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Diagnostic analyses for the study of materials, technique and state of preservation of a gilt and painted leather of the XVIII Century

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Abstract

In this study we report on the restoration work for the gilded and painted leather from the Sanctuary of the Santissimo Crocifisso di Papardura in Enna, Italy. The work started with a historical and stylistic examination of the artwork which dates back to 18th Century. The study of the leather and its decoration was deepened thanks to specific scientific analysis (such as XRF spectroscopy, Raman and SEM) in order to assure the integrity of the material during the restoration work. To this end, a diagnostic procedure was set up to provide a clear picture of constitutive materials (type of leather, silver leaf and pigments), technique, and state of preservation.

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Introduction

The Sanctuary of the Santissimo Crocifisso di Papardura of Enna is a small sanctuary, which was carved out of Monte di Papardura hill rock (Enna). In 1659 the sacred picture of the crucified Christ was discovered [1]. This important discovery led to the construction of the sanctuary building, where the iconography is entirely dedicated to the Christ sacrifice, a recurrent theme in XVII Century Sicilian sacred iconography.

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The frontal altar of the Sanctuary, with the Crucifixion theme (Fig. 1) summarizes the manufacturing features, which in Venice were called "cuoridoro" (literally translated from Italian as ‘Golden Hearts’). Leather has been used in decorative arts since the Middle ages, when it was mainly used in furniture and in the making of armours. This gilded leather technique ‘a Ghadâmes’ was invented in the VI Century in North Africa and then it spread across Spain and then to France, Germany, Flanders and in Italy, where, in the XV Century, Venice had undisputed prestige. In fact, the 'cuoridoro' organization (grouping the craftsmen and of their products) is documented as a craft-guild in 1656 [2]. Their handcraft consisted in a laborious manufacturing: silver leaf was applied onto a leather surface, and then the surface was gilded with gilt varnish in a way that would emulate true gold. On this gilded background the decorative motif was stamped using woodblocks. Then oil paint was applied onto this design. The decorative pattern would then be finished with different punch marks (lines and dots, circles, squares, etc.).

Historical research shows that the production of decorated leather was widespread in Sicily [3]. In fact, the frontal altar herein examined is part of a series of the five Antependia depicting "The Five Sorrowful Mysteries of Jesus Passion".

![Fig. 1. Frontal altar in gilded and painted leather, 18th century, Sanctuary of the Santissimo Crocifisso di Papardura, Enna. After the restoration work.](image)

Such artifacts in leather have been only recently credited as ‘artworks’; previously, there was little interest in such crafts, and this explains why it has been very difficult to find information about when Enna’s Sanctuary’s frontals had been made. Research in the archive has led to the hypothesis that the Sanctuary frontals were created between 1659 (date in which the sanctuary had been finished) and 1736 [3].

The diagnostic work was aimed at answering questions about technique and constitutive materials. With this purpose the surface was first investigated with a digital microscope, and then with the X-Ray Fluorescence (XRF) spectroscopy in order to identify the pigments’ composition. Raman spectroscopy and Scanning Electron Microscopy (SEM) were also carried out in order to identify the materials’ composition, and cross-section was applied to find a correspondence between the bibliographical data and this sort of manufacture. Diagnostic data also helped to determine the state of preservation of the work of art. To see if there was any hydrolytic degradation, the pH level of the leather extract was measured. Another important analysis the team has assessed is the evident level of biological degradation, carried out by means of microbiological and entomological tests.
1.1 Diagnostic work to know materials and the executive technique

The gilded leather manufacturing process started the tanning: the transformation of leather into a material ready to work for creating artifacts. Subsequently, the leather was decorated with silver (or gold) leaf, gilt varnish and color or varnish, and also stamped. The search for certain features and the newly-acquired possibility to decorate leather, led to a specific selection of animal species for the production of the artifacts: generally, small animals (sheep, goats, and calves) were used as a source for the leather artwork [4].

Every animal species is characterized by a particular kind of tissue, depending on thickness and size of fibres, which makes it possible to recognize the particular species by carrying out a microscopic analysis of the leather surface. In this study, this operation was challenging because of the decoration, but the species was recognized thanks to a small exposed fragment, where the silver leaf had left the leather surface visible.

The investigation was carried out taking instant photos with a digital microscope. These were compared to available bibliographic data, and therefore it was possible to verify the nature of the leather used in the manufacture of this work of art.

In order to identify the decorative materials the screening started with the analysis of the painted surface with a digital microscope. The macro-photographs provided important information, which were especially useful to identify the points where future investigations could be performed more precisely. These macro-photographs have shown some areas of particular diagnostic interest, representing different states of preservation or chromatic alteration situations. (Fig. 2 a-e).

XRF analysis was subsequently conducted on all coloured areas. Thanks to its non-destructive nature, the XRF is the instrument of choice in the analytical field of pigment identification. The XRF spectrometry was carried out by Dr. Cosimo Di Stefano, a chemist from Palermo's Regional Centre for Design and Restoration. The
analysis was performed with an XRF portable spectrometer, LITHOS 300 by Assing. It was equipped with a low-energy source, which could detect chemical elements with a higher-than-potassium atomic number.

The results obtained with the XRF analysis were later correlated with the Raman Spectroscopy data. The latter was used to further compile more comprehensive information, especially in the case of some pigment’s chemical composition, which the XRF analysis could not identify perfectly – for example when it came to the lighter elements. In addition, the leather substrate and the presence of the silver leaf can alter the measurements, which is why XRF analysis by itself would’ve been insufficient, if not complemented with another type of analysis for the pigments that XRF could not identify. Raman spectroscopy was then chosen as an auxiliary technique, for which it was necessary to take some representative micro-samples.

Diagnostic data (SEM, Raman and XRF) where then analyzed to identify any overpaint presence, and in some cases Energy Dispersive X-ray spectroscopy (EDS) analysis was carried out to confirm further the material that was under investigation. To this end, the cross-sections consisted of two representative samples of the relevant areas. The position of the samples was carefully chosen during the preliminary screening, which helped to understand the initial situation and to limit destructive analysis to a few points.

Both the Raman and SEM analyses were carried out by Mr. Bartolo Megna, a materials engineer from the Laboratory of Materials for Restoration and Conservation, Dept. of Materials Engineering, University of Palermo. The instrument used in the Raman spectroscopy is an InVia Raman microscope, equipped with a laser source He-Ne a 633nm with Notch filter and a grating with 1800 lines/cm, produced by Renishaw. The other instrument was the ESEM XL30 with a low vacuum FEG electrons generator, produced by Philips.

1.2 Results

The study for the identification of materials allowed for the identification of the animal species whose skin was used as a base for the decoration. The cross-section has also given information about the executive technique.

Every animal species is characterized by a particular kind of tissue. These differences are well-visible when observing the hair-follicles distribution and their particular pattern on the leather surface. The macro-photography (taken with a digital microscope) of leather used on the frontal altar was compared to the sample images of the most common animal species used in artistic leather manufacturing. This helped to assess that the leather used for creating this artwork was sheepskin. As shown in the picture, the sheepskin has a fiber tissue with grouped follicles. The secondary follicles are in larger numbers compared to the primary ones (Fig. 3a). To make a macro photo for the research, a small part of leather, where the decorations have been lost, was photographed. It shows the same irregular distribution of follicles (Fig. 3b).

For the interpretation of XRF spectra it was crucial to study that of the leather: this is not a single substance but rather a group of related materials with many characteristics in common. For this reason the leather’s elements could influence the signals of the other decoration materials.

Spot 1. The leather spectrum has detected Iron, Potassium and the high Calcium presence (fig.4). This might be due the leather working process as the unhairing phase. In the tanning industry the unhairing stage concerns the removal of animal hair from the skin by chemical degradation of the hair shaft. Traditionally, alkalis such as lime (calcium hydroxide) or soda ash (sodium carbonate) were used. The lime causes an immunisation of the keratin to the action of chemicals and remains between the leather fibres.
Spot 2. A second spectrum was taken on the silver leaf in order to understand if the silver was pure or not. Moreover, as mentioned before, oil paint was traditionally applied onto the silver surface. In the same way studying the silver spectrum was important to understand the other materials’ signal. The spectrum detected the presence of only Silver, besides the same elements found in the first measure (fig.5).

Other spots: the analysis was carried out on the others coloured areas, previously observed with a microscopic examination, in order to identify every pigment used in the painting. Every spots and the elements found are visible in the summarising graphic of the sampling spots (fig.6) and are listed in the table (Tab.1).
| N.spot | Description      | XRF (elements detected) | Raman               | SEM/EDS (elements detected) |
|--------|------------------|-------------------------|---------------------|----------------------------|
| 1      | Leather          | Ca, Fe                  |                     |                            |
| 3      | Silver           | Ca, Fe, Ag              |                     |                            |
| 2      | Varnished silver | Ca, Fe, Ag              |                     |                            |
| 18     | Punched silver   | Ca, Fe, Ag              |                     |                            |
| 4      | Brown            | Ca, Fe, Ag, Cu          |                     |                            |
| 13     | Turquoise        | Ca, Fe, Pb              |                     | C, O, Al, Pb, Ca, Fe       |
| 31     | Turquoise        | Ca, Fe, Pb              |                     | Prussian blue              |
| 23     | Blue (Mary)      | Ca, Fe, Pb (> %)        | Prussian blue       |                            |
| 24     | Dark blue (Mary) | Ca, Fe, Pb (< %)        |                     |                            |
| 25     | Green (S. John)  | Ca, Fe, Pb              |                     |                            |
| 28     | Dark green (S. John) | Ca, Fe, Pb       |                     |                            |
| 20     | Green (landscape)| Ca, Fe, Pb              |                     |                            |
| 8      | Dark red         | Ca, Fe, Ag, Hg          | Vermillion           | C, N, O, Al, Si, Pb, Ag, Ca, Hg |
| 21     | Red (Mary)       | Ca, Fe, Ag, Hg          | Vermillion           |                            |
| 30     | Red (S. John)    | Ca, Fe, Pb, Hg          |                     |                            |
| 27     | Incarnate        | Ca, Fe, Pb, Hg          |                     |                            |
| 29     | White            | Ca, Fe, Pb              | White lead           |                            |
| 32     | Dark             | Ca, Fe, Pb              |                     |                            |
| 15     | Yellow (overpainting) | Ca, Fe, Pb, Cr, Zn |                     |                            |
| 11     | Indian red (overpainting) | Ca, Fe, Pb, Ba |                     |                            |
| 14     | Dark (overpainting) | Ca, Fe, Pb, Cr, Zn |                     |                            |
| 16     | Dark (overpainting) | Ca, Fe, Pb, Cr, Zn | Artificial ultramarine |                            |

Tab. I: Summarising table of the sampling spots.

XRF analysis allowed for the identification of the overpaintings artificial composition (Tab. I, in grey). Two overlapping layers of overpaintings were located in the entire leather' perimeter. Modern artificial pigments such as Zinc White, synthetic ultramarine and Lead-Tin Yellow were identified thanks the XRF.

XRF cannot identify organic pigments, therefore it wasn't detected any peak ascribable to the dark pigment. It might thus be a pigment with an organic composition, as Carbon black, Cork black, etc. While the Lead White was used as white pigment and also mixed to obtain other colour graduation as incarnates.

The brown pigment was oddly used in the floral decoration. The copper's peak and the floral brown coloration might be ascribable to a green pigment as the Copper Resinate. Its tendency to alter itself brown is known since the XVI Century.

The blue and red pigments were more difficult to identify, this is why more than one diagnostic technique was needed to study their composition. The contextual reading of XRF, Raman and SEM data allowed understanding the nature of red pigment. The fluorescence measurements of XRF did not allow to identify if the plumb and Mercury concentration were been attributable to the Red Lead ($\text{Pb}_3\text{O}_4$) or to the Cinnabar /Vermillion ($\text{HgS}$). Raman Spectroscopy identified it as Cinnabar/Vermillion (fig. 7) but with both analyses it was impossible to determine the natural or artificial composition. Since XRF is not able to detect impurities, EDS microanalysis from SEM images was used, indicating the artificial nature of the pigment. The red pigment was identified Vermillion. The artificial pigment used since the VII Century [5]. While the blue one was identified as Prussia Blue by the Raman spectroscopy. The presence of Pb might be ascribable to its use in the mixing with the White Lead. In Table I, in fact, the concentration of Pb is higher when the blue coloration is lighter.
The analyses of the cross section confirmed the bibliographical data and the information available from visual observation of the artwork. As demonstrated by the study of Fioravanti in the XVI Century [6], the decoration is constituted by (fig.8 a, b):
- Leather as a first layer and as a material used for the decoration;
- The silver leaf was applied evenly on the leather. The glue layer was not visible where the silver leaf was applied, but micro-photos, taken with SEM, showed fibres closer to the silver layer in certain spots;
- The silver leaf was used as support material for the decoration (painted surface).

1.3 Discussion

The small number of similar cases studied has made the data interpretation difficult. The executive technique, the nature of binder and of pigments has never been studied scientifically. This has been the motivation to use analytical methods in order to identify the range of materials and colours used by the artist. The analyses have given important information about the nature of the pigments and have uncovered a large variety of colours used by the artist. Thanks to this study it was possible to clarify some doubts about the artist's choices. For example the use of a brown colouration in the floral decoration is unusual. Comparing the floral area of this frontal altar (fig. 9b) with the others four frontals of the same series (fig.9a), where the floral decoration was still in green, it was clear that a chromatic alteration had been occurred. This hypothesis was confirmed by the diagnostic work.

Fig. 9. Frontals in gilded and painted leather, Sanctuary of the Santissimo Crocifisso di Papardura, Enna.
(a) The Crowning with Thorns, decoration' particular;
(b) The Crucifixion, decoration' particular.
2.1 Diagnostic work for the study of the preservation state

When the frontal altar in gilded and painted leather reached the Regional Centre for Design and Restoration of Palermo laboratories, it appeared to be in a considerably bad state of preservation. Its surface was totally hidden by deposits and showed evident deformations. The paint seemed to have changed its colours, and the varnish had oxidised and turned yellow. For this reason, preliminary analyses were necessary to evaluate the preservation condition of the leather before starting the conservation work.

Measurement of the pH level helped to determine if there any chemical degradation processes were present, such as acid degradation or demineralization of the material. Leathers have a very complex mixture of chemical structures. They vary according to the chemicals used in hide pretreatment, the chemicals that occur naturally in the tannin extracts that are used in the tanning process and the chemicals used for the various finishing operations. They also vary in the chemicals they come into contact with in use and the chemical absorb from their varying environments. Sulphuric acid in leather, originating from the adsorption of sulphur dioxide from industrial air pollution, is commonly considered as the primary agent of acid hydrolysis in historical leathers.

A chemical test was considered necessary to undertake before deciding on a conservation programme. A sample has been manually taken from an almost detached piece of leather and was measured the pH of its aqueous extract. The sample with a weight of 0.25 grams has been put in a flask with deionized water (pH 7.0) and hermetically sealed. The flask with the sample has been shaken up and then left to rest. Twelve hours later, the pH level of the water extract of the sample was measured with a traditional pH meter.

Entomological analyses were necessary as a consequence of the biological degradation signs, such as small white and powdery spots, and insect tracks. Signs of the biological damage spread were well visible. A big quantity of not still dry rosune allowed thinking that the insects were still in activity.

Observation was the first moment in the sampling. In this phase were identified the different insect signs and the presence of rosune. Two different kinds of insect track were observed. The first one (fig. 10a) had an irregular trend, deep ruts and there were numerous wormholes nearby (1-2 mm diameter). The second kind of insect track was more superficial and widened than other one. In this case there weren't any wormholes nearby (fig. 10b).

Subsequently rosune samples were studied through the microscopy exam.

2.2 Results

Some studies have shown that the pH safety range for artistic leather is between 3.5 and 6.0 In this case, the pH of the extract was 5.9, which was considered adequate [7].

Observations showed that there was an entomological damage caused by larvae, and the examination with a digital microscope indicated that these belonged to two particular species of insects: wood boring beetles (fig. 11a) and clothes-moths (fig. 11a). For this reason, an anoxic disinfection before starting the restoration was performed. To this end an
anoxic chamber with an inert gas (nitrogen) was built. The leather was left in the chamber per a period of thirty
days with a data logger as a means of evaluating the environmental condition inside the chamber. After that
period, the frontal altar was submitted to an accurate dusting-phase with a macro-vacuum cleaner, and with the
use of a micro-vacuum for the interstices.

2.3 Discussion

The scientific analyses that have been carried out were very important in order to determine the preservation
state and to ensure appropriate measures concerning restoration work.

It is unusual to find biological damage in leather due to the conservation, offered by this type of vegetable
tanning. Nevertheless, the unfortunate coincidence between more factors has facilitated good conditions for the
insects’ proliferation. These conditions were firstly environmental as the high humidity. Moreover this damage
was due to the use of a wooden rigid frame onto where the leather was nailed around its entire perimeter.

Studies have suggested that the hydrolytic breakdown in vegetable-tanned leather is chiefly due to the actions
of sulphur dioxide and nitrogen dioxides present in acid air pollution. After the chemical test with the pH
evaluation, it was possible to determine the leather is in safe conditions for its conservation, this is partly due
with the high altitude of the Sanctuary and its distance from the urban centres.

3.2 Restoration work

After the preliminary analyses, which were conducted to identify the executive technique and the preservation
state of the frontal, it was possible to start the actual restoration work.

As with the scant bibliography, the complications of working with this sort of object lie in the necessity to
consider both the leather's features and its decoration in their context. The leather support has intrinsic qualities
that require superficial work in order to prevent fibre felting or tannin solubilisation. The decoration (that
includes silver leaf, pigments and varnish) demands specific solutions.

Like the surface, which was completely covered by deposits, the painted and gilded leather had more layers of
re-painting on the edge and a visibly degraded, thick coating of varnish. Taking cue from recent studies, the
"Water-Based Cleaning Systems" were used in the altar frontal cleaning process (fig. 12a, b) [8]. It was thus
possible to use the cleansing qualities of water while lessening intrinsic risks, by carefully adjusting the chemical
properties of the water used:
- Choosing and controlling the pH with the use of buffer solutions;
- Adding chelating agents, able to improve the solvent power;
- Making the solutions denser with gelling agents, useful to reduce the scant power of water to wet the surfaces
  (hydrophobe surfaces, like varnish, oil painting), but also useful to reduce the high power of water to wick in
  under the surface.

Fig. 12.
(a) After the cleaning phase;
(b) Result of the cleaning.

After the cleaning phase, a humidification of the frontal altar was necessary in order to re-give the correct
flatness to the leather and to relax the leather fibres. It was performed with the use of a GoreTex® membrane
(fig. 13a). Losses were integrated with the use of new leather, compatible in elasticity and thickness with the
original (fig. 13b). The restoration work was completed with the construction of an elastic tensioning frame where the tensioning was assigned to a sprung-stretcher system (fig. 13c, d).

Finally, a display cabinet was designed with controlled microclimate and lighting in order to guarantee the comeback of the painted leather to its original place of conservation, protected from adverse environmental conditions, which exist in the Sanctuary.

![Fig. 13.](image)

(a) Integration of losses; (b) humidification with the GoreTex® membrane; (c) construction of the elastic tensioning frame; (d) calibration of the frame to the correct degree of tensioning;

**Conclusion**

Low interest in art objects made of artistic leather causes a delay in this type of research. The current investigation standards lack appropriate codification for a common procedure for the restoration of artistic leather artifacts. This is why a thorough knowledge of the original artistic processes is always important as well as an assessment of the degradation processes. The only way to obtain such data is via a thorough study and observation of the artwork and a careful diagnostic work. The nature of leather, its working process, and the function, for which it is destined, influence the dynamics of the degradation and its state of preservation. This observation was carefully considered during this diagnostic work.

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