Nuclear Instruments and Methods in Physics Research B 348 (2015) 291–295

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

# Paintings on copper by the Flemish artist Frans Francken II: PIXE characterization by external microbeam

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ARTICLE INFO

*Article history:*
Received 25 July 2014
Received in revised form 23 December 2014
Accepted 23 December 2014
Available online 2 February 2015

*Keywords:*
Oil paintings on copper
External microbeam
Nuclear microprobe
IBA techniques
Pigments composition

ABSTRACT

Resorting to an external proton microbeam, PIXE analyses of three oil paintings on copper support dated from the XVII century and attributed to the Flemish artist Frans Francken II, were undertaken. The present work aims to contribute to the compositional study of the painting materials employed by XVII century artists that exploited copper as a support for oil painting, and specifically the materials used by Francken's workshop, particularly copper plates. Because of the low thickness of the pictorial layers of this type of paintings and its non-destructive character, PIXE is the ideal technique to study the elemental composition of the paintings. Several spots in each painting were chosen for analysis in order to cover almost all the pigments used in the colour palette. Lead and calcium were detected in practically every analysed regions, probably related to the presence of lead white and chalk, usually used as ground layer on copper paintings. Small quantities of gold were also detected, which is present in many of this artist's works to embellish some details of the representations. Also this work reports the first application of the external proton microbeam set-up available at CTN/IST in Portugal for the characterization of oil paintings.



## 1. Introduction

The use of copper as support for oil paintings had its major expression in the XVI and XVII centuries (1575–1650), at first in Italy and then in the Netherlands. Despite the first experiences by Sebastiano del Piombo, Correggio and Parmigianino in the 1520s [1], only when Vasari, Agnolo Bronzino and Alessandro Allori in the 1560s executed oil paintings on copper plates for the court of Florence, does the interest in this type of support seem to have grown. Soon it was adopted by the Flemish painters working in Italy that exploited this technique when returning to Northern Europe [2]. This expansion was probably due to the interest that artists revealed for painting on unconventional supports and also to the accessibility of copper plates for etching, engraving and enamelling [1]. Furthermore, copper prices were similar to those of wooden panels, so it was an economic solution and available on the market [3].

These plates offer a flat, smooth, rigid and non-absorbent surface, where it is possible to perform more detailed images than in a traditional canvas or wooden support, providing also a particular finishing and colour brightness. Moreover, copper plates offer good conservation conditions for the paintings, since they are not very responsive to humidity or heat variations. Furthermore, the paint layer isolates the copper from air, avoiding also the corresponding corrosion process.

According to some authors, these supports are quite difficult to paint, presenting serious problems related to the adhesion of the pigments [4]. On the other hand, the preparation of copper plates for painting is simpler than that of other supports. The first step consists in scraping the copper plates prior to painting, then applying garlic juice over the surface (to reduce superficial tension and improve adhesion) and finally a thin preparatory layer, typically of white lead in oil (to which colourful pigments like umber can be added), to even the surface and promote paint adhesion [4].

Several painters, mainly in earlier stages of the career, executed a few paintings on copper, but remarkably Frans Francken II (Antwerp, 1581–1642), like Jan Brueghel I, painted more than a third of his works on copper supports [2]. His paintings are characterized for representing large groups of people with mythological, biblical and historical subjects. He also introduced new themes, revolving around the representation of exotic objects and animals,

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http://dx.doi.org/10.1016/j.nimb.2014.12.072
0168-583X/

natural and artistic treasures, which became popular in Flemish painting of the time. Francken specialized in small-scale paintings, intended for «*cabinet de curiosités*» or private collections belonging to the nobility and the ascending middle class, which are the ancestors to the contemporary museums.

Despite the relatively high quantity of paintings on copper supports around the world, few information is available about them in terms of conservation and restoration procedures and also of scientific records, although some results are recently available [5,6]. This type of paintings is characterized, among others, by very thin pictorial layers and because of that, PIXE, which is a superficial and non-destructive characterization technique under the adequate experimental conditions [7–13], was used to study the elemental composition of these paintings. The present work aims to contribute to the study of the painting materials used by the painters who used copper as metal supports and specifically the materials used by Frans Francken II workshop.

The measurements were performed using the external proton microbeam set-up installed at the CTN/IST [14], which for the first time was used to study the composition of pictorial layers on easel paintings.

## 2. Materials and experimental methods

### 2.1. Objects

Along this work, three oil paintings executed on copper supports were studied. The paintings are attributed to Frans Francken IÍs workshop, based on its stylistic and technical features, and they should have been executed during the first half of the XVII century (c. 1605–1645). All the paintings exhibit religious scenes from the New Testament: *The wedding at Cana*, *The resurrection of Lazarus* and *The conversion of Gentiles*. These medium-scale (38.5 × 55.5 cm$^2$) devotional paintings were executed in very thin copper supports (1 mm thick). They are rectangular-shaped, almost regularly cut, with non-rounded corners and surface free of deformations by hammer-marks. On the reverse of the plates, no punch-mark of any kind was found, which occurred frequently despite of guild regulations [3] on those times. Instead, on the reverse of *The resurrection of Lazarus* and *The conversion of Gentiles*, there are handwritten inscriptions made with a black-bluish ink, with the numbers 12 and 14, respectively. This could be an inventory number or a placement reference for displaying (in an altarpiece, a cabinet or a collection), which indicates that there may be other paintings belonging to this set.

All paintings exhibit a fairly good state of conservation however they reveal several mechanical damages caused by inadequate framing options and poor handling. The paintings showed scratches (caused by nails used in the frames), deformations and cleavage caused by flexing and harmful handling. The pictorial layers revealed an excellent adhesion to the copper plate, but also some fillings and retouched areas were found.

Consequently, they were submitted to a conservation and restoration intervention that took place in CCR installations. The varnish layer applied in a past intervention, which is not reported, was removed for conservation procedures with a solution of isooctane and isopropyl alcohol, in 1:1 proportion. During the cleaning procedures of the paintings, some of the fillings from previous restorations were removed. On the backside of these layers, which were in contact with the copper substrate, a thin green layer was found. This green layer has been reported by other authors [6,15] and it was related with the presence of copper organometallics compounds as a result of the corrosion process in the copper plate.

It should be highlighted that along this study no sampling was allowed. The conservation treatment presented, therefore, as a great opportunity to gather technical information on the paintings. PIXE measurements were performed without this protective layer, before the new varnish layer was applied.

### 2.2. Experimental

Digital photographs using a Nikon 5700 camera under ultraviolet (UV) light were acquired to detect retouches and to verify that the varnish was completely removed. The UV source is composed by 4 lamps of long wave UV light at 350 nm oriented at 45° with the paintings. Digital photographs under infrared (IR) light were used to record specific details and to detect the presence of underdrawings or strokes not visible under normal white light.

PIXE experiments were done using the external microbeam set-up installed at the nuclear microprobe at the CTN/IST [16], in Portugal. In this set-up, the 2 MeV proton beam produced by a 2.5 MV single ended Van de Graaff accelerator is extracted from the vacuum chamber through a 100 nm thick $Si_3N_4$ exit window, encountering the sample after 3 mm of air with a final energy of 1940 keV. The beam incidence is normal to the sample surface and the X-ray detector (Si Bruker SDD) with an active area of 30 mm$^2$ is placed at 2.8 cm from the sample at an angle of 45° to the beam direction. The proton beam (with dimensions of 70 × 70 μm$^2$) can raster the surface under study with maximum dimension of 800 × 800 μm$^2$. More technical details can be found in [17]. The OMDAQ V5.2 software package is used for data acquisition and treatment [18]. This software also allows us to control the beam by the scanning control.

The X-ray spectra were acquired with a 50 μm thick Mylar foil in front of the SDD detector and GUPIXWIN [19] software was used for data analysis. During the experiments, beam current was maintained between 300 and 500 pA.

Under these experimental conditions, the beam produced no visible marks on the surface of any of the different colours analysed [9,11,13], even on carbonate based natural pigments as noticed in other research works [20].

Several spots on the principal colours of the paintings were analysed. Retouched regions (previously determined by UV light) were also characterized.

## 3. Results and discussion

### 3.1. Copper plates

As a first step, the metallic support of the three paintings was analysed. In some areas of the paintings, due to the presence of small gaps, it was possible to observe the copper plate to the naked eye (Fig. 1a). Nevertheless for the composition analysis, the backside of the paintings was analysed. According to the PIXE composition results, very pure copper plates were used, being Pb (0.15–0.20 wt.%), Au (0.03–0.06 wt.%), Hg (0.03 wt.%) and As

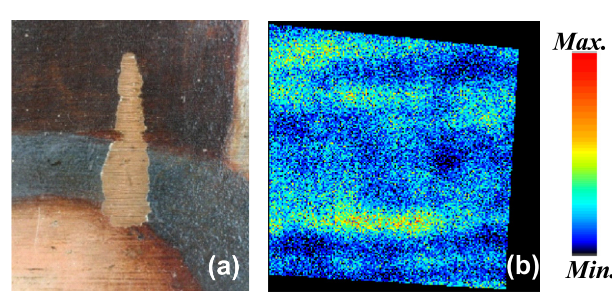


**Fig. 1.** (a) Detail of a gap on *The resurrection of Lazarus* (8×). The substrate copper plate is visible showing horizontal lines as a consequence of surface treatment. (b) 2D PIXE Cu-map (800 × 800 μm$^2$), also showing the surface lines distribution.

(0.02–0.04 wt.%) the trace impurities detected. The high quality of these plates reflects the high level of technical development in their production, where the use of very pure copper was demanded in order to be possible to produce thin hammered objects [21]. The purity of these plates contrasts with the composition of coeval copper coins or objects which do not present that degree of purity [22].

The chemical analyses of the black-bluish inked areas on the back of *The resurrection of Lazarus* and *The conversion of Gentiles* show high quantities of S and Fe, being compatible with the use of iron gall ink to mark the paintings. A welded area in *The resurrection of Lazarus* was also analysed, revealing the use of a tin brass alloy, with a composition of Cu (68.0 wt.%), Zn (18.8 wt.%), Sn (10.1 wt.%), Pb (2.9 wt.%) and As (0.2 wt.%).

### 3.2. Paint layer

As it was previously reported, the paint layer of this type of paintings is characterized by its extreme thinness. In fact, in some cases it was possible to detect the Cu signal coming from the substrate using the proton beam (~2 MeV energy) and furthermore, it was possible to reproduce the substrate topography when 2D maps were acquired considering the Cu-Ka signal. In Fig. 1b is shown one of these 2D maps recorded during the experiments, where parallel lines in the substrate are observed as a consequence of the surface preparation previously explained.

In general, copper, calcium and lead were detected in almost all the analysed areas. The copper could be associated with the substrate or with some specific colours, as it will be described later on. The presence of calcium and lead is related to the presence of lead white (as a pigment) and chalk (as extender) used as preparatory layers [5]. From the 2D PIXE maps, it was observed that lead distribution is quite homogeneous while calcium appears in most of the cases as small agglomerates (average of 80–100 μm in size). In the following lines, results obtained for specific colours will be presented and correlated with the pigments used during the period of the paintings.

#### 3.2.1. Red

Different hues of red are found in the three paintings (Fig. 2a), which in terms of composition results in small differences in elemental concentration. Fig. 2b shows the X-ray spectra recorded for two different hues of red belonging to the mantle of St. John, the Baptist (which are representative of other red analysed points). In all of them, Hg and S are found in major concentration, suggesting the use of vermilion (HgS), being the light red areas those with the highest concentration of Hg and S. The presence of this compound is further suggested when analysing selected point spectra and their deconvolution using GUPIXWIN, since PIXE, being an elementary composition technique (like other similar techniques as X-ray fluorescence or energy-dispersive X-ray spectroscopy), cannot give information about the presence of compounds.

Fig. 3 shows the 2D PIXE maps for Hg, Cu, Pb and Ca elements recorded in the light red colour. It can be observed that Cu and Ca maps have an opposite distribution to those exhibit by Hg. As a general tendency, Hg follows a small aggregates distribution (100–200 μm) which can be related to the production method of vermilion. Known from ancient times (~800 AD), the black sulphide of mercury flakes obtained after evaporation and condensation should be grinded for the red colour begins to appear, and the longer it is ground, the finer the colour becomes. When considering the darkest regions on red, the presence of Hg is drastically reduced (see PIXE spectrum on Fig. 2b), while Pb and Ca signals increase. In this case, interpretation of data is more complicated, since the presence of Pb and Ca has been previously associated to the presence of lead white and chalk in the preparatory layers. Nevertheless, the high intensity of the Pb-L lines can be related

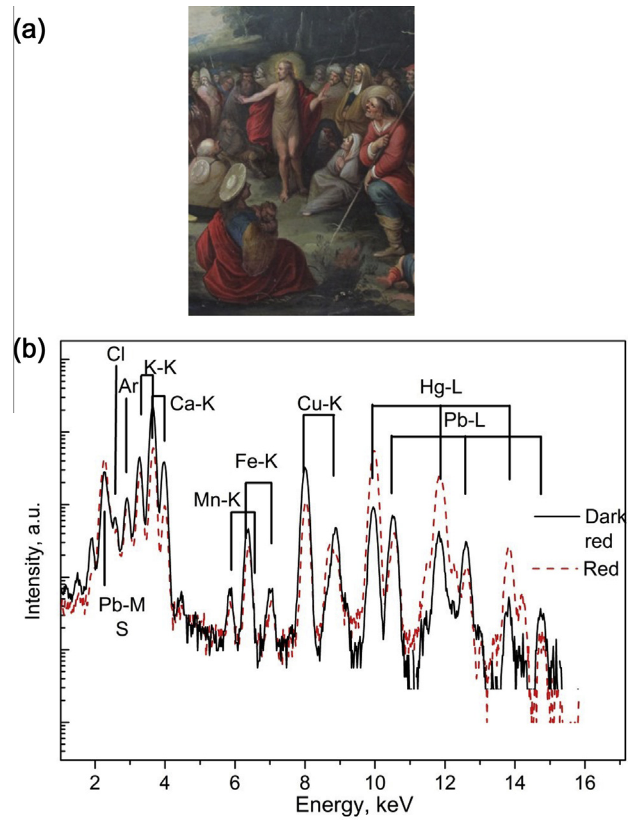


**Fig. 2.** (a) Detail of *The conversion of Gentiles* showing different hues of red in two of the characters. (b) representative PIXE spectra for light (red) and dark red (black). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

to the presence of minium or red lead ($Pb_3O_4$), which was frequently added to vermilion, due to its lower price [23]. Other pigments as iron oxide red or sienna can be neglected since the quantities of iron are not very different between the reds. However, organic sources as cochineal dye or madder lake cannot be excluded. Whatever the origin of these dark red colours, the difference between these two hues is clear when infrared photography is used (Fig. 4). Under infrared light, the light and intense red regions are seen whitish, while the dark red areas are transparent to the radiation.

#### 3.2.2. Blue

The blue colour can be found in diverse regions on the paintings such as garments or sky. On those regions, different X-ray spectra and thus different composition were registered. Fig. 5 shows two of those X-ray spectra recorded, one in Lazarus's shroud in *The resurrection of Lazarus* and other in the tunic belonging to a man in *The conversion of Gentiles*. The shroud is dominated by the presence of Pb, Cu, Fe, Co, with contributions of Ca, K and Si (small contribution of the K-line can be distinguished in the spectrum). The presence of Co is the key element for this blue colour. Its presence is probably related with the cobalt smalt pigment KCo(Al)-silicate. Although the Al signal cannot be detected under the experimental conditions used, if we consider the presence of Si we can correlate this colour with the use of this pigment mixed with lead white. Considering the tunic, the main signal is related to the presence of Cu and Pb. The high concentration of Cu undoubtedly relates this colour with the azurite pigment ($2CuCO_3{\cdot}Cu(OH)_2$). The correlation of Cu with the pictorial layer in this region can also be ascertained by the Cu $K\alpha/K\beta$ ratio (7.0–7.1). In fact, as determined by the GUPIXWIN

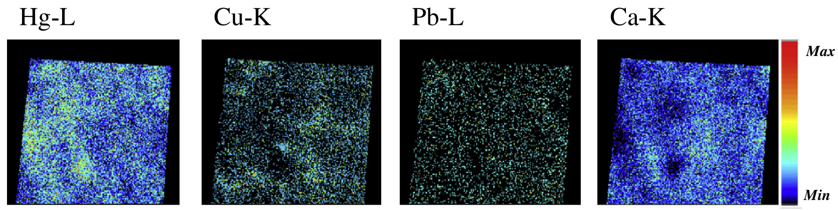


**Fig. 3.** 2D PIXE maps for Hg, Cu, Pb and Ca recorded in a light red area. (800 × 800 $\mu m^2$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Fig. 4.** Detail of *The conversion of Gentiles* photography and its corresponding photo under IR light.

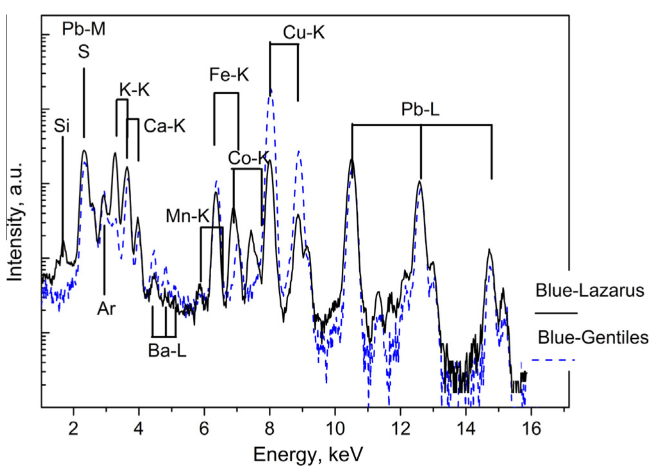


**Fig. 5.** X-ray spectra recorded on blue colours from several points of the paintings under study: one in Lazarus's shroud (solid black) in *The resurrection of Lazarus* and in the tunic belonging to a man in *The conversion of Gentiles (dash blue).* (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

software code, the value of the Cu Kα/Kβ yield ratio for a thin target is 7.3 upon considering the transmission through the 50 μm Mylar filter and the 2.8 cm of air in front of the detector. Furthermore, most of the analysed spots where the Cu X-rays are mainly produced in the Cu plate, result in a measured Cu Kα/Kβ yield ratio with values between 6.0 and 6.3, due to the different X-ray absorption through the lead white preparation layer and the corresponding pictorial layer.

### 3.2.3. Gold

It was also possible to detect small quantities of gold in two of the three paintings: in *The conversion of Gentiles*, the gold is restricted to St. John's halo, while in *The wedding at Cana*, gold was also detected in the wall drapery pleats. The use of "shell gold" or powder gold was very characteristic of this painter, being present in many of this artist's works. However in *The resurrection of Lazarus*, the most distinctive painting of this group because of the different scale of the composition, it was not possible to identify the presence of gold, which could indicate a more mature stage of Francken's career.

### 3.2.4. Fillings

Regarding the fillings which can be found in all the three paintings, they are characterized by the presence of Ti and Zn in different amounts, depending on the area. These elements reveal the use of modern white pigments as titanium white and zinc white which appeared in the middle of the XIX century and they were widely used at the beginning of the XX century. These white pigments were mixed with other pigments to obtain the desired colour, according to the restored area.

## 4. Conclusions

This work has allowed not only to report the first application of the external proton microbeam set-up available at CTN/IST in Portugal for the characterization of oil paintings, but also to contribute to the literature regarding this type of paintings on metal supports. These results will add valuable data to the scarce literature that can be found based on the scientific research of this type of paintings. The use of PIXE and the nuclear microprobe were an advantage to the study of these paintings, which have very thin pictorial layers.

This first study of the paintings attributed to Frans Francken II has been useful to produce a first identification of the pigments used, and to increase our knowledge of the construction methods and pigments mixtures used by this master. The suggested pigments are usually found in coeval paintings, although several retouched areas were found, which show the presence of modern pigments containing Ti and Zn.

The complex determination of the elemental colour composition and its relation with the pigments showed the importance of using more than one analytical technique. Other techniques, not available for the present study, such as Raman spectroscopy or SEM could also be successfully used in the future for further analysis [24,25], if sampling is allowed.

## Acknowledgements

V. Corregidor acknowledges FCT for the Ciência program. The work was partially supported by FCT-Portugal (PEST-OE/FIS/UI0275/2011).

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