

## DEGRADATION OF WOOD DECORATIONS FROM 18<sup>TH</sup> CENTURY OLD HOUSES

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**Abstract:** A particular house built in the second half of the century XVIII<sup>th</sup> with a special note in Romanian architecture of this period, has been evaluated in this paper. Now this house is in an advanced damaging situation and needs to be restored urgently. It is an unique architectural house from the south part of Romania region (with wood decoration), and the analysis from this paper had been recorded 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 permits one to observe the structure of layers, EDXRF and ICP-AES allow elemental composition of samples and to identify the chemical groups present here. Raman spectrometry method was widely used for investigating the aging of wood 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 magnitudes: chroma ( $C^*$ ) and tone ( $H^*$ ). The differences between treated and non-treated samples have been calculated, too ( $\Delta H^*$ ,  $\Delta C^*$ ), correlated with the overall colorimetric difference between treated and not-treated samples:  $\Delta E^*$ .

Keywords: wood decorations, stucco, EDXRF, CIELAB

### 1. INTRODUCTION

Wood has been used by humans for thousands of years [1]. Met as decorations, the wood stucco could be found on churches and monasteries (attached on building and roof structure), and on different facades (as goals, pilasters, cornices, spirals and arches) [2]. As an organic material, wood can easily support a degradation process, this being the reason for which the historical wood artefacts have been lost due to the fragile nature of the material [3].

Mostly of the buildings with stuccoes and decorations are dating from XIX<sup>th</sup> - XX<sup>th</sup>. These can be divided in large public buildings, residential buildings and traditional, and houses with floor to floor, the public buildings being the most spectacular in the down town of many cities. Components with artistic value are recognized as: frames, decorative strips, pilasters, statues, arches, bosses; profiled cornice, richly ornamented – all of them whether from masonry or wood [4]. A large number of buildings, some of them with unclassified valuable artistic components inside (balustrade, mosaic floors, stucco decorations), need works of conservation and restoration, very important for maintenance of the building: roof structure, artistic components: stucco facades, gates, joinery, fittings.

Significant deterioration of wooden constructions are produced when they come in direct contact with water

from rain or condensation, moisture gradient case is favoring biological attack. Paint was also observed to have cracked as the stucco beneath the paint developed cracks, thus making the paint ineffective in preventing water intrusion [5].

Raman spectrometry methods is widely used for investigating the natural aging of wood in historical buildings but a drawback in these studies was that the age of the wood was estimated based on the architectural history and style of the buildings [6].

The present study deals with the color change of wood during natural aging in the context of public buildings. Experience shows that color properties are in direct relation to aging, i.e., the lightness of wood decreases and the hue is shifted slightly to red [7,8], similar with the change induced by thermal treatment [9,10].

Wood has been and remains a material deeply rooted in the conscience of society by its values and material properties of machinability, wooden objects as a heritage and education, which is transmitted from generation to generation as part of cultural heritage, cultural heritage national wooden objects occupying approximately 60% of all movable and immovable cultural property [11]. But wood is an organic material subject to degradation and damage permanent and irreversible, so to maintain a long lifetime as wooden objects conservation actions are needed both and restoration.

Since the wood has a predisposition to such degradation. Degradations are those that change the chemical nature of a material of chemical, radiation and biological agents frequently co-assisted and climatic factors [12]. On the other hand, the deterioration of physical condition changes to a structural or functional element, under the action of physical, mechanical and climatic factors, such as the breaking of a beam, swelling or shrinkage of a panel of the timber [13]. Factors other climatic factors that lead to such natural aging (UV, water, variations in atmospheric humidity, temperature variations, frost-thaw) are fire abiotic factors leading to the deterioration of wood [14].

In this study, colors of wood samples of historical buildings, were evaluated. The results will show the main components responsible for color change during aging.

## 2. EXPERIMENTAL SECTION

### 2.1. Materials and methods

Cioflelea house built in the second half of the century XVIII<sup>th</sup> introduces a special note in Romanian architecture of the houses of this period. It is characterized by continuous porch off the main facade, stained glass and polygonal turret. Now this house is in an advanced damaging situation and needs to be restored urgently. It is the only house from this region with wood stucco(decorations), and the analysis from this paper had been recorded from detached not useful fragments behind the building. The degree of deterioration/preservation of materials can be checked before intervention, in order to search for compatibility of materials.

### 2.2. Characterization techniques

The samples were analyzed by using the following techniques:

**Raman spectra** have been obtained with a portable dual wavelength Raman analyzer IR - XANTUS 2 – RIGAKU, with the following parameters: Dual wavelength source 1064nm & 785nm, spectral range (cm<sup>-1</sup>) 200 – 4000, Spectral Resolution (cm<sup>-1</sup>) 7 – 10, Laser Output Power (mW) 400 – 490, Laser Output Power (mW) 30 – 490, cooled detectors – CCD and InGaAs. The paint cross sections were analyzed using Raman spectroscopy in order to identify pigments and fillers. The laser beam was focused on a diameter of about 25, 5 and 1.5–2 μm, respectively. Spectra were acquired using 10 s of signal collection time and five accumulations.

**X-Ray Fluorescence** was used to identify the elements in certain pigments, fillers. A dispersive wavelength X-ray fluorescence spectrometer (EDXRF) with a Benchtop spectrometer sequential type, energy dispersive. The system is equipped with 3 crystals.

A Varian Liberty 110 Series spectrometer was used for the **ICP-AES analysis**. The samples were cut off from the original shreds and were finely powdered in an agate mortar. Multielement, matrix matched standards were used for the quantitative determinations. Microwave assisted digestions were performed in a Berghof microwave oven with the use of high-pressure closed Teflon PFA vessels and online pressure and temperature control.

**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<sup>0</sup>. The CIELAB color parameters clarity (L\*), red/green colour component (a\*) and yellow/blue colour component (b\*) and their derived magnitudes: chroma (C\*) and tone (H\*). The differences in  $\Delta L^*$ ,  $\Delta a^*$ , and  $\Delta b^*$  and the total color differences  $\Delta E^*$  were calculated using specific formulas [15,16]. The differences between treated and non-treated samples have been calculated, too ( $\Delta H^*$ ,  $\Delta C^*$ ), correlated with the overall colorimetric difference between non-treated and treated samples:  $\Delta E^*$ [17]. According to the literature  $\Delta E^* < 5$  was considered as corresponding to a not significant variation [18].



Fig. 1. Cioflelea House (XVIII<sup>th</sup> century)



Fig.2. Images of different wood decorations

### 3. RESULTS AND DISCUSSIONS

This building is in an advanced state of degradation and deterioration, and all delay of interventions is injurious

to this valuable monument (Fig.1). The main cause for this deteriorations and degradations is the losses of tightness of shingles cover, due to exposure to direct sun light, wind and rains, and cannot provide protection to the weathering. Could be observed a loss of resistance - as the damage progresses, the wood is soaked and fragile. Decayed wood breaks easily perpendicular to the fiber break without being crushed chips. Weight loss - very degraded wood is lighter than healthy wood of the same species, due to the destruction of wood substance by fungi. Changing the color - is often the most obvious sign of degradation. The appearance of brown islands - closed or some lighter may indicate an incipient decay (Fig.2).

**Raman spectra** were registered in the region 200-2000  $\text{cm}^{-1}$ . These are shown in Fig. 3. Read lead, different red iron oxide pigments and cadmium red can be identified. In some cases the method can be used alone for pigment identification and in many cases it provides useful additional evidence for pigment identification using other instrumental techniques (optical microscope analysis, XRF).

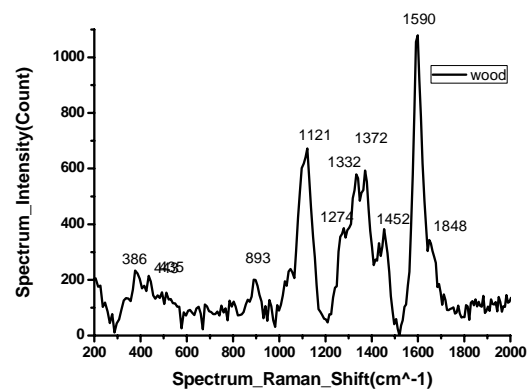


Fig. 3. Raman spectra of the wood

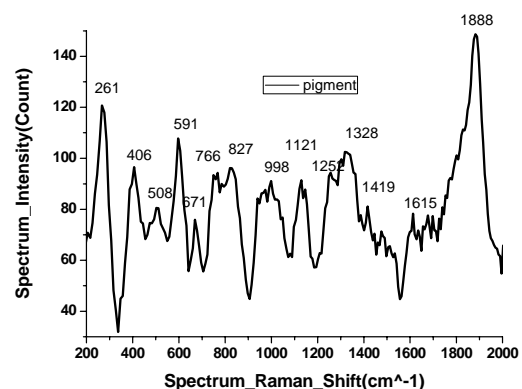
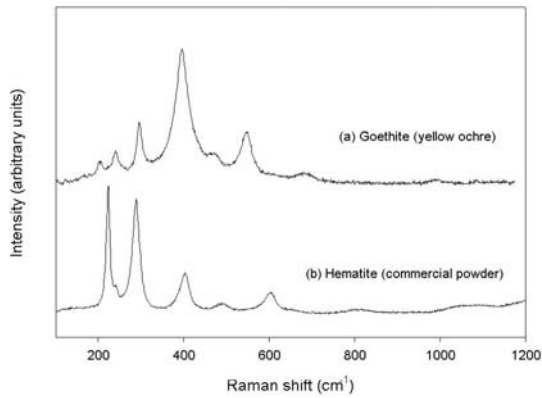
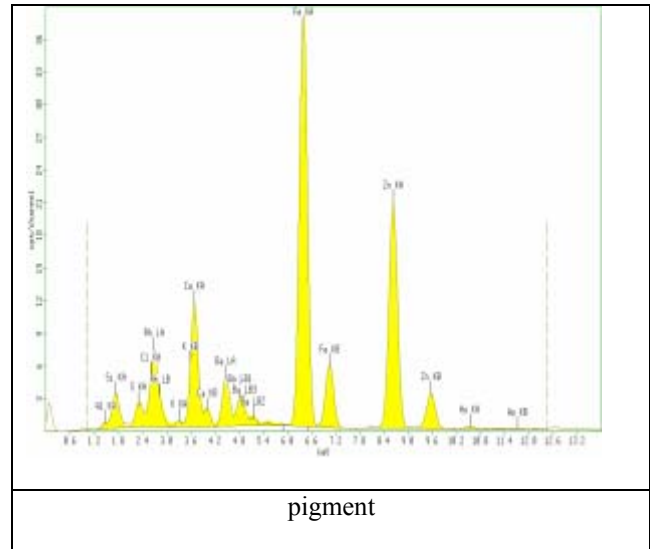


Fig.4a. Raman spectra of the pigment



**Fig.4b.** The Raman spectra of goethite and hematite

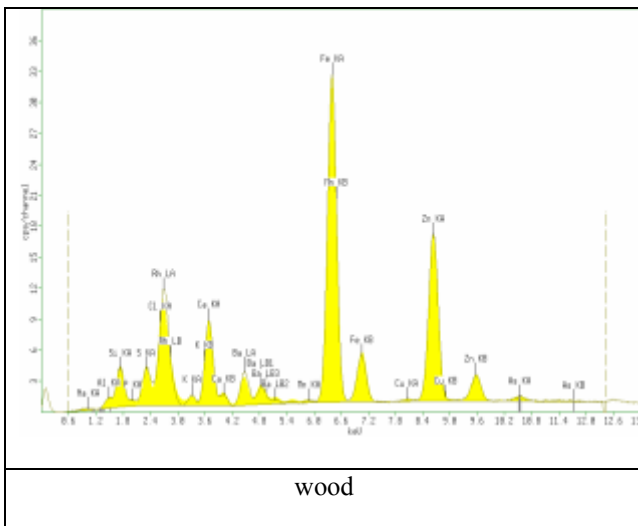
The black pigment is charcoal black, the yellow pigment is yellow ochre, a hydrous iron oxide ( $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ). The red pigment is red ochre, or red iron oxide ( $\text{Fe}_2\text{O}_3$ ). These oxides could be observed by Raman spectra, Figs.4a and 4b. The copper green pigment is either verdigris, a copper acetate salt ( $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot [\text{Cu}(\text{OH})_2]_3 \cdot 2\text{H}_2\text{O}$ ), or malachite, a natural copper carbonate ( $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ), both of which contain copper, carbon, and oxygen. Venetian red is a light and warm (somewhat unsaturated) pigment that is derived from nearly pure ferric oxide ( $\text{Fe}_2\text{O}_3$ ) of the hematite type. Also, could be identified cobalt phosphate, which is an inorganic compound with the formula  $\text{Co}_3(\text{PO}_4)_2$ , known as cobalt violet. These presumptions could be supported by the results obtained by EDXRF and ICP-AES, too, Fig. 5 and Table 1.











**Fig.5.** EDXRF analysis of wood and pigment

**Table 1.** The elements detected by ICP-AES

Element	Wood	Pigment
Al	115.2ppm	0.03 %
Ca	1.90%	4.1%
Ba	96.3 ppm	282 ppm
Co	-	1.17 ppm
Ni	-	23 ppm
Fe	985.3 ppm	11.1 ppm
Mn	15.49 ppm	1.02 %
Mg	245.16 ppm	962 ppm
Na	320.81 ppm	1005 ppm
Zn	178.33 ppm	3.9 %
Cu	112.1 ppm	0.9 %
Li	98.4 ppm	-
K	253.2ppm	173 ppm



Colorimetric measurements (CIELab) were performed to verify the colour modification ( $\Delta E^* = \sqrt{\Delta L^* + \Delta a^* + \Delta b^*}$ ), where  $L^*$ ,  $a^*$  and  $b^*$  are the brightness (0 for black – 100 for white), the red–green component (positive for red and negative for green) and the yellow–blue component (positive for yellow and negative for blue), respectively. and their derived magnitudes: chroma ( $C^*$ ) and tone ( $H^*$ ).

					
Indoor wood (A)			Pine wood (B)		
L=63.24	a=14.23	b=31.67	L=85.98	a = 5.19	b= 23.7
					
1			2		
L=61.8	a=11.9	b=29.32	L=56.17	a=8.79	b=15.26
					
3			4		
L=40.30	a=9.25	b=19.01	L=49.47	a=8.66	b=19.48
					
5			6		
L=40.82	a=9.61	b=18.88	L=50.07	a=11.00	b=19.73

**Fig.6.** The chromatic parameters for all the samples

The differences between treated and non-treated samples have been calculated, too ( $\Delta H^*$ ,  $\Delta C^*$ ), correlated with the overall colorimetric difference between non-treated and treated samples:  $\Delta E^*$ : the difference between all faces of the artifact versus the indoor wood (quiet clean surface), the results indicated: that color properties are in direct relation to aging, i.e., the lightness of wood decreases and the hue is shifted slightly to red colour, Fig.6.

From the calculus, have been observed the following results vs. Sample A:

Face 1:  $\Delta L = -1.44$ ;  $\Delta C = -3.08$ ;  $\Delta H = 1.209$  and  $W_i = 4.80$ ;

Face 2:  $\Delta L = -7.07$ ;  $\Delta C = -17.11$ ;  $\Delta H = 2.41$  and  $W_i = 38.17$ ;

Face 3:  $\Delta L = -22.94$ ;  $\Delta C = -13.58$ ;  $\Delta H = 0.79$  and  $W_i = 10.30$ ;

Face 4:  $\Delta L = -3.77$ ;  $\Delta C = -13.41$ ;  $\Delta H = 0$  and  $W_i = 16.47$ ;

Face 5:  $\Delta L = -22.42$ ;  $\Delta C = -14.07$ ;  $\Delta H = 1.47$  and  $W_i = 6.82$ .

From the calculus, have been observed the following results vs. Sample B:

Face 1:  $\Delta L = -24.18$ ;  $\Delta C = 7.38$ ;  $\Delta H = 4.67$  and  $W_i = -61.2$ ;

Face 2:  $\Delta L = -29.81$ ;  $\Delta C = -6.65$ ;  $\Delta H = 5.36$  and  $W_i = -15.83$ ;

Face 3:  $\Delta L = -45.68$ ;  $\Delta C = -2.95$ ;  $\Delta H = 5.37$  and  $W_i = -4.67$ ;

Face 4:  $\Delta L = -36.51$ ;  $\Delta C = -2.95$ ;  $\Delta H = 4.54$  and  $W_i = -37.53$ ;

Face 5:  $\Delta L = -45.16$ ;  $\Delta C = -3.61$ ;  $\Delta H = 5.92$  and  $W_i = -43.18$ .

In the first set of data the samples vs. Indoor wood (sample A) show negative values for  $\Delta a$  (green component), while the samples vs. new wood (sample B), the same parameter shows positive values (red component);  $\Delta b$  parameter shows only negative values for both data sets, indicating only blue colour. Because the parameter  $\Delta L$  has only negative values, this is a proof for negative (to darken) aspects of the samples. Also, chroma ( $C^*$ ) has only negative values, and tone ( $H^*$ ) has positive values versus sample A and negative values vs sample B. The lightness of wood decreases and the hue is shifted slightly to red colour, the most pronounced value being for pigment (sample 6). All these results are in good agreement with the literature data [19].

#### 4. CONCLUSIONS

For wood decoration belonging to Cioflkea House (XVIIIth century) from chromatic parameters, has been observed that by degradation, the lightness of wood decreases and the hue is shifted slightly to red colour.

The black pigment is charcoal black, the yellow pigment is yellow ochre, a hydrous iron oxide ( $Fe_2O_3 \cdot H_2O$ ). The red pigment is red iron oxide ( $Fe_2O_3$ ). Also, could be identified cobalt phosphate, which is an inorganic compound with the formula  $Co_3(PO_4)_2$ , known as cobalt violet. These presumptions could be supported by the results obtained by Raman, EDXRF and ICP-AES, too.

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## 6. REFERENCES

- [1] T. Nilsson, R. Rowell, *Wood Science for Conservation, Historical wood – structure and properties*, Journal of Cultural Heritage, 13(3), Supplement, 2012, pp. S5–S9
- [2] K. Haneca, K. Cufar, H. Beeckman, *Oaks, tree-rings and wooden cultural heritage: a review of the main characteristics and applications of oak dendrochronology in Europe*, Journal of Archeological Science, 36(1), 2009, pp. 1-11
- [3] D. Hunt, *Properties of wood in the conservation of historical wooden artifacts*, Journal of Cultural Heritage, 13(3), supplement S, 2012, pp.S10-S15.
- [4] UNGER A.; SCHNIEWING A.P.; UNGER W. (2001). Conservation of Wood Artifacts. Springer Verlag Berlin.
- [5] Popescu, C.M., Dobeles, G., Rossinskaja, G., Dizhbite, T., Vasile, C., *Degradation of lime wood painting supports. Evaluation of changes in the structure of aged lime wood by different physico-chemical methods*. J. Anal. Appl. Pyrolysis 79, 2007, pp.71–77
- [6] Marengo, E., Robotti, E., Liparota, M.C., Gennaro, M.C. *Monitoring of pigmented and wooden surfaces in accelerated ageing processes by FT-Raman spectroscopy and multivariate control charts*. Talanta 63, 2004, pp. 987–1002
- [7] Kohara, J. *Study on the old timber*. Ind. Eng. Chiba Univ.9, 1958a, pp. 1–55.
- [8] Kohara, J. *Study on the old timber*. Ind. Eng. Chiba Univ.9, 1958b, pp. 23–65.
- [9] Bekhta, P., Niemz, P. *Effect of high temperature on the change in color, dimensional stability and mechanical properties of spruce wood*. Holzforschung 57, 2003, pp. 539–546
- [10] Matsuo, M., Yokoyama, M., Umemura, K., Gril, J., Yano, K., Kawai, S. *Color changes in wood during heating: kinetic analysis by applying a time-temperature superposition method*. Appl. Phys. A99, 2010, pp. 1–6
- [11] Gregory, D., Matthiesen, H. and Björndal, C. *In situ preservation of artefacts in Nydam Mose: Studies into environmental monitoring and the deterioration of wooden artefacts*. In Proceedings in the 8<sup>th</sup> ICOM Group on Wet Organic Archaeological Materials Conference, ICOM, Stockholm, 2001, pp. 213-223.
- [12] Sanya A.E., *Analyse du traitement hyrdo-thermique de boi gorge d'eau; application à la restauration-préservation du bois archéologique* – University of La Rochelle- FR, 23.11.2000.
- [13] Ippoliti R., *L'ambiente e il legno: tipologie di ambienti umidi*, published on the Internet site: <http://www.team.it/arke/manualearke/manualegno>
- [14] Eaton, R.A. and Hale, M.D.C., *Wood. Decay, pests and protection*. Chapman & Hall, London, 1993
- [15] JIS (2009) Z 8730, *Colour specification- Colour differences of object colours*
- [16] JIS (2008) Z 8729, *Colour specification-CIELAB and CIELUV colour spaces*
- [17] Derrick M.; Stulik D.; Landry J. (1999). *Infrared Spectroscopy in Conservation Science*. The Getty Conservation Institute, Los Angeles.
- [18] Millett, M.A., Gerhards, C.C. *Accelerated aging: residual weight and flexural properties of wood heated in air at 115°C to 175°C*. Wood. Sci. 4(4), 1972, pp. 193-201
- [19] M. Alberghina, S. Schiavone, F. Prestileo, E. Cacciatore, L. Pellegrino, D. Perrone, *Spectrophotometric investigations at the museum: monitoring of colour changes during differentiated cleaning of the marble statues*, YOCOCU. Contribute and Role of Youth in Conservation of Cultural Heritage, (Editors: A. Macchia, E.Greco, B.A. Chiarandà and N. Barbabietola), Italian Association of Conservation Scientist, Rome, 2011, pp. 267-280.