Archaeometric non-invasive study of a Byzantine Albanian icon

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Abstract
The present study is part of a project concerning the characterization of Albanian Byzantine and post-Byzantine icons, through the identification of pigments, of painting technique and the state of conservation of the artworks.

The Albanian iconographers produced an incredible number of icons from the 14th to the 19th century and about 6000 of them are conserved in the Museum of Medieval Art of Korça (Albania). The study of these artworks is conducted by non-destructive methods, X-ray fluorescence, visible light reflectance spectrophotometric measurements and UV fluorescence analysis, according to an analytical procedure developed in our Laboratory. With this procedure we can recognize the inorganic pigments from their typical features. Moreover, the study of the optical properties of paintings is of fundamental importance for correct restoration. Eleven areas were chosen where to carrying out our measurements. The present work, concerning the study of an icon of 14th century, has allowed us to recognize the palette and the painting technique used in this work of art by the anonymous painter. We have also compared this icon with other Byzantine works housed in the same Museum.

Keywords: Byzantine icons, Albanian icons, X-ray fluorescence, UV fluorescence, reflectance spectrophotometry

1. Introduction

Entire Albania maintains countless artistic treasures, especially related to the Byzantine and post-Byzantine wall paintings and icons. The Museum of Medieval Art of Korça, located in the southeast Albania, near the border with Greece, keeps over 6000 icons in addition to many other important artistic objects. Among the icons we mention the masterpieces of leading painters such as Onufri, Onufri Qiprioti, Konstantin the Teacher, Konstantin Jeromonaku, Konstantin Shpataraku, David of Selenika, and the Çetiri brothers, a family of painters from Grabovë, a village in the Korça district. Onufri, who was a great exponent of icon and mural painting of 16th century, is the most important painter in this museum. He painted in many churches in Elbasan, Berat, Kastoria (Greece), Zerze (Prilep-Macedonia) and elsewhere. Albanian artworks, for various reasons, are not sufficiently studied in terms of preparation techniques and materials used.

Some research on Albanian Byzantine and post-Byzantine icons have been done in recent years which led to the publication of the results [1,2,3,4] (Civici et al. 2005; Civici 2006; Franceschi et al. 2010; Franceschi et al. 2011), but these are only few studies considering the huge amount of not yet studied artworks held in the Museum of Medieval Art of Korça and in the other Albanian art sites.

This article reports the study of a Byzantine icon, painted on a wooden panel by an anonymous Albanian artist of the 14th century, with the tempera technique. The wooden table is carved out forming a frame, adorned by a band in red. This icon, shown in figure 1, is very famous and it is known as the Albanian Mona-Lisa [5] (Arapi and Czerwenka-Papadopoulos 2002).
Figure 1. Anonymous, 14th century, *The Archangel Michael*, 108.5x83.5 cm, inventory number 2764, painted for the church of Ascension in Mborje (Korça district). Numbers indicate the spots where X-ray fluorescence and spectrophotometric measurements have been performed.

The image represents the archangel Michael, against the originally gold ground, in armour and with his sword in his right hand, as guardian of the church. The helmet, held in his left hand, completes the traditional iconography of archangel. On the green-grey helmet, between the arms of the cross, in white lettering is the inscription: \[ IC \quad XC \quad N \quad K \]
indicating the victorious Christ, \[ I(HCOY)C \quad X(PICTO)C \quad N(I)K(A) \] (see detail in Fig. 2).
In addition from the detail shown in Fig. 2 it is possible to observe, between the damaged areas and the detachments of the paint film, the brown colour of the preparative layer. The conservation state of the painting is fairly good, but the icon has been restored in the past without performing analyses on pigments and on preparatory layer. The main purpose of this research was the identification of the original pigments used by the painter, those added during restoration interventions, the restored areas, as well as the painting technique used by the anonymous painter, so supplying useful information to art historians and restorers. The comparison with previous studied icons of 14\textsuperscript{th} and 15\textsuperscript{th} century [3,4] (Franceschi et al. 2010; Franceschi et al. 2011) is of great interest in highlighting analogies and differences in the traditional iconographic Albanian tradition.

2. Methodology

Given the historical, artistic, religious and cultural importance of this icon we decided to use non-invasive methods in this study. A variety of areas were chosen for the purpose of identifying the pigments and the painting techniques of the anonymous artist. The following archaeometric techniques were applied.

2.1. Optical microscopy and macrophotography

Optical observation and photographic documentation was achieved using a Dino-lite portable digital microscope and a Canon EOS 350D camera equipped with a Canon Zoom Lens EF-S 18-55 mm.

2.2. X-ray fluorescence spectrometry

Elemental analysis was performed using a Lithos 3000 portable system and an appropriate Lithos program by Assing to process the data. The apparatus consists of a molybdenum tube, a zirconium filter and a semiconductor silicon (Li) detector, cooled by Peltier effect. The operating parameters were: 25 kV, 0.1 mA, and 240 seconds of acquisition time. The elements with the highest intensity detected on the paintings, such as lead, iron or mercury, have been used as internal standards.

2.3. UV fluorescence

This analysis was carried out using a ceiling light with 4 Sylvania black light-blue F18W/BLB-T8 tubes. The digital camera used for recording images is the Canon EOS 350D without barrier filter. It is a non-destructive superficial analysis that identifies the presence of one or more film-forming substances such as varnishes applied on the work (resins, oleoresins, proteins, etc.) and generally
every previous intervention. This technique allows assessing the condition of the paint, enhancing the presence of restorations, biological attacks, even when they appear indistinguishable to the naked eye. Also it can give some information on pigments that may have their own particular fluorescence, for example: the yellow green of arsenic trisulphide, the brightness of lead white, the darkening of iron oxides.

2.4. Reflectance spectrophotometry
Reflectance spectrophotometric and colour measurements have been performed using a Minolta CM-2600 portable spectrophotometer provided with a Xenon lamp to pulsate the light on the sample surface and with an integrative sphere inside the apparatus. Light is reflected by the pigment with an angle of 8°. It is captured by a silicon photodiode that measures the colour spectrum between 360 and 740 nm with an interval of 10 nm. Colour coordinates are based on the CIEL*a*b* system using an illuminant D65 with an observer angle of 10°. In this system \( L^* \) represents colour lightness while \( a^* \) and \( b^* \) are the coordinates of chromaticity. Coordinates \( +a^* \) and \( -a^* \) indicate red and green values while \( +b^* \) and \( -b^* \) indicate the yellow and blue values, respectively.

3. Results and discussion
Looking at the edges of the table and cracks in wooden planks, it is evident that no intermediate canvas was used beneath the painted surface. The inorganic pigments employed for the painting could be identified by means of the principal characteristic elements, their relative abundance and by comparing their reflection spectra with the literature data and with those of a pigment database developed in collaboration with the Soprintendenza per i Beni Architettonici e il Paesaggio della Liguria. The results, helpful to identify the pigments and the painting technique of this artwork, are discussed, showing the contribution that each technique has provided.

3.1. X-Ray fluorescence
From the data obtained by XRF measurements processed as discussed in literature [6](Seccaroni and Moioli 2004), we could detect the presence of various elements in the different layers of the painting. The experimental data obtained by X-ray fluorescence are collected in Table 1 and visually summarized in figure 3, where the occurrence of the principal elements - detected on the basis of the counts measured for the main peak of each element - in the different analysed spots is plotted. In the case of simultaneous presence of arsenic and lead, their principal peaks As K\( \alpha \) and Pb L\( \alpha \) are
superimposed at about 10.5 keV. We considered the counts of Kβ (11.73 keV) and Lβ (12.61 keV) respectively. The counts of the peaks of the elements have been normalized for graphical presentation.

Table 1. The counts of the main peaks of the elements detected in the analysed areas of Archangel Michael

| spot | colour           | P  | K  | Ca | Ba | Mn | Fe | Co | Ni | Cu | Zn | Au | Pb | As | Ka | Pb | Lα | Lβ | Sr |
|------|------------------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| 1    | preparative layer| 9  | 868| 6  | 5  | 54 | 3  | 1  | 4  | 14 | 23 | 30 | 192| 300| 100| 32 |
| 2    | brown hair       | 4  | 126| 11 | 1600| 70 | 103| 16 | 11 | 110| 610| 4537| 2990| 1140| 655| 376| 40 |
| 3    | dark-incarnate   | 12 | 167| 20 | 730| 199| 13 | 13 | 45 | 4245| 2670|
| 4    | white-incarnate  | 10 | 10 | 20 | 14 | 103| 17 | 11 | 610| 4537| 2990|
| 5    | incarnate        | 10 | 5  | 15 | 8  | 106| 36 | 10 | 100| 5050| 3435|
| 6    | brown            | 6  | 333| 25 | 4  | 171| 7  | 58 | 7  | 20 | 640| 3  |
| 7    | red-brown        | 4  | 21 | 265| 2655| 10 | 45 | 275| tr | 20 | 43 | 6 | 7 | 43 | 6 | 4 |
| 8    | red              | 7  | 43 | 6  | 32 | 6  | 4  | 2300| 820| 512 |
| 9    | dark green       | 74 | 8  | 16 | 106| 5400| 56 | 6  | 32 | 1187| 786 |
| 10   | white            | 15 | 2  | 5  | 48 | 11 | 8  | 10 | 10 | 5050| 3435|
| 11   | light brown      | 12 | 640| 3  | 77 | 6  | 23 | 25 | 6  | 40 | 2450| 25 | 10 | 43 | 6 | 4 |

Barium was found in six spots (1, 2, 4, 6, 9, 10) and zinc in three (6, 9, 10) thereby indicating the occurrence of restoration interventions. In fact, these elements have to be attributed to white pigments BaSO₄, blanc fixe [7](Feller 1986) and ZnO, zinc white [8](Kühn 1986) or lithopone, white pigment developed from 1870, mixture of barium sulphate and zinc sulphide: such pigments have been used starting from the 19th century. The visual observation of painting’s surface permitted the detection of extensive colour detachment (spot 1); we can observe that from these data we achieve the elemental composition of preparative layer, containing mainly phosphorus, calcium, iron; strontium is generally low or absent. Noteworthy the presence of arsenic (spots 1, 6, 7, 9) and gold (spot 1): the latter is a reman of the upper layer, formed, probably, by a gold leaf, as it was in the Byzantine traditional technique. The presence of phosphorus in addition to calcium suggests the use in the preparative layer of ivory/bone black. The presence of calcium in correspondence of light brown colour of spot 11 indicates the use of calcium white for the particular shade. Also considering the iron content (iron is accompanied by manganese in this icon, indicating the use of a brown earth), we can note that the painter used it, in small quantity, to obtain the colour
of the preparation layer. As we found the same ensemble of elements in an other icon of the same period coming from the same church [4](Franceschi et al. 2011), we took the suggestion of a traditional use for the purpose to obtain a dark ground for the next paint layer, in the style of that age [9](Sendler 2001). In addition the presence of iron derives from successive paint layers, in particular to give brown and dark incarnate tones (spots 2,3,7). The association of iron and arsenic is found in correspondence with the dark red colour of the wings (spot 7). Interesting the presence of arsenic, that indicates the use of an arsenic sulphide (realgar, $\text{As}_4\text{S}_4$, or orpiment, $\text{As}_2\text{S}_3$); noteworthy also the association of these pigments with a copper compound in correspondence of the armour (spot 9).

Orpiment and realgar are known to occur in some Orthodox countries in paintings of icons during a long period of time, lying from 12th to 16th century [10](West FitzHugh 1997); recently their use has been reported also in 14th and 15th century Albanian icons [4](Franceschi et al. 2011). Mercury is present in many areas, indicating the use of cinnabar ($\text{HgS}$), as shade in brown hair or to obtain the intense red colour of the mantle of the Archangel. To achieve flesh tones and to give highlights white lead was also used (spots 4,5,10).
3.2. UV observation
Under the UV illumination areas containing cinnabar or vermillion become purple; iron oxide presents a typical darkening behaviour, clearly showing the painting technique used by the artist, with strokes applied to form continuous layers as painting basis and thin strokes as overlayers (fig. 5).
The presence of lead white is clearly evidenced by the strong response to UV illumination [11] (Aldrovandi et al. 1996) (Fig 6). The use of arsenic sulphide, orpiment, is indicated by a greenish yellow UV fluorescence [4] (Franceschi et al. 2011). The fresh, more or less recent varnish appears as black areas, denoting restoration interventions [12] (Aldrovandi 1999).
The flesh tone was obtained by the use of brown and dark-brown brushstrokes and a series of highlights consisting of almost pure lead white (see fig. 5) in addition to the brown colour of preparative layer.

Looking at fig. 5, where a detail of Archangel Michael, corresponding to the face and the background, is shown, we can make some considerations, regarding the different areas:

- In the areas where the preparatory layer is emerging due to the loss of metal coating we can notice the preparatory drawing.
- The presence in the background of iron oxide (bole residue?) can be seen here and there,
where the lower the UV fluorescence;
• Areas where there is lead white are revealed by the strong UV fluorescence;
• Cinnabar strokes under UV radiation change to a red-purple tone;
• Dark brown colour reveals the presence of iron oxides that darken under UV radiation.
• The green colour, where copper compounds are present, turns from green to black.

Observing the figure 6, in the areas corresponding to detailed wings of the Archangel, we can note the overlap of the brushstrokes with various shades of colour formed by overlays of arsenic sulphide to cinnabar. The mantle is obtained using cinnabar with broad dark lines to give the shadows that under the UV radiation appear to have a different response with a darker colour.
Figure 6. Comparison between visible light (top) and UV (bottom) images. Detail showing Archangel Michael’s clothing and wing.
Figure 7. Comparison between visible light (top) and UV (bottom) images. Detail showing
Archangel Michael's red wing. Yellow lines are obtained by using orpiment. Red strokes are probably obtained with realgar.

The colour of the wings was obtained with ochre, as a base, realgar (dark red strokes) and orpiment (yellow points and lines), the latter giving a green fluorescence in the UV image. The blade of the sword and the areas containing iron oxides become darker under UV light.

3.3. Reflectance spectrophotometric measurements

The reflectance Vis spectrophotometric investigations were made on all the areas examined by X-ray fluorescence. On the basis of the measurements made, it was possible to confirm some results obtained by the other techniques or to establish new as following:

3.3.1. Red and flesh tones

The hue range of red pigments varies from light orange to dark red/brown. The red inorganic pigments generally used in this icon were red ochre, realgar and cinnabar (HgS). In some cases red tonalities were obtained from appropriate mixtures of these pigments with lead white. There is no evidence of the use of lakes.

The graph obtained by data processing in the first derivative [13] (Bacci et al. 2003) improves the reading of data, and highlights the behaviour of the examined reflectance spectra. The method may allow identifying the pigments that mainly contribute to the perception of colour. The technique, which offers the best results in the examination of mural paintings, where there is little or no paint binder on surface film, poses more difficulties in easel painting, as in almost all the icons of the Korça Museum, veiled with thick, unequal and misleading varnishes.

Figure 8 shows the results obtained by measuring three different red spots of Archangel Michael, 4, 7 and 8, and comparing them with the spectra of cinnabar [14] (Gettens et al. 1993b), red ochre and red lead.
Figure 8. Reflectance curves referring to Archangel Michael’s two red spots 7 and 8, and three flesh tones, spots 3, 4, 5, comparing them with the spectra of red ochre, red lead and cinnabar and their second derivative.

Cinnabar is revealed in four of the examined areas, but it is highlighted the contemporaneous presence of other pigments, with their less or more strong spectral response. So it is explained the XRF signal of copper in the spot 4; whose presence is revealed by the deformation of line of second derivative in the range 400-500 nm. The curve corresponding to the dark red wings (spot 7) reflects the predominant presence of red ochre and ivory/bone black. Finally the red tone of mantle was obtained using cinnabar with lower amounts of lead white (note the slight shift of the peak in the second derivative curve toward higher wavelengths).

3.3.2. White
Areas containing lead white are clearly evidenced (fig. 4) by the strong response to UV illumination (Aldrovandi et al. 1996) and by XRF in various spots, both as white colour and in mixture with other pigments. White pigments ZnO and BaSO₄, as already remarked, are due to restoration interventions.

In this icon we did not found the presence of a filler layer formed using lead white (Civici et al. 2008) or the presence of a second thick white or slightly coloured preparatory layer, known as
imprimatura [15](Gettens et al. 1993a).

Figure 9. Reflectance curves referring to spots 1 and 10 in *Archangel Michael* compared with the curve typical for lead white and its second derivative.

As we can see, the preparative layer (spot 1), composed primarily of white lime, behaves differently from that of lead white, as highlighted by the second derivative shapes. With regard the curve of spot 10 (white wings), we can note two important signals: in the shortest wavelengths the deformation is linked to the presence of copper and cobalt, while in the red region the peaks are relative to the underlying paint layer.

3.3.3. Dark green

The XRF measurement on the dark green of the armour reveals the high presence of copper with iron, arsenic and lead. The colour should be attributed to the strong presence of copper, while the darkness can be related with an iron-based pigment, like the burnt umber [16](Helwig 2007), but it is also possible the use of carbon black, not identifiable by means of this technique.
Figure 10. Reflectance curves (on the left) referring to spots 10 in Archangel Michael and 9 in St George with scenes (Franceschi et al. 2011), compared with the curves typical for malachite and verdigris and their second derivatives (on the right).

It is not possible, by the simple comparison with typical reflectance spectra of malachite and verdigris, to assess the actual nature of the copper based pigment. We have also considered the possibility of the use of a blue pigment, like azurite, with the yellow orpiment, to obtain the green tonality. The use of Vergaut (a mixture of orpiment and indigo) in medieval paintings is well known. On the other hand, it is possible to recognize a close similarity between the mixture of pigments found in the previously analysed Albanian icon, St. Nicholas of 14th century (Franceschi et al. 2011) and that of the present work (see in particular the second derivative of the reflectance spectra).

3.3.4. Brown

We have compared three different brown areas (see figure 11), corresponding to the spots 2 (brown hair), 6 (brown sword) and 11 (light brown of the sword handle). Appropriate layers containing ivory/bone black, white lime, ochre, red lead and cinnabar give the different tones. Looking at the figure 11 we can infer the high content of cinnabar used to render the hair hue (spot 2). As well as...
you can see the same feature for points 6 and 11, where the slope of the reflectance curves is dominated by the ratio of white lime and black in the mixture. The presence of red ochre on the layer under the sword handle (spot 11) is shown by the slight curvature around 570 nm.

![Figure 11. Reflectance curves referring to spots 2, 6 and 11 in Archangel Michael and their second derivatives compared with the spectra of burnt umber](image)

4. Conclusions

The icon studied in the present work represents an interesting example of the Albanian Byzantine art of 14th century. Its anonymous author follows the iconographic tradition, with some peculiarities.

The non-destructive methods that we have used provide information to identify the pigments and the preparation of the icon worked by the anonymous artist.

For the preparatory layer, the painter employed lime coloured with brown ochre (as suggested by the contemporary presence of manganese and iron) and, in limited areas, ivory/bone carbon (as indicated by the contemporaneous presence of calcium and phosphorus) or copper based compounds. The absence of sulphur suggests the main use of calcium carbonate rather than the more usual gypsum. Noteworthy a difference is related to the nickel content: this element is present only in three areas, at the contrary it always accompanies iron in ochre in the other artwork of 14th century, St Nicholas, painted for the same church of Mborje, investigated in a previous study (Franceschi et al. 2011).

Through our study we also detected the previously restored areas of the icon and the kind of pigments utilized by restorers in a period of time from the first half of 1800 (as denoted by the presence of blanc fixe).

The anonymous painter's palette of the 14th century previously studied was very poor, including lead white, cinnabar, red and yellow ochre, brown earth, realgar and ivory/bone black and probably indigo.

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This icon of the same century, object of the present study, is more richly coloured. The use of mixtures of various pigments, in different proportions, allowed the artist to get a more wide variety of colours. To be noted the presence of green with different shades obtained using a copper compound with arsenic sulphide.

Furthermore, the spectral reflectance measurements of the different pigments gathered in this work, in addition to recognizing the conservation status of the examined artwork, will also be useful for future restoration intervention. In conclusion, the set of non-destructive techniques employed in this study has proved to be very useful for recognizing pigments, including those not detectable with certainty by means of X-ray fluorescence.

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