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Application of a Portable XRF Spectrometer for *In-Situ* and Nondestructive Investigation of Pigments in Two 15th Century Icons

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Abstract

A simple portable X-Ray Fluorescence (XRF) spectrometer was successfully used for *in-situ* and nondestructive identification of the painting materials in two 15th century icons from the Onufri Museum in Beart, Albania. The spectrometer is based on a low power X-ray tube, a thermoelectrically cooled Si PIN detector and the spectrum acquisition system. It was assembled and adjusted at our laboratory for the investigation of the icons. A small number of pigments were clearly identified by X-Ray Fluorescence (XRF) measurements in both icons. This includes Lead white for the white color, gold and yellow ochre for the yellow color, red lead, cinnabar and red ochre for the red color, as well as cooper based pigments for the green color. At the same time, the investigation raised some new questions that need further investigations by the use of additional analytical techniques. The results show that in both icons are used similar pigments, which are in accordance with the Byzantine icon painting tradition.

Keywords

Portable X-Ray Fluorescence (XRF) Spectrometer, Pigment Analysis, Icons, Albanian Icons, Berat, Albania

1. Introduction

The town of Berati is an important historical and cultural centre in Albania. The old part of the city comprises buildings with a unique style of architecture and an old fortified castle filled with old churches and mosques decorated with beautiful wall paintings. Berati is designated "Museum town" in 1961 by the Albanian

government and from 2008 it is designated a UNESCO World Heritage Site.

The "Onufri" museum is situated within the old castle and has a big collection of icons and other Christian religious objects. It is named after Onufri from Neokastra, who is considered the best painter that had ever worked in Albanian territory and in the 16th century founded a school of painters known as the Berati School [1] [2].

This article reports the study of materials used in two beautiful Byzantine icons from the collection of the museum. The main purpose of this research was the identification of the original pigments, as well as the painting technique used by the anonymous 15th century painters. The reconstruction of the palette of old painters will provide useful information to restorers and art historians. While, there have been a number of studies on the materials used in various post-Byzantine icons in Albania [3] [4] [5] [6] the information regarding the materials utilized by the icon painters of 13-15th centuries are scarce [7] [8].

In this study, a portable XRF spectrometer, assembled and adjusted at our lab, is used for *in-situ* analysis of the decorated areas of the icons. The application of XRF techniques to pigment identification is based on the identification from the spectrum of one or more "key elements", which are the main constituents of the pigment. In most of the cases the combination of color and "key elements" lead to effective inorganic pigment identification. The technique fulfills some of the main requirements for the examinations of cultural artefacts, like portability, nondestructive, non-invasive and multi elemental nature. However, the main limitation of the technique is the inability to identify organic pigments due to the insufficient sensitivity of XRF for low Z elements [9] [10].

2. The Studied Icons

The studied icons are painted with the technique of tempera on wooden supports. They are exposed at the "Onufri" museum in Berat, Albania (inventory No 6 and 178). The icons are not signed and art historians attribute them to anonymous painters of the 15th century [11].

The first icon named "The Annunciation" (dimensions 37 × 32 cm, **Figure 1(a)**) belonged to the church of Assumption of the Virgin in the castle of Berat. The composition of the scene follows the old Byzantine tradition. The Archangel Gabrielle, on the left side, has just descended from the heaven and is addressing to the Virgin. She is sitting on her throne accepting the announcement with modesty and obedience. The Holy Spirit is coming down from the heaven, like a dove flying towards the Virgin.

The second icon is titled "Saint Nicholas" (dimensions 60 × 30 cm, **Figure 1(b)**) and belonged to the church of Saint Nicholas in the castle of Berat. The icon is not preserved in full; a part of the right side is missing. The saint is depicted in bust, dressed in Episcopal vestments, holding the Bible with the left hand and blessing with the right hand. A miniature image of Christ blessing the Saint is depicted in the golden background.

(a) (b)

Figure 1. Photos of the icons with the respective positions of the measurements.

3. Experimental

The portable EDXRF spectrometer was assembled at our laboratory. It consists of a small thermoelectrically-cooled Si-PIN X-ray detector (model XR-100CR from AMPTEK INC., USA), a self-contained miniature X-ray tube system (Mini-X) and the signal processing unit (Amptek PX4).

The Si-PIN photodiode has an area of 7 mm^2, thickness of 300 μm and is thermo-electrically cooled down to −30˚C. The signal processing unit consists of an Amptek PX4 unit, which is an interface between Amptek's XR100 series of X-ray detectors and a personal computer equipped with data acquisition, control, and analysis software. The PX4 includes three major components: 1) a shaping amplifier, based on a state of the art, high performance, low power DP4 digital pulse processor, 2) a multichannel analyzer, and 3) power supplies. The detector and PX4 are connected and adjusted in accordance with the recommendations of the respective manuals [12] [13] and at the working conditions the system has FWHM of 190 eV for MnK_α (**Figure 2**).

Mini-X is a self-contained, miniature X-ray tube system, which includes the X-ray tube, high voltage power supply and USB controller, designed for X-ray fluorescence analysis applications [14]. It features a 50 kV/80μA power supply, silver(Ag) transmission target, and a beryllium and window.

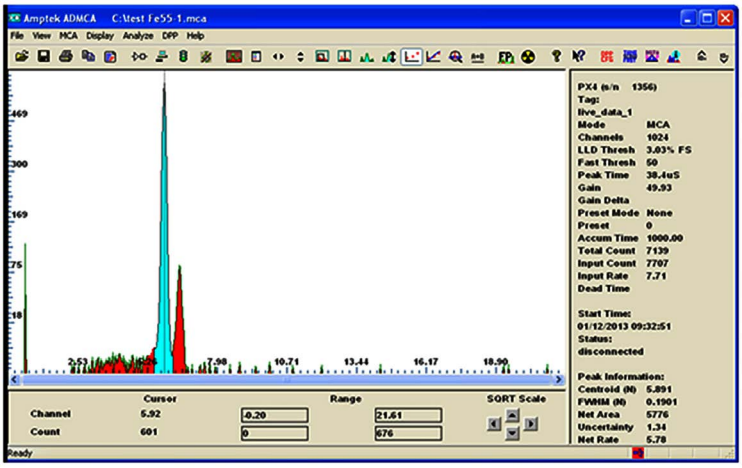


Figure 2. The spectrum of Mn K_α from Fe-55 radioisotope.

The X-ray tube and the detector were mounted on the geometrical setup in perpendicular directions so that both their axes are intersected on the sample surface at 90˚. Two laser pointers mounted on both sides of the detector provide for the optimal and repeatable positioning of the sample (laser spots are overlapped on the optimal position). The X-ray beam from the tube is collimated through a brass collimator with aluminum insert 2 mm diameter hole, which allows the positioning of filters. A similar collimator with 2.5 mm hole is used in front of the detector. In this arrangement the spot of the radiation on the sample surface is an ellipsis with diameters of 10 and 6 mm. During the measurements the X-ray tube was operated at 40 kV and the current was 10 μA. The primary X-ray radiation was not filtered and the spectra with sufficient intensity of the main elements were collected for 25 s at each point.

The intensities of the elements of the X-ray spectra were calculated by the program AXIL [15] included in the QXAS [16] package distributed by the International Atomic Energy Agency. The intensity of each element was later normalized to the sum of the intensities of all the elements identified in the spectrum. This allows us to have a better idea of the relative intensities of the different elements appearing in the spectrum, making clear the identification of major elements. On the other side the normalization enables the comparison of the spectra measured at different positions of the icon because it reduces the errors due to not perfect positioning of the measuring head.

During *in-situ* operations the measuring head of the spectrometer was mounted on a tripod that allowed its correct positioning towards the object.

4. Results

The measurements were performed at the museum under the supervision of the responsible restorer of the museum, who suggested the most interesting colors and areas of the original paintings for investigation in each icon. In each icon we performed measurements at 15 different points, which cover the main colors

and some of the different hues. The positions of the measured points in each icon are presented in Figure 1.

Table 1 and Table 2 are presented the intensities of the elements detected at each of the measured points in both icons. The measured points are grouped according to their main colors category.

In Figure 3 are presented the relative intensities of the white color (A-11) and two areas with blue color (A-4, A-10) from the icon "The Annunciation".

The fact that Pb is the only major element in the spectrum of the white color A-11 indicates the use of Lead White ($2PbCO_3 \cdot Pb(OH)_2$), as the white pigment.

Although it was not directly measured, lead white is used as white pigment in the icon Saint Nicholas mainly mixed with other pigments (ochre's, etc.) and in the small details of the beard (N-5). The spectra measured at those points show Pb as a major element (Figure 5, Figure 9).

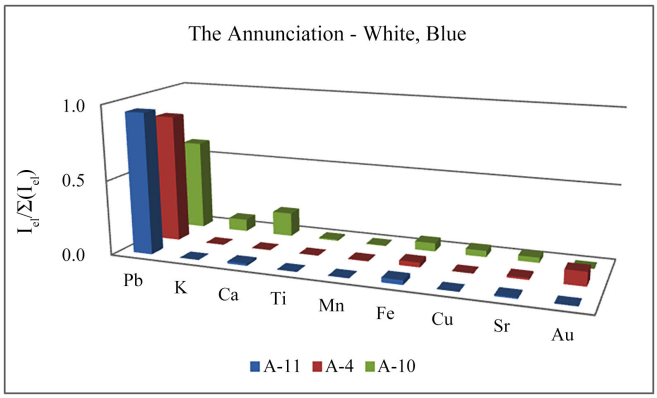


Figure 3. The relative intensities of the elements in the spectra of white and blue painted areas.

Table 1. Intensities (cps) of the elements detected at the measured positions of the icon "The Annunciation".

	White	Blue		Yellow		Ochre			Red				Brown		
	A-11	A-4	A-10	A-9	A-3	A-7	A-13	A-6	A-1	A-14	A-5	A-8	A-2	A-12	A-15
K	0.0	0.0	16.3	12.5	22.4	7.5	5.5	14.3	12.5	6.2	7.5	14.2	4.1	11.5	32.9
Ca	9.4	0.0	31.8	197.6	75.5	42.6	65.4	181.3	157.4	98.6	71.5	115.9	94.3	195.3	91.6
Ti	0.0	0.0	1.8	1.4	1.0	0.0	1.2	1.7	2.8	0.0	1.4	1.1	0.0	0.0	2.4
Mn	1.5	0.8	0.8	5.9	21.9	4.0	4.7	12.4	12.2	6.1	2.1	7.6	13.5	23.9	17.3
Fe	20.2	6.3	11.1	95.5	**479.6**	**55.5**	39.8	**350.5**	**280.0**	**180.3**	37.0	**234.0**	**271.0**	**344.0**	**289.3**
Cu	0.0	0.0	8.3	0.0	9.4	0.0	0.0	0.0	0.0	0.0	0.0	0.9	0.0	0.0	29.6
Sr	5.8	2.4	6.9	16.1	10.2	7.5	2.4	14.1	12.7	8.6	2.0	8.5	8.4	18.4	12.4
Au	0.0	18.6	0.0	**64.4**	**115.7**	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hg	0.0	0.0	0.0	0.0	0.0	0.0	**654.3**	**87.9**	**72.9**	**64.0**	0.0	0.0	0.0	0.0	0.0
Pb	**633.0**	**169.4**	**119.6**	19.4	72.6	126.9	0.0	**24.4**	**21.8**	**89.6**	**528.3**	**60.2**	**117.4**	**226.0**	**370.0**

Table 2. Intensities (cps) of the elements detected at the measured positions of the icon "Saint Nicholas".

	Yellow		Ochre		Brown			Red			Green				
	N-2	N-1	N-3	N-13	N-5	N-4	N-12	N-7	N-11	N-14	N-6	N-8	N-9	N-10	N-15
K	21.4	20.5	0.8	2.4	1.4	25.0	25.8	7.7	12.5	3.3	17.9	7.1	8.0	4.0	3.4
Ca	387.6	195.3	27.9	17.9	23.3	288.7	316.5	61.8	40.8	23.3	52.2	33.5	20.1	16.6	13.3
Ti	3.1	1.4	9.4	0.0	0.0	5.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mn	3.5	6.0	6.0	8.2	14.7	10.8	17.0	6.4	9.4	2.3	0.0	0.0	0.0	0.0	0.0
Fe	78.2	85.2	**25.3**	**68.2**	**167.9**	**336.2**	**451.0**	37.3	142.8	15.5	241.2	40.3	67.3	32.9	32.1
Cu	3.8	2.3	0.0	0.0	0.0	9.2	16.6	0.0	0.0	0.0	**4093.1**	**852.9**	**1529.8**	**686.8**	**967.2**
Sr	5.6	4.4	0.0	11.5	13.4	5.8	7.4	0.0	2.6	0.0	4.2	7.2	9.0	6.4	4.4
Au	**107.5**	**94.5**	0.0	0.0	0.0	28.3	0.0	0.0	0.0	0.0	8.2	0.0	0.0	0.0	0.0
Hg	0.0	107.9	0.0	0.0	0.0	0.0	15.1	**496.6**	**447.1**	**330.4**	0.0	0.0	0.0	0.0	0.0
Pb	0.0	122.1	1286.6	1153.1	968.4	32.3	18.0	**557.7**	**475.5**	**291.0**	69.8	782.3	671.9	879.1	347.4

The results of the measurements at the blue areas with different hues A-4 and A-10 of the icon "The Annunciation" do not allow direct identification of the blue pigments. The major element detected in these areas is lead and this suggests that the blue colors should have been prepared by a mixture of lead white with a blue pigment composed of low atomic number elements such as Indigo ($C_{16}H_{10}N_2O_2$) or Ultramarine ($Na_{8\text{-}10}Al_6Si_6O_{24}S_{2\text{-}4}$) whose major elements can't be detected by the present XRF instrument. However, the presence of small amounts of Ca and Fe at A-10 can indirectly indicate the presence of ultramarine. They can indicate some calcite and pyrite, which are referred as impurities of natural Lapis lazuli (ultramarine) [17]. On the other side, Ultramarine was identified by μ-XRF measurement in the wall paintings of the church to which the icon originally belonged [18].

In both icons we couldn't find spots of ground free from the paint layer to measure its composition. However we can deduce its composition from the measurements at other points, such as gold painted areas. The presence of high amounts of Ca in the spectra of gold painted aureoles of the Virgin (A-9) at the icon "The Annunciation" and Saint Nicholas (N-2) at the other icon suggests that the ground should have been prepared by a calcium rich compound, probably gypsum (**Figure 4**). The layers over the ground in these areas are sufficiently thin to not strongly attenuate the Ca K radiation.

The presence of Fe in the spectra from both icons should indicate that the gold leafs have been applied using the so called "water gilding" technique [19], which involved adhesion of the gold leaf on a so-called bole; a fine-grained clay colored by iron oxide pigments and bound by water-based glue. Examples of the application of this gilding technique in post-Byzantine icons are widely reported [20] [21].

Additional analyses are needed to explain the presence of small amounts of Pb

in the spectra A-9 in the icon "The Annunciation". It can either indicate the practice of preparing the ground layer by applying lead white on gypsum, which was used in some cases as reported by Kouloumpi [22], or it can be related with the application of "mordant (oil) gilding" technique, during which the gold leaf is applied over a thin layer containing siccative oils and/or resins mixed with Lead-based materials, to speed up the drying process and to obtain the desired color [19].

Figure 5(a) and **Figure 5(b)** are presented the relative intensities of the spectra measured at different yellow colored areas in both icons. As was previously discussed, the bright yellow used for the aureoles and the backgrounds in both icons (A-9, A-3 and N-2, N-1) are made of gold. In the spectra of A-3 and N-1, apart from Au, we observe the constituents of the pigments used for over paintings. In A-3 the high presence of Fe can be related with the dark tree painted over the gold (probably green earth mixed with carbon black), while Pb and Hg in N-1 are related with the pigments used for the red letters.

In both icons there are some yellow areas that are not prepared with gold (A-7 and N-3, N-5, N-13). The presence of Fe in the spectra of A-7 confirms the use of yellow ochre ($FeO(OH)\cdot nH_2O$) mixed with lead white for the yellow color of the walls in the icon The Annunciation. The flesh tones at the icon Saint Nicholas N-3, N-13 should have been prepared by mixing yellow and red ochre with lead white. In the case of N-5 at the beard of the Saint thin brushstrokes of pure white lead are applied directly over the red/yellow ochre.

Different hues of red color are widely used in the icon The Annunciation. The relative intensities of the spectra measured on those areas are presented in **Figure 6**. In some areas (A-13, A-5) the main elements are respectively Hg and Pb, indicating the use of the red pigments cinnabar (HgS) and red lead (Pb_3O_4) without other additions. In the other areas (A-1, A-6, A-14) the main elements are Fe and Ca with small amounts of Hg and Pb, indicating the use of red ochre (Fe_2O_3) mixed with small amounts of cinnabar and white/red lead.

In **Figure 6** are also presented the relative intensities of the spectra measured on areas with dark brown color (A-2, A-8, A-12, A-15). The measurements, showing Fe as the main element in those spectra, indicate that red/brown ochre mixed with some white/red lead and probably carbon black was used for the dark brown colors.

In the icon "Saint Nicholas" the red color is used for the vestments of Christ, the Saint and the Bible. In those areas it is used in two main shades: a red color (N-7, N-11, N-14) and a dark brown color (N-4, N-12). The relative intensities of the elements in the spectra of red and brown painted areas in this icon are presented in **Figure 7**. In the spectra of the parts with the red color we observe the presence of two main elements, Hg and Pb that indicates a mixture of cinnabar with lead white or red. It is interesting to notice that the intensity ratio of these elements is almost constant from one point to the other. This suggests that the same mixture of cinnabar and lead white or red is used for the bright red areas.

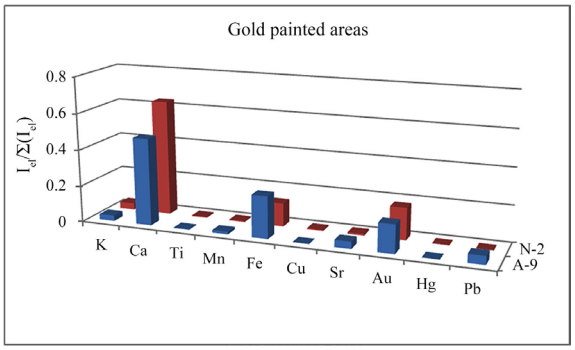
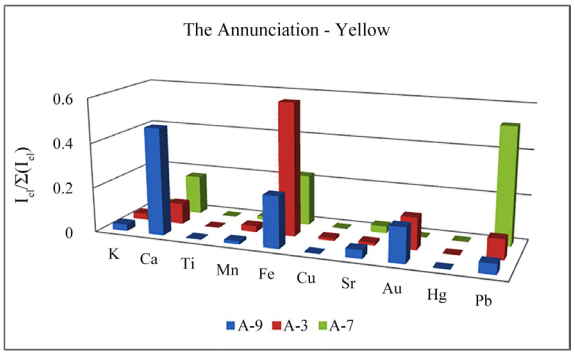
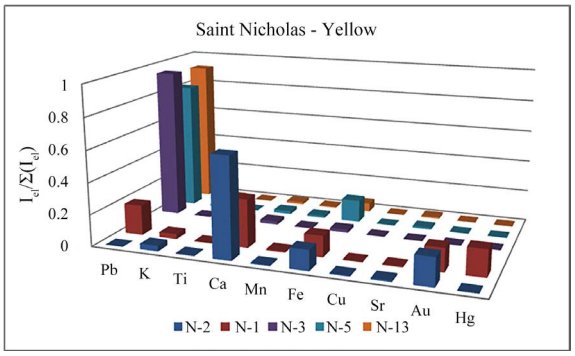


Figure 4. Comparison of the gold layers from both icons.

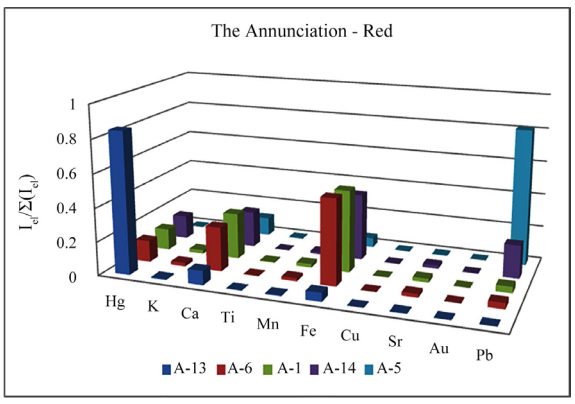


(a)

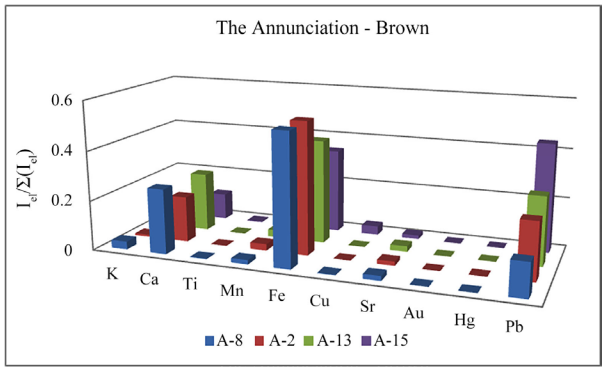


(b)

Figure 5. The relative intensities of the elements in the spectra of yellow painted areas.



(a)



(b)

Figure 6. The relative intensities of the elements in the spectra of red and brown painted areas in the icon "The Annunciation".

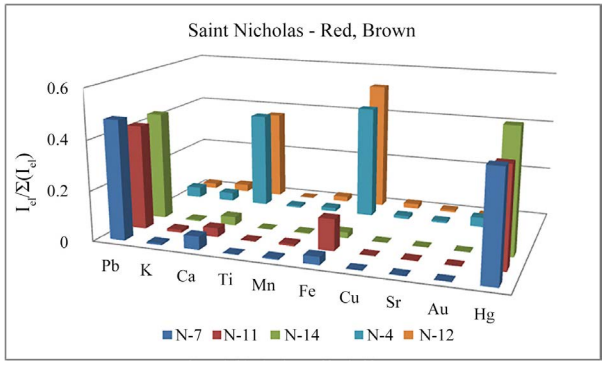


Figure 7. The relative intensities of the elements in the spectra of red and brown painted areas in the icon "Saint Nicholas".

The high presence of Fe in the areas with dark brown colour of the Saint's vestment and the hairs of Christ (N-4, N-12) suggest the use of red/brown ochre mixed with some black pigment. The Ca present in the spectra can originate from different sources like the composition of the ochre, the ground layer and probably can be part of the black pigment (black bone is a black pigment rich in Ca) [17].

Based on these results it looks that the painter had first painted the vestment of the Saint with the dark brown color and then had used the prepared red color (mixture of cinnabar and white/red lead) to give light and contrast to the figure.

In **Figure 8** are presented the relative intensities of the spectra measured at the hair of Archangel Gabriel (A-8) in the icon "The Annunciation" and the hair of Christ (N-4) in the icon "Saint Nicholas". The results show that the painters of both icons had used a similar mixture of red/brown ochre with small additions of white/red lead and black pigment for the dark brown color of the hairs.

The green color in different hues was used in the icon "Saint Nicholas". The results of the measurements are presented in **Figure 9**, where the green areas contain mainly copper and lead. The green color of the Christs's himation (N-6) is prepared with pure copper based greens (there exist two copper based green pigments, malachite ($CuCO_3 \cdot Cu(OH)_2$) and verdigris ($Cu(CH_3COO)_2 \cdot nCu(OH)_2$),

which cannot be distinguished by XRF techniques). The same copper based greens mixed with lead white are used for the green grayish color of omoforion of the Saint (N-9, N-10, N-15), while the dark colored crosses of the omoforion (N-8) should have been prepared by the application of a black colour pigment over the green grayish color.

As was previously mentioned XRF measurements cannot directly identify the black pigments, but from the above discussions we can suggest the application in both icons of carbon based black, like charcoal and/or black bone (C + $Ca_3(PO_4)_2$), which have widely used during that period.

5. Conclusions

A simple XRF spectrometer assembled at our lab was successfully used for *in-situ* and nondestructive identification of the painting materials in two 15th century icons from the Onufri Museum in Berati, Albania.

A small number of pigments were clearly identified by XRF measurements in both icons (Table 3). This include Lead white for the white color, gold and yellow ochre for the yellow color, red lead, cinnabar and red ochre for the red color, as well as cooper based pigments for the green color.

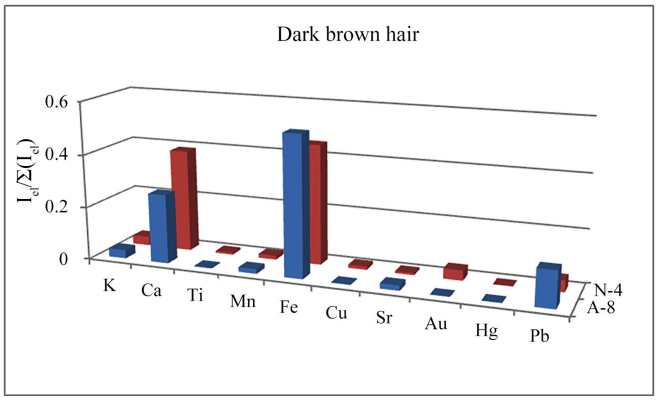


Figure 8. Comparison of the dark brown colors used to paint the hairs in both icons.

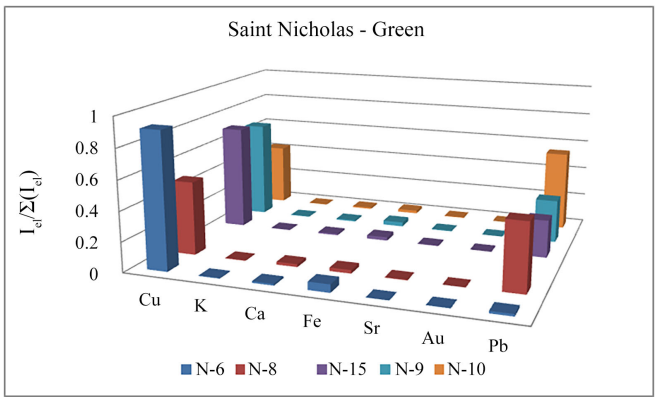


Figure 9. The relative intensities of the elements in the spectra of green painted areas in the icon "Saint Nicholas".

Table 3. Summary of the main pigments identified in each icon.

	The Announcement	Saint Nicholas	
Ground	Gypsum/Calcite (?)	Gypsum/Calcite (?)	Ca
White	Lead white	Lead white	Pb
Yellow	Gold	Gold	Au
	Yellow Ochre	Yellow Ochre	Fe
Red	Red Ochre	Red Ochre	Fe
	Red lead	Red lead	Pb
	Cinabar	Cinabar	Hg
Green	Green earth (?)	Cu based green	Cu
Blue	Indigo or Lapis lazuli (?)	-	-
Black	Carbon black (?)	Carbon black (?)	-

(?), Not directly identified.

At the same time, the obtained results raised some new questions that need further investigations by the use of additional analytical techniques. These include the clear identification of pigments composed of low Z elements (charcoal and bone black in the black and gray colors and indigo or lapis lazuli in the blue ones) as well as the clarification of the ground layer preparation or the gilding technique used at the icon "The Annunciation".

The results show that in both icons are used similar pigments, which are in accordance with the Byzantine icon painting tradition. The same type of pigments is reported to have been found in a 15th century Greek icon of "The Mother of God, Hodegetria" [21].

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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