NON-DESTRUCTIVE AND MICROANALYTICAL TECHNIQUES FOR COMPOSITION AND STRUCTURE IDENTIFICATION OF THE WALL MATERIALS FROM PALACE OF POTLOGI

Rodica-Mariana ION [1, 2], Mihaela-Lucia ION [3], Valentin RADITOIU [1], Ioan DARIDA [4], Dana POSTOLACHE [4]

[1] *National Research and Development Institute for Chemistry and Petrochemistry – ICECHIM, Bucharest, Romania*
[2] *Valahia University, Materials Dept., Targoviste, Romania*
[3] *Valahia University of Targoviste, History Department, Romania;*
[4] *SC DANART SRL, Bucharest, Romania*

E-mail: rodica_ion2000@yahoo.co.uk

Abstract: 45 km from Bucharest there is an example of Brancoveanu architecture, the Palace of Potlogi. Built in 1698, the first royal residence built in the new style. Exterior and interior decorations of the building are the most interesting parts of the palace, including the decorations, sculptures, galleries, portraits, even the garden and courtyard entrance plane, have some oriental influences. Although simple or torso columns, capitals neo-corintic, fretted railings, doors and windows frames, consoles with original heraldic signs disappeared. Also, some fragments of stucco decoration have been used in abundance with a rare delicacy floral. Even the restoration started some years ago, is almost ready, some analysis have been imposed (from detached not useful fragments behind the building), in order to identify the existing materials and to select the proper materials useful for restoration. Microscopy allows observing the presence of resin; WDXRF allows elemental composition of sample, while FTIR spectrometry method was widely used for investigating the composition and aging compounds from this building. The CIELAB color parameters were calculated and have been determined clarity (L*), red/green colour component (a*) and yellow/blue colour component (b*) and their derived magnititudes: chroma (C*) and tone (H*). The differences between treated and non-treated samples have been calculated, too (ΔH*, ΔC*), correlated with the overall colorimetric difference between treated and not-treated samples: ΔE*.

Keywords: stucco, FTIR, EDXRF, CIELAB, Potlogi

1. INTRODUCTION

In 1698 on the property Potlogi, Constantin Brancoveanu starts raising new royal houses, for his four sons: Constantin, Stefan, Radu and Matei. The new building, a very large building unusual for that era, was fully completed in autumn 1699 [1]. The historical circumstances have made 15 years after the end of palace, to be robbed and left in desolation. One hundred years later this palace was already in ruins. Since then the building has been exposed to weather that, year after year, they brought in an advanced state of ruin. The architect restorer and the team and describe the approach to the restoration carried out in the mid 50s restoration made by the team led by Şt.Balş wanted to be a reconstitution to restore their shape, volume and its original decoration, executed based on original documents, surveys and interpretations after children or other similar items from the same era monuments [2].

The restoration works were started virtually from its foundations in 1955, during the communist regime, closely following the restoration of models developed during the Brancoveanu Mogosoaia Palace, another important building of that period, restored in 1920 by the great architect George Matei Cantacuzino. He contemplated also ruin Mogosoaia, only partially intervened on her by a fellow Italian with a decade ago, and had to use plenty of imagination in the process of restoration, drawing mainly from Văcăreşti monasteries (most important architectural monument of Brancoveanu dinasty destroyed in turn by the dictator Ceausescu in the 1980s), Hurezi, Stavropoleos or Doamnei Church [3].

The preservation-restoration interventions of the original plasters and stuccos, executed in the period 2014-2015, aimed at creating the unity of the assembly based on the existence of four physical realities: original plasters, new elements originated from the reconstruction intervention executed by Bals, the sporadic repairs of poor quality and the preservation-restoration interventions approved by the present Ministry of Culture [4]. Because in Bals team were non-profesional persons, too, the quality of stuccoes was not very good. So, under such circumstances, the present paper aims to show some analytical results about these stuccoes, if they are from Bals restoration or they are original.

The church supported was submitted in time complex interventions, and only few of them had the role of conserving the artistic components. This is why the original mural painting is only preserved in the narthex, and unfortunately this was also altered irreversibly by repaintings. Now, after the last restoration procedure, these were already removed, however in the past the surface of the painting was thoroughly hammered in order to increase the adhesion of a new layer. Therefore, there are areas where the representations can hardly be identified.

Due to its nature, the rock is subject to many alteration and degradation forms (chromatic alteration, efflorescence, decohesion, exfoliation and detachment). In this study, through a diagnostic analysis, the degradation materials occurring in the Palace of Potlogi, have been identified.

2. EXPERIMENTAL SECTION

2.1. Materials and methods

The sample prelevated from the Palace of Potlogi was from detached not useful fragments behind the building, Fig.1.

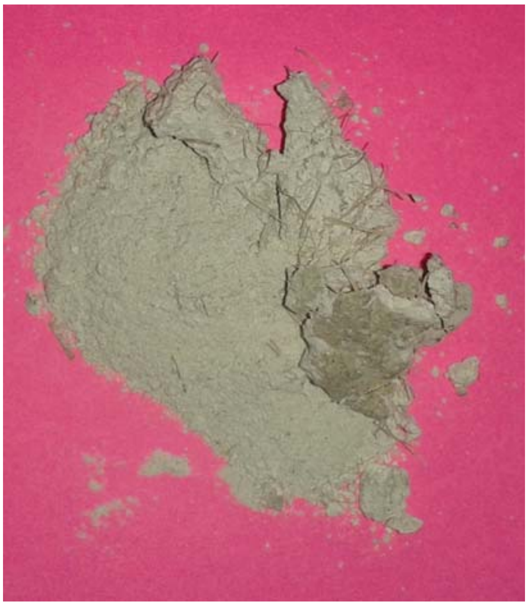

Fig.1. The analyzed sample

2.2 Characterization techniques

The FTIR spectra have been recorded by Attenuated Total Reflectance, ATR, with a Perkin Elmer Spectrum GX spectrometer (PerkinElmer Ltd., UK), in the following conditions: range 4000 cm^{-1} to 580 cm^{-1}, 32 scan, resolution 4 cm^{-1}.

X-ray fluorescence analysis, has been performed with an wavelength dispersive instrument, WDXRF PW4025, type Benchtop, X-ray tube from Pd power 200W, limit of detection: 1ppm - 10ppb.

Light Optical Microscopy (LOM) has been used for a stratigraphic characterization of polychrome surfaces by Light optical microscopy (LOM) using Leica DM 1000 stereoscopic microscope with a Leica EC3 camera under a magnification of 40x to 600x, to determine the matrix heterogeneity, particle size, color, shape and transparency.

Color measurements, achieved with a spectrophotometer (Carl Zeiss Jena M40) under a D65 light source and an observer angle of 10^{O}. The CIELAB color parameters clarity (L*), red/green colour component (a*) and yellow/blue colour component (b*) and their derived magnititudes: chroma (C*) and tone (H*). The differences in ΔL^*, Δa^*, and Δb^* and the total color differences ΔE^* were calculated using specific formulas [5, 6]. The differences between treated and non-treated samples have been calculated, too (ΔH*, ΔC*), correlated with the overall colorimetric difference between non-treated and treated samples: ΔE*[7, 8].

3. RESULTS AND DISCUSSIONS

The infrared spectroscopic analysis carried out on the sample prelevated from Potlogi Palace allowed the identification of different inorganic phases and organic products, as follows (Fig.2):

- stretching vibrations of calcium carbonate ($CaCO_3$), peaked at 1409, 705 and 611 cm^{-1}.
- typical vibrational bands of gypsum ($CaSO_4 \cdot 2H_2O$), centered at 1109, 669 and 596 cm−1, and its related forms (bassanite and anhydrite). Common forms of Ca-sulfate are anhydrite CaSO4, bassanite $CaSO_4 \cdot 0.5H_2O$ and gypsum $CaSO_4 \cdot 2H_2O$ [9]. Anhydrite typically forms at higher temperatures and gypsum at lower temperatures [10] and transformations between these two forms of Ca-sulfates do not occur readily under dry conditions at low temperatures.
- The characteristic bands of thenardite, centered at 1034 cm^{-1}, were also found, as a first proof for degradation process of the rock.
- stretching vibrations of some organic compounds, most probably from an organic resin (identified by optical microscopy, Fig.3) and from the twine, centred at 944 cm^{-1} (C-O), l365 cm^{-1} (C-H), 1735 cm^{-1} (C = O).
- bands clay minerals were recognized, through the peaks from 1032 cm^{-1} (Si–O–Si bond) [11].

Finally, in the samples taken from the Potlogi Palace calcite and gypsum (together with related forms – bassanite and anhydrite), organic resin, twine (flax and hemp) were identified. Representative FTIR spectra of the analyzed wall and flax samples are shown in Fig. 3.

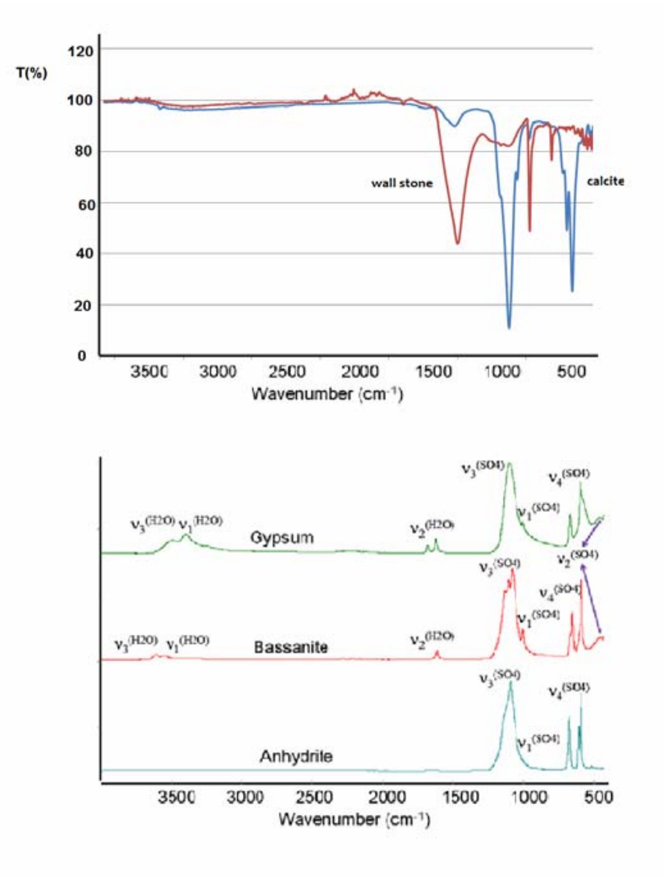

Fig.2. FTIR spectra of Potlogi stone sample

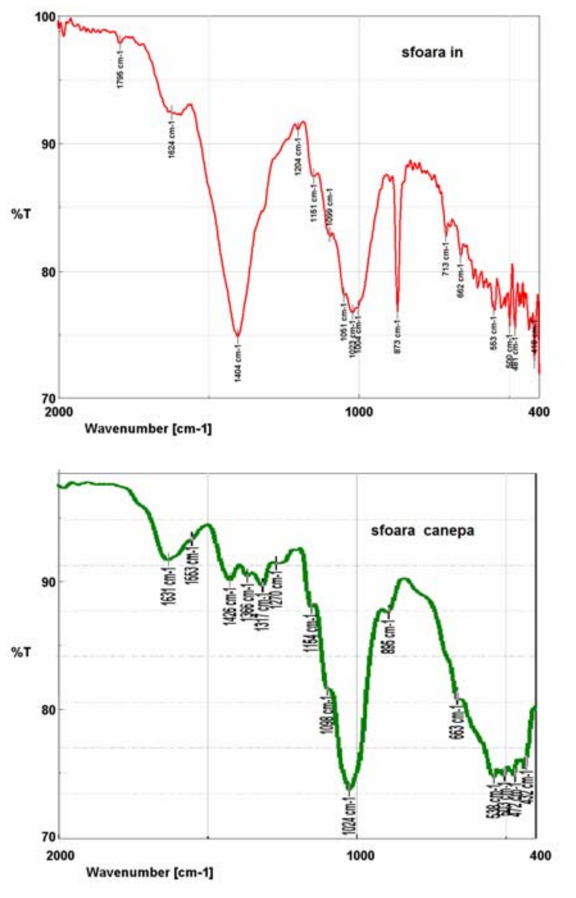

Fig.3. FTIR spectrum of the twine: flax (up) and hemp (down)

Correlated with FTIR spectra there are EDXRF determinations, Table 1. Also, by optical microscopy was possible to put into evidence the presence of resin (Fig.4) and the presence of flax and hemp fibers (Figs.5, 6).

Table 1. Results obtained by EDXRF

Compound	Concentration (%)
Na_2O	9.4
Al_2O_3	3.4
SiO_2	4.6
K_2O	1.41
CaO	79.09
Fe_2O_3	2.1

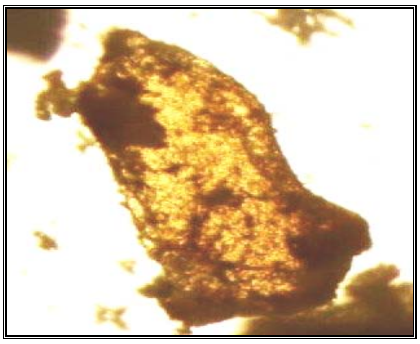

Fig.4. Resin from the wall

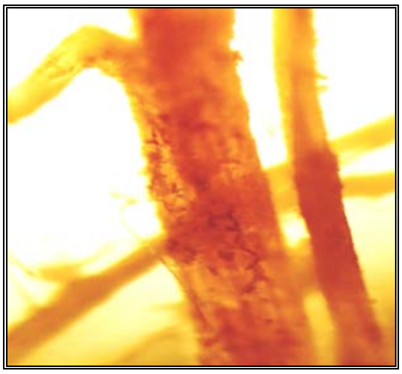

Fig.5. Fiber present in the wall

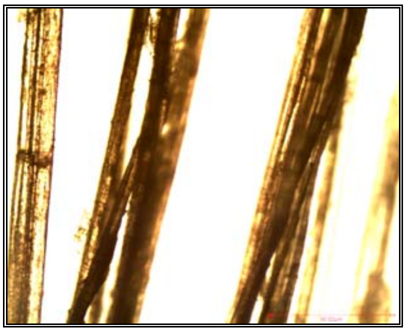

Fig.6. Flax fiber as reference

The differences between treated and non-treated samples have been calculated, too (ΔH*, ΔC*), correlated with the overall colorimetric difference between degraded and reference samples (limestone with gypsum), the results indicated that color properties are in direct relation to ageing, i.e., the lightness of wall decreases even the hue is changed a little ΔH=1.45.

4. CONCLUSIONS

For the sample prelevated from Potlogi Palace, optical microscopy allows to observe the presence of resin, WDXRF allows elemental composition of sample, while FTIR spectrometry method was widely used for investigating the aging of the material used for this building, puing ino evidence the composition: calcite, gypsum, bassanite, anhydrite, flax and hemp fibers. The CIELAB color parameters calculated demonstrated that the differences between treated and non-treated samples yielded to a decreased lightness even the hue is changed a little ΔH=1.45.

5. ACKNOWLEDGEMENTS

This paper has been prepared with the financial support of the projects **PN II 261/2014 and PNII 222/2012**.

6. REFERENCES

[1] BALŞ, Stefan, *Curtea Brâncovenească din Potlogi*, Ed. Meridiane, Bucureşti, 1968, p.5

[2] POPA Corina, GRECEANU Eugenia, JUVARA CHILIMAN Alexandra, DOBJANSCHI Ana, GEORGESCU Maria, IACOVESCU Ioana, MIHAIL Bogdan, BĂDĂRĂ Doru, TOMA Ileana, ŢIGLIU Iolanda, *Moştenirea Brâncovenească*, ed.Centrul Cultural Palatele Brâncoveneşti, 2008, Mogoşoaia.

[3] BALŞ, Stefan, *Curtea Brîncovenească din Potlogi*, Ed. Meridiane, Bucureşti, 1968, p.8.

[4] SAVA, Irina, *Palatul Potlogi, ctitorie brancoveneasca*, Restitutio, 9(2015), pp. 350-352.

[5] JIS (2009) Z 8730, *Colour specification- Colour differences of object colours*

[6] JIS (2008) Z 8729, *Colour specification-CIELAB and CIELUV colour spaces*

[7] DERRICK M.; STULIK D.; LANDRY J. (1999). *Infrared Spectroscopy in Conservation Science*. The Getty Conservation Institute, Los Angeles.

[8] BALŞ, Ştefan, *Restaurarea Palatului de la Potlogi*, în Revista Arhitectura, nr.2/1955

[9] DYAR M.D., GUNTER M.E. (2007) *Mineralogy and Optical Mineralogy.* 708. p. Mineralogical Society, Chantilly, VA

[10] HARDIE L.A. (1967) The gypsum-anhydrite equilibrium at one atmosphere pressure. American Mineralogist, 52, 171-200

[11] La RUSSA M.F., BARONE G., MAZZOLENI P., PEZZINO P., CRUPI V. AND MAJOLINO D. (2008), *Characterisation and differentiation of pigments employed on the facade of "Noto's Valley" monuments (Sicily).* Applied Physics A, 92, 185-190.