

## THE ROLE PLAYED BY THE SCIENTIFIC TECHNIQUES USED IN THE EXAMINATION AND ANALYSES OF THE MURAL PAINTING OF WOODEN ROMANIAN CHURCHES

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**KEY WORDS:** Chemical analysis, Church, Conservation, Patrimony;

### ABSTRACT

The paper presents the analytical examination of colour samples taken from the frescoes of “Pogorarea Sfantului Duh” wooden church (sec. XVII), Dretea Village, Cluj County, Romania. The pigments were investigated through FT-IR spectroscopy, completed by UV – VIS – NIR spectroscopy, by ICP – AES and by observations of the optical microscopy. Was determined the whole palette of colours used by the popular masters, the pigments having mineral nature (red lead, blue ultra-marine, yellow ochre).

### 1. INTRODUCTION

The wooden church, “Pogorarea Sfantului Duh”, Dretea Village, Cluj County, was built in 1672, from oak wood on the foundations of an older church. It is one of the most representative monuments of religious architecture from Cluj County.

Because of the advanced deterioration it was decided to save the church through its movement at The Astra Museum, Sibiu, Romania, one of the most important ethnographical museum in Romania. This way the monument will be integrated to the world touristic circuit. The code of registration in the List of Historic Monuments is 13B0361.

The restoration and conservation of this monument supposes a deep knowledge of the materials it was created of, but also the interactions of those materials with the environment.

The respect for the work of art imposes the usage of some techniques of investigation less destructive, if it is possible.

In the last years, the objects belonging to the cultural patrimony were investigated through FT-IR spectroscopy, too. But in order to have a complete image of the palette of colours used by the popular masters, we need to use other analytical techniques, too. The literature dealing with this problem shows us that we can use successfully, other techniques such as: XRD, SEM-EDAX, the RAMAN micro-spectroscopy, the UV-VIS-NIR spectroscopy and ICP-AES.[1-3]

### 2. EXPERIMENTAL PART

The samples analyzed were taken from the characteristic areas of the painting, so that to cover the entire surface of the painting and the chromatic gamma. From this church were taken the following samples:

Sample	The area from which it was taken	The color of the painting coat
P 1	Altar	Red
P 2	Altar	Ultramarine
P 3	Nave	Yellow
P 4	Narthex	Red-brown

The color samples were analyzed through optical microscopy, FT- IR and UV-VIS-NIR spectroscopy, and ICP-AES, in order to identify the pigments' type.

- The analyze of the pigments through FT-IR spectroscopy

The pigments were submitted to a spectral analysis in the IR domain (400 – 4000 cm<sup>-1</sup>), using the FT-IR apparatus, 620 JASCO, Japan. The technique in direct transmission was applied using the KBr pellet procedure.

- The analyze of the pigments through the UV-VIS spectroscopy

The samples were analyzed using the UV-VIS spectroscopy, in the 200 - 2300 nm domain, with the V 570, JASCO apparatus, made in Japan. The technique used was that of the direct examination of the material, by putting it in the tub of the device for diffuse reflection. By using this technique, the main spectral and chromatic characteristics have been identified.

For the identification of the spectral characteristics there were used standards.

- The determinations were made with the ICP-AES technique, using the Spectroflame P (Analytical Spectro-Instruments, Germany).

The above mentioned apparatus permits simultaneous determinations of more elements, the correction of the environment and the scanning of the separation spectral lines.

### 3. RESULTS AND DISCUSSIONS

The conservation status of the mural painting from the above mentioned monument is precarious. In time, the monument acted as a live organism, being caught up in a dynamic relation with the environment.

In the application of the restoration and conservation treatments, this behavior of the monument must be taken into account. Any treatment that is wrongly applied, any use of a bad product, could damage irremediably the monument.

That is why the making of some chemical investigations was imposed. In the realization of these investigations we avoided the diagnose based on only one type of clues (it is not enough to determine the nature of the materials, based on the analyses of one clue).

When examining the sample **P 1**, in the IR spectrum (Fig. 1), we observed the predominant presence of the priming (based on CaCO<sub>3</sub>). Besides the above mentioned chemical compound, the sample contains also a compound based on Pb<sub>3</sub>O<sub>4</sub>, situated in the wavelength of 455 cm<sup>-1</sup>, 530 cm<sup>-1</sup> and 1680 cm<sup>-1</sup>. [4]

The analysis in UV-VIS of the same sample (Table 1) showed a relatively intense band at 540 nm and shoulders in the 600-800 nm domain. The 540 nm band belongs to the pigment

containing  $Pb_3O_4$ . The presence of the shoulders in the 600 – 800 nm areas indicates that the pigment was contaminated by other colors that in the photos with stratigraphical sections had a shade of yellow.

The colour characteristics (Table 2) indicate the presence of a large quantity of priming ( $L^*$  had a high value), besides the red coloring pigment ( $a^*$ ) and the traces of yellow pigment ( $b^*$ ).

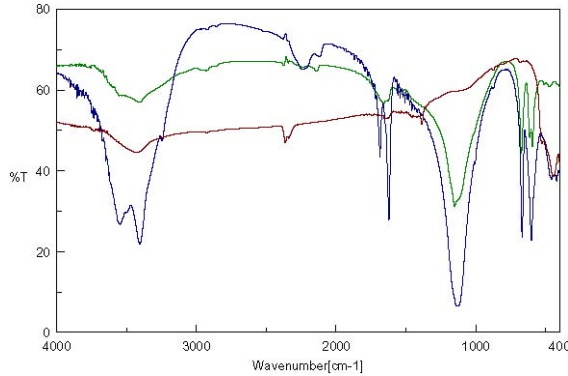


Figure 1. IR spectra of sample P 1

— P 1  
 —  $Pb_3O_4$   
 — First layer of paint

The IR spectrum of the P 2 sample (Fig.2) indicates the predominance of the  $CaCO_3$  based priming. Besides this in the sample there are bands at  $3626\text{ cm}^{-1}$ ,  $3440\text{ cm}^{-1}$ ,  $1110\text{-}1088\text{ cm}^{-1}$ ,  $1016\text{-}1010\text{ cm}^{-1}$ ,  $610\text{ cm}^{-1}$  and  $504\text{ cm}^{-1}$ , that indicates the presence of the ultra-marine pigment. [4,5]

In the UV - VIS domain (Table1) there were low intensity bands in the areas 480-800 nm, 450 nm, 505 nm and 714 nm, indicating the presence of the blue pigment and green impurities.

The colour characteristics (Table 2) indicates the presence of the blue pigment ( $b^*$ ) and that of a green shade impurity ( $a^*$ ).

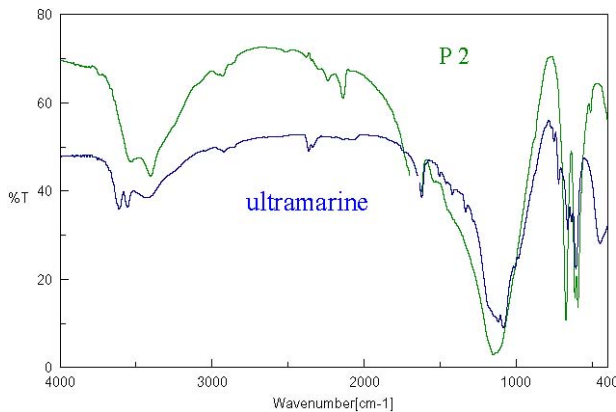


Figure 2. IR spectra of sample P 2

For the P 3 sample the IR spectrum reveals the presence of the yellow pigment, with FeO component. (Fig.3)

The UV-VIS-IR spectrum (Table1) indicates a wide band in the 400-650 nm area, centered at 512nm and another band at 668 nm, indicating the presence of the yellow pigment, modified by the priming support and contaminated, probably, with traces of the blue pigment, from the neighborhood area.

The chromatic analysis (Table 2) indicates the presence of the yellow pigment ( $b^*$ ) and that of an impurity.

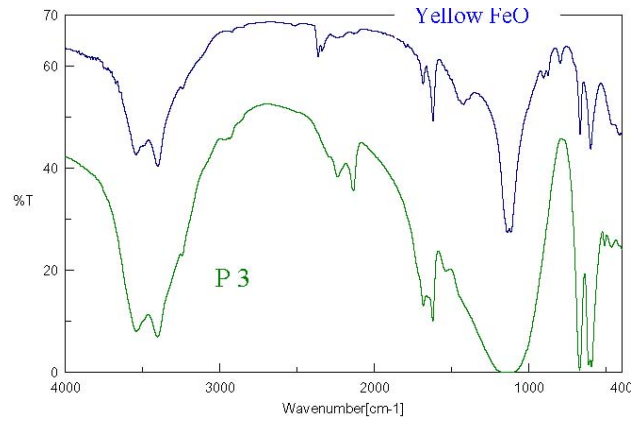


Figure 3. IR spectra of sample P 3

At the sample P 4, the IR spectrum (Fig.4) indicates the presence of a pigment, based on FeO, marked by the  $520\text{ cm}^{-1}$  band, derived from the pure pigment.

The UV-VIS-IR (Table 1) presents a wide band in the area 350-600 nm, centered at 540 nm, belonging to the red pigment and low intensity bands at 630 nm, 760 nm and 800 nm, that indicate the presence of some blue-greenish impurities.

The chromatic analysis (Table 2) indicates clearly the presence of the red pigment ( $a^*$ ), but, also, the presence of a slightly bluish shade ( $b^*$ ).

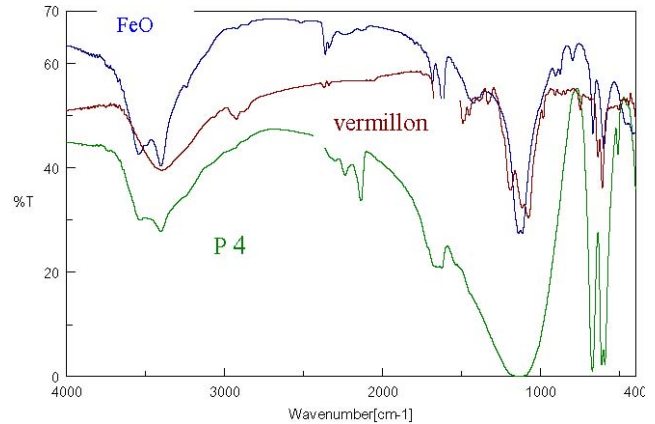


Figure 4. IR spectra of sample P 4

Table 1. Characteristic bands in the UV-VIS spectrum - Dretea Church- Cluj County

Sample	$\lambda_{\text{sample}}$ [nm]	$\lambda_{\text{standard}}$ [nm]
P 1 - red	540	530; 1380
P 2 - blue	450; 505; 714	370; 540; 710; 1090
P 3 - yellow	512; 668	360; 490; 630; 800; 1420; 1920
P 4 - red	540; 630; 760; 800	292; 525; 1146; 1926; 360; 490; 630; 800; 1420; 1920

Table 2 – The colour characteristics - Dretea Church- Cluj County

Sample	$L^*$	$a^*$	$b^*$	$C^*$	H
P 1	88,58	2,00	0,04	2,01	1,15
P 2	93,19	-0,26	-2,61	2,60	84,31
P 3	89,93	0,07	0,53	0,53	7,52
P 4	92,29	1,03	-0,73	1,24	35,33

Where: L\* - luminosity; a\* - green/red; b\* - blue/yellow; c\* - chroma; H - shade angle;

The results obtained by using the ICP-AES method confirm the dates obtained through the FT-IR and UV-VIS-NIR spectroscopy. (Table 3 and 4).

Table 3. The composition (%) of the pigments used at the Dretea Church– Cluj County

Sample	Pb %	Zn %	Si %	Mg %	Fe %	Cu %
P 1	2,58	0,036	0,09	0,04	0,098	0,006
P 2	1,96	0,029	0,14	0,086	0,14	0,021
P 3	0,05	0,007	0,09	0,046	0,11	0,113
P 4	0,027	0,005	0,05	0,018	0,10	0,001

Table 4. The composition (%) of the pigments used at the Dretea Church– Cluj County

Sample	Al %	P %	Sn %	Cr %	Mn %
P 1	0,002	0,031	≤ 0,005	0,007	0,004
P 2	0,21	0,019	≤ 0,005	0,006	0,008
P 3	0,07	0,014	0,014	0,002	0,006
P 4	0,046	0,004	≤ 0,005	0,0019	0,003

Sb,Ti,Ni ≤ 0,005; Cd ≤ 0,001

Table 3.a. The chemical composition of the pigments used at the Dretea Church– Cluj County

Sample	Predominant elements	Results
P 1	Pb	Red pigment (red lead)
P 2	Si, Al, Pb, Fe	Blue pigment, ultramarine type
P 3	Fe	Yellow-ochre pigment, hydrated iron oxides
P 4	Fe	Red-brown pigment (cinnabar mixed with hydrated iron oxides)

#### 4. CONCLUSIONS

The results presented in this paper represent a first stage of a new methodology based on complementary techniques, which can be applied in a systematic study. These results are used in the election of the similar to the original mixture of materials, in order to avoid the risk of ulterior rejections.

The modern analytical techniques (the FT-IR,UV-VIS-NIR spectroscopy, and ICP-AES) together with the classical ones (the optical microscopy) permitted the identification of the nature of the pigment used by the popular masters and the use of an adequate conservation-restoration treatment.

The respect for the artwork supposes the usage of the least destructive techniques of investigations.

The ICP-AES method is adequate for the analysis of the pigments because it has low limits of detection, it is very quick and permits the investigation of several elements simultaneously, reducing the quantity of solutions necessary for the measurements.

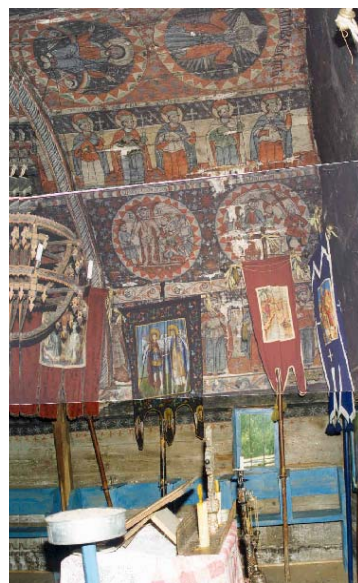
The FT-IR spectroscopy makes exact determinations through the comparison of spectra, so it needs standards. Anyway the possibility offered by the apparatus to analyze very small quantities of substance it is an advantage that must be used.

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Ensemble of the Nave Wall



Ensemble of the Nave Wall



Nave – detail



Iconostasis – detail



Narthex Ensemble