Village from Muscel by Ion Marinescu Valsan
State of Conservation and the Chromatic Palette

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Ion Marinescu Vålsan (1865 - 1936) was a Romanian painter belonging to the modern Romanian art from the beginning of the 20th century. Many of the paintings painted by him have picturesque landscapes in his native town, Malureni, Arges County. He was influenced by Nicolae Grigorescu. Village from Muscel painting, by Ion Marinescu Vålsan, was examined by several non-invasive techniques (VIS, UV & grazing light examination, IR reflectography, optical microscopy and X-rays fluorescence spectrometry) to obtain information on its chromatic palette and state of conservation. Zinc white, Lead white, Prussian blue, Cinnabar, Chrome yellow, Yellow ochre, Red ochre, Viridian and Burnt umber were used as the pigments, while the preparation layer is from Chalk, Zinc white, Lead white, identified by XRF analysis.

Keywords: oil painting on canvas, VIS, UV & grazing light examination, IR reflectography, optical microscopy(OM), X-rays fluorescence spectrometry (XRF)

The work of art Village from Muscel, undated and signed I. Marinescu, made in oil painting on canvas technique, part of the collection of the Art Museum in Constanta, presents a landscape of countryside with low wooden houses, low walls, light roof. In the foreground you can see a green field on which cattle graze and hens peck. A peasant woman is schematically drawn on the right. Trees and hills are shown in the background. The state of conservation and the chromatic palette of the studied painting were determined based on an analytical protocol using non-invasive techniques: Vis, UV & grazing light examination, IR reflectography, optical microscopy and X-rays fluorescence spectrometry [1-6].

The research is part of the extensive process of conservation-restoration and capitalization of this painting belonging to the modern Romanian art from the beginning of the 20th century.

Experimental part
The areas analyzed by different analytical techniques were selected observing the requirements for works-of-art analysis and the complex composition of the painting. The X-rays fluorescence spectrometry analyzes were carried out in 12 selected points.

Visible (Vis), Ultraviolet (UV) and grazing light examination
The surface of the painting was thoroughly examined in VIS and UV wavelength domains, using a SMZ 800 NIKON stereomicroscope, a lamp with magnifier and fluorescent light CTS ART LUX 20 and a lamp with magnifier and black light CTS ART LUX 70.
Visible fluorescence with UV excitation was useful for gaining information regarding the degradation of varnish, the reflocces and other interventions on the painting surface.
Grazing lights allow documentation of the cracks, loss of colour and highlights the painting technique.

Infrared reflectography
Examination of painting by IR reflectography, a non-destructive method used in art forgeries detection, can reveals the preparatory drawing, changes in painting composition, damages, fillings and retouches. The painting was studied using an infrared reflectography system MOD M-IR 10 new, CTS Italy, using 0.70-2 mm wavelength [2, 3].

Optical Microscopy (OM)
The painting was examined by OM using a SMZ 800 NIKON microscope, at magnification between 50X and 100X. This investigation concerned the colour layers, superposition and mixture of pigments, the working technique, the possible fissures, cracks and other types of degradations [3, 7, 8].

X-rays fluorescence spectrometry (XRF)
The elemental analysis of mineral pigments and ground layers was carried out in-situ [7, 8, 9-14] using a XRF spectrometer type INNOV-X Systems Alpha Series Bruker, non-destructive portable instrument. The apparatus is equipped with an X-ray tube with W anode, working at the maximum parameters of 35kV voltage and 40ìA current intensity; the fluorescence radiation is detected and analyzed with a PIN Si detector, thermoelectrically cooled, controlled by a minicomputer. For spectra acquisition and semi-quantitative analysis, for heavy matrix, the analytical mode software has been selected, with 30s excitation duration, and for light matrix (60s excitation), the Soil mode software was used.

Results and discussions
The purpose of our research was the identification of the pigments used in the painting Village from Muscel, to assess the deteriorations, to identify previous paintings as well as possible the changes of the original pictorial composition.
The first information was provided by visual examination in order to determine aspects concerning the deterioration state of the pictorial layer. This investigation allows us to estimate the most efficient techniques of analysis which should be applied in order to identify the set objectives.
The preparation layer is applied by the painter after previously stretching the canvas on the frame. The examination of the painting showed that the preparation layer is made out of animal clay and chalk, as identified by physical and chemical analyses. The high concentration of clay provided the ground with a pronounced rigidity, which led to strong cracks that influenced the paint layer.
The paint layer is applied by the author in several stages. In the areas containing the sky, grass, hill in the background, trees and signature, the paint layers were applied after the painting had dried. The time difference is confirmed by the fact that in these areas the paint is matted, as the quantity of binding agent is showing a deficit and the quality of the paste is poor. These differences are also emphasized by the UV lamp; the image obtained following the UV examination shows clear evidence on the fluorescence of the initial painting and the lack of fluorescence of following interventions. The paint layer has a good adherence to the ground layer, its degradations being the same as the ones met in the entire pictorial layer. It presents few areas in which the paint was thickly applied and traces of brushing.

The varnish layer is missing, the specific fluorescence being very poor when exposing the painting to UV radiations. The paint subsequently applied by the author stands out by the total lack of fluorescence of the paint layer.

At the painting Village from Muscel (fig.1) are visible small fissures and cracks of the pictorial layer. The back side is oxidized with much adhering dirt.

In the grazing light (fig.2) are visible the network of cracks and plain deformation of the canvas frame.

Figure 3 shows the following: front side in UV light (a), UV light detail, emphasizing the lack of fluorescence of the paint layer subsequently applied by the author (b), UV light detail, emphasizing the signature subsequently applied by the author (c).

IR reflectography study of the painting was focused on the identification of preparatory drawings and the characteristics of the author’s working technique (fig.4). Details of the signature, made by means of IR reflectography, grazing light and UV examination show in figure 5.

The optical microscopy was useful for the assessment of the chromatic and compositional characteristics of the pictorial layers. The analytical points on the painting were selected under optical microscopy in order to choose the representative areas for pigments and preparation layer analysis.
The X-ray fluorescence spectrometry (XRF) was used in order to analyze the inorganic chemical elements present. Thus, the basic pigments used in the creation of the painting were identified. The aim of the XRF study was to identify inorganic pigments, the collected X-ray fluorescence data showing the main elements in the composition of pigments in the work of art. XRF analysis points and images of the colour film visualized by optical microscopy are presented in fig. 6.

Table 1

| Analysis point | Microscopic study | Specific elements (XRF) | XRF analysis results |
|----------------|-------------------|-------------------------|----------------------|
| 1. Blue sky (Fig. 7 a) | The colour is made up of a combination of pigments. Particles of blue pigment are visible | Zn, Pb, Fe | Zinc white, Lead white, Prussian blue |
| 2. White sky (Fig. 7 b) | The colour is made up of a combination of pigments. A white film applied over the blue background is visible. Particles of blue pigment are visible | Zn, Pb, Fe | Zinc white, Lead white, Prussian blue |
| 3. Green tree (Fig. 7 c) | The colour is made up of a combination of pigments. Particles of ochre, green and blue pigment are visible | Fe, Cr, Zn, Pb | Yellow ochre, Viridian, Prussian blue, Zinc white, Lead white |
| 4. Copper tree colour (Fig. 8 a) | The colour is made up of a combination of pigments. Particles of red and yellow ochre pigment are visible | Hg, Fe | Cinnabar, Yellow ochre |
| 5. Black – face (Fig. 8 b) | Particles of dark brown pigment are visible | Fe | Burnt umber |
| 6. Red girdle (Fig. 8 c) | The colour is made up of a combination of pigments. Particles of red ochre and cinnabar pigment are visible | Fe, Hg | Red ochre, Cinnabar |
| 7. White – skirt (Fig. 9 a) | The colour is made up of a combination of pigments. White and yellow ochre spots are visible | Zn, Pb, Fe | Zinc white, Lead white, Yellow ochre |
| 8. Green grass (Fig. 9 b) | The colour is made up of a combination of pigments. Green and blue spots are visible | Fe, Cr | Prussian blue, Viridian |
| 9. Yellow grass (Fig. 9 c) | The colour is made up of a combination of pigments. Particles of yellow and blue pigment are visible | Cr, Pb, Fe | Chrome yellow, Prussian blue |
| 10. Signature (Fig. 10 a) | Particles of brown pigment are visible | Fe | Burnt umber |
| 11. Preparation layer (Fig. 10 b) | Particles of white pigment are visible | Ca, Zn, Pb | Chalk, Zinc white, Lead white |
| 12. Purple- sky (Fig. 10 c) | The colour is made up of a combination of pigments. Particles of white, blue and red are visible | Zn, Pb, Fe, Hg | Zinc white, Lead white, Prussian blue, Cinnabar |
In table 1 are presented the results of optical microscopy, XRF analysis and the pigments identified in Village from Muscel.

XRF spectra of Blue sky, White - sky and Green - tree are presented in figure 7 a, b, c.

XRF spectra of Copper tree colour, Black - fence and Red - girdle are presented in figure 8 a, b, c.

XRF spectra of White -skirt, Green -grace and Yellow -grace are presented in figure 9 a, b, c.
Fig. 10. XRF spectrum Signature (a), Preparation layer (b) and Purplish -sky (c)

XRF spectra of Signature, Preparation layer and Purplish -sky are presented in figure 10 a, b, c.

Conclusions

Ion Marinescu Vălsan uses in Village from Muscel the following pigments: Zinc white, Lead white, Prussian blue, Cinnabar, Chrome yellow, Yellow ochre, Red ochre, Viridian and Burnt umber, identified by XRF analysis.

From results by XRF analysis performed on Village from Muscel art work it follows that the preparation layer is from Chalk, Zinc white, Lead white.

The state of conservation of the painting was assessed under the grazing light examination. Are visible the network of cracks and plain deformation of the canvas frame.

The UV light study of the painting highlights the lack of fluorescence of the paint layer subsequently applied by the author, as well as the signature.

The IR reflectography did not revealed any underdrawings or previous designs, but showed the ratio of black and white tones used in the plastic composition, as well as the artist brushstrokes, helping in characterizing the painter’s working technique.

The results have brought new data to current knowledge and augment the database of materials and techniques used in the beginning of the 20th century in the modern Romanian art.

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