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EVALUATION OF THE GOLD LEAF THICKNESS IN THE COATING OF THE IMPERIAL HORSE-DRAWN CARRIAGE EMPEROR D. PEDRO II

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ABSTRACT

In this study, the presence of gold in the coatings of the emperor D. Pedro's II Berlin device, part of the Imperial Museum of Petropolis, Brazil, was verified. Then perform was evaluation of the thickness of the gold leaf, using the technique of X-Ray Fluorescence, measuring peak intensities (Kα / Kβ or Lα / Lβ) of the elements of interest in the layer. It was possible to verify in the XRF spectra the presence of four elements: Ti, Fe, Au and Pb. The Pb was present at all sampling points, which indicates the presence of lead carbonate (lead-white) as preparation layer. The presence of Au at some sampling points indicates that several parts of the Berlin devices were covered with gold leaf. The presence of Ti and Fe is due to the application of golden mica over the entire length of the berlin device during the process of last restoration. The presence of the mica layer on the gold covering was relevant for gold thickness determination. The average value of the gold thickness obtained was 0.62 ± 0.51 µm, with a coefficient of variation of 83% and a confidence interval of 0.49-0.75 µm ($\alpha = 0.05$). The values are compatible with the thickness of gold foil normally found in the coating of pieces of wood from the same period that the Berlin device was built.

1. INTRODUCTION

Analysis of objects of historical value in museum collections around the world has intensified in the last decades, promoting an interaction among professionals of diverse areas: restorers, conservatives, archaeologists, historians, physicists, chemists, etc., around a common goal [1,2].
X-Ray Fluorescence (XRF) is a non-destructive technique that enables a qualitative and quantitative analysis with good accuracy [3,4]. It has been applied quite successfully in the determination of coatings thickness in a range of materials of historical-cultural value [5,6].
The studies and characterizations of the coating sheets thickness in a variety of materials are extremely important in archeological.
One of the important points is a possibility of analyzing the artisan's techniques, in the use and application of gold foils in the coatings of materials, as well as the thicknesses. The documentation of the coatings can help in the establishment of the technique used, reconstructing its history, old restoration processes, techniques that were carried out in its conservation and also detecting possible forgeries [7,8].
The objective of this study was the verification of the presence of gold in the coatings of the emperor D. Pedro's II Berlin device, part of the Imperial Museum of Petropolis, Brazil. Then perform was evaluation of the thickness of the gold sheets, using the X-Ray Fluorescence technique.

2. MATERIAL AND METHODS

2.1. Art artefact

The emperor D. Pedro's II Berlin device (Figure 1) was built by the British company Pearce & Countz, responsible for building the carriages of the British monarchy, for its coronation ceremony in 1841. It was incorporated into the collection of the Imperial Museum in the 40s, XX century. The Berlin device has undergone several restoration processes over the years. The most recent took place in the period 2011-2013 and was sponsored by the GE Celma Company based on the Culture Incentive Law, the support of the Society of Friends of the Imperial Museum (SAMI) and the coordination of Eliane Zanatta, responsible for the Laboratory of Conservation and Restoration of the Imperial Museum [9,10].

Figure 1: The Imperial Horse-drawn carriage Emperor D. Pedro II.

2.2. Sampling

Figure 2 shows some of the points analyzed in the Berlin. The measurement points were previously selected by the Museum's restoration team, where there were indications of the existence of gold. In the restoration treatment, the metallic parts received a thin layer of maritime matt lacquer, diluted in mineral turpentine. After drying, synthetic paint was applied to metal. Finally, the elements, originally gilded, received on protective synthetic paint, monochromatic reintegration with golden Mica diluted in Paraloid-B72

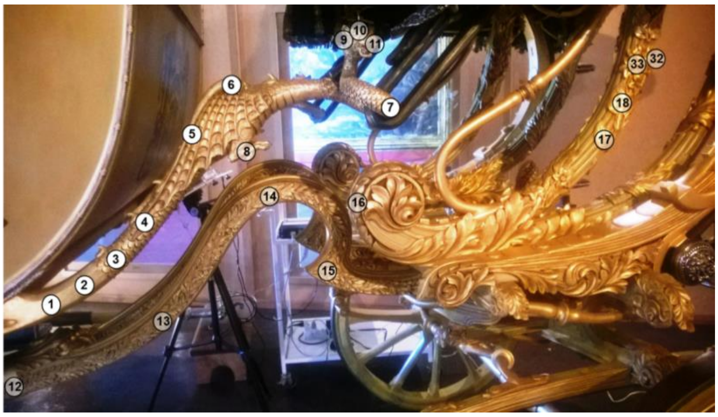

Figure 2: Points in the Berlin where measurements were taken.

Figure 3: The Berlin's right frontal serpent.

2.3. Instrumentation

The XRF analysis of the Berlin was performed using a portable XRF system developed by the Electronic Instrumentation and Analytical Techniques Laboratory (LIETA, UERJ) together with the Polytechnic Institute of UERJ, Nova Friburgo (IPRJ, UERJ). Figure 4 shows the portable X-ray Fluorescence system used in this study. The portable XRF system was developed with the intention of being used for several areas of research, especially in archaeological studies. The portable XRF system can be used to obtain qualitative information, identifying the elements present in the samples and quantitative information, providing the concentrations of the elements present in the samples. The portable XRF has an X-ray tube with silver anode (Ag) and a SiPIN type semiconductor detector. The X-ray tube was operated at 35 kV, 50 μA and during an acquisition time of 600 s. All XRF spectra were evaluated using the AXIL software provided by the International Atomic Energy Agency (IAEA).

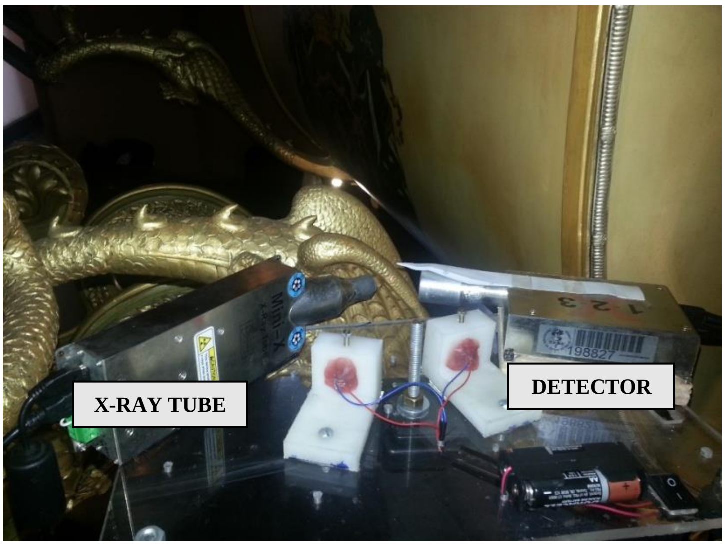

Figure 4: Experimental setup for the measurement of Au thin sheets.

3. METHODOLOGY

The technique of measuring the thickness of a thin sample (film) deposited on a substrate using the ratio between XRF lines of the elements present in the substrate has been used with great success in the archaeological area [11,12]. In the model used in this study, the elements Lead, Gold and Mica were considered. This model consists of a mica layer of thickness t on the thin gold film of thickness d which lies over a thicker lead sample of thickness L, as shown in Figure 5. In this model, both the mica layer and the gold contribute to the attenuation of lead L_α and L_β lines.

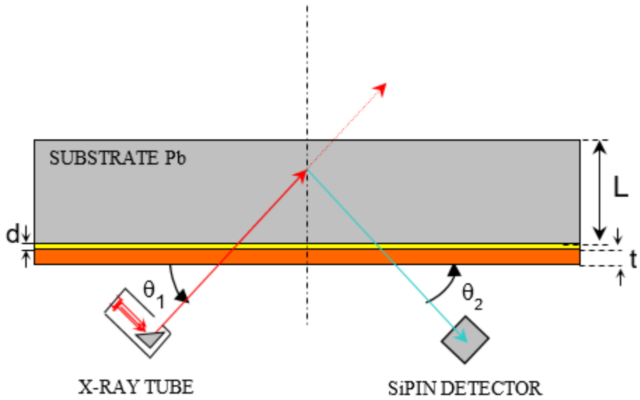

Figure 5: Basic model: Lead + Gold + Mica. X-ray beam incident on the angle θ_1 and the beam coming out, in the direction of the detector, at the angle θ_2

In this model, the intensity for the L_α and L_β lines of the lead attenuates the mica layer and gold layer, so the XRF equation for the lines L_α and L_β of the Pb will be:

$$I_{Pb-L_\alpha} = \frac{W_{Pb} S_{L_\alpha}\left(1-e^{-\chi_{L_\alpha}\rho.L}\right)}{\chi_{L_\alpha}}\left[\left(e^{-\mu_{mica}(E_o).\frac{t}{sen(\theta_1)}}\right).\left(e^{-\mu_{Au}(E_o).\frac{d}{sen(\theta_1)}}\right)\cdot\left(e^{-\mu_{mica}(E_{L\alpha}).\frac{t}{sen(\theta_2)}}\right)\left(e^{-\mu_{Au}(E_{L_\alpha}).\frac{d}{sen(\theta_2)}}\right)\right] \quad (1)$$

$$I_{Pb-L_\beta} = \frac{W_{Pb} S_{L_\beta}\left(1-e^{-\chi_{L_\beta}\rho.L}\right)}{\chi_{L_\beta}}\left[\left(e^{-\mu_{mica}(E_o).\frac{t}{sen(\theta_1)}}\right).\left(e^{-\mu_{Au}(E_o).\frac{d}{sen(\theta_1)}}\right)\cdot\left(e^{-\mu_{mica}(E_{L\beta}).\frac{t}{sen(\theta_2)}}\right)\left(e^{-\mu_{Au}(E_{L_\beta}).\frac{d}{sen(\theta_2)}}\right)\right] \quad (2)$$

Where $\mu_i\left(L_{\alpha,\beta}\right)$ is the linear attenuation coefficient of the coating material i at L_α or L_β energy; ρ is the material density $\left(g \cdot cm^{-3}\right)$; $I_{Pb}\left(L_{\alpha,\beta}\right)$ is the intensity of the L_α or L_β line of the Pb; S_i is called the system sensitivity of the element i in the sample; W_{Pb} is the concentration of Pb in a sample and χ_i can be understood as a coefficient of total mass absorption of the element i in the sample.

The value of the gold thickness d may be deduced from equations 1 and 2 as follows:

$$d = -.\left\{\left(\frac{\mu_{mica}(E_{L\alpha})-\mu_{mica}(E_{L\beta})}{\mu_{Au}(E_{L\alpha})-\mu_{Au}(E_{L\beta})}\right).t+\left(\frac{sen(\theta)}{\mu_{Au}(E_{L\alpha})-\mu_{Au}(E_{L\beta})}\right)\ln\left[\frac{\left(\frac{I_{L\alpha}}{I_{L\beta}}\right)}{\left(\frac{I_{L\alpha}^{\infty}}{I_{L\beta}^{\infty}}\right)}\right]\right\} \quad (3)$$

Where $\left(\frac{L_\alpha}{L_\beta}\right)_\infty$ is the ratio for the base material (Pb) of infinite thickness.

4. RESULTS

The Figure 6 shows the XRF spectrum of the measurement on the serpent's chest. In this spectrum the presence of Titanium, Iron, Gold and Lead can be observed. To understand the presence of these elements in the spectrum, a new measurement was performed at a point that had no gold coating. The measurement was made on the wood part of the berlin. Figure 7 shows an XRF spectrum comparing the measurement performed on the saw with the measurement performed on the wood. It can be observed that the elements Ti, Fe and Au do not appear in the spectrum referring to wood. However, the presence of Pb in the two spectra is observed.

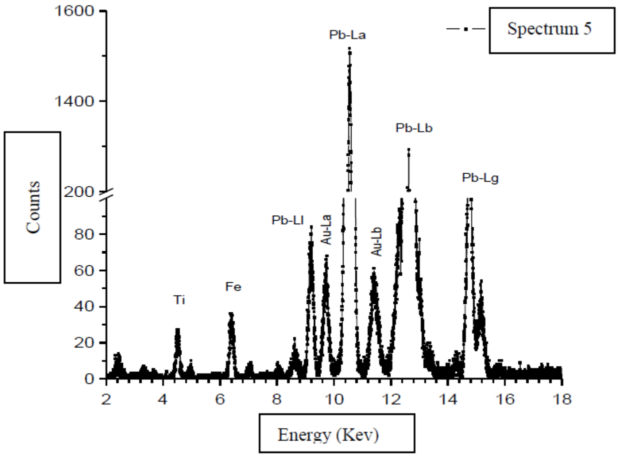

Figure 6: XRF spectrum of the snake's chest.

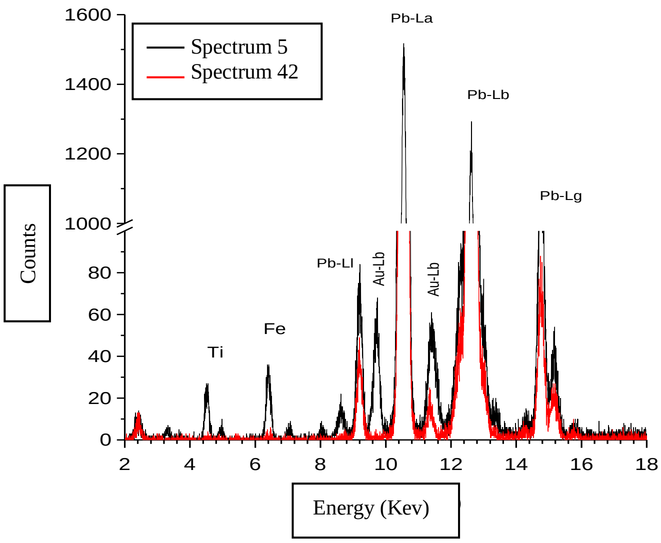

Figure 7: Overlap of two spectra: Spectrum 5 referring to the golden serpent and spectrum 42 obtained from the part of wood without golden coating.

The fact that this Berlin was built in 1837 raises the hypothesis of the presence of lead (lead carbonate) in its base coat. Lead carbonate occurs in nature in the form of Hydrocerussite, a rare mineral, but it has been synthesized for more than 2,000 years. Also known as lead white and is, since antiquity, one of the most used white pigments in the preparation of surfaces that will receive adornments such as paints and / or the like. Therefore, there is evidence, from the XRF spectra, that the preparation base for the gold coating was made using lead-white throughout the Berlin. The presence of Fe and Ti detected in the serpent, are not seen in the region of wood. This information evidences that these elements are in fact referring to the layer of mica.

4.1. Thickness of gold

To obtain the gold thickness, the thickness of mica layer must be considered. It was used the methodology developed by Cesareo [13], which results to equation 3. However, for the accomplishment of this methodology it was necessary to obtain experimentally the mica attenuation coefficient. For the calculation of the mica attenuation coefficient, the same product used in the covering of the Berlin was used when restoring (Mica + Paraloid B72, in this work it is called mica only).The mica was brushed with a silk brush on a smooth surface. After drying, this mica film was removed and its thickness was measured using a micrometer. The obtained value the thickness of the mica was approximately 74 μm. The mica attenuation coefficient was calculated using the transmission method [14]. The transmission method is based on Figures 8 and 9. In this method, the intensity of the Pb plate is first measured I_0 (Figure 8). Subsequently, the mica sample is positioned between the Pb plate and the detector (Figure 9), without altering the configuration (without removing the Pb plate from the site) and the measurement of the Pb plate with the sample of absorbing the characteristic X-rays (I). From the initial Pb intensity and the attenuated Pb intensity of the mica, the mica attenuation coefficient can be calculated through equation 4.

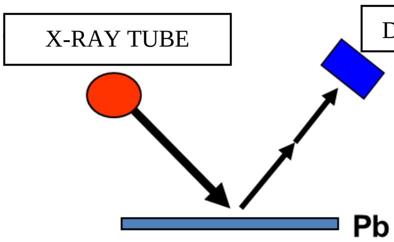

Figure 8: Scheme for the transmission method (obtaining I₀).

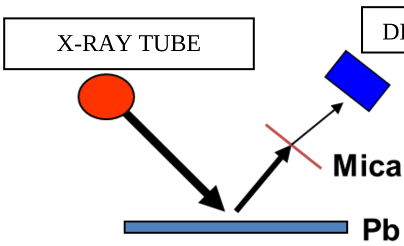

Figure 9: Scheme for the transmission method (obtaining I).

$$I = I_0 e^{\mu d} \rightarrow \mu_{mica} = \frac{1}{d} \ln \frac{I_0}{I} \qquad (4)$$

Where I_0 is the intensity of the Pb plate; I is the intensity of the Pb plate attenuated by the mica layer; d is the thickness of mica layer and μ_{mica} is the mica linear attenuation coefficient.
The table 1 shows the mica linear attenuation coefficient values for the energies of lead L_α and L_β (10.5 kev and 12.6 kev, respectively) obtained by the transmission method.

Table 1 – Mica attenuation coefficient for the energies of the L_α and L_β lines of Pb were obtained in the laboratory

$\mu(L_\alpha)$ (cm^{-1})	$\mu(L_\beta)$ (cm^{-1})	d (µm)
34	23	74

After calculating the mica attenuation coefficient, the equation 3, which reproduces the lead + gold + mica model, was validated. Four samples were prepared: Pb, Pb + Au, Pb + mica and Pb + Au + mica. Figure 10 shows the 4 samples being analyzed. The thickness of mica values were obtained (using the Pb + Mica sample) and two different ways of obtaining the thickness of gold values. First, the thickness of gold methodology was used and the thickness of gold methodology with mica attenuation (using the Pb + Au and Pb + Au + Mica samples, respectively) was used. XRF measurements were performed on the samples in the same manner as the in Berlin analyzes (35 kV and 50 µA). Table 2 shows the mica and gold thickness values obtained in this analysis.

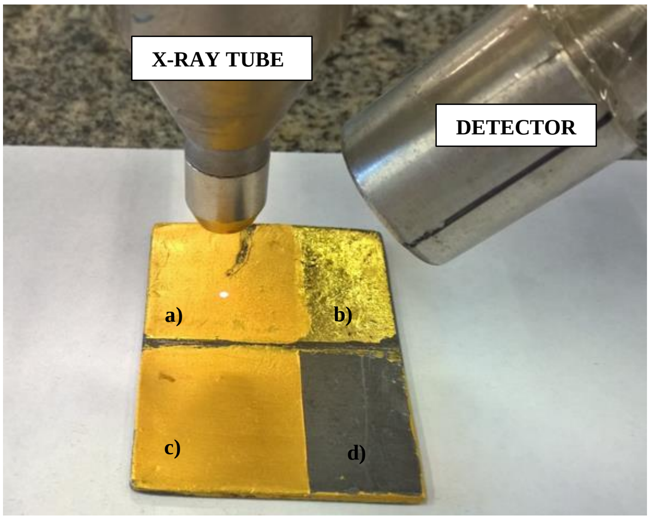

Figure 10: Samples for validation of the methods of calculating thickness. a) Pb+Au+Mica; b) Pb+Au; c) Pb+Mica; d) Pb

Table 2: Thickness of mica and gold obtained experimentally in the laboratory.

Material	Thickness measurement process			E_{rel} (%)$^{b)}$
	Micrometer	XRF		
	d (µm)	d (µm)	CV$^{a)}$ (%)	
Mica	74 ± 1	85 ± 9	11	13$^{c)}$
Gold	---	0.43 ± 0.12	28	---
Mica + Gold	---	0.35 ± 0.08	23	19$^{d)}$

a) CV = Coefficient of variation; b) E_{rel} = relative error; c) Relative error between the thickness of Mica measured by micrometer and XRF; d) Relative error between the thickness of the gold obtained in the plate Pb + Au and Pb + Au + Mica.

Figure 11 shows a histogram of the thickness values obtained from the 71 points analyzed using the Pb + Au + Mica methodology. For a better analysis of the value corresponding to the thickness of the gold layer, the Extreme Value Test (Grubbs Test) was performed. The Grubbs test is a statistical tool that verifies the presence of extreme values in sample observations. The Grubbs test showed that seven points could be removed. Figure 12 shows the histogram of the new data distribution.

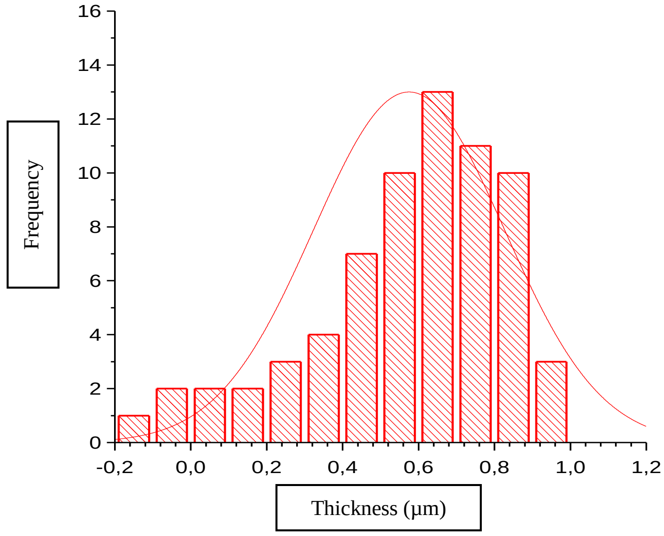

Figure 11 - Histogram of the thickness of the gold layer considering the presence of the mica in the coating.

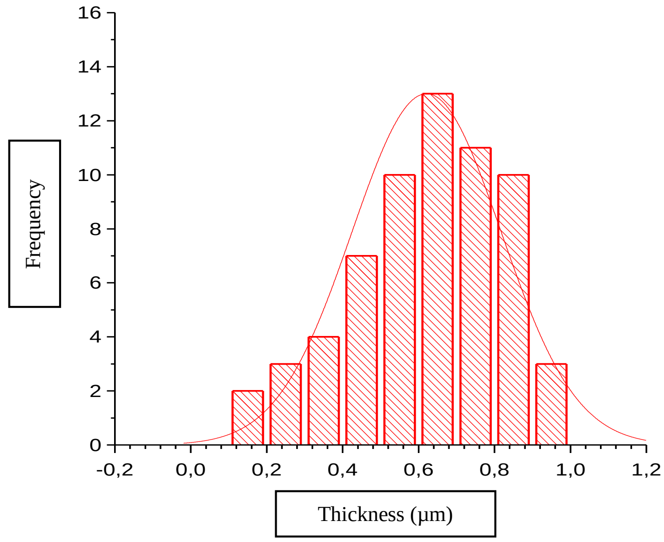

Figure 12 -Histogram of the thickness of the gold layer considering the presence of the mica in the coating after statistical analysis (Grubbs test).

The mean value of the thickness of gold obtained was d = 0.62 ± 0.51 µm, with a coefficient of variation about 83%, and a confidence interval of 0.49 - 0.75 µm ($\alpha = 0.05$). The values found for thicknesses of gold are consistent with the thickness of gold sheets normally used in the coating of pieces of wood from the period that the Berlin was built [15]. A large dispersion was found in the values of the thickness of gold (CV = 83%). This large dispersion can be associated with the process of degradation and cleaning during the various restoration processes that the Berlin has undergone.

CONCLUSION

From this work, it was possible to confirm that several parts of the Berlin were covered with gold leaves. The applied coverage of gilt mica over the entire length of the Berlin, during the restoration, has a signature through the presence of Ti and Fe in the XRF spectra. XRF spectra showed the presence of lead at all measurement points. These results may be indicative that the preparative base was made with lead white.
The results show that the thickness of gold, considering the thickness of mica, has values in a confidence interval of 0.49 - 0.75 μm ($\alpha = 0.05$).

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