# Manuscript Details

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| **Manuscript number** | SAB_2019_70_R1 |
| **Title** | Monte Carlo simulation of portable XRF setup: non-invasive determination of gold leaf thickness in Indo-Portuguese panel paintings |
| **Article type** | Research Paper |


**Abstract**

In this work, we present the combined use of in situ X ray Fluorescence spectroscopy and Monte Carlo simulation using PENELOPE code for the completely non-invasive determination of gold leaf thickness in artworks using lead white as mordant. The methodology used is based on the detection of different characteristic lines of Pb in the X ray fluorescence spectra, attenuated trough the gold leaves, and determining the thickness of gilding by comparing their attenuation. Firstly, this methodology was calibrated using model samples of simple stratigraphy, namely pure Au leafs of 1, 2 and 2.5 μm thickness covering a Pb infinitely thick sheet. The modelled X ray setup was then used to study the gilding thickness of three panel paintings belonging to the Museum of Christian Art in Old Goa (India): two paintings, from the 18th century, concerning to the same series but different themes: Our Lady of Sorrows (MoCA1) and Our Lady of Seven Sorrows (MoCA2), and a third painting entitled Monstrance (MoCA3), from the 17th century. These panel paintings were analyzed to understand the differences and similarities between techniques, according to the time/epoch and technique of its manufacture. The obtained values for MoCA2 tend to be slightly lower than for MoCA1, however, the t student test revealed that the differences were not statistically different ($p = 0.37$). Regarding the MoCA3 painting, the average thickness was determined to be statistically different ($p<0.001$) and higher than for the other two paintings. These results emphasize the use of different techniques concerning gold leaf beating. In the 17th century painting it was verified the use of a thicker gold leaf while in the group of the 18th century gold leaf was thinner and manufactured with a similar thickness in both paintings. These results are in consonance with the accuracy of leaf beating technology, increasing with the experience acquired during the ages.



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| **Keywords** | XRF; thickness determination; Monte Carlo; gilding; PENELOPE |



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## Submission Files Included in this PDF

**File Name [File Type]**

cover letter.docx [Cover Letter]

letter_reviewers.docx [Response to Reviewers]

highlight.docx [Highlights]

Graphical Abstract.tif [Graphical Abstract]

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Fig.1.jpg [Figure]

Fig.2a.JPG [Figure]

Fig.2b.JPG [Figure]

Fig.3.tif [Figure]

Fig.4a.JPG [Figure]

Fig.4b.JPG [Figure]

Fig.5.JPG [Figure]

Fig.6.tif [Figure]

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## Research Data Related to this Submission

There are no linked research data sets for this submission. The following reason is given:
Data will be made available on request

Dear editor,

I am sending you the paper “Monte Carlo simulation of portable XRF setup: non-invasive determination of gold leaf thickness in Indo-Portuguese panel paintings” for your appreciation to Spectrochimica Acta B.

This paper describes the development of a methodology for the completely non-invasive determination of gold leaf thickness in artworks that present lead-white as mordant. The common approach for such determinations is the collection of samples to be inspected using SEM. However, this leads to two main drawbacks: the need for sampling, not always allowed, and the lack of representability of one collected sample. X ray Fluorescence analysis allows for complete non-invasive inspection of the full artwork and our methodology enables the determination of the gold leaf thickness with an accuracy that complies with the demands of Cultural Heritage studies.

The established approach is grounded on the modelling of the portable XRF setup using Monte Carlo simulation and the detection of different characteristic lines of Pb in the X ray fluorescence spectra, attenuated trough the gold leaf, hence, determining the thickness of gilding by comparing their attenuation. The method was calibrated and certified using mock samples of simple stratigraphy, reference materials of pure Au leaves (1, 2 and 2.5 µm thickness) covering a Pb infinitely thick sheet. A calibration curve was then obtained, that could be applied to any artwork presenting lead (belonging to the lead-based mordant) in the underlayer, to be analyzed with our spectrometer.

As case study for this application, the modelled X ray setup was then taken to the Museum of Christian Art in Old Goa (India) and used to study the gilding thickness of three panel paintings: two paintings, from the 18$^{th}$ century, concerning to the same series but different themes: Our Lady of Sorrows (MoCA1) and Our Lady of Seven Sorrows (MoCA2), and a third painting entitled Monstrance (MoCA3), from the 17$^{th}$ century. The obtained results emphasized the use of different techniques concerning gold leaf beating techniques.

I hope the methods here presented and the results obtained are compliant with the standards of SAB and the paper is accepted for reviewing process.

On behalf of the remaining authors,

Best regards,

Sofia Pessanha

## Dear professor De Giacomo,

**Here is the detailed response to the review of our paper. Alterations in the manuscript were made in orange shade for clarity.**

**Authors would like to recognize the effort of the reviewers and editorial board to the improvement of our paper, hoping it is in an acceptable form for publication in SAB.**

**On behalf of the remaining authors,**

**Best regards,**

**Sofia Pessanha**

## Reviewer 1

**- This manuscript reports a method of determination of gold leaf thickness using X-ray fluorescence and Monte Carlo simulations. Calibration measurements are performed on Au/Pb samples to assess the reliability of Monte Carlo simulations, which are then used to determine the Au thickness of paintings with white lead substrates. The method is applied to three paintings from the XVII and XVIII centuries. The manuscript is generally clear and it appears to be a useful contribution. I would recommend it for acceptance after the points listed below are addressed.**

R: the authors recognize the effort of the reviewer to improve our paper and present the reply to your queries:

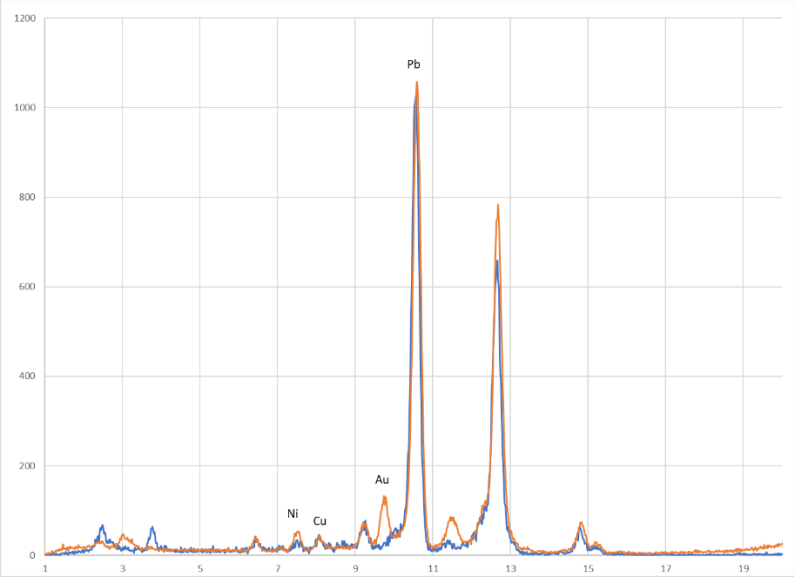
**-The simulated detectors include the effect of the beryllium window and the silicon active layer but at the same time the measured spectra are corrected for detector efficiency, using data given by the manufacturer. Therefore, the drop in the detector efficiency appears to be corrected twice. Please clarify.**

R: The detector efficiency is contemplated in the response function of the detector corresponding to a drop of efficiency in the higher and lower energies, as the reviewer mentions. The other time the efficiency is used is in the determination of the spectrum out coming from the x ray tube to be used as input spectrum in our simulation: because the direct spectrum had to be measured with an x ray detector (the same) we had to deconvolute the obtained spectrum from the detector efficiency in order to obtain what would be the output from the x ray tube. This time, the deconvoluted spectrum will have an enhancement of intensity in the lower and higher energies. As can be seen in Fig. 2a, the input spectrum has higher intensity than the direct spectrum so. This way, we are not considering a drop twice. The explanation was improved, hopefully with more clarity:

*“The efficiency curve of the detector was then deconvoluted from the measured spectrum to obtain the input spectrum for the simulation file. As can be seen in Fig.2a, the spectrum used as input has increased intensity in the lower and higher energies when comparing to the direct measured spectrum.”*

**-If the Ni and Cu peaks that appear in the spectrum of Fig 3 are originated from the collimator system, why such peaks do not show up in the direct filtered output spectrum? Could these peaks result from the purity of the gold leaf itself?**

R: There are two main contributions for the presence of Ni and Cu in the experimental spectrum: Ni does appear in the direct filtered spectrum of Fig. 2a, but Ni and Cu are more intense in the experimental spectra due to the excitation of the materials of the collimator with radiation scattered in the sample and then collected in the detector because of the geometry (detector placed in a 90º geometry) and because of the smaller distance between them. Moreover, these two peaks appear in all the spectra collected with this setup. The following figure presents the spectrum of a white area in in panel painting MOCA1 and the comparison with a gilded area. The Cu and Ni peaks are similar in intensity:




The sentence: “*Two bands corresponding to Ni and Cu, present in the experimental spectrum are missing in the simulated one as they come from the collimator that was not modeled in the simulation*.” Was rewritten:

“*Two peaks corresponding to Ni and Cu, present in the experimental spectrum are due to the excitation of the materials of the collimator with scattered radiation in the sample*.”

There is always the possibility of Cu being present as an impurity in the real gold samples, however with this setup, this was not considered. We also added some remarks regarding this issue in the conclusion section:

“A limitation of this methodology is only contemplating high-grade gold leaf gilding. Further simulations would be necessary to consider the use of gold leaf with significant contribution of Cu and/or Ag that would change the mass attenuation coefficients and density of the gilding layer, or to consider other forms of gilding, such as fire gilding or depletion gilding, were the gilding layer could present voids, hence, altering its density[15]. This methodology was applied to a case study that present these characteristics, absence of Ag peak and no further presence of Cu than the usually found with this spectrometer.”

**Minor remarks:**

**-Line 114: delete "eq."**
R: “eq” was deleted;

**-Line 150: none of the listed Monte Carlo codes is commercial. Please correct**
R: Indeed, all of the packages are freely available, commercial was deleted.

**-Line 150: replace "XMI-SIM" with "XMI-MSIM"**
R: the typo was corrected.

**-Line 270: how was the detector efficiency "deconvoluted"?**

**-Line 282: replace "characteristic elements" with "characteristic lines"**
R: phrase was rewritten;

**-Line 288: delete "eq."**
R: “eq” was deleted;

**-Line 289: replace "Si=3.7 w=eV" with "Si, which is 3.7 eV"**
R: phrase was rewritten;

**-Line 306. replace "bands" with "peaks"**
R: bands was replaced with peaks

**-References: the authors use version 2014 of the PENELOPE program but they cite a reference from 1995. I suggest citing a more update reference.**
R: reference 24 was replaced by:
F. Salvat, PENELOPE-2014 A Code System for Monte Carlo Simulation of Electron and Photon Transport, Nuclear Energy Agency, NEA/NSC/DOC(2015)3

-**Reviewer 2**

**- This paper concerns thickness determination by Monte Carlo simulation and XRF measurements. This approach is not completely new because several papers concerning both thickness estimation by XRF and by Monte Carlo have been published as well as papers about other methods using the XRF alone. The authors' approach to the simulation was optimal in the sense that the experimental setup has been completely characterized making so, from this point of view, reliable the Monte Carlo simulation of the experiment. I also appreciated the use of statistical analysis. Nevertheless, I have a main concern about the authors' use of some certified modern foils samples as reference. Samples of this kind are homogeneous while the same does not hold for ancient ones, where dishomogeneities can be found due to the blacksmith or the corrosion action, when applicable. Regardless of the use of reference samples, the fact that dishomogeneities could compromise thickness estimation is claimed in a recent paper by F.J Ager et al. (Spectrochimica Acta B 135, 42-47 2016) and I agree with the latter authors. I would like to know how the present authors address this problem.**

R: authors acknowledge the reviewer for the positive feedback. It is true that thickness estimation using XRF and Monte Carlo has been a subject of interest and continuous improvement of the used methodologies. What distinguishes our paper is the modelling of the XRF setup using an X ray tube and not a radioactive source, as it was more common and, also, simpler.

It also true that the gold leaf applications in real artworks are seldom homogeneous. This is why a non-destructive approach using XRF is more consistent than relying on the measurements of one (or if possible two) collected samples. To overcome this inhomogeneity hindrance, several measurements (and thickness determinations) were undertaken, in order to gauge the average thickness of the used gold leaf. This was also why the results were presented also as ranges of values and a t student test was performed to assess if the obtained values were significantly different between paintings.

This discussion should be, of course included in the manuscript, so, the following paragraph was added to the 4.2. section:

“The determined thicknesses were presented as a range of values, as well as the average value of 12 measurements. As can be seen, there is a distribution of values, that can be explained with irregularities during the gold leaf application. To better gauge the significance of the results obtained, a t student test was performed.”

Regarding the density question discussed in the paper by Ager at al., it is true that our determinations are highly reliant on the estimated density for the layer and, if there are

porosities the final density of the layer would be overestimated, hence, the thickness underestimated. However, and as the paper discusses, these porosities would be highly probable when using fire gilding and depletion gilding. Our artworks were gilded using gold leaves so, the presence of voids would be less likely. This way, we believe that using the attenuation coefficient determined by MC simulation of pure gold leaves is a good enough approximation.

We added some remark regarding this issue in the conclusion section:

“A limitation of this methodology is only contemplating high-grade gold leaf gilding. Further simulations would be necessary to consider the use of gold leaf with significant contribution of Cu and/or Ag that would change the mass attenuation coefficients and density of the gilding layer, or to consider other forms of gilding, such as fire gilding or depletion gilding, were the gilding layer could present voids, hence, altering its density[15].”

And in the introduction section:

“…and Proton Induced X-ray Emission[13,14] are often used to determine the thickness of coatings in art and Cultural Heritage”

Was replaced by:

“…and Ion Beam Analysis techniques[13-15] are often used to determine the thickness of coatings in art and Cultural Heritage”

Completely non-invasive determination of gold leaf thickness in artworks;

Application to artworks using lead-white as mordant;

Monte Carlo simulation of portable XRF spectrometer;

Distinction between apoch of manufacture through gold leaf thickness;