elevation in the Hg content for some objects. A closer look shows that the situation for the 1st century (38 objects) is complex: there are some examples that are obviously fire-gilded (#40, #42, #61, and #62, some with an Hg content even above 15%), while alternative gilding techniques (Hg content < 0.5%, e.g., #25–#28) are still present. However, there are several objects (e.g., #24, #30, #31) that show clearly elevated Hg contents of a few percent. These do not match the expectations for fire-gilding as described above. Their Hg contents are not readily explained with the current understanding of the different gilding techniques.

Two possible explanations for these findings are either (i) that the relevant objects are fire-gilded as described in this paper, suggesting an incomplete understanding of the chemical and physical processes during the procedure, or (ii) that Hg was introduced as a contamination, either during or after the gilding process.

Another relevant question regarding fire-gilding is the presence of distinct Hg enrichments along the profile of fire-gilded layers. From our own results, there was already evidence of the accumulation of Hg at the interface between the base metal and Au plating layer. Also, Anheuser prepared cross-sections from some historical samples, showing distinct non-uniform Hg distribution within the gilded layer (Anheuser, 1999).

The presence of a distinct Hg profile—for example, an enrichment of Hg at the Au/base metal interface—might influence the results of bulk measurements. It is therefore necessary to identify and characterize such possible enrichments to accurately evaluate the results of such measurements. A distinct Hg profile might also result in a signature that could be identified in non-destructive measurements (see discussion below). This would allow the identification of objects as fire-gilded independent from the bulk Hg content.

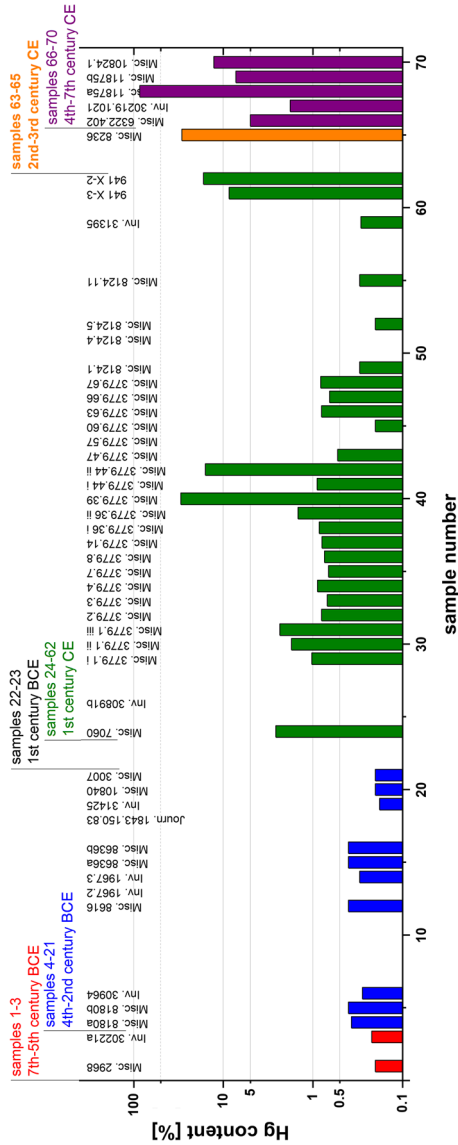


FIGURE 1 Hg content of the gildings of 70 different objects from the Antikensammlung Berlin. Note that the x-axis is chronologically ordered, but not scaled to equal time intervals. The sample names given at the top correspond to the registration numbers. Solid lines are added for Hg content of 0.5 to highlight the relevant limits in the discussion. Results previously unpublished in this form. Although in the original data some values are referred to as “0”, we consider this to be rather below the limit of detection “< 0.1%”

MATERIALS AND METHODS

We prepared artificial fire-gilded samples under laboratory conditions and measured Hg contents of the gold layers. To be consistent with the vast data set available to us (Niemeyer, 2018), we measured Hg contents using SR-XRF. We performed several experiments in which we tried to obtain Hg contents as low as possible to gain a deeper understanding of the gilding process. The use of micrometer-focused SR-XRF allowed us also to measure the Hg distribution along cross-sections (Hg profiles).

Gilding method

In preliminary studies (Margreiter, 2016), we developed our gilding method based on information by Anheuser (1997) and goldsmith Dirk Meyer, in Maierhöfen, Germany, who specializes in restoration work with fire-gilding (Meyer, 2016).

Fire-gilded samples were prepared on Ag foil from various sources: (i) 0.5 mm, 99.9% (metals basis) ALFA 39181.FI; (ii) 1.0 mm, 99.9% (metals basis) ALFA 11438.FI; (iii) 0.5 mm 999.7 fine Ag sheet (Goetze refinery, Berlin) and 1.0 mm copper sheets (ALFA 10954.FI). Ag foils were cleaned with acetone. Cu was treated with diluted acetic acid to remove the oxide layer. Gold leaf (refined gold “24 ct Doppelgold”, Wilhelm Wasner Blattgold GmbH 010012101) was dissolved in a fivefold amount of Hg. This yielded a firm but ductile amalgam paste. The amalgam was applied to the base material using a spatula and brush. Subsequently, the samples were heated in the open flame of a Bunsen burner until the yellowish color appeared, indicating the formation of the ζ -phase (see Supporting Information video, Supplement 3).

Part of the preliminary studies (Margreiter, 2016) was the comparison of the Hg content of fire-gilded Cu and Ag substrates by the specialized goldsmith Dirk Meyer and the authors. The Hg contents were determined from SR-XRF bulk spectra from the BESSY II BAMline, through rudimentary data analysis with OriginPro software. The data do not show significant differences between samples prepared in our laboratory and samples prepared by the goldsmith (see Supporting Information, Supplement 4), bolstering the legitimacy of the applied gilding procedure.

The choice of base material was motivated by serial measurements at the Antikensammlung. As we aimed for a replication of the results, Ag was chosen as the base material. Cu was chosen as a comparison, based on the fact that it was a commonly gilded material and allowed for a similar preparation procedure.

Although there are a variety of recipes for the preparation of the amalgam, ranging from Au–Hg ratios of 1:4 up to 1:8, the actual ratio only influences the consistency of the amalgam paste, not its chemical composition. The amalgam paste is always a mixture of solid Au_2Hg particles suspended in liquid Hg (Anheuser, 1997); therefore, our ratio was chosen so that the amalgam paste was the easiest to work with during sample preparation.

Instead of a defined temperature/heating time set-up, we opted for a visual approach to the gilding process: The samples were heated in a colorless flame until a color change was observed. This is in line with the procedure of D. Meyer (personal communication) and most likely the way ancient gilders determined when to stop the heating process.

It is well established that a pretreatment of Cu with Hg or an Hg salt (commonly $\text{Hg}_2[\text{NO}_3]_2$) simplifies the application of the amalgam on the base material and was commonly performed in the Middle Ages. However, we limited the pretreatment of the base materials to the superficial cleaning process, as described above, as we found no evidence that this method had been used in ancient times.

Artificial aging of laboratory samples

Directly after preparation as described above, all samples show Hg content above 5%; even Hg content below 10% seems to be the exception (detailed results see below). This observation prompted our hypothesis, that a natural gradual loss of Hg in fire-gilded layers throughout the ages might result in modern Hg content $< 5\%$.

For this reason, a set of fire-gilded Cu samples were heated in a temperature-controlled oven at 200°C, 190°C, and 180°C for 6 h, 1 day, 3 days, 7 days, and 10 days as a rudimentary artificial aging process.

The temperatures were chosen so that they would significantly increase the rate of naturally occurring processes, while staying well below the necessary temperature for phase transitions and boiling points.

Cross-sections

Identification of possible Hg profiles requires the measurements of elemental profiles within the samples. It must be emphasized that typical layer thicknesses in the range of 10–20 μm , especially in combination with the chemical composition (Au/Hg), provide serious challenges for depth profiling techniques. For example, the application of Rutherford backscattering (RBS) is not promising because Au and Hg will not be clearly separated in RBS spectra.

Laser ablation inductively coupled mass spectrometry (LA-ICPMS) might be a possible alternative. Although relevant setups exist, the availability of beamtime at the BESSY II prompted the decision to cut cross-sections of artificial samples and to characterize them mainly with SR-XRF.

These cross-sections were prepared by embedding the samples in resin (Struers EpoxyFix) and cutting them perpendicular to the sample surface.

Such a treatment is out of the question for ancient samples. However, if our research could identify a distinct Hg profile in fire-gilded layers, the same distinct profile might later be identifiable by non-destructive techniques that can resolve at least limited profile information.

Non-destructive identification of profile characteristics

With the possibility of distinct Hg profiles as an unambiguous characteristic of fire-gildings, the need for a non-destructive approach of identifying such a signature in archeological objects arises. A preliminary test for such a system was performed with a new compact grazing-exit XRF (GEXRF) spectrometer (Baumann et al., 2021) on one fire-gilded Cu and fire-gilded Ag sheet. The system collects fluorescence radiation with a CCD camera under shallow exit angles. The advantage of the used technique as opposed to varying the incidence angle for depth profiling is that only a small lateral spot is probed, which enables measurements at specific points.

A small variety of other possible approaches for the non-destructive identification of profile characteristics is discussed in Section 4.3.

SR-XRF measurements

All SR-XRF measurements were performed at the BAMline at BESSY-II Berlin (Görner et al., 2001) using an excitation energy of 20 keV. This choice of energy suppresses the appearance of Ag K lines, which in turn significantly reduces background noise and allows for a simultaneous analysis of the dominant Hg and Au L lines. The analysis of the obtained spectra was

performed with the AXIL (analysis of X-ray spectra by iterative least squares) computer package (Van Espen et al., 1986). The term “Hg content” henceforth refers to the Hg L line intensity, normalized to the sum of measured Hg and Au L line intensities.

Line scans on sample cross-sections

Line scans on sample cross-sections were performed using a set-up with compound refractive lenses (CRL); for details see Strub et al. (2008). The CRL were set to reduce the beam spot size of the X-ray excitation to an area of about $1 \times 1 \mu\text{m}^2$.

Line scans were typically performed several times at various positions of the cross-section.

Bulk analysis

SR-XRF bulk measurements have typically been performed with a beam size of $2 \times 2 \mu\text{m}^2$. “Bulk measurements” hereby refers to measurements from the surface, with the “bulk” being the whole of the gilding layer and interface region, as opposed to the cross-section measurements that probe layers at a certain depth.

Correction for self-absorption

The characteristic X-rays of Hg and Au are prone to self-absorption when passing through the upper layers of the gilded surface. This becomes particularly important if the self-absorption for one of the elements’ X-rays is higher than the others, as it would skew the measured composition toward the less absorbed element.

To account for this factor, a variety of XRF simulations were performed utilizing the Monte Carlo software XMI-MSIM by T. Schoonjans (Schoonjans et al., 2012). With this, a total of 54 XRF spectra of amalgam layers of homogeneous but varying composition and different thicknesses were simulated.

The Au X-rays were generally more affected by self-absorption, with the effect increasing with higher layer thickness up to a penetration depth of $\sim 30 \mu\text{m}$. This first approximation correction for self-absorption was taken into account for every sample prepared in the laboratory.

RESULTS AND DISCUSSION

Bulk analysis of artificially aged samples

The results of a systematic bulk analysis of artificially aged fire-gilded Cu substrates are shown in Figure 2.

The main purpose of these measurements was the investigation of sample aging as an explanation for Hg content below the accepted 5% limit for fire-gilded samples by means of Hg diffusion into the environment. Although the results do point to a decrease of the Hg content over time, the samples never conclusively undercut the 5% limit—not even the visually destroyed samples after longer heating periods.

Figure 2 suggests a logarithmic relation between Hg content and heating time. To assess the general applicability of this hypothesis, the data presented in Figure 2 were adapted to represent the relative decrease in Hg content during the aging process.

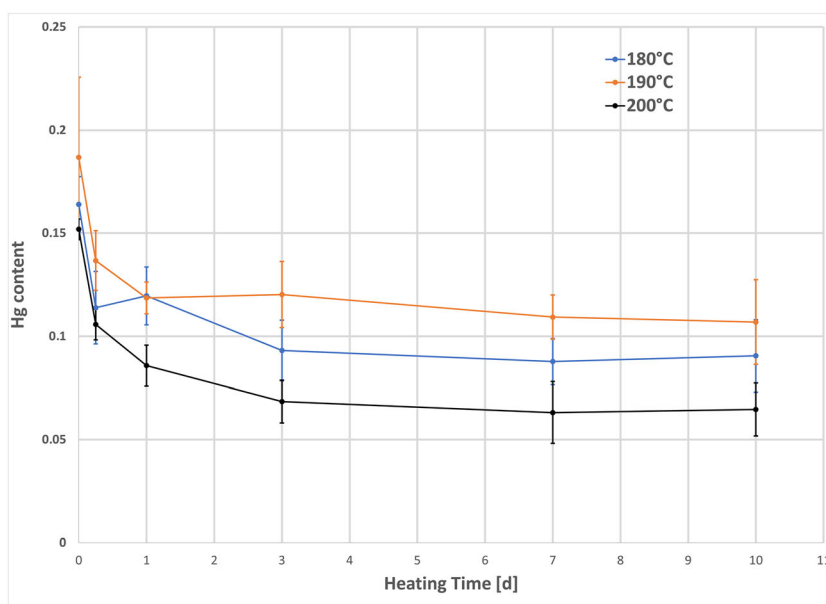


FIGURE 2 Absolute Hg content of the artificially aged fire-gilded Cu substrates plotted against the heating time in days, for different temperatures. Different points in a temperature series are connected by lines to enhance readability. “Hg content” refers to the Hg L line intensity, normalized to the sum of the measured Hg and Au L line intensities

The data in Figure 2 were therefore adjusted, on the one hand, to give the Hg content not in absolute but in normalized values, and, on the other hand, to show an approximation of the sample age as simulated by the chosen experimental conditions.

Each temperature series was normalized individually with the respective highest Hg content as corresponding reference. This allows for better comparability between the different temperature series.

The basis for the simulated age conversion is the rough rule of thumb that a temperature increase of 10°C doubles the reaction rate, with room temperature at 20°C. Storing a sample for 10 days at 30°C would therefore correspond to storing the same sample for 20 days at room temperature. By this approximation, the sample stored for 10 days at 200°C maps to the same sample stored for several thousand years (10×2^{18} days) at room temperature.

Figure 3 shows a weak logarithmic relation between the Hg content and the simulated aging period. It must be noted that the basis for this figure is a very rough approximation, intended as a starting point for further adjustments and analysis.

This study focused solely on the effects of aging. Although chemical interactions between the burial soil and sample material have been shown to some extent (Graziani et al., 2020), we expect their influence on the measured Hg content to be minimal, based on our observation below that large parts of the Hg are located at the gilding interface rather than the surface of the gilding.

Overall, the results of these bulk measurements show that it seems to be difficult to obtain low bulk Hg concentrations: in all our experiments, we never reached values < 6%. This holds true even for samples that were heated to a point that the gilding lost its desired golden appearance through oxidation of the base material.

Therefore, we conclude that gilded objects with an Hg content < 5% are likely not fire-gilded.

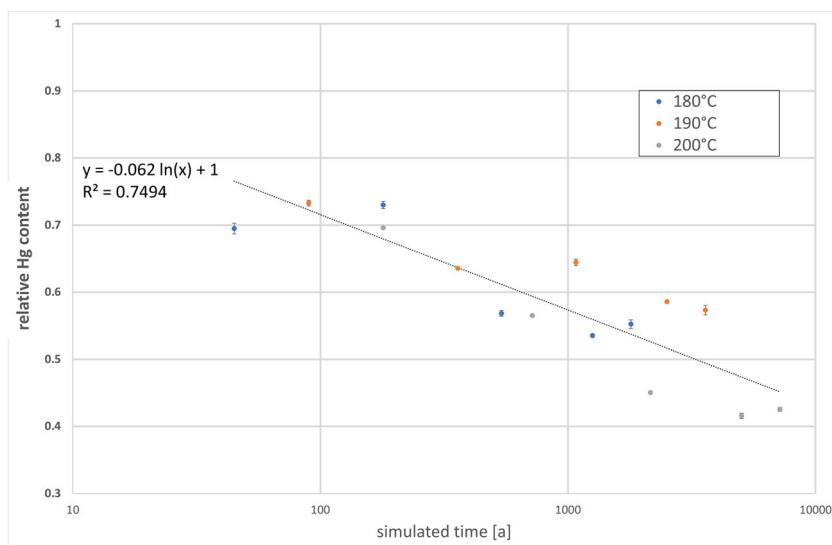


FIGURE 3 Plotting relative Hg contents of artificially aged Cu substrates at different temperatures against the simulated aging period. Simulated aging period is determined with the ad hoc assumption that $+10^{\circ}\text{C}$ doubles the reaction rate. The data suggest a weak logarithmic relation between both parameters. The first data point in each series, representing the non-heated sample of the series, is omitted due to the logarithmic scale of the x -axis. “Hg content” refers to the Hg L line intensity, normalized to the sum of the measured Hg and Au L line intensities

Elemental profiles

Through the analysis of cross-sections of the interface between the gilded layer and the substrate, profile information of the Hg distribution was obtained. Figures 4 and 5 present an averaged profile for Ag and Cu, respectively.

The results conclusively show a distinct Hg enrichment at the interface of fire-gilded Ag substrates. This was not observed for Cu substrates. Previous studies by Anheuser had shown a similar Hg enrichment at the interface, but only for the particular case of Ag substrates that were treated with an Hg salt solution before the application of the amalgam (Anheuser, 1999). Anheuser therefore attributed the enrichment to the surface treatment with Hg salt and the formation of an Ag–Hg alloy before the amalgam was applied. Our results show that such an enrichment is characteristically found at the interface of the golden layer and an Ag substrate, even without a pretreatment with Hg salt. This characteristic might be identified by non-destructive means for unambiguous identification of fire-gilding (see Section 3.3).

Another observation, not as apparent as the Hg accumulation, is that the determined Hg content after the interface—that is, within the substrate—stays constant for more than $10\ \mu\text{m}$ in Ag substrates and starts fluctuating just a few micrometers in the substrate for Cu. Both observations likely depend on amalgam/Hg diffusion into the substrate. This suggests that Hg diffusion is significantly easier into an Ag substrate than a Cu substrate, in agreement with previous studies (Anheuser, 1999).

From these profiles we conclude that if Ag is used as a base layer a typical Hg enrichment can be found at the Au/base metal interface. With the given resolution it is not possible to decide whether the enrichment is rather small in a layer of around $1\ \mu\text{m}$ thickness or whether the enrichment is stronger, albeit in a narrower layer.

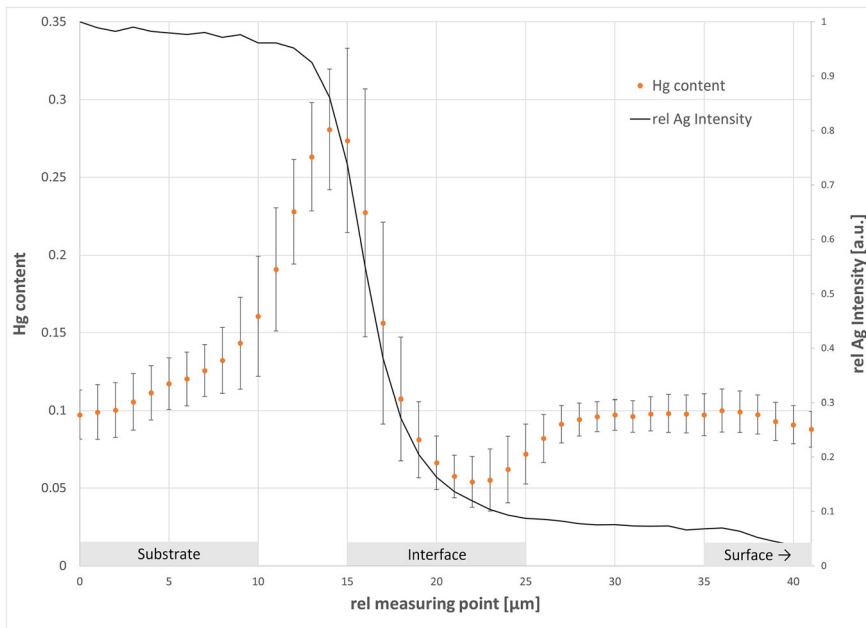


FIGURE 4 Elemental profiles of a fire-gilded layer on silver (XRF data of a cross-section mapping scan along the sample interface averaged over 141 linescans). “Hg content” refers to the Hg L line intensity, normalized to the sum of the measured Hg and Au L line intensities. “Rel Ag intensity” is the measured Ag L line intensity normalized to the maximum value

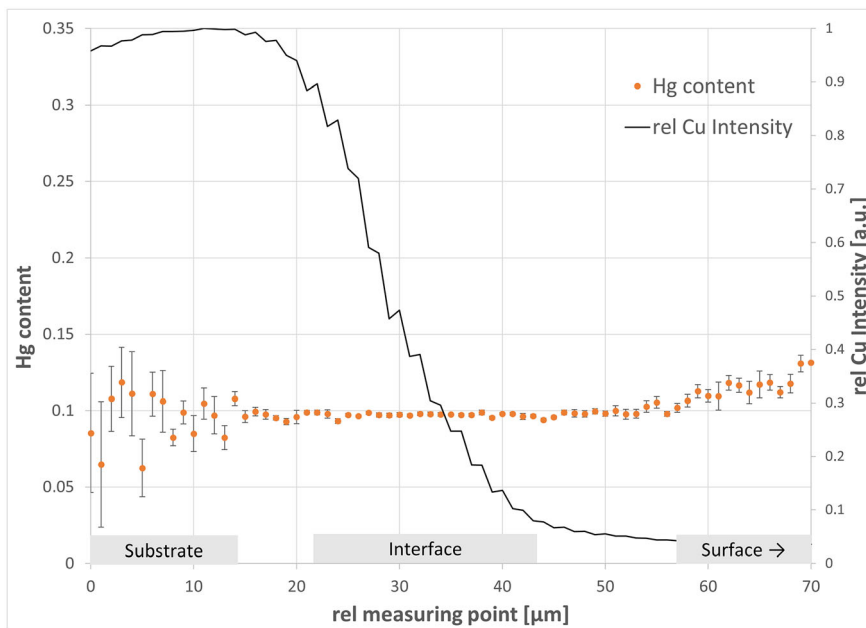


FIGURE 5 Elemental profiles of a fire-gilded layer on copper (XRF data of a cross-section mapping scan along the sample interface averaged over six linescans). “Hg content” refers to the Hg L line intensity, normalized to the sum of the measured Hg and Au L line intensities. “Rel Ag intensity” is the measured Ag L line intensity normalized to the maximum value

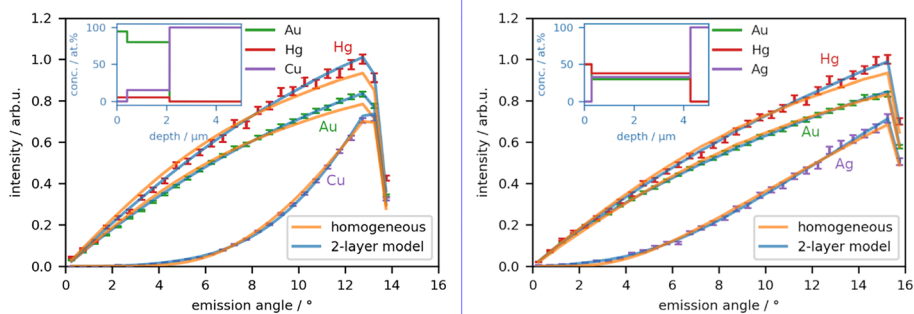


FIGURE 6 Angle-resolved XRF profiles on two prepared samples with Cu (left) and Ag (right) support. The insets show the layer thicknesses and compositions for the two-layer model. Measurement parameters: Mo microfocus X-ray tube with 50 kV and 200 μ A/150 μ A for the Cu/Ag measurement, respectively; 1 h measurement time with 19 min lifetime, spot size on sample $3 \times 1 \text{ mm}^2$

Possible non-destructive identification of fire-gilded layers

With the identification of a characteristic Hg distribution in fire-gilded Ag substrates (see Section 4.2), the question arises whether and how this feature can be utilized for a non-destructive identification of fire-gilding separate from the absolute Hg content.

Figure 6 shows GEXRF angular scans on two samples differing in support material (left: Cu; right: Ag). The experimental values for the Au L, Hg L and Ag-K/Cu-K fluorescence intensities are shown, with an analytical fitting of the experimental data. In a first step, a homogeneous model was assumed (Hg/Au on Cu or Ag) and then the gilding layer was modeled with two layers: Hg/Au on Hg/Au/Cu on Cu or Hg/Au on Hg/Au/Ag on Ag, respectively. The two-layer model represents the experimental data considerably better, showing unambiguously diffusion of elements inside the sample. In this example, the interface between gilding and support cannot be probed due to the large thickness of the gilding layer, but differences between the two samples are discernible, originating from either a thinner gilding layer in the Cu sample and/or more diffusion.

These test measurements show that the thickness of the gilding layer limits the applicability of benchtop XRF measurements for the identification of interface enrichments. The system might, however, still be applicable at specific points of the gilded object where the layer thickness is reduced by wear or damage.

Another conceivable method for the identification of such an Hg distribution might be the combination of different methods or of two different experimental set-ups of the same method that probe different depths of the sample, resulting in limited profile information.

PIXE might be one of the most promising candidates for such a procedure. A combination of PIXE at different detection angles or acceleration energies can be adapted such that they are optimized for the detection of such an interface enrichment and/or the presence of Hg diffused deeper into the substrate (see, for example, Denker et al., 2005; Miranda et al., 2006; Neelmeijer & Mader, 2002).

Albeit minimally destructive, another conceivable method for the identification of an enrichment layer is the use of a time-resolved LA-ICPMS system, as discussed above (Section 3.3).

CONCLUSIONS

With this article we report our findings of various SR-XRF studies on laboratory-prepared fire-gildings of Cu and Ag substrates. The work was motivated by previous results in the

Antikensammlung Berlin and focused largely on two main aspects: (1) the analysis of sample cross-sections for the identification of characteristic Hg profiles, which could be used for a non-destructive identification of fire-gildings; and (2) an investigation of the lowest possible Hg content in fire-gildings, prompted by findings of low Hg content in historic samples that do not seem to agree with the current understanding of the fire-gilding process.

Regarding the sample cross-section, we report the identification of a distinct Hg enrichment during fire-gilding at the interface between the substrate and golden layer on Ag substrates. Similar enrichments were previously reported, but our findings generalize the presence of the enrichment, independent of the substrate's pre-treatment.

Hg enrichment is a feature unique to fire-gilded samples and, therefore, opens a possible route toward a non-destructive identification method. A combination of several measurements (or several techniques) that probe the sample up to different depths can be used for this purpose: a method that probes only the first few micrometers will not include the enrichment zone, thereby giving a smaller Hg content than a method that reaches deeper into the material. From the combination of the results, limited information on the Hg depth profile can be derived. Benchtop XRF and PIXE are possible candidates for methods that could reliably and non-destructively identify these enrichments at the interface by varying incident beam angle or particle energies. The first benchtop XRF measurements show promising results. However, such measurements are highly susceptible to factors such as sample roughness and inhomogeneities as well as the thickness of the gilded layers. These factors might therefore limit the applicability of the method to spots of a historical object where the gilded layer is thin and homogeneous enough to obtain a clear signature of an Hg enrichment at the Au/Ag interface. On the other hand, it can be expected that such spots can be identified on many historical objects—for example, spots where the gilded layer is thinned or damaged. A combination of different methods might also contribute to an unambiguous identification of an Hg enrichment at the interface.

So far, the distinct interface enrichment was only observed for fire-gilded Ag substrates and was absent on fire-gilded Cu substrates. A method based on the identification of the enrichment would therefore be limited in scope to certain base materials.

We established, through previous data by various authors, and practical considerations, that low Hg content below ~5% cannot be expected in fire-gilded objects. This, however, conflicts with recent findings in the Antikensammlung Berlin, which found elevated Hg content in several antique objects from the 1st century CE, below 5%. The possible explanations for these findings are either that (i) the loss of Hg during the gilding process can be far larger than previously thought, (ii) a process after the gilding process reduces the Hg content of fire-gilded objects significantly, or (iii) a significant amount of Hg is introduced into gilded objects that are not fire-gilded through a yet unknown process, be it during burial, storage in the museum, etc.

Neither our studies nor the published literature seem to suggest the first option, leaving two possible hypotheses. In this article we present our findings regarding the subsequent loss of Hg from gilded objects caused by aging. The initial hypothesis that aging might lead the Hg content of a sample to fall below 5% could not be verified. Independent of the base material, aging samples by storing them at elevated temperatures for set amounts of time led to a significant decrease in the samples' Hg content. However, even visually destroyed samples showed Hg content above 5%, therefore confirming the suggested limit. It seems improbable to us that contents below 5% will be reached by simple aging; however, physical and chemical interactions—for example, with the soil in the case of buried archeological objects—were not considered.

This leads us to the conclusion that the gilded Ag objects in the Antikensammlung Berlin with elevated Hg contents below 5% were probably not fire-gilded—a conclusion contrary to previous assumptions by Niemeyer (2018). Further studies are necessary to identify the particular reason for the Hg elevation in these samples. A possible explanation might be based on uptake of Hg from the atmosphere: previous studies on Ag point drawings show clear evidence for the natural uptake of Hg into Ag aggregates from the atmosphere (Reiche

et al., 2007). Due to the similar behavior of Ag and Au in the formation of amalgams (see also Reiche et al., 2004), an analogue uptake of Hg by Au aggregates might explain the observations on the objects of the Antikensammlung.

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PEER REVIEW

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are openly available in dryad at <https://doi.org/10.5061/dryad.8gtht76nd>.

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