STRUCTURAL AND COMPOSITIONAL INVESTIGATIONS OF MOSAICO BIZANTINO DECORATION FROM PALACE OF CULTURE, IASSY

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***Abstract*:** In this paper we are proposing a complex study about the structure and composition of a sample prelevated from Palace of Culture, Iassy (as fragment detached from the building,   without value), in order to identify the existing materials and to select the proper materials useful for restoration. Microscopy allows to observe the presence of the main weathering signs (chromatic alteration, alveolization, blistering, differential disaggregation, efflorescence, decohesion, exfoliation and detachment, cracking, delamination, disaggregation, flaking, loss), EDXRF and ICP-AES allow elemental composition of sample, while GC-MS allow us for the first time in the literature, the identification of the coniferous resin from the glue in mixture with fatty acids, plant oils and possibly beeswax used to bind the paint to the wall support. The composition and aging compounds found in this sample have been analyzed by FTIR and Raman spectroscopy. Also, 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*), together with their differences and the overall colorimetric difference between treated and not-treated samples: ΔE*.

Keywords: *FTIR, Raman, EDXRF, ICP-AES, GC-MS, CIELAB, Palace of Culture, Mosaico Bizantino decoration*

1. INTRODUCTION

The Palace of Culture, recognized as the most important Gothic monument from Iassy is one of the last expressions of Romanticism in Romanian architecture [1]. The edifice was built in the period 1906-1925; it is the most outstanding work of Romanian architect I.D, Berindei, which demolished the old buildings in the courtyard great princely courts and barracks. The exterior walls were decorated with heraldic elements [2].
Despite its archaic design, the Palace, the stone blocks have been replaced with lightweight and less expensive materials. Foe example, some rooms were decorated, using a special material patented by Henri Coanda, called bois cement or "concrete bois", and imitating oak [3]. This new construction material has been obtained through a patent in France, and even now its receipee is not completely known.
After 1977, when the palace became a museum, the original harmony has turned into kitsch typical communist era. A firm state monopoly, fully covered walls and ceilings those were painted and therefore very beautiful.
Being in a long restoration process, this palace needs optimal and correct solutions and materials, compatible with the initial ones. That's why, by using a fragment detached from the the building, we tryed now to identify the structure and composition of some painted surface, and the glue used to link the paint to the support.
Stone monuments worldwide are suffering from weathering and erosion due to natural causes and causes created through human impact [4]. Some known weathering processes work simultaneously to decompose rocks: physica (induced by the action of heat, water and pressure), chemical (due to the effects of atmospheric chemicals) and biological (provoqued by the microorganisms) in nature. Also, the stone surfaces exposed to intense sunlight or to high/low temperature variations can lead to shock on stones which can expand and contract differently, sometimes with coupled with salts in stone structure [5,6].
In this paper we are proposing a complex study about the structure and composition of a sample prelevated from

Palace of Culture, Iassy (as fragment detached from the the building), in order to identify the existing materials and to select the proper materials useful for restoration. Microscopy allows to observe the presence of the main weathering signs (chromatic alteration, alveolization, blistering, differential disaggregation, efflorescence, decohesion, exfoliation and detachment, cracking, delamination, disaggregation, flaking, loss), EDXRF and ICP-AES allow elemental composition of sample, while GC-MS allow us for the first time in the literature, the identification of the coniferous resin from the glue used to link the paint to the wall support. The composition and aging compounds foung in this sample, have been discussed. Also, 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*), together with their differences and the overall colorimetric difference between treated and not-treated samples: ΔE*.

2. EXPERIMENTAL SECTION

2.1. Materials and methods

The investigated sample is shown in Fig.1

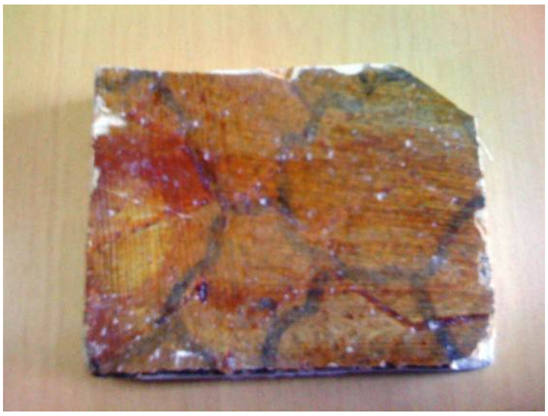


Fig.1. The photo of Mosaico Bizantino decoration

2.2 Characterization 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^{-1}) 200 – 4000, Spectral Resolution (cm^{-1}) 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.

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, performed with an energy dispersive instrument, EDXRF PW4025, type Minipal-Panalytical, with a Si(Li)-detector of 150 eV resolution at 5.89 keV (Mn-Kα-line).

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.

Gas-chromatography with mass spectrometry (GC/MS) has been achieved with GC/MS Triple Quad Agilent Technology (for compounds identification we based on NIST Library).

GC method: Column DB-WAX (L=30m, D=250 μm, d=0,25 μm; Oven Program: 50^{o}C for 5min., then 4^{o}C/min to 150^{o}C , then 10^{o}C/min to 320^{o}C; Carrier gas: He, Flow=1ml/min; Injector Temp.: 250^{o}C; Injection Volume: 0,5 μl

MS Method: QQQ Collision Cell: Quench Flow Gas (He) = 2,2 ml/min; Collision Flow Gas (N_2) = 1,5 ml/min; Type of Source : EI; Electron Energy : 70 eV; Source Temperature: 230^{o}C ; Aux Temp2. : 280^{o}C ; Scan Segment : 40-400; Type of Chromatogrm : TIC

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 [7, 8]. 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*[9]. According to the literature ΔE* < 5 was considered as corresponding to a not significant variation [10].

3. RESULTS AND DISCUSSIONS

The infrared spectroscopic analysis carried out on the sample prelevated from Palace of Culture allowed the identification of different inorganic phases and organic products, as follows (Fig.2):
- stretching vibrations of calcium carbonate ($CaCO_3$), peaked at 1962, 1409, 715 and 603 cm^{-1}.
- typical vibrational bands of gypsum ($CaSO_4 \cdot 2H_2O$), centered at 667 cm^{-1}, and its related forms (bassanite and anhydrite, as the main degradation forms of gypsum)
- bands of clay minerals were recognized, through the peaks from 975 cm^{-1} (Si–O–Si bond) from clay, and of calcite (1018 cm^{-1}) [11].
-the bands from 1010 cm^{-1} could be attributed to cellulose/silicate, as a proof for wood pieces and clay in the binder and support [12,13].
- The strong bands at 1409 and 1452 cm^{-1} are characteristic of pigments (ex.Verdigris or red lead);
- the bands below 700 cm^{-1} are assigned to TiO_2.
- the presence of S is from cadmium/zinc sulphide, used as yellow pigment.

Representative FTIR spectra of the analyzed samples are shown in Fig. 2.

Some of the FTIR bands are not visible in Raman spectra, most probably due to the absorption of different pigments used for painting and due to used binders.
- Raman bands associated with the glyceride carbonyl groups (1739 cm^{-1}), suggest the presence of a drying oil. Also, fatty acid carboxylate bands at 1519 and 1325 cm^{-1}, are identified, those being responsible for the reaction between the copper-containing pigment and the drying oil.

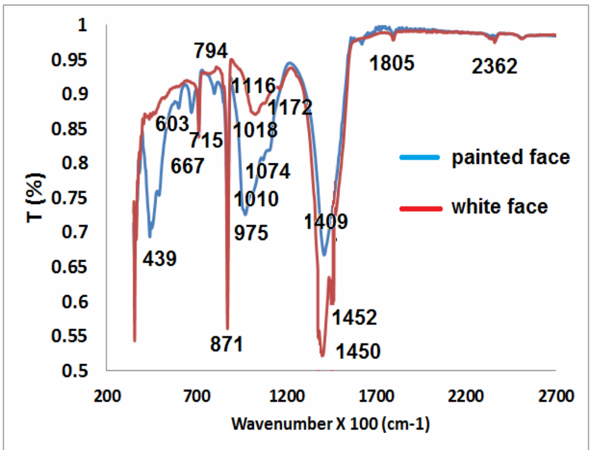


Fig.2. FTIR spectra of painted surface and support surface

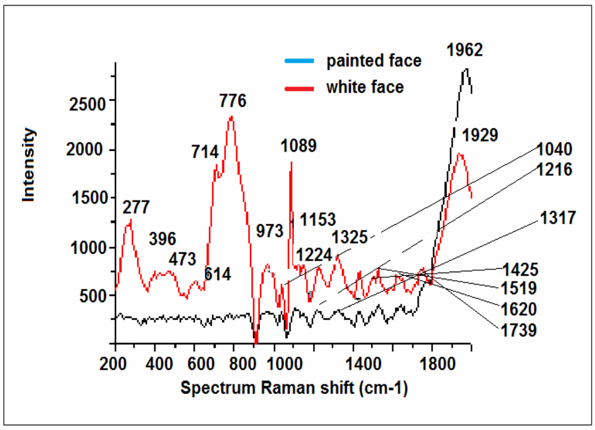


Fig.3. Raman spectra of painted surface and support surface

- Bands at 1409, 1074 and 667cm^{-1} demonstrate that the lead carbonate is present in the basic or hydrocerussite form, $2PbCO_3 \cdot Pb(OH)_2$, element visible from EDXRF investigations, too.
-the Raman bands from 1425 cm^{-1} could be attributed to calcium oxalate, most probably formed by degradation, but majority on the support [14].

Table 1. The ICP-AES results for Mosaico Bizantino decoration

Painted surface		Support surface	
Element	Concentration (%)	Element	Concentration (%)
Al	0.071259843	Al	0.008229167
Ca	0.866141732	Ca	1.90625
Sr	0.056496063	Sr	0.0528125
Mn	0.023031496	Mn	0.0053125
Fe	0.442913386	Fe	0.003333333
Cr	0.003149606	Cr	0.001041667
Mg	0.024212598	Mg	0.016979167
Na	0.076771654	Na	0.043020833
Zn	17.32283465	Zn	0.02090625
Cu	0.004330709	Cu	0.006875
K	0.013188976	K	0.006875
Pb	0.093503937	Pb	

Table 2. The EDXRF results for Mosaico Bizantino decoration

Support surface		Painted surface	
Element	Concentration (%)	Element	Concentration (%)
Al_2O_3	3.0	Al_2O_3	3.8
SiO_2	1.4	SiO_2	5.8
P_2O_5	2.7	P_2O_5	1.8
SO_3	55.7	SO_3	30.1
CaO	35.5	CaO	11.2

		TiO_2	0.51
		V_2O_5	0.17
		Cr_2O_3	0.11
Fe_2O_3	0.17	Fe_2O_3	3.98
ZnO	0.03	ZnO	42.0
		PbO	0.60
Cl	1.5		

The main conditions associated with the deterioration of stucco are: blistering (bubbles beneath the stucco), cracking (hairline to wide-open), delamination (the finish, brown, and scratch coats detach from one another), detachment (the stucco actually detaches from the wall beneath), disaggregation (loss of binder), flaking (thin, small layers of the finish coat loosen and flake off), loss (sometimes sheets of stucco detach and fall exposing the substrate beneath). Excessive water infiltration (through cracks or loss, for example) leads to a high moisture content. If salts are present in the stucco itself, cyclical wetting and drying can lead to damaging efflorescence. The leaching of the salts which then crystallize, expands, and attracts more moisture. Repeated freezing and thawing processes cause internal deterioration, detachment of stucco from the substrate, and delamination of the stucco's layers. Similar effects of water are responsible for cracking in stucco. All these stucco deterioration are visible in Fig.4.

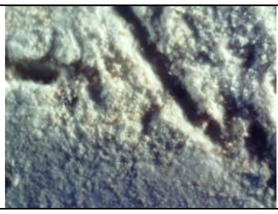
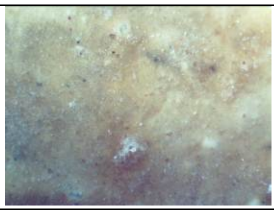
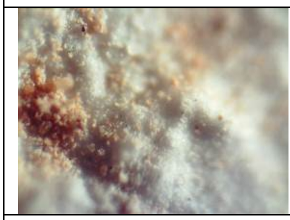
	
chromatic alteration and cracking	loss and exfoliation
	
alveolization	blistering and disaggregation
	
efflorescence	exfoliation, decohesion and detachment

Fig.4. Optical microscopy of deterioration of Mosaico Bizantino decoration

The main problem in thus case is the binder (glue) substrate, which is visible in Fig. 5.

Fig.5. The image of all layers from Mosaico Bizantino decoration

This binder powder prelevated with a spatula, has been extracted in methanol, filtered and and after that has been analyzed by GC-MS, Fig.6.

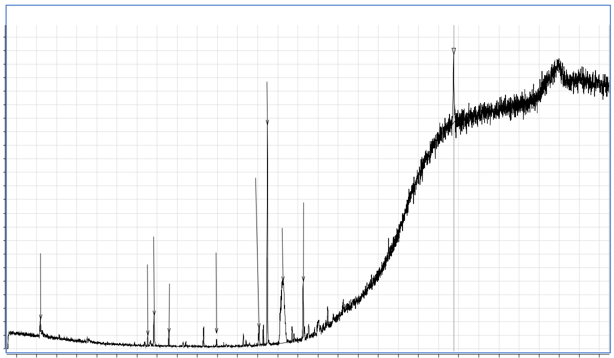


Fig.6. GC-MS results from Mosaico Bizantino decoration

Table 3. The compounds identified by GC-MS

RT	Area Sum %	Attribution
2.196	1.09	dl-phenylephrine
7.531	1.23	α-cubebene
7.851	3.62	δ-cadinene
8.592	1.46	Germacrene D
10.326	1.9	α-thujene
10.96	0.81	Dihydro-cis-α-copaene-8-ol
11.45	Not quantified	3-thujene-2-one
11.47	Not quantified	borneol
11.59	Not quantified	Terpinene-4-ol
13.083	2.44	Manoyl oxide
13.297	1.88	α-Terpinyl- acetate
13.489	22.89	Thubergen

13.68		α-copaene
14.236	41.43	sclareol
14.726	1.71	N.D.
15.09		α-Muurolene
15.27	6.25	Pimara-7,15-dien-3-one
16.492	2	α-cadinol
22.749	11.29	N.D.

The presence of fatty acids, diacids, hydroxy-acids, long chain alcohols and specific alkane patterns highlighted the presence of beeswax, animal fats, plant oils and pine resin. GC-MS analysis of the binder showed that the medium consisted of oil with addition of natural resin.

As a weathering sign, the chromatic alteration is visible from the chromatic parameters: ΔE=0.91; ΔL=0.24, ΔC=0.83; ΔH= 0.29. These very small differences of the chromatic parameters of the painted face vs. white face indicated that:

- during the time, the painted face supported a bleaching process;
- the adsorbtion of the pigments into binder and substrate;
- during the degradation, many islands are formed, containing white efflorescence, fragments loss, all together contributing to the whitening of the painted face of the examined sample [14].

4. CONCLUSIONS

In this paper we are proposing a complex study about the structure and composition of a sample prelevated from Palace of Culture, Iassy (as fragment detached from the building, without value), in order to identify the existing materials and to select the proper materials useful for restoration. Microscopy allows to observe the presence of the main weathering signs (chromatic alteration, alveolization, blistering, differential disaggregation, efflorescence, decohesion, exfoliation and detachment, cracking, delamination, disaggregation, flaking, loss), EDXRF and ICP-AES allow elemental composition of sample, while GC-MS allow us for the first time in the literature, the identification of the coniferous resin from the glue used to link the paint to the wall support. The composition and aging compounds found in this sample have been analyzed by FTIR and Raman spectroscopy. The presence of fatty acids, diacids, hydroxy-acids, long chain alcohols and specific alkane patterns highlighted the presence of plant oils and pine resin. Also, The CIELAB color parameters were calculated and indicated a very small difference between painted and white surface, as a proof of the weathering process in time.

5. ACKNOWLEDGEMENTS

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

6. REFERENCES

[1] Cheptea Stela, Lăcrămioara Stratulat, *Cercetări arheologice din Palatul Culturii – Iaşi,* A XLV-a Sesiune Naţională de Rapoarte Arheologice, Sibiu, 26-29 mai 2011.

[2] Cheptea Stela, *Cercetările arheologice de la Curtea domnească din Iaşi*, Sesiunea anuală a Centrului de Istorie şi Civilizaţie Europeană al Filialei Iaşi a Academiei Române, în cadrul „Zilelor Academice”, Iaşi, 15 septembrie , 2011.

[3] Cheptea Stela, Apăvăloaei B, *Cercetări arheologice din Palatul Culturii – Iaşi. O altă viziune*, Simpozionul Naţional Monumentul. Tradiţie şi Viitor, ediţia a XIII-a, Iaşi, 12-16 octombrie 2011.

[4] Pope Gregory A, Meierding Thomas C, and Paradise Thomas R. *Geomorphology's role in the study of weathering of cultural stone.* Geomorphology, 47(2-4):211–225, 2002.

[5] Bonazza A, Sabbioni C, Messina P, Guaraldi C, and De Nuntiis P. *Climate change impact: Mapping thermal stress on Carrara marble in Europe.* Science of The Total Environment, 407(15):4506–4512, 2009

[6] Lipfert Frederick W.. *Atmospheric damage to calcareous stones: Comparison and reconciliation of recent experimental findings.* Atmospheric Environment (1967), 23:415–429, 1989.

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

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

[9] Derrick M., Stulik D., Landry J. (1999). *Infrared Spectroscopy in Conservation Science.* The Getty Conservation Institute, Los Angeles.

[10] 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

[11] Mihalache Victor, Aur Virgil, Ciobănasu Corneliu, *Aspecte Privind Lucrările De Consolidare, Restaurare Si Amenajare La Palatul Culturii Iasi,* Monumentul. Traditie si Viitor, VIII, 2012, 1-12.

[12] Jokilehto, Jukka – *A history of architectural conservation*, Elsevier Butterworth Heinemann, London, 2004

[13] Pedemonte Enrico, Fornari Gabriella – *Chimica e restauro. La scienza dei materiali per l'architettura*, Marsilio Editoru, Venezia, 2003

[14] Ion RM, Turcanu-Caruțiu D, Fierăscu R.C., Fierăscu I., Bunghez I.R., Ion M.L., Teodorescu S., Vasilievici G., Rădițoiu V., *Caoxite-Hydroxyapatite Composition As Consolidating Material For The Chalk Stone From Basarabi-Murfatlar Churches Ensemble*, Applied Surface Science, 2015, doi:10.1016/j.apsusc.2015.08.196,