APPLICATION OF X-RAY FLUORESCENCE ELEMENTAL ANALYSIS FOR MURAL PAINTING RESTORATION OF OTETEȘANU CHURCH IN MĂGURELE (PAINTED BY GH. TATTARESCU)

DANIELA CRISTEA-STAN, B. constantinescu, catalina chioideanu, corina anca simion

Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering, P.O.Box MG-6, RO-077125 Bucharest-Magurele, Romania, E-mail: daniela@nipne.ro

Received October 6, 2016

Abstract. Pigments used in 1853 by famous Romanian painter Gh. Tattarescu for oil mural painting and icons-iconostasis of Church St. Constantine and Helena located in Măgurele, Ilfov County analyzed using a portable X-Ray Fluorescence spectrometer are discussed. The chemical element predominant in all spectra for the red areas is mercury suggesting the pigment is cinnabar (HgS - mercury sulfide). In pink areas we detected Hg together with Pb, which means cinnabar was mixed with lead white – (PbCO3)2·Pb(OH)2. Yellow pigment was made from a mixture of chrome-yellow (PbCrO4) and ochre (Fe based yellow ochre – Fe2O3 • H2O, – hydrated iron oxide). In a blue area (an iron-based pigment – very probably Prussian blue – Fe₃(CN)₆·H₂O) we detected the presence of zinc suggesting a late repainting with zinc white (ZnO) on the original lead white layer.

Key words: XRF, pigments, oil mural painting.

1. INTRODUCTION

Conservation-restoration is an activity devoted to the preservation of cultural heritage for the future. The traditional definition of the role of the conservator-restorer involves the examination, conservation, restoration and preservation of cultural heritage using any methods that prove effective in keeping that property in as close to its original condition as possible for as long as possible.

The conservator-restorer applies some simple ethical guidelines, such as:

– minimal intervention to avoid modifications of initial concept (e.g. no oil-painting restoration on old tempera mural painting);

– appropriate materials (close to original) and methods that aim to be reversible to reduce possible problems with future treatment, investigation, and use [1];

– full documentation of all work undertaken [2].
In the spirit of these guidelines, our investigation helps a correct and an efficient conservation-restoration of oil-painted (mural and on wood-icons) items, through in situ characterization of the original painting materials and from ulterior restorations-interventions based on a portable X-Ray Fluorescence (XRF) spectrometer.

2. REGIONAL SETTING

Orthodox Church St. Constantine and Helena from Măgurele, Ilfov County, is a church built in the late eighteenth century, after 1791. Between years 1851–1853, Ioan Oteteleşeanu with his second wife, Elena, born Filipescu, decides to re-build it. The “new” church is built of thin bricks and was endowed with religious objects, having the patrons Sts. Constantine and Helena, and the second patron St. John the Baptist. We don’t know the name of the founders, the author and the craftsmen who initially raised this Church (after 1791). We have no information on the original architecture and paintings, but it seems that in the second half of the nineteenth century, when it was rebuilt, the architecture was changed and the 18th Century painting disappeared. The new (mural and iconostasis) painting was realized by Gheorghe Tattarescu in 1853, in a special style that makes the transition from Byzantine to the Renaissance style. The icons painted by Tattarescu are true masterpieces, the harmony of lines, proportions, details and the predominant colors of pink and blue being remarkable. Tattarescu is considered the greatest religious painter of our country, being the “artist-author” of many churches as: Zlătari, Sf. Spiridon Nou and Crețulescu in Bucharest, Bistrița and Câmpulung Monasteries.

Fig. 1 – King David portrait before and after restoration.
After 2000, a long difficult process of repair of the Church started. In 2010 the restoration of the mural painting begun under the expertise of a team lead by painter-professor Silviu Petrescu (Fig. 1).

For a correct restoration it was necessary to identify the mineral pigments used by the old master and the eventual re-paintings.

3. MATERIALS AND METHODS

The XRF elemental analysis method is completely nondestructive and can be performed directly in situ [3, 4]. For that, we used a portable Oxford Instruments X-MET 3000TX+ XRF spectrometer. The pigments identified by scanning specific areas were inorganic pigments containing Fe, Co, Cu, Zn, As, Pb, Hg, Ag, Au, Sn, Sb, Ba. The exciting X-ray beam of the spectrometer is generated by a 40 kV – Rh anode tube. The detection system is a PIN silicon diode detector with Peltier cooling. The resolution of the detector is 270 eV for the K$_a$ line of Mn (5.89 keV). The measurement spot size is about 30 mm$^2$. The spectrometer has a Hewlett-Packard (HP) iPAQ personal data assistant (PDA) for software management and data storage [5]. Light elements (e.g. C, N, O, Na, Mg, Al, Si, S, P, Cl) can not be determined in in situ analysis due to their absorption into the air. From our analysis we can’t identify the chemical compounds, but only the main metals found in mineral pigments and some relevant impurities.

4. RESULTS AND DISCUSSION

As general rules our investigation showed the use of mixed pigments, both in the icons and mural painting. We measured zones of different colors both for the iconostasis icons and for Church frescoes proving Tattarescu used the same pigments both for wood painting and for mural painting.

In order to be easily identified, investigated areas were photographed and marked with letters.

For St. George wall picture (Fig. 2) we measured the area of his legs: carnation, golden shoes, red jacket and blue mantle. Red color (Fig. 3) is from a mercury-based pigment (cinnabar – HgS) which is found in small quantities in carnation too.
Yellow pigment (Fig. 4) was probably made from a mixture of chrome-yellow (PbCrO$_4$) + yellow ochre (Fe$_2$O$_3$ $\cdot$ H$_2$O – hydrated iron oxide). Blue color (Fig. 5) is from an iron-based pigment (most probably Prussian blue – Fe$_7$ (CN)$_{18}$·H$_2$O). Note the presence of chrome yellow in all areas. White lead – (PbCO$_3$)$_2$·Pb (OH)$_2$ is also present in all measured areas. However, in some blue areas we detected a relatively high presence of zinc, most probably from zinc white. The simultaneous presence of Pb and Zn in the region of the cupola, and the variations of the ratio of the relative intensities for Pb-L$_{\alpha}$ and Pb-L$_{\beta}$ lines indicate a later re-painting based on zinc white, probably in the first half of the XX$^{th}$ century. We also note the presence of iron – an indicator for ochre – in all colors.
For Church’s iconostasis painted by Tattarescu were measured areas of different colors to compare the pigments with those used for mural painting. Our study confirmed the use of the same pigments by Tattarescu both for wood and wall oil painting.

On “The Last Supper” – icon (Fig. 6) we measured a red area (no. 1 – mantle), blue area (no. 5 – mantle), yellow area (no. 3 – Jesus halo and no. 2 – mantle), white-blue area (no. 4 – table).

As was pointed, red pigment contains mercury (most probably cinnabar HgS) – Fig. 7, which is also found in smaller quantities in pink shirt of Jesus, suggesting cinnabar was mixed with white lead.

As in oil mural painting of the Church, for icons yellow – Fig. 8 – was probably made from a mixture of yellow ochre with chrome yellow. Note the presence of iron – an indicator of ochre in all colors. Blue color – Fig. 9 – was made from an iron-based pigment (most probably Prussian blue) mixed with small
quantities of chrome yellow. Green is made from a mixture of chrome yellow and blue pigment. Note the presence in all the icons of white lead.

Gold (Fig. 10 Apse – nave area) was detected in one ornamental star (see Fig. 11 – no. 1) – probably a gold powder layer deposed on a lead white background. The significant presence of iron in this spectrum suggests red iron oxide (Fe₂O₃ – hematite) was used in preparation of the last layer of gilding.

5. CONCLUSIONS

The pigments used by Tattarescu both for mural oil painting and for the iconostasis of the Măgurele Church are:
- red pigment is based on mercury, most probably cinnabar;
- in Pink areas we also detected Hg, suggesting cinnabar was mixed with lead white;
- yellow pigment was made from a mixture of chrome-yellow and ochre;
- blue pigment is based on iron, most probably Prussian blue; in some blue areas we also observed the presence of zinc suggesting a later repainting with zinc white on the original lead white layer.

As a general observation, iron is present in practically all measured areas which suggest a widespread use of ochre.

Our research shown Tattarescu used multiple layers of color put on a ground, for example a thin layer of ochre (about 20–30 microns) overlapped by a 50–70 microns layer of cinnabar (our capacity of analysis between 30 and 100 microns in depth depends on the layers’ constitutive chemical elements).
In conclusion, our study demonstrated the XRF screening method based on portable spectrometers and applied for in situ analysis is an important help for painting restorers in their work on religious and civil cultural heritage monuments.

**Acknowledgements.** Financial support by Romanian National Scientific Research Agency ANCS grant PN-II-ID – PCE – 2011 – 3 – 0078 is gratefully acknowledged. Many thanks to Mr. Silviu Petrescu for the opportunity to perform the analyses and to take the pictures.

**REFERENCES**
