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Dedicated to Professor Liviu Literat
On the occasion of his 85th birthday

SCIENTIFIC INVESTIGATION OF PIGMENTS EMPLOYED FOR „CRUCIFIXION" PROCESSIONAL FLAG PAINTING FROM THE ETHNOGRAPHIC MUSEUM OF TRANSYLVANIA HERITAGE

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ABSTRACT. The processional flag is a cult object belonging to the churches. Nowadays, as well as it was in the past, the flag is carried by people, preceeding the religious processions; it is used on the occasion of bringing icons and holy relics from one place to another; the flag is also used at different ceremonial moments and at funerals. The Ethnographic Museum of Transylvania owns 10 processional flags in various conservation stages. Pigment samples were taken and we present the result of the samples expertise achieved by using the FTIR spectrometry, X-Ray diffraction, X-ray fluorescence and gas chromatography-mass spectrometry for the processional flag with the inventory number 8254. The results will be used to recommend several correct conservation and preservation methods.

***Keywords**: processional flag, painting materials, XRF, XRD, FTIR, GC-MS*

INTRODUCTION

Inside the Romanian space the flag had different hypostases: in military and political life, as well as the state flag and banner for the fight; in traditional manifestations, as the wedding, and symbol of the groups of male slime; in religious life that processional flag [1].

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The processional flag is an object of worship kept in churches and used in religious processions, solemn moments and at funeral. His successor Byzantine battle flags, wearing on him the crucifix or representations of religious themes, is a symbol of the fight against sin, against the known and unknown enemies and also a triumph of Christianity [2].

The processional flags are encountered since the IVth century and after Eusebiu Cezarea description's it had the following form: a long spearhead with gold-plated trims intersect with a stick of wood, forming a cross; in the top was placed a crown and trim of gold and precious stones. Horizontal arm of the cross was hanging a flag or a square red canvas, decorated with precious stones and sewn with gold yarn [3].

The processional church, as an object of worship, is a result of association of Roman Legions symbols with Christian icons [1].

At present, processional flag is made from a piece of canvas approximately 1(one) meter long and 60 cm wide or larger dimensions, fixed on a wooden support, an T form stick, which had a cross on the top. On this canvas are painted both sides icons representing: Saints, Christ, Virgin Mary, the Saint protector of the Church and religious themes.

As to the existence of processional flags in the Romanian world, with its poor little churches, it seems they were missing from the majority of Orthodox communities up to the middle of the 18-th century.We could encounter it only in cathedrals and big and wealthy monasteries.

The conservation of processional flags has to be made taking into account the diversity of materials of which they are composed and their functions well defined. Without an adequate scientific method, based on the principles and rules for conservation [4], we will not be able to stop processes of degradation and parts with great historic value will disappear.

Processional flags may be made of two woven fabrics removable, painted separately, or from a single fabric painted on both sides. It is important to study both structure of fabrics from which it was carried out the flag, as well as the technical execution, because during the years the painted fabric had different reactions to the environmental factor, physical-chemical and mechanical.

The support that has to be painted can be made of cotton, line, natural silk, wool or sinthetic fabrics. It is necessary to determine the exact material of support because each of this materials had his own methods and rules of conservation.

The primer, next layer, made from binder and filler material is thin, transparent and irregular. Primer composition helps us in the choice of methods of restoration. Analysis of the primer and its components is usually reduced to determining the chemical composition and microscopic cross-sectional research. In the primer, animal or plant glue, plaster and powdered chalk can be found.

Color layer is homogeneous and thin, in terms of composition, being made up of mineral origin or pigments and organic binder. A layer is made up of two or more color grains. The glue is organic and can be of vegetable or animal origin. The binder is made from egg yolk and egg white, sometimes mixed with resins in tempera paintings or vegetable glues and resins in oil paintings.

The color painted layer is the most important part of the processional flag because it is determining the historical-documentary and artistic value. That is why most of the physical, chemical and physical-chemical research studies with priority the color layer, in order to determine its composition and physical properties.

The protective layer, lacquer, applied for protecting the painting, is prepared in the past from natural resins, which until the late 16 th century, were blended with vegetable glues. Starting with 17th century it was used the topal lacquer and in the 19th century, dammar lacquer [5].

Ethnographic Museum of Transylvania, Cluj-Napoca owns 10 processional flags in different conservation states. Within the project "Modern Methods of Investigation, Authentication and Storage of Icons of the Ethnographic Museum of Transylvania's heritage", developed in collaboration with the Faculty of Orthodox Theology and National Institute for R&D of Isotopic and Molecular Technologies, Cluj-Napoca, different methods have been used for separation, identification and analysis of pigments, support layer and primer layer of processional flags.

The color layer samples for analysis of pigments processional flag inventory no.8254 were taken in the Restoration and Conservation Laboratory of the Ethnographic Museum of Transylvania, in accordance with the rules of restoration and conservation [6].

The investigation of patrimony objects can be performed with mechanical, thermal, optical, spectroscopic, magnetic, X-ray (diffraction and fluorescence) methods, etc. One can identify the metal, mineral, pigments, dyes [7], binders, nature [8-12], etc. With modern methods are clarified the structure of layers and materials composition of the ethnographic pieces, thus discovering the way in which they were made, the initial mode of preparation and technologies used for obtaining this objects. The spectroscopic methods can be useful in identifying substances or their mixtures, purity degree and the impurity nature. The microscopic methods allow in several cases the determination of the nature and the origin of the materials. The thermal methods can characterize the durity, fragility, fluidity and plasticity of materials [13]. These methods allow the identification and the study of various ethnographic materials.

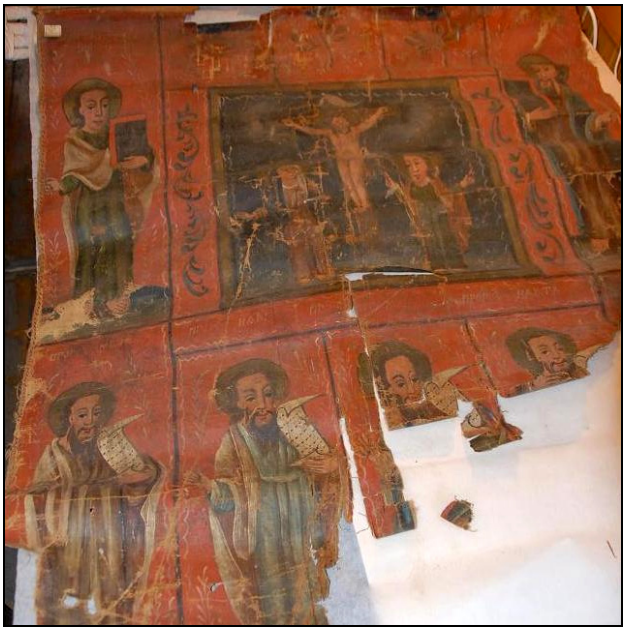

Figure 1a. Front 1 of Processional flag inventory no. 8254

Figure 1b. Front 2 one sequence of Processional flag inventory no. 8254
(St. Arch. Michael only)

The processional flag painted on both sides was analyzed, inventory no. 8254 (Figs. 1a and 1b). Front 1 painting: The Crucifixion with the Evangelists Mark and Matthew on the sides, and below with five Prophets, two partially present and one missing. Front 2 (verso) painting: St. Arch. Michael with Evangelists John and Luke on the sides and below five Prophets only four visible. The processional flag was purchased by Ethnographic Museum of Transylvania in 1939 from the Turda area. The object has a width in the upper part of 94 cm and a maximum length of 108 cm.

The investigation process of a processional flag, must be carried out by analizing the multilayers structure; the fabric support, primer, painted layer and protective layer being the main elements and the paper aim.

RESULTS AND DISCUSSION

FTIR spectroscopy

FTIR spectra recorded in different spectral domains for all collected samples are presented in Figs. 3-5.

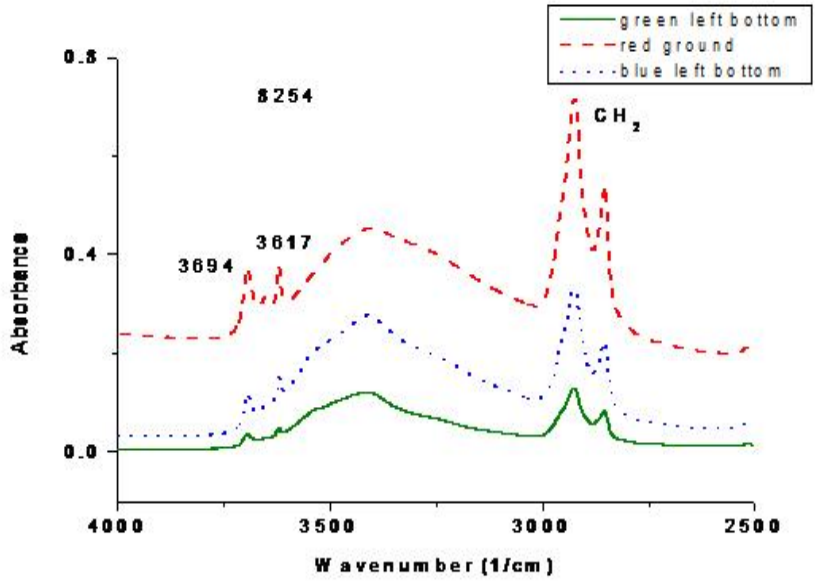

Figure 3. FTIR spectra for samples **1-3** of painted flag on both sides (8254), 4000–2500 cm^{-1} spectral domain. Legend: 1-middle; 2-top; 3-bottom

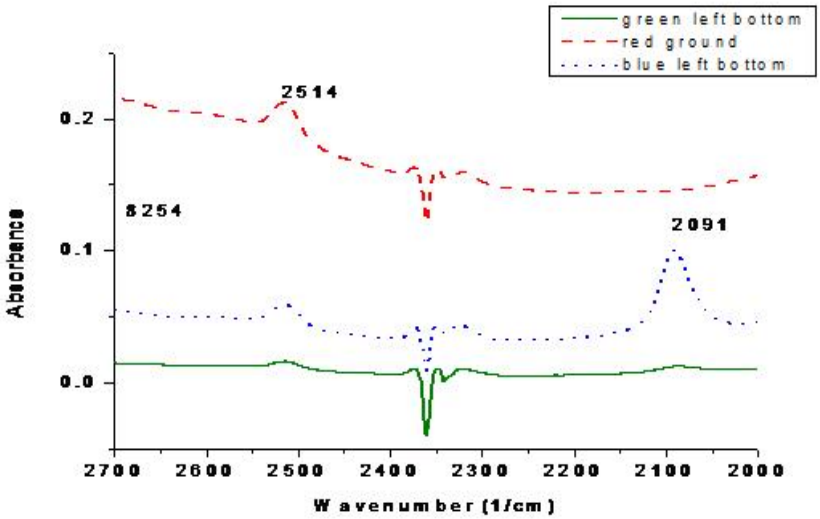

Figure 4. FTIR spectra for samples 1-3 of painted flag on both sides (8254), 2700-2000 cm^{-1} spectral domain. Legend: 1-middle; 2-top; 3-bottom

Identified compounds: derivatives containing SH group (2514 cm^{-1}), CN group (2091 cm^{-1}), probably Prussian blue - $Fe_4[Fe(CN)_6]_3$.

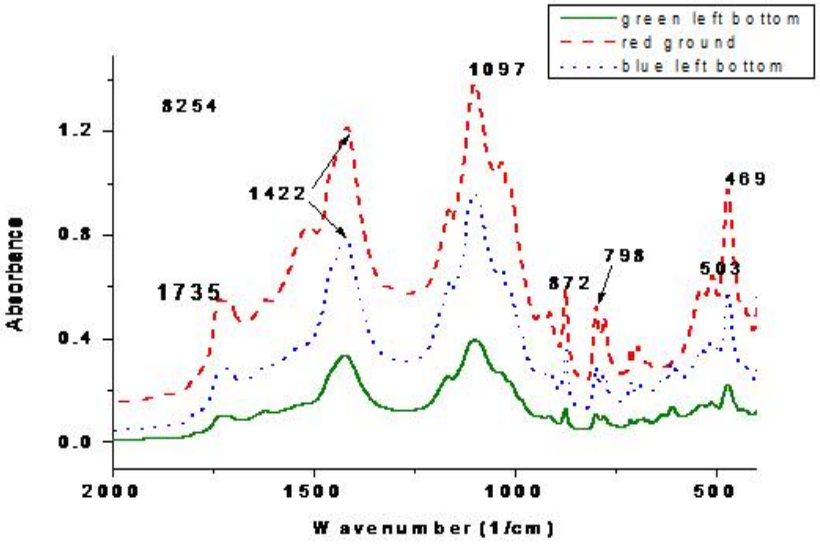

Figure 5. FTIR spectra for samples 1-3 of painted flag on both sides (8254), 2000–400 cm^{-1} spectral domain. Legend: 1-middle; 2-top; 3-bottom

Identified compounds [14], see Figs. 3-5: free OH groups (3697 and 3617 cm^{-1}, probably gypsum bands $CaSO_4$. $2H_2O$), CH_2 groups (aliphatic compounds), esters (1735 cm^{-1}, of line oil), $PbCO_3$ absorbtions at~ 1422 and 870 cm^{-1}, 1097 cm^{-1} ($BaSO_4$ and possible some contribution of Si-O-Si band), SiO_2 (quartz-798 cm^{-1}), Pb_3O_4 (469 and 530 cm^{-1}). In line oil a sicative agent (lead minium), litharge or ceruse is added. Lead minium (Pb_3O_4) was found in all coloured samples. During the time, derivatives that contain SH group appear (absorption at ~2514 cm^{-1}). For green painting material malachite ($CaSO_4$. $2H_2O$, 1097 cm^{-1}) was proposed, containing white pigment (carbonate) as diluant, also.

X-ray fluorescence

Red painting material: Hg (HgS) and Pb also (probably red lead), as major cations employed also for the ground of the processional flag. For the book contour one can identify Hg as major cation (cinnabar).

Blue painting material: major cations Cu (azurite, $2CuCO_3.Cu(OH)_2$) and Fe (Prussian blue), mixed in order to obtain a dark blue touches.

For the greenish dress, Cu was identified as major element: malachite can be the green pigment.

Lead was identified in all samples and in oil also as lead minium employed as siccative agent.

The halo contains a lot of As, so one can speak about auripigment (As_2S_3). The ground could contain a mixture of gypsum, barite and Ca carbonate for color "dilution".

X-ray diffraction

The identification of pigments was as follows:

- for red pigment, see Fig.6, HgS (cinnaber) was the major component but PbO, PbO_2 and Pb_3O_4 were identified also;
- as concerned blue pigment, azurite and Prussian blue were identified, see Fig. 7.

The crystallinity of the processional flag texture was: 31.4%, 34% for blue painted processional flag and 43.5% for red-painted processional flag. The higher crystallinity for the processional flag painted texture can be due to the crystalline status of the employed pigments.

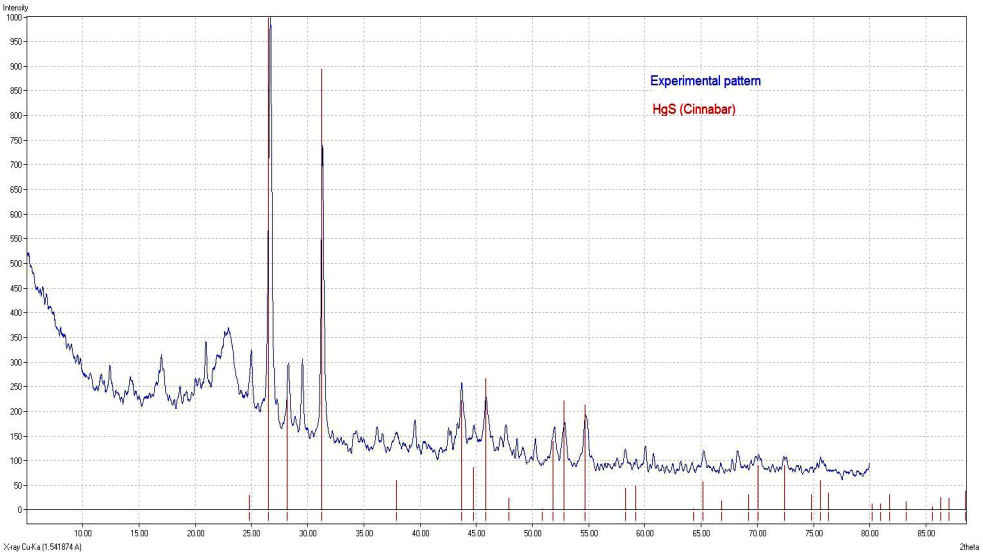

Figure 6. XRD pattern of red painting material as compared to HgS pattern from PDF-2 database.

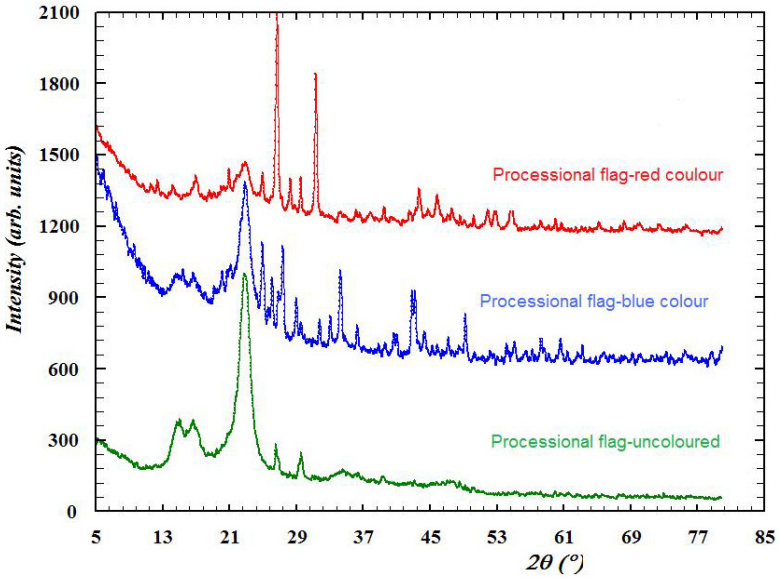

Figure 7. XRD patterns of Processional flag support and of painting materials.

Mass spectrometry

Red pigment

The analysis by mass spectrometry of the collected sample near red pigment zone indicates the presence of vegetal oil (taking into account the compounds ratio, one establish the presence of line oil). For temperatures higher than 250 ^{0}C are identified the following molecular ions corresponding to peaks at m/z 64, 101 and 202 that are specific to red pigment HgS (cinnaber or vermillion). These peaks are due of to S_2^+, Hg^{++} and Hg^+, respectively being produced from HgS by electron impact.

Blue pigment

The ions attributed to fatty acids having the carbon atom number between 9 and18 were identifed. The intensities ratio of palmitic and stearic acids confirmed the use of line oil as painting material. The maximal intensity is due to palmitic acid followed by stearic one, their summ represents 60 % relative to all acids. There were also identified the molecular ions corresponding to M= 172, 186, 200, 214, 228, 242, 256, 270 and 284 that are molecular ions of C_{10}-C_{16} and C_{18} acids. One can mention that the peaks corresponding to fatty acids with even molecular masses are more abundant relative to those with odd molecular masses. The used pigment looks to be Prussian blue, confirmed also by FTIR band corresponding to CN group belonging to $[Fe(CN)_6]_3Fe_4$ compound.

Green pigment

In the case of sample collected from the green pigment zone the ions similar to those of blue pigment were identified. One can therefore confirm the use of line oil and the pigment was a combination of blue and yellow pigments, the last one being inorganic, impossible to be detected by mass spectrometry with electronic impact.

CONCLUSIONS

As a result of the previous analyses, one cand establish that the processional flag was painted with pigments based on line oil and the employed pigments were Prussian blue, red Cinnaber or Vermillon, green malachite, red lead and other lead oxides. These results will help in conservation and a future restoration of this processional flag.

EXPERIMENTAL SECTION

The following samples, see Figures 8a and 8b, were collected from the processional flag: red pigment (background verso), green pigment (left down verso) and blue pigment (left down, front). The quantities taken were of the order micrograms. Sampling was carried out in sterile plastic mini tubes with lid. Each tube was numbered.

Figure. 8a Front 1 of Processional flag inventory no. 8254:
the place of blue sampling

Figure. 8 b. Front 2 one sequence of Processional flag inventory no. 8254:
the places of red and green samplings

The collected samples were investigated by FTIR spectroscopy, X-ray fluorescence, X-ray diffraction and mass spectrometry.

FTIR measurements were performed with a JASCO 6100 spectrometer in the 4000-400 cm^{-1} spectral domain and a resolution of 4 cm^{-1} employing KBr pellete technique.

X ray fluorescence measurements were performed using an INNOV-X Alpha-6500 portable instrument. All colours on both sides of the processional flag- red, green, blue, black and aura were analysed.

The diffraction data were collected in the 2θ = 3-85° angular domain with a Bruker D8 Advance diffractometer, using Cu $K\alpha_1$ radiation (λ = 1.5406 Å) (40 kV; 40 mA). In order to increase the resolution, a Ge 111 monochromator was used to eliminate the $K\alpha_2$ radiation. Data collection was performed at room temperature with the programs package DIFFRAC plus XRD Commander. The pigment identification was made by comparing the obtained patterns with PDF-2 database. The amorphous/crystalline ratio was calculated by using Material Studio software.

Mass spectrometry measurements were done with a coupled GC-MS system. Mass spectrometer with ionic trap Polaris Q, gas chromatograph Trace GC Ultra and Autosampler AS2000 (ThermoFinnigan San Jose, USA)

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