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Modelling an XRF method for determining gilding thickness in silver cultural heritage objects without sample collection: case studies on 16th century Portuguese silverware

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ABSTRACT

In situ X-ray fluorescence is a non-invasive technique that is widely used in historical objects, namely in pieces of gilded silver, to determine the composition of the alloy and gilding. In the case of gilded silver, fire gilding was a mercury-based historical technique that is no longer practiced. Moreover, with traditional XRF analysis is possible to determine the thickness of the gilding by using given intensity ratios of the characteristic lines of silver. However, this requires the analysis of the substrate, for the calculation of the intensity ratio without gilding, which is not always accessible. This study presents and validates a methodology for the calculation of the thickness of fire gilding silver pieces using XRF analysis with a commercial spectrometer and without the need to analyse the isolated substrate. Six silver alloy mock-up samples were produced following historical techniques and generic intensity ratio for Kα and Kβ lines of silver in the alloy was calculated (6.35 ± 0.05), to be used in any alloy with a silver composition over 75 %. Since attenuation of the silver's characteristic lines depends on the gilding composition, different Hg concentrations (5 %–20 %) were tested. The results obtained with this approach for the mock-ups was compared with SEM-EDS measurements for gauging uncertainty and the methodology was then applied to three pieces of 16th century Portuguese silverware. This adaptation of previously established principles, proved to be effective to calculate the thickness of fire gilding on silver and was validated to be applied, *in situ*, in real museum artworks without the need for sample collection.

1. Introduction

Fire gilding, also known as gold amalgam process, is thought to have appeared in China between the 2nd and 3rd centuries BCE. Although there is no consensus on when this technique was first introduced in Europe, it is thought to have been between the 1st and 2nd centuries AD (Oddy, 1993; Anheuser, 1997). This technique became the predominant method for gilding metals from the Middle Ages until the 19th century, when electrolysis gilding was invented (Oddy, 1993; Anheuser, 1997; Martinón-Torre and Ladra, 2011). With this gilding technique, the mercury is never completely evaporated, and a small percentage remains to allow it to be identified in non-invasive elemental analyses such as XRF.

Measuring the thickness of fire gilding is extremely important for the study of historical and museum objects. Methods for measuring the thickness of gilding on cultural heritage objects include the use of an optical microscope on gilded silver objects (Serrano et al., 2023), SEM-BSE on silver sculptures (Wu et al., 2021a, 2021b), SEM-EDS on gilded copper pieces (Barcellos Lins et al., 2020a), and FEG-SEM on fire-gilded copper (Ottenwelter et al., 2022). However, these methods are mostly invasive. For cultural or historical heritage objects, non-invasive techniques are always preferable and, in many cases, the only feasible option.

Building on this principle, Cesareo et al. (2009, 2013, 2022) proved

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that the intensity ratio of the characteristic lines of an element in the substrate can be used to determine the thickness of a coating. A similar approach was used by Pessanha et al. (2019a) to analyse the gilding of a 16th century illuminated manuscript. A related study was conducted by Buccolieri et al. (2025) who use portable ED-XRF to measure the thickness of gold coatings on wooden paintings, using the Au-Lα/Fe-Kα intensity ratio. XRF, a non-invasive technique that can be carried out using portable equipment, is one of the most suitable methods for this purpose. Although it is a method that has proven to be effective, it is based on a comparison between the coated and uncoated substrate. However, in many cases, such as when the object is completely coated, it is not possible to have access to the isolated substrate.

Additional methods have been explored to overcome this limitation, such as the study of the thickness of gilding on silver carried out by Ferretti et al. (2013), who obtained the thickness of the gilding through the mass fraction of silver in the Kα and Kβ lines. Brocchieri et al. (2021), describes several methods for estimating the thickness of a silver coating on metal using a commercial portable XRF spectrometer, discussing its limitations and including the use of references to obtain calibration curves to estimate the thickness of silver objects. Sabbarese et al. (2021) also use portable XRF to measure the thickness of gold coatings on metals (Ag, Cu, Fe, Pb) using a commercial portable instrument, evaluating thickness through intensity ratios. Non-invasive calculations of gilding thickness have also been explored using simulations, such as Monte Carlo Simulation (Pessanha et al., 2019a, 2019b; Barcellos Lins et al., 2020b). However, the application of these methodologies requires accurate knowledge of the equipment, namely, emitted X-ray spectrum, detector's efficiency curve and geometry between the X-ray tube and detector, which is not always available when using commercial portable spectrometers.

So far, existing research on Portuguese cultural heritage in gilded silver has not focused specifically on determining the thickness of the gilding, and studies addressing the thickness of fire gilding on silver in the broader European context remain scarce. For the first time on medieval Portuguese silverware, this work aims to expand the limited research corpus in this area by presenting and validating a methodology to calculate the thickness of fire gilding on silver without the need to have access to areas of clean silver, using XRF analysis with commercial equipment.

Additionally, we aim to transpose this method to calculate the thickness of gilding on 16th century Portuguese silverware pieces. To do this, tests were carried out on standard silver samples with different compositions, using traditional techniques. This methodology will enable an initial approach to calculating the thickness of fire gilding on Portuguese silver pieces *in situ*, using a commercial portable spectrometer, without the need for access to the isolated substrate. It represents a first attempt to address the gaps in current research on this topic and to provide a standardised, cost-effective, and easily applicable methodology for routine *in situ* characterisation of gilded silver artworks, contributing both to museum practice and to the broader understanding of these objects.

2. Methods and materials

2.1. Background and validation

As several authors have shown (Vázquez et al., 1988; Cesareo et al., 2009, 2013, 2022; Pessanha et al., 2019b; Gójska et al., 2024), it is analytically possible to calculate the thickness of multiple layers using the intensity ratios of a given element. Cesareo et al. (2009) explains the use of these ratios to obtain the thickness when a metal is covered by another metal, using the following Eq. (1):

$$\left(\frac{K\alpha}{K\beta}\right) = \left(\frac{K\alpha}{K\beta}\right)_{s.a.} \exp\left(-[\mu_1 - \mu_2]\rho d\right) \quad (1)$$

Where (Kα/Kβ) is the intensity ratio of the characteristic lines of an element on the coated substrate; $(K\alpha/K\beta)_{s.a.}$ is the same ratio for the isolated substrate, only due to self-absorption; μ_1 (in cm^2/g) is the mass attenuation coefficient of the coating at the energy of Kα emission line considering the element of the substrate; μ_2 (in cm^2/g) is the mass attenuation coefficient of coating at the energy of Kβ emission line considering the element of the substrate; ρ is the density of the coating alloy; and the path length (in cm) is $d = \frac{x}{\cos\theta}$ where x is the thickness of the layer and θ is the angle between the detector and the normal to the sample.

This calculation has two relevant variables: the $(K\alpha/K\beta)_{s.a.}$, referring to the substrate without coating; and the composition of the coating, since the mass attenuation and density considered in the calculation depend on this composition.

2.2. Preparation of mock-up samples

Six mock-up silver alloy samples (Fig. 1), were prepared, with different concentrations of silver, copper and gold: A – 75 % Ag, 25 % Cu; B – 83.3 % Ag, 13 % Cu, 3.7 % Au; C – 91.6 % Ag, 8.4 % Cu; D – 92.5 % Ag, 7.5 % Cu; E – 94.5 % Ag, 5 % Cu, 0.5 %Au; F – 95 % Ag, 3 % Cu, 2 % Au.

The metals used to make the alloys were 99.999 % pure (Albino Moutinho Lda. Portugal). The alloys were made by melting the metals in a crucible and pouring the mixture into a mould, creating an ingot (Vitobello and Rehren, 2009). The ingot was rolled in a manual rolling mill to a thickness of 0.5 mm.

The percentage of silver in the different samples was chosen considering the alloys most commonly used in Portugal in the 16th century (mock-up samples A, B, and C) (Vidal, 1974), the current sterling silver (mock-up sample D) and in two (mock-up samples E and F) it was chosen for higher percentages of silver based on recent studies carried out on 16th century Portuguese silver objects (Borges, 2018).

Given that in 16th century Portuguese objects contained gold in the composition of silver alloys (Borges, 2018; Borges et al., 2018), different percentages of gold were added to three mock-up samples. This was done to assess whether the presence of gold, and its varying concentrations, influences thickness calculations.

The samples were gilded using the traditional fire gilding method described by Oddy (1993) and Anheuser (1997) and previously reproduced effectively by Margreiter (2016, 2022). The gilding was carried out in the workshop of specialist goldsmith Dirk Meyer in Maierhöfen, Germany.

The mercury amalgam used for gilding can be produced in different proportions (Anheuser, 1997), which only influences the consistency of the amalgam and not its chemical composition (Margreiter et al., 2022). The amalgam used to prepare the standard samples was produced with a proportion of 1:5 of gold and mercury respectively (the proportion used by goldsmith Dirk Meyer). The samples were gilded in layers, between 1 and 4 layers of gilding. They were then polished with a haematite burnishing stone.

2.2.1. Evaluation of the gilding thickness and composition

SEM-EDS analysis was carried out to measure the actual thickness of the coating layer and to check the concentration of Hg that remained in the gilding. The equipment used was the HITACHI S3700 N interfaced with a QUANTAX EDS microanalysis system. This QUANTAX system was equipped with a BRUKER AXS 5010XFlash® Silicon Drift Detector with 129 eV Spectral Resolution at FWHM/Mn Kα. Standardless PB/ZAF quantitative elemental analysis was performed using the Bruker ESPRIT software. The EDS analysis was carried out under the following conditions: backscattered electron mode (BSEM), 20 kV accelerating voltage, ~10 mm working distance and 120 μA emission current. According to the manufacturer, the detection limits with this configuration for major elements (>Na) were in the order of 0.1 wt%.

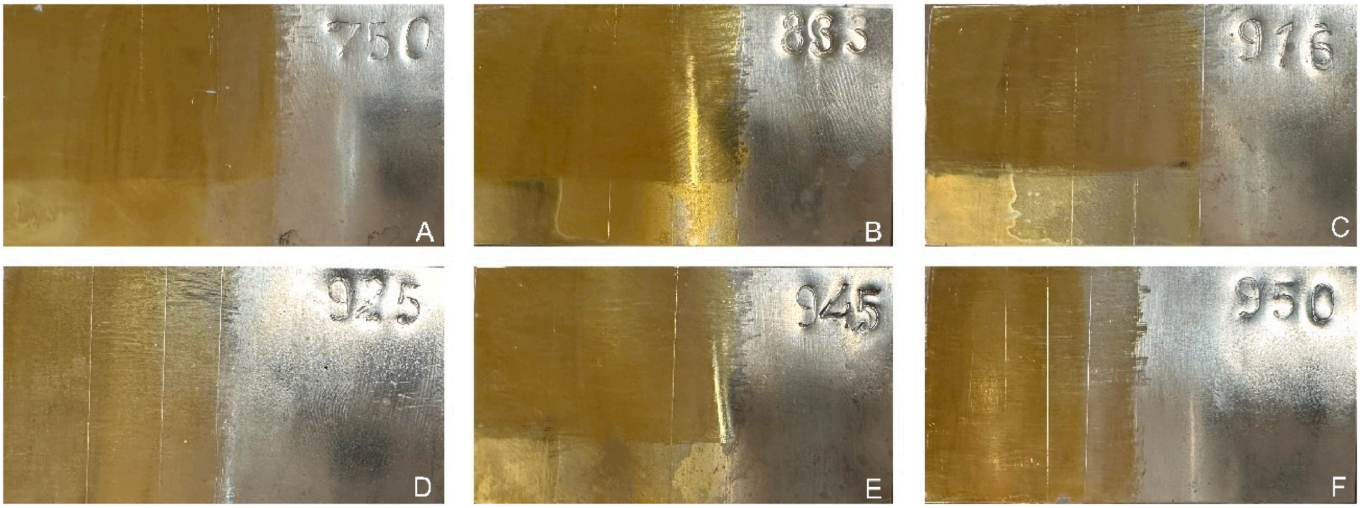

Fig. 1. Detailed view of the six fire gilded silver mock-up samples: the inscribed numbers represent the proportion of silver in the alloy, in parts per thousand, and the letters identify each mock-up sample. The vertical lines in the gilding separate the layers: from four layers to one layer, from left to right.

To measure the thickness of the coating layer, a strip was taken from each of the samples and embedded in acrylic resin (VariKleer, Buehler). The thickness was measured on cross-sections prepared in resin along the entire length of the samples, the average of the measurements and the respective standard deviation (Table S1) were considered for comparison with the experimental data.

The concentration of Hg (w/w %) was analysed on the same resin assembled strips, 3 to 6 points in each layer were analysed and the average concentration obtained was considered for each layer (Table S2).

2.3. Portable XRF setup

The portable spectrometer used in this work is a Bruker Tracer III-SD handheld spectrometer equipped with an Rh anode tube and a Silicon Drift Detector (SDD). The operating conditions were set up at 40 kV, 11 μA current, with an Al/Ti filter (304.8 μm Al/25.4 μm Ti) and 60 s acquisition. Analyses were carried out at 4 points in the gilded zones and 3 points in the non-gilded zones, repeating the analysis 3 times for each point.

The geometry of the system was determined by taking into account the Compton effect and the energy difference between the Compton and Rayleigh peaks of the Kα characteristic line of the X-ray tube's anode.

Spectra deconvolution and fitting was performed using the PyMCA v5.9.2 software.

2.4. Validation of the methodology

The gilding thicknesses of the mock-up samples were calculated using Eq. (1).

The first issue to be investigated was the amount of Hg reminiscent in the alloy after fire gilding. Two coating compositions were considered: 95 % Au – 5 % Hg and 80 % Au – 20 % Hg. These values are based on the results of the SEM-EDS analyses carried out on the samples where, for all layers/sample, percentages of Hg between 6 % and 21 % were identified, which corresponds to what is expected according to recent studies by Margreiter et al. (2022), supported by practical tests and studies by other authors, that demonstrated that the percentage of Hg in fire gilding is never less than 5 % and can be up to 20 %. The variation in the amount of Hg in fire gilding is also influenced by the ageing of the objects.

In the mock-up samples under study, the areas with fewer layers normally have a lower percentage of Hg than the areas with more layers, which is due to the number of times they were heated during the production of the fire gilding. The zone with 1 layer was heated 4 times, the zone with 2 layers was heated 3 times, the zone with 3 layers was heated 2 times and the zone with 4 layers was heated only 1 time.

For the purposes of comparison with the real measurements, the average of the calculated thicknesses of the 4 points analysed by XRF was taken for each layer/sample. The uncertainties in the calculations were obtained using the propagation of uncertainties formula. The calculated results compared with the actual SEM-EDS measurements are shown in Fig. 2 (Table S3).

Since the analysed coating composition is generally between 5 % Hg and 20 % Hg, it can be seen from Fig. 2 that the calculations made considering the two very different coating compositions are very similar and the uncertainties overlap. This way, we can conclude that the difference in gilding composition does not affect significantly the determined thickness, at least considering the uncertainty of our method. When comparing to the measured thickness, the calculated thicknesses are also very similar. It can also be seen that these calculated values, in 78 % of cases, are within the real values previously measured. The other 22 % are the samples *D – 4 layers*, *E – 3 and 4 layers*, with an overestimated thickness and *F – 1 and 2 layers,* with an underestimated thickness. However, we believe that these discrepancies are more likely due to the unevenness of the layers and different probing spots by XRF and SEM-EDS.

Based on the results obtained, as described in the literature and confirmed by the measurements, we believe that it is correct to assume a general coating composition of 90 %Au–10 %Hg for the calculation of the thickness of fire gilding silver.

In order to determine the value of Kα/Kβ intensity ratio due to self-absorption that could be used on real objects, where it is not possible to access clean silver zones (without coating), and without introducing major uncertainty to the calculation, the following procedure was undertaken. Apart from the mock-up samples, three certified reference materials were used to gauge a representative value for this parameter in silver alloys (compositions of certified reference materials in Table S4). Table 1 shows the $(K\alpha/K\beta)_{s.a.}$ of the mock-up samples and certified reference materials.

Observing the $(K\alpha/K\beta)_{s.a.}$ of the different mock-up samples and certified reference materials, considering the different compositions (either % Ag or % other elements), an average value of $(K\alpha/K\beta)_{s.a.}$ of 6.35 ± 0.05 was determined and used henceforward. To verify the suitability of this model value of $(K\alpha/K\beta)_{s.a.}$ for calculating fire gilding thicknesses, this value was used to calculate the thicknesses of the six mock-up samples. These calculations are reflected Fig. 3 (Table S5).

Analysing the data shown in Fig. 3 it is possible to understand that

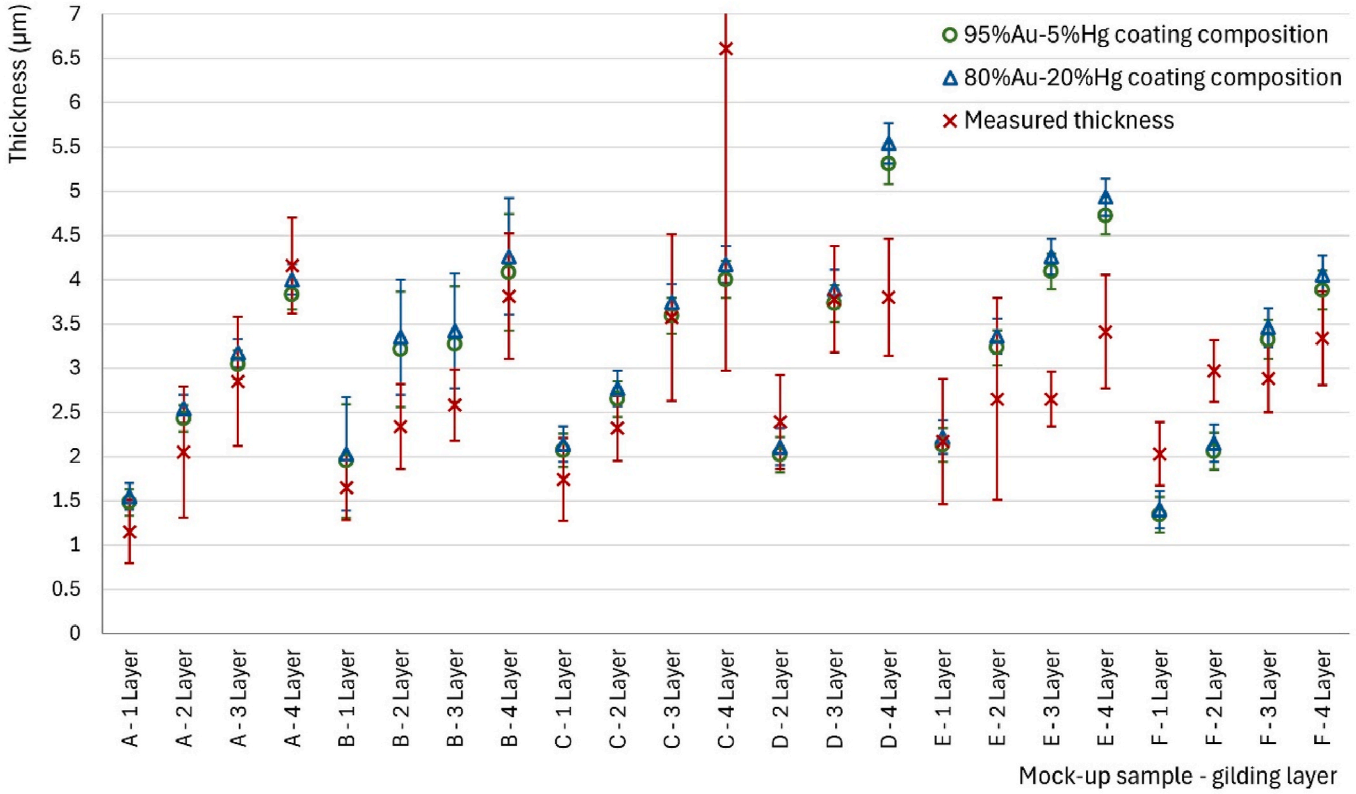

Fig. 2. Thickness calculated using $(K\alpha/K\beta)_{s.a.}$ for 95 %Au - 5 %Hg and 80 %Au - 20 %Hg compositions and thickness measured with SEM-EDS of mock-up samples.

Table 1
$(K\alpha/K\beta)_{s.a.}$ of mock-up samples and certified reference materials. Average of these values and respective deviation from the average: $(K\alpha/K\beta)_{s.a.\ model}$.

Sample	Ag Content	$(K\alpha/K\beta)_{s.a.}$
A	75 % Ag	6.25
B	83.3 % Ag	6.31
C	91.6 % Ag	6.40
D	92.5 % Ag	6.39
E	94.5 % Ag	6.39
F	95 % Ag	6.38
Ag Check Sample Bruker Tracer 5g	92.774 % Ag	6.39
133X AGQ2 (batch C) from MBH Analytical Ltd	92.745 % Ag	6.37
133X AGA2 (batch A) from MBH Analytical Ltd	86.96 % Ag	6.25
Average: $(K\alpha/K\beta)_{s.a.\ model}$		**6.35**
Deviation from average: Uncertainty of the $(K\alpha/K\beta)_{s.a.\ model}$		**0.05**

using the $(K\alpha/K\beta)_{s.a.\ model}$ to calculate the thickness, we also obtain an agreement between the obtained values and the values measured with SEM-EDS, considering a greater uncertainty, with the only exception being sample *E - 3 layers*. By comparing Figs. 2 and 3, we can realise that the approach of using the model value and a general coating composition, although less precise, is more accurate.

The thicknesses calculated using the $(K\alpha/K\beta)_{s.a.\ model}$ and general coating composition of 90 %Au–10 %Hg for the mock-up samples and compared with the values measured in the SEM-EDS allow us to verify that the results obtained are 96 % consistent.

3. Results and discussion

3.1. Case study: 16th century Portuguese silverware

This method was applied to real objects produced in Portugal in the 16th century. Three masterpieces (Fig. 4) were selected from different museums: i) a chalice from the *Museu da Misericórdia do Porto* (MMIPO O0001), ii) a chalice from the *Museu Nacional Frei Manuel do Cenáculo* (MNFMC ME1482/1) and iii) a chalice from the *Museu de Arte Sacra da Sé de Évora* (MASSE EV.SE.1.028/1–2). These pieces were selected considering the possibility of accessing the isolated substrate (ungilded silver) to validate the viability of this method for calculating the thickness of original 16th century objects.

Three points in the gilded areas and three points in the non-gilded areas were analysed by XRF, with the gilded and non-gilded areas analysed corresponding to the same silver foil. The three pieces are composed of an Ag–Cu alloy, containing trace elements such as Pb, Bi, Fe, Hg, Au, and Zn. The composition of these pieces is consistent with what would be expected for a 16th-century Portuguese silver alloy (Borges, 2018; Borges et al., 2018). The presence of these elements may reflect natural impurities from the metal ores, suggesting the origin of silver, external contamination introduced during the metallurgical process or could be related with the incorporation of recycled metal, practices often associated with economic constraints or resource shortage (Flament and Marchetti, 2004; Borges, 2018; Borges et al., 2018).

The quantification of the alloy analysed in the non-gilded areas was carried out in the CloudCal v3.0 software (Drake, 2018), using the certified reference materials discussed in section 3.1 (Table S4). as standards for quantification. The averages of the concentration of the three points were considered. An Ag concentration of i) 93.38 ± 0.95 %, ii) 89.23 ± 0.95 % and iii) 93.21 ± 0.94 % was obtained, corresponding to the legal standard established in the 16th century in Portugal (Vidal, 1974). These values are within the range of the values of the mock-up samples tested previously.

The $(K\alpha/K\beta)_{s.a.\ measured}$ obtained for these pieces were: i) 6.29 ± 0.03; ii) 6.26 ± 0.02; and iii) 6.23 ± 0.05. The averages of the three points were considered and the uncertainties in the calculations were obtained using the uncertainty propagation formula.

The results obtained for the thickness calculation using the $(K\alpha/K\beta)_{s.a.\ model}$ and the $(K\alpha/K\beta)_{s.a.\ measured}$ for coating compositions of 90 %

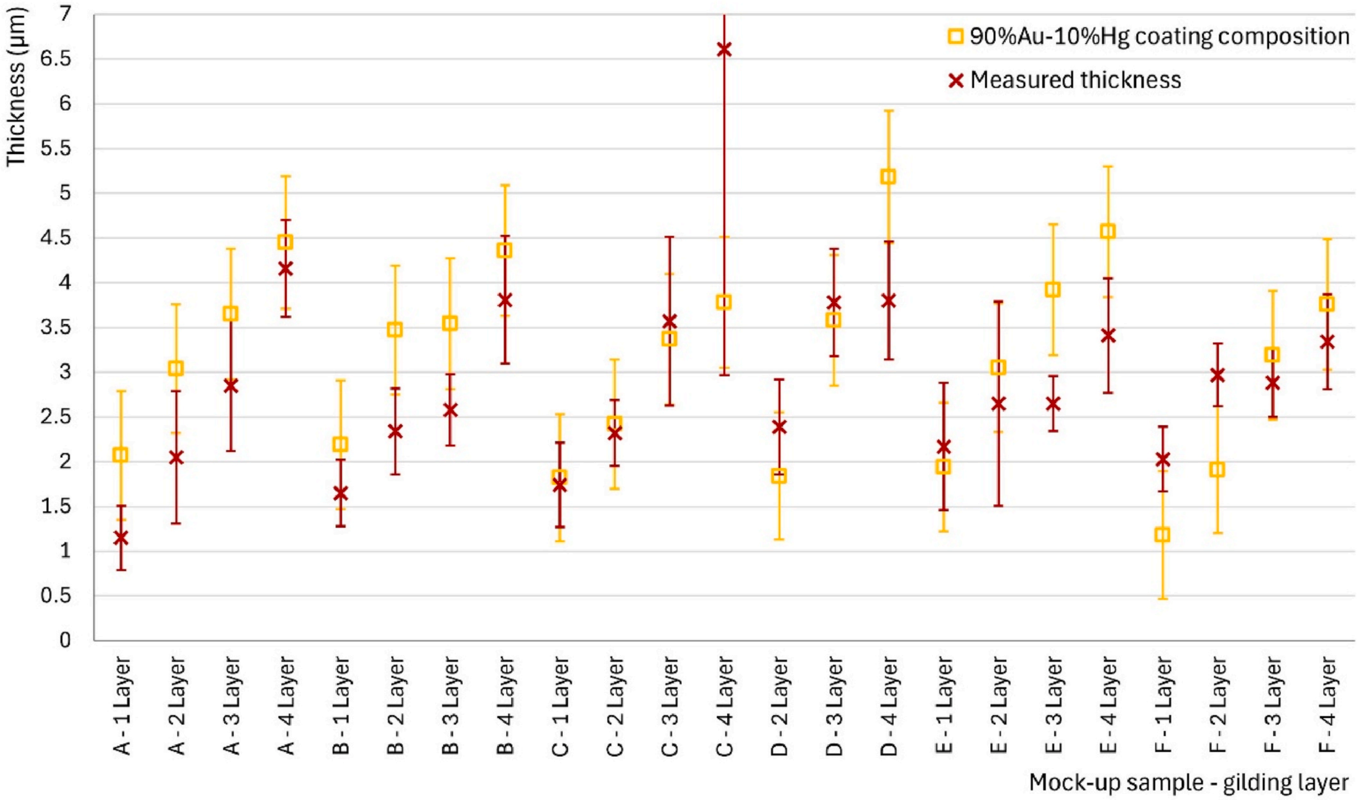

Fig. 3. Thickness calculated using the $(K\alpha/K\beta)_{\text{s.a. model}}$ for 90 %Au–10 %Hg composition and thickness measured with SEM-EDS of mock-up samples.

Fig. 4. General view of the three 16th century Portuguese silver chalices under study: i) MIPPO O0001, ii) MNFMC ME1482/1, iii) MASSE EV.SE.1.028/1–2.

Au–10 %Hg are shown in Fig. 5 (Table S6). The averages of the thicknesses of the three points were considered.

As expected, the thicknesses determined with the model intensity ratio were higher than the thicknesses determined with measured intensity ratio values, given that the $(K\alpha/K\beta)_{\text{s.a measured}}$ is lower than the $(K\alpha/K\beta)_{\text{s.a. model}}$. However, considering the uncertainties, the value calculated using the $(K\alpha/K\beta)_{\text{s.a. model}}$ was within the value calculated using the $(K\alpha/K\beta)_{\text{s.a. measured}}$. It can therefore be considered a reliable value. It should be noted that the geometry of both the object and the analysing equipment can lead to different and less accurate results. Also, an alloy composition very different from those studied in this article could lead to unrealistic results since in this study was used a general

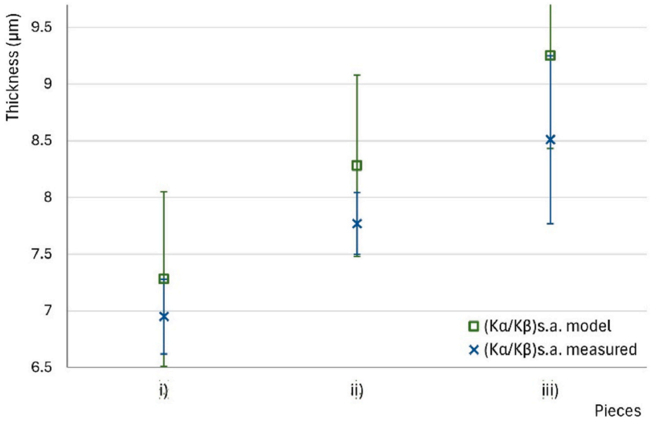

Fig. 5. Calculated thickness using $(K\alpha/K\beta)_{s.a.\ model}$ and $(K\alpha/K\beta)_{s.a.\ measured}$ for 90 %Au–10 %Hg coating composition.

value of $(K\alpha/K\beta)_{s.a.}$ taking into account samples produced with concentration of silver based on Portuguese objects from the 16th century.

This method of calculating the thickness of fire gilding on silver, based on methods previously developed by other authors (Cesareo et al., 2009; Buccolieri et al., 2018, 2025; Brunetti et al., 2022) but using a value of $(K\alpha/K\beta)_{s.a.}$ general, has shown good results for studying the thickness of gilding on 16th century Portuguese pieces without the need to access the isolated substrate, which represents an important development in the study of these pieces, since many objects are completely covered with gilding, making thickness calculation very difficult through analysis with commercial portable spectrometers and without sampling.

This study is the first of its kind on 16th century Portuguese pieces, having demonstrated good applicability and usability to measure the thickness of the fire gilding in silver. Previous studies on European pieces have gilded silver earrings from the western Iberian Peninsula (Serrano et al., 2023), gilded copper buckles and jewellery from the province of Rome and Prague (Barcellos Lins et al., 2020b; Ottenwelter et al., 2022) and gilding on silver sculptures from Germany (Wu et al., 2021a, 2021b), obtaining thickness values through OM and SEM measurements, in the order of tens of micrometres. Similar thicknesses to those obtained in these studies were reported in research more directly comparable to ours, such as in the case of gilding in Italian silver crosses measured using the mass fraction of silver in the Kα and Kβ lines (Ferretti et al., 2013). While these methods provide accurate results, they usually require either sampling and surface polishing, which are invasive, or simulations that require precise knowledge of the analysis equipment, so that this non-invasive calculation is possible. In contrast, the present study requires neither sampling nor simulation, nor extensive knowledge of instrument geometry. This approach broadens the applicability of fire-gilding thickness measurements in silver and enhances usability for cultural heritage professionals as it can be applied to a wider range of objects and contexts using commercially available, portable equipment.

4. Conclusion

The main contribution of this article is the development of a non-invasive and rapid methodology for determining the thickness of fire gilding on fully gilded silver objects, which represents a significant advance for cultural heritage studies. This approach allows gilding thickness to be calculated using generic model values of $(K\alpha/K\beta)$ which account for self-attenuation and general coating composition. This method does not require sampling, surface preparation or detailed knowledge of instrument geometry. Combining accuracy with ease of use, this method provides heritage professionals with a practical tool applicable to a wide range of objects and conservation contexts.

The results indicate that the $(K\alpha/K\beta)_{s.a.}$ of a substrate differs, not only due to the concentration of Ag, but also to the presence of other elements in the alloy and their respective concentrations. The presence of Au has a negligible effect the value of $(K\alpha/K\beta)_{s.a.}$. An alloy with many elements has a lower $(K\alpha/K\beta)_{s.a.}$ than an alloy with the same concentration of Ag but fewer elements. Considering the results, an average value of $(K\alpha/K\beta)_{s.a.}$ of 6.35 ± 0.05 and a coating composition of 90 %Au–10 %Hg gives consistent results for calculating the thickness of fire gilding on silver alloys under study. In addition, this type of gilding has a very heterogeneous thickness, as evidenced by the SEM-EDS measurements, which can lead to a difference between the zones measured and those analysed by XRF.

This methodology proved to be suitable when applied to 16th century Portuguese gilded silver objects. Despite its limitations, it can be used to estimate the thickness of gilding using commercial X-Ray spectrometers, even when the isolated substrate cannot be analysed, for fire-gilded silver alloys with a silver content between 75 % and 95 %. Further studies are needed to assess its applicability to silver alloys of different compositions.

CRediT authorship contribution statement

Catarina Lopes Cordeiro: Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. **Carlo Bottaini:** Writing – review & editing, Supervision, Resources, Project administration, Data curation, Conceptualization. **Rui Bordalo:** Writing – review & editing, Supervision, Project administration, Data curation, Conceptualization. **Gonçalo de Vasconcelos e Sousa:** Writing – review & editing, Supervision, Project administration, Conceptualization. **Sofia Pessanha:** Writing – original draft, Validation, Methodology, Formal analysis, Conceptualization.

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Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Catarina Lopes Cordeiro reports financial support was provided by Foundation for Science and Technology. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.radphyschem.2025.113300.

Data availability

Data will be made available on request.

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