SPECTROMETRIC INVESTIGATION OF PIGMENTS AND SUBSTRATA IN WOOD PAINTINGS

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A polychrome and gilded wooden artifact was found, in a heavily deteriorated state, in the stores of the Mdina Cathedral Museum, Malta. The object represents two zoomorphic angels holding a coat of arms. Stylistically, the artifact matches with parts of a late 16th century Organ balcony, currently exhibited at the same Museum. The present study aims to establish whether or not the newly recovered artifact might have formed part of the balcony ensemble by means of material identification techniques. The combined use of XRF, FT-IR and FT-Raman spectroscopy ensure a detailed characterization of the material used. In the case of pigments, for both artifacts the blue pigment was smalt, while cinnabar was used for red and flesh tones. The metallic decorative parts of the panels are gilded, confirmed by the presence of Au peaks in the X-ray spectra. The supporting structure of both artifacts was manufactured from poplar wood.

Keywords: Polychrome wood; FTIR; XRF.

1. Introduction

Recent years have seen an increasing number of cases where a variety of analytic methods have been introduced for the characterization of pigments and manufacturing techniques of polychrome art works, such as paintings and sculptures. These studies use methods such as energy-dispersive X-ray fluorescence micro-Raman, and Fourier-transformed infrared spectroscopy to provide significant information to conservators, museum curators and art historians alike, leading to better insight for the preservation of cultural heritage.¹⁻³

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The first step in identifying the pigments used in the manufacturing of a polychrome artifact is typically XRF analysis. XRF is an elemental analysis technique, not a molecular one: each element has a characteristic XRF spectrum regardless of its molecular environment. The technique cannot be applied for elements of low atomic mass and is primarily utilized for the analysis of inorganic materials. The presence or absence of an element could suggest the use of a particular pigment. For example, the detection of mercury can be correlated with the use of vermilion, a red pigment produced artificially since the 8th century; whereas the presence of lead might suggest the use of lead white (a basic lead carbonate, $\text{Pb}(\text{OH})_2\text{CO}_2$) in the case of a white pigment, or the use of minium (lead tetraoxide, Pb_3O_4) in the case of a red one. The analysis may in some cases lead only to a reduction of possible pigments of the same color, since several pigments might contain the same element or elements. For example, for black, the presence of iron may suggest either ochre or another iron-containing pigment (e.g., Black Ochre: a mixture of a native impure oxide of carbon called black mineral, iron and alluvial clay, or Mars Black: Fe_3O_4 iron oxide pigment developed in the 20th century).⁴

This methodology presents, however, a number of risks owing to the possibility of identifying several pigments containing the same element or elements, or even identifying a pigment only because in the XRF spectrum the elements appear to be present together, while they may be present in separate layers. Due to these issues, this method is typically used in combination with fingerprinting techniques such as Raman. The Raman technique is highly effective in identifying unknown materials, both organic and inorganic. Molecular specificity is inherent in vibrational spectroscopy, since molecular group frequencies and crystal lattice modes lead to unique vibrational spectra for specific materials, and even for materials that are compositionally identical but differ in either connectivity, e.g., realgar vs. pararealgar (α - and γ - As_4S_4 , respectively), or in their crystal structure, e.g., massicot vs. litharge (orthorhombic and tetragonal PbO , respectively). Comparing the Raman spectrum of a sample to a library of spectra of possible materials usually yields an unambiguous match that leads to the identification of the otherwise unknown compound.⁵⁻⁷

In this work, a complementary use of the above mentioned techniques was applied during the restoration process of two 16th century polychrome wood artifacts to establish by material identification if they are part of the same ensemble.

2. The Artifact

A heavily deteriorated polychrome and gilded wooden artifact (Fig. 1, left) was recovered from the stores of the Mdina Cathedral Museum, Malta. During the documentation of the state of preservation, it was observed that the artifact matches stylistically to remnant parts of a late 16th Organ Balcony (Fig. 1, right) exhibited in the same Museum. The study of the manufacturing technique, carving style and approach, leads us to hypothesize that the recuperated artifact might have belonged to the organ loft ensemble.

The work, in an unfortunate state of preservation, is a fine example of Late Mannerist gilded and polychromed wood carving. The center of production is not known, but a

Neapolitan or Sicilian workshop seems likely. The possibility that it reached Malta with the new organ should not be overlooked. As a matter of fact, the entry concerning it is recorded along with the expenses for the importation and fixing of the new organ.

The gallery's three sides (119 cm height), preserved to respective lengths of 69 cm, 417 cm, 73 cm, are remarkable for the decorative fantasy of their carved decoration in which the ornately rich balustraded rails carry grotesque masks and mermaids alternating with foliated columnettes.⁸

Fig.1. Left: the recovered polychrome wood artifact; Right: the Organ Balcony.

3. Experiment

Carefully collected samples of blue pigment, flesh tones and gold were analyzed for each artifact. The locations of the samples are identified as (i) the Angels artifacts (A) for samples collected from the two angels and (ii) The Organ Balcony (OB) for samples collected from the remnant parts of the Organ Balcony.

A preliminary characterization of the samples was obtained with an X-MET 3000TX+ portable XRF spectrometer (Oxford Instruments). The excitation X-ray beam for this spectrometer is generated by a 40 kV tube with Ag anode. The detector resolution (a PIN silicon diode detector with Peltier cooling) is 270 eV for the Mn K α line (5.89 keV). The measurement spot size is about 30 mm². The analyzer has a Hewlett-Packard (HP) iPAQ personal data assistant (PDA) for software management and data storage.⁹

FT-IR and FT-Raman spectra were acquired using a FT-IR/Raman Bruker Vertex 70 instrument equipped with two mobile probes, a MIR fiber with a LN₂ cooled LN-MCT Mid detector and a RAMPROBE fiber with a LN₂ cooled Ge detector, and a Nd:YAG laser of 1064 nm and 1–500 mW. FT-IR spectra were recorded between 650 and 4500 cm⁻¹ with 1000 scans and FT-Raman between 50 and 3500 cm⁻¹ with 500 scans. Resolution was in all cases 4 cm⁻¹. The identification of pigments was made by comparison of their Raman spectra to our reference databases.^{10,11} A Micros Crocus II MCX100LCD biological microscope with integrated computer and real-time camera was used for the wood identification.

4. Results and Discussions

Pigments were first identified by means of XRF analysis according to the X-ray characteristic energies (keV) in each spectrum, corresponding to specific chemical

elements. Attribution of different pigments is based on previous consideration from literature.⁴ FT-Raman spectra provided more information on the pigments, while FTIR spectra gave more information on the organic content of painting.

4.1. The blue pigment

The results of the blue pigment analysis revealed a significant presence of Co and other elements such as Ni and As and traces of Bi. The presence of cobalt is a key element for smalt, while the metal impurities (Ni, As, Bi) are indicators of mineral provenance used.

According to literature, only two possible sources were geologically rich enough in Co to support, for a long period of time, a trade route over Europe, North Africa and the East as far as China. These are the areas of Qamsar and Anarak in Persia and the Erzgebirge region in Saxony. The source localized in Erzgebirge mountain range, a center of cobalt pigment production (cobalt was obtained as secondary extraction products from silver ores, whose minerals are found admixed in the so-called ‘five-element’ Ni–Co–As–Ag–Bi veins) from as early as the 12th century, matches with the pattern of the blue pigment collected from the Angels (A) as well as from the Organ Balcony (OB) artifacts.¹²

The amount of pigment used varies with the tone area — in the darker parts we found more Co (smalt) and less lead while opposite for lighter areas (less Co and more Pb), making the correct identification of As and Bi difficult because of the interference of these elements with the Pb L lines.

Fig. 2. XRF spectra obtained for the blue pigment collected from the Organ Balcony (OB).

Studies of the evolution of pigments used in 16th–19th century polychrome wood objects¹¹ suggest the occurrence of Ni, As and Bi impurities in Co-Blue pigment as an indicator of a 16th–17th century object. No spectral features except the ones characteristic of gypsum (1010 cm⁻¹) and calcite (1083 cm⁻¹) were identified from Raman spectra collected for the blue pigment. According to literature, smalt, the pigment identified by XRF analysis, cannot be detected using a 1064 nm laser as the excitation source.¹³

4.2. The red/ flesh tone pigment

The chemical element identified in the flesh tone sample spectra is mercury (Hg), the presence of which indicates that the red pigment used was cinnabar, a mercury sulfide (HgS) — see Fig. 3. The K_{α} (2.30 keV) and K_{β} (2.46 keV) peaks of S are covered by the M_{α} (2.34 keV) and M_{β} (2.44 keV) peaks of Pb and therefore cannot be seen (Fig. 3).

Fig. 3. XRF spectra obtained for the red pigment sample collected from the Organ Balcony (OB).

The Raman spectrum (Fig. 4) for the flesh tone samples revealed evidence of cinnabar, mercury (II) sulfide (HgS), with bands at 254, 286 and 345 cm^{-1} , thus confirming the XRF results. The spectrum contains also a band at 1054 cm^{-1} . This band is representative of calcium carbonate, which is probably the white pigment used to make the flesh tones from a red base color.

Fig. 4. FT-Raman spectra obtained for the a) red pigment, b) white lead standard, c) cinnabar standard flash color sample from the Angels (A), and d) skin flash color sample from the Organ Balcony (OB).

4.3. The metallic decorative parts

High Au peaks confirm the presence of gold (Fig. 5) in the gold samples. High peaks of Fe in all the spectra reveal the presence of bole, red iron oxide, used in the preparation procedure in the gilding technique known as water gilding. Like many metals, gold does not give a first-order Raman spectrum, so it is virtually undetectable by this technique.

Fig. 5. X-Ray spectra obtained for gold samples from Angels (A) and Organ Balcony (OB).

4.4. The preparation layer

The occurrence of Ca, Fe, and Sr in all of the analyzed samples, suggests that these elements belong to the preparation layer. The presence of Pb in all the measured samples suggested that lead white ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$) was the white pigment used. White lead is omnipresent: all the recorded Raman spectra contain the intense Raman band at $1,056 \text{ cm}^{-1}$ (see Fig. 4), whereas the less intense bands of white lead at 260, 203 and 154 cm^{-1} are only observed in a few spectra. Apparently, this pigment was applied to modify the hue of the colored areas, making them appear brighter.

A compound based on Ca was used for the preparation layer (see X-ray spectra presented in Fig. 4). Two bands can be found at 1136 and 1010 cm^{-1} and three other very weak peaks at 674 , 499 and 417 cm^{-1} that are consistent with the presence of gypsum–calcium sulphate (Fig. 6).

4.5. Wood identification

The FT-IR spectra (Fig. 7) of the two wood samples show one strong hydrogen bound O–H stretching absorption around 3400 cm^{-1} and a C–H stretching at 2917 cm^{-1} . In the fingerprint region (between 1800 and 900 cm^{-1}), some discrete absorbance bands due the various functionality of the wood constituents groups can be seen clearly: C=O stretching (unconjugated) at 1733 cm^{-1} , the aromatic skeletal vibration in lignin at 1508 cm^{-1} , and other complex peaks describing carbohydrates and lignin various vibration modes localized in the fingerprint region below 1463 cm^{-1} .

Fig. 6. FT-Raman spectra obtained for the preparation layer: a) & b) the gold samples from Angels (A) and Organ Balcony (OB), respectively; c) Flash color sample from the Angels (A); d) Flash color sample from the Organ Balcony (OB); e) Blue sample from the Angels (A); f) Blue sample from the Organ Balcony (OB).

Fig. 7. FT-IR spectra of wood samples collected from the a) Angels (A) and b) Organ Balcony (OB).

No remarkable spectral differences were noticed in the case of the two samples; at this point we can conclude that the wood specie used is the same. It should be mentioned that the use of FTIR as a detection tool capable of differentiating between various wood types is conditioned by the existence of large reference databases containing FTIR spectra of the different species.

4.6. Microscopic identification

At microscopic inspection, the specie that has been analyzed was found to have diffuse porosity, with radially oriented vessels in multiples (see Fig. 8). The average vessel

diameter was calculated as being 40-65-95 μm . No helical thickenings have been observed, and tyloses were scarce but present. Rays were composed of a single cell type (homocellular) and exclusively uniseriate. Simple vessel perforations and large vessel-ray pits were observed. This structure is similar to the structure described in Ref. 14 for *Populus* (Poplar). Correlating these results with the visual analysis, we can finally validate that poplar was used for both artifacts.

Fig. 8. Left: radial section of the wood sample showing ray tracheids and simple perforation plate. Center: radial section showing intervessel pitting. Right: Transverse section showing diffuse-porous.

5. Conclusions

This paper has presented the results of our analysis and material comparison of a late 16th century polychrome wood organ balcony and a salvaged polychrome artifact. Such a detailed characterization of the materials and their successive stratification is a necessary task that must be accomplished prior to the commencement of any restoration intervention.

The analysis of the materials (pigments and preparation layer wood, *etc.*) was accomplished by combining the information obtained from X-ray fluorescence (XRF), Fourier-transform Raman spectroscopy (FT-Raman) and Fourier transform infrared (FT-IR) spectroscopy. The materials used — blue pigment smalt, red pigment, cinnabar and gold for the decorative parts, and poplar for the wood — are identical, thus leading to the conclusion that the two artifacts are part of the same ensemble.

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