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STUDIES ON PIGMENTS OF RELIGIOUS MURAL PAINTINGS USING A PORTABLE X-RAY FLUORESCENCE SPECTROMETER – THE CASES OF URECHESTI-CICANESTI ARGES AND ICOANEI BUCURESTI CHURCHES

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Abstract. Samples from mural painting of Urecheşti-Cicaneşti Church, Argeş County and of Icoanei Church, Bucharest, were analyzed by X-Ray Fluorescence (XRF). For Urecheşti-Cicaneşti Church relevant results are the use of cinnabar in original painting and the presence of Paris-green and lemon-yellow (barium chromate) – both toxic chemicals – from 1950 restoration. For Icoanei Church we identified gold remnants in original haloes and four white pigments: lead white, zinc white (probably from 1873 or 1889 oil re-painting), smaller quantities of lithopone but also titanium white probably used for retouching (completing gaps-lacunae) after 1930.

Key words: X-Ray Fluorescence, pigments, mural painting, restoration.

1. INTRODUCTION

Mural painting has a major importance in the case of a Church in Orthodox world. Starting from the Middle Ages, rulers or boyars who took care of painting a church were considered founders, just as those who had built it. Moreover, mural painting, besides being an "adornment", represents a moralizing, theological and educative discourse, having a historical-aesthetic value and an extra-aesthetic one at the same time. Mural painting restoration has become an interdisciplinary field, including a previous investigation of the monument, of the specific microclimate conditions, the analysis of materials - especially of pigments. The physicist role is to identify the original and the re-painting added pigments to give to restorer very important information how to eliminate the over-painting and to choose identical or very similar with the original pigments for restoration [1, 2].

2. REGIONAL SETTING

The wooden Holy Trinity Church from Urecheşti-Cicaneşti, Argeş County (Fig. 1a) was built around 1832 by people having leading positions in local community. The original painting is from 1832, but major restorations, including repaintings, were made in 1871 and in 1950 [3].

Icoanei Church from Bucharest (Fig. 1b) was built between 1784-1786 by Panait Babeanu, an important captain in the local military forces "lefegii". The church is a product of Turkish-Fanariot regime troubled times. The initial ensemble painted by Grigore Zugravul (1784-1786) in a fresco technique was over-painted in many stages with different procedures, the final layer being an oil painting, unfortunately chemically not compatible with the fresco. Recent (2010-2017) restoration work highlighted the evolution of painting interventions in time, in many cases leading to the re-discovery of the original 18th Century iconography [4].

Fig. 1a – Holy Trinity Church from Urecheşti-Cicaneşti (in the background a modern brick Church).

Fig. 1b – Icoanei Church from Bucharest.

3. MATERIAL AND METHODS

Small samples from the mural paintings – internal and external from the Holy Trinity Church in Urecheşti village – Cicaneşti and only internal from Icoanei Church, Bucharest, were analyzed in our institute's laboratory of archaeometry. For the first church the sampling was performed on some icons from iconostasis, on painting of the founders and on few external Saints images. In the case of Icoanei church the sampling was performed on some areas of Altar painting.

The over-paintings (re-paintings) often distort or completely hide the original image. This problem is extremely important since it may lead to irreversible alteration of the original painting. This is the case of Icoanei Church where the oil over-painting covered original gold leaves put on initial fresco images.

Because X-Ray Fluorescence (XRF) elemental analysis method is completely nondestructive [5,6,7], we used an X-MET 3000TX+ portable XRF spectrometer (40 kV – Rh anode tube) to identify the elemental composition of pigments from original and restoration or re-paintings. The measurement spot size was about 30 mm^2 – a description of the spectrometer in Cristea-Stan et al. [8]. Few measurements were performed with our new portable TRACER 5 'BRUKER spectrometer (40 kV tube Rh–anode) which features as a novelty a CCD camera for viewing samples and the data acquisition done by a built-in microcomputer coupled with a Laptop for a remote control.

The identified pigments are Fe, Co, Cu, Zn, As, Pb, Hg, Au, Ba. Low Z elements (C, N, O, Na, Mg, Al, Si, S, P, Cl) are difficult to be determined due to their absorption into the air. XRF analysis can't identify the chemical compounds, only the main elements (especially metals) and some relevant impurities from mineral pigments.

4. RESULTS AND DISCUSSION

4.1. The Holy Trinity Church From Urecheşti-Cicaneşti, Arges County

We measured areas of different colors on icons from iconostasis and on external and internal mural paintings, the investigation indicating the use of the same mixed pigments, practically all containing ochre.

Relevant for the red color from iconostasis (see Fig. 2) is the original cinnabar (mercury sulfide HgS) overlaid with minium (red lead Pb_2PbO_4), probably from 1871 restoration. Traces from the original painting of 1832 are also found in the painting of the founders, where red is also given by cinnabar mixed with minium (see Fig. 3). The pecularity in the case of founders (see Figs. 4 and 5) is the brown (darkened) aspect generated by the transformation of cinnabar in meta-cinnabar (a polymorph of cinnabar) due to the exposure to light with a wavelength between 400 and 570 mm (this is the light spectrum region corresponding to cinnabar). Currently, this alteration may be removed mechanically [1].

Fig. 2 – The iconostasis of the Holy Trinity Church from Urecheşti-Cicaneşti, Argeş County.

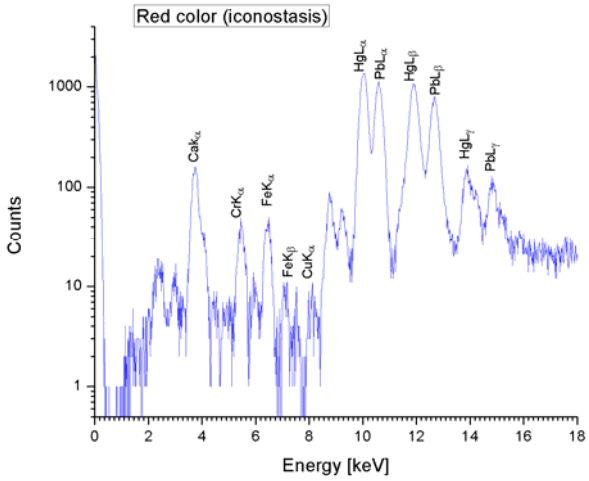

Fig. 3 – XRF spectrum – red area (iconostasis).

Fig. 4 – Founders painting (in pronaos – narthex).

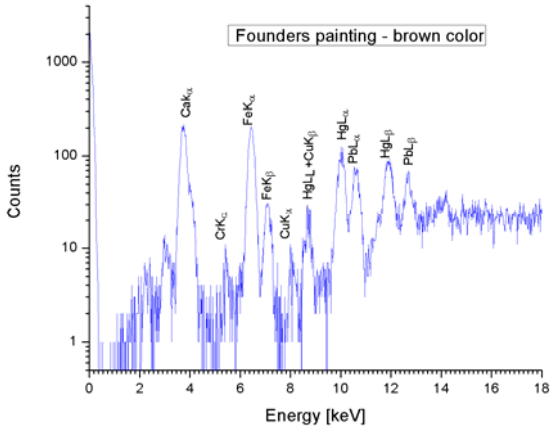

Fig. 5 – XRF spectrum – brown area from founders picture.

The green color was originally an artificial copper pigment, over-painted with Paris green (arsenic-copper combination) – $(Cu(C_2H_3O_2)_2 \cdot 3Cu(AsO_2)_2)$ probably in 1950 – see Figs. 6 and 7 of external mural painting in the altar area. Paris green ("verde de Paris" – Scheele's green) is a strong toxic insecticide if it is inhaled or eaten, probably used because it was a cheap chemical.

Fig.6 – External wall mural painting – altar area.

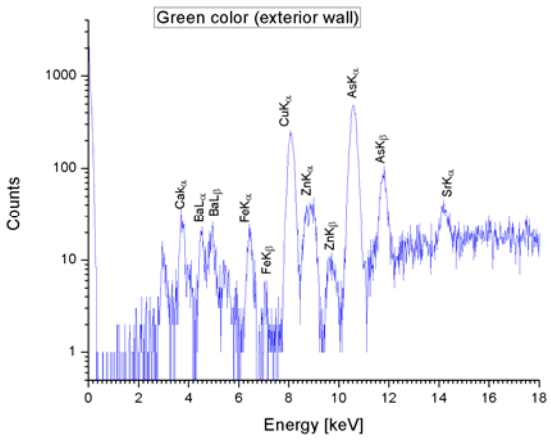

Fig. 7 – XRF spectrum – green area from external mural painting.

An interesting case is the yellow color, initially realized with gold ochre (yellow ochre $FeO(OH)\cdot nH_2O$) and re-painted in XXth Century in the area of Saints halo with the pigment known as lemon-yellow (barium chromate - $BaCrO_4$), also a toxic chemical Figs. 8–9.

Fig. 8 – Some Saints (mural painting from South internal wall).

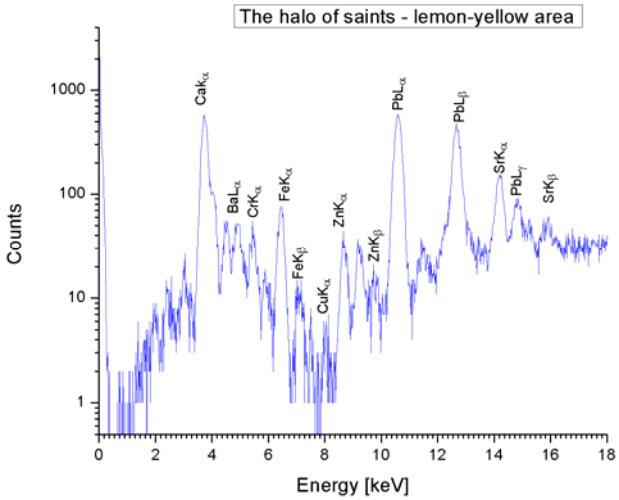

Fig. 9 – XRF spectrum – The halo of Saints (lemon-yellow area).

The blue pigment is Prussian blue ($C_{18}Fe_7N_{18}$).

The white color was originally from lime white – $Ca(OH)_2$. Repainting (1871 or even later) was done with zinc white (ZnO), and in 1950 with titanium white (TiO_2).

4.2. The Case of Icoanei Church from Bucharest

The analyses performed on the samples showed that the painting is composed from two layers (initial fresco and oil) applied on mortar. Oil repairs were the result of two stages of restoration: 1873 and 1889 – see Figs. 10 and 11. The color oil film was sometimes applied directly to the original fresco painting, other times had an intermediate layer of lime-sand or gypsum [3].

Fig. 10 – Icoanei Church, Bucharest – Painting on internal wall after removal of oil re-painting and conservation-restoration (Gabriela Ştefăni□ă [9]).

Fig. 11 – Pronaos-narthex, Northern part – exfoliations of oil re-painting are observed (Gabriela Ştefăni□ă [9]).

Our most spectacular result is the identification of gold (remnants of thin foils) in the golden halo, put on a yellow ochre layer (most probably bole) – see Fig. 12. Four white pigments were identified: lead white,

zinc white (probably from 1873 or 1889 oil re-paintings), smaller quantities of lithopone ($BaSO_4$*ZnS), but also titanium white probably used for retouching (completing gaps-lacunae) after 1930. The red pigment is minium – see Fig. 13.

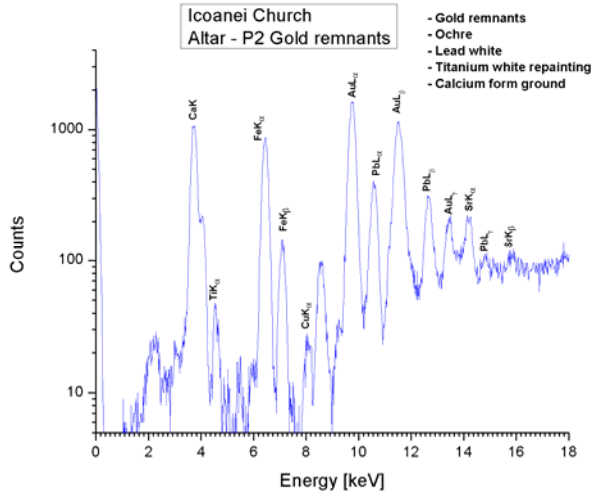

Fig. 12 – XRF spectrum – gold remnants (Altar).

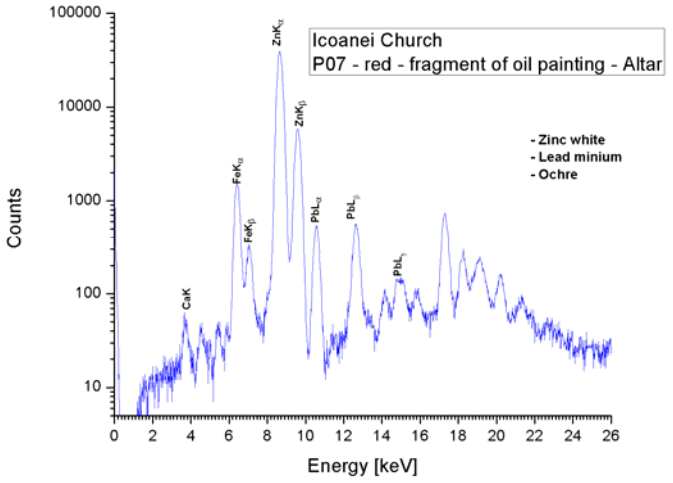

Fig. 13 – XRF spectrum – red area (fragment of oil painting – Altar).

The green pigment is green-earth, a copper-based pigment – malachite $Cu_2CO_3(OH)_2$ – copper acetate $Cu(CH_3COO)_2$ mixed with chrome green (Cr_2O_3) – see Fig. 14. For blue color we identified cobalt-blue ($CoAl_2O_4$), probably the original pigment of the fresco, but also some Prussian blue from restorations. Orpiment (As_2S_3) was also used probably to obtain a more pale color – see Fig. 15. Ochre (Fe_2O_3) is present almost everywhere, as well as calcium from the primer.

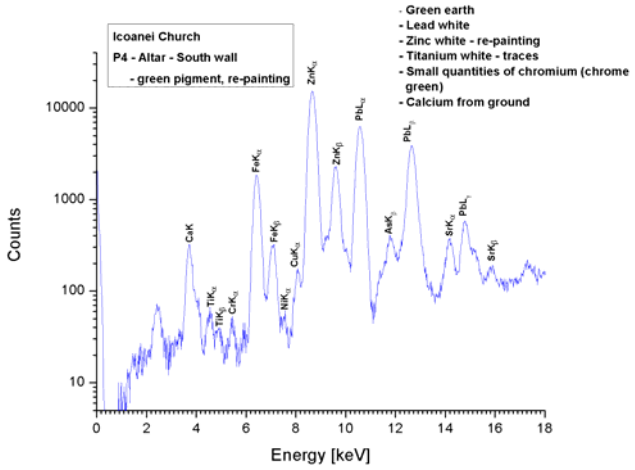

Fig. 14 – XRF spectrum – green area (Altar – South wall).

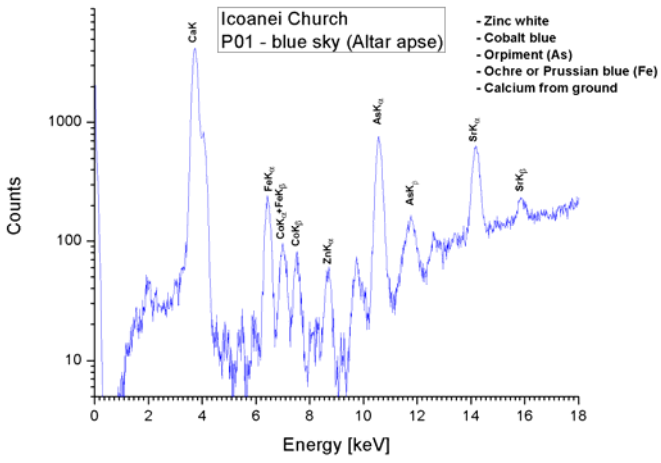

Fig. 15 – XRF spectrum – blue area (Altar apse).

5. CONCLUSIONS

Our studies demonstrated the important role portable analytical instruments plays in the correct restoration of mural paintings, in this case X-Ray Fluorescence (XRF) spectrometers. We identified both original and over-painting pigments for two historical churches, focusing on the case of an original fresco painting covered with later oil colors layer. This information is essential for a good restoration, helping restorers in cleaning, remove of bad repairs and in selection of adequate pigments to obtain a painting very close to the original one.

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