Romanian Reports in Physics **71**, 804 (2019)

ARCHAEOMETRIC STUDIES OF MURAL PAINTS FROM MATIA LOGGIA (CORVINS' CASTLE)

R.M. ION[1,2], S. TINCU[3], N. ION[1], I.A. BUCURICA[4], S. TEODORESCU[4], I.D. DULAMA[4], R.M. STIRBESCU[4], A.I. GHEBOIANU[4], C. RADULESCU[4], M.L. ION[5], L. IANCU[1,2], R.M. GRIGORESCU[1]

[1] ICECHIM, Group of Evaluation and Conservation Cultural Heritage, 202 Splaiul Independentei 06621-Bucharest, Romania
E-mails: *rodica_ion2000@yahoo.co.uk; ionpnelu@gmail.com; lorenna77ro@yahoo.com; rmgrigorescu@gmail.com*
[2] "Valahia" University, Materials Engineering Dept., 13 Aleea Sinaia, Targoviste, Romania
E-mails: *rodica_ion2000@yahoo.co.uk; lorenna77ro@yahoo.com*
[3] Corvins' Castle, 1–3 Strada Castelului, 331141-Hunedoara, Romania
E-mail: *sorin_tincu@yahoo.com*
[4] "Valahia" University of Targoviste, Institute of Multidisciplinary Research for Science and Technology, 13 Aleea Sinaia, Targoviste, Romania
E-mails: *bucurica_alin@yahoo.com; sofiateodorescu@yahoo.com; dulama_id@yahoo.com; stirbescu_nic@yahoo.com; anca_b76@yahoo.com; radulescucristiana@yahoo.com*
[5] "Atelierul de Creatie" NGO, Bucharest, Romania
E-mail: *lucia.mihaella@gmail.com*

Received October 10, 2018

Abstract. The analysis of the pigments from the Matia's loggia of Corvins' Castle, have been achieved in this paper in order to collect informations about the composition and weathering/deterioration processes of this mural paint. X-ray diffraction (XRD) correlated with optical microscopy (OM), scanning electron microscopy with energy-dispersive spectrometry (SEM-EDS), have been used for identification and quantification of the main components, in relationship with FTIR and Raman spectrometry and with chromatic parameters, too.

Key words: Corvins' Castle, OM, SEM-EDS, XRD, FTIR, Raman, chromatic parameters.

1. INTRODUCTION

A mysterious fresco (Matia's loggia), barely visible in the Corvins' Castle, depicts one of the most beautiful accounts of the family of John of Hunedoara over time [1, 2]. This fresco, in danger of disappearing because of its degradation stage, is one of the most impressive mural paintings in the Corvins' Castle, and is almost erased due to time degradation [3–5]. The mysterious fresco dates back to the end of the 15th century, according to historians, and its remnants can be seen today on the arch of Matia's wing floor of the castle. **The first group** was a woman with the apple of the kingdom in her hand, and in front a male figure, holding a round, undefined object. **The second group** consisted of a man who offered the woman a seal ring similar to the Huniad's ring, while the woman made a gesture of refusal. **The third group** depicted a woman, this time with a raised head, a sign that she was a mother, also represented with the prominent belly, and holding a circle with two wedding rings in her hand, and in front of her the man, making this time a gesture of refusal. On a side column there is a child with the apple of the kingdom in his hand, and a filater was carried over his head with a worn inscription, which Stefan Moller believed he could read the name of Johannes [6].

The results offered by som analytical techniques, developed in the field of materials science for objects of art and archaeology offer to the archaeologists the informations about the material composition and manufacturing technology of such objects [7, 8]. X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy-dispersive spectrometry (EDS) have been widely used for the analysis of archaeological objects of art [9], being known that such techniques are non-destructive and non-invasive techniques for analyzing valuable objects. Also, FTIR, Raman, chromatic parameter measurements, will be used for analysis of paints and pigments and for the evaluation the weathering/ deterioration processes of the investigated artifacts.

2. MATERIALS AND METHODS

2.1. SPECIMENS SAMPLES

The prelevated samples were collected from the monument wall, without any value for this monument (Fig. 1).

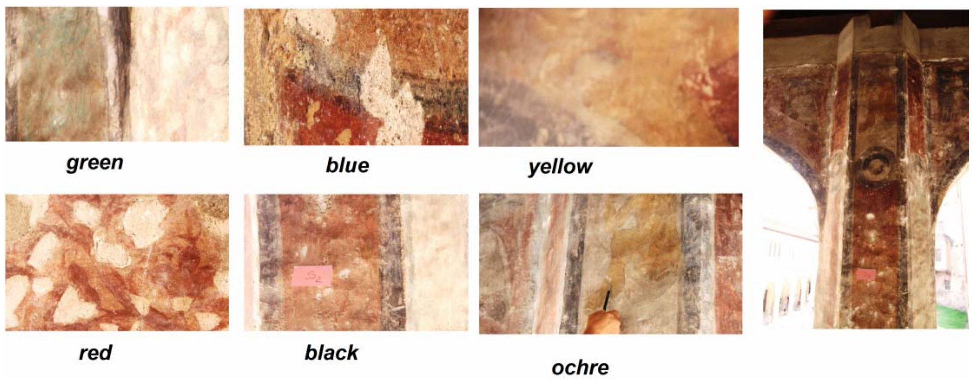


Fig. 1 – (Color online). The aspects of the wall with different pigments.

2.2. CHARACTERISATION TECHNIQUES

The diffraction data (XRD) for the powder were recorded on a X-ray diffractometer Rigaku Ultima IV, equipped with software for control, control acquisition and data conversion, with the technical features: X-ray tube – Cu anode (2 kW); detector – NaI with limitation > 700,000 cps; Bragg-Brentano focused high-resolution geometry; Software: PDXL 2.2. (processing), ICDD-PDF4 + 2016.

Fourier transformed infrared spectroscopy (ATR-FTIR) measurements has been recorded with a Vertex 80 spectrometer (Bruker Optik GMBH, Germania) in the range of 4000 – 400 cm^{-1}, 32 scan, resolution 4 cm^{-1}, equipped with DRIFT accessory. Also, this apparatus could work in Attenuated Total Reflectance, ATR module.

For Raman spectra, a portable dual wavelength Raman (Rigaku, USA) analyzer equipped with with a standard diode-pumped, air-cooled Nd:YAG laser source (power of 252 mW) (785 nm and 1064 nm) with high sensitivity, resolution of 4 cm^{-1}, have been used. Data were collected and processed with the software Opus 7.0 (Bruker Optics GmbH).

The optical microscopy was performed with a Primo Star ZEISS optical microscope in transmitted light at a magnification between 4× and 100×. The equipment had attached a digital video camera (Axiocam 105) which, by the microscope software, allowed real-time data acquisition.

The Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) was obtained with a SU-70 (Hitachi, Japan) microscope, with a magnification range of 30×–800.000×. SEM has been coupled with an energy dispersive spectrometer (EDS) which allows qualitative and quantitative analysis (from Be ($Z = 4$) to Pu ($Z = 94$)).

Color measurements have been recorded with CM-2600d spectrophotometer (KONICA MINOLTA) (Japan) under a D65 light source and an observer angle of 10°. The total color differences ΔE^*_{ab}, the lightness (L^*), a^* and b^* as the color coordinates under any testing condition.

3. RESULTS AND DISCUSSION

In the object of art studies, the analysis is more difficult due to severe limitations imposed on sampling. This is the reason of an increasing demand for nondestructive or microanalytical techniques that minimize the amount of analyzed sample without compromising the quality of results about the samples is demanded, that provide fully comprehensive material characterization [10]. For ancient decorative layers from mural pictures that cover external surfaces of architectural heritage (patinas), multidisciplinary analyses in archeology, conservation and chemistry, are necessary [11, 12].

Ussually, a wall is made from stone blocks bound with a mortar made of clay and lime. The arricio is rough and composed of lime and fine aggregates of quartz and volcanic stone, while the intonaco is very fine and thin, made from lime and clay and fine aggregates of phytoliths, quartz and volcanic stone. The pigments used for paintings are constituted from different minerals as follows: white: calcium carbonate, black: carbon black, red: iron oxide (hydroxide)-hematite; ochre: hydrated iron oxide (limonite) or goethite; blue: natural indigo/azurite and clay as paligorskyte [13] or blue earth is vivianite [$Fe_3(PO_4)_2 \cdot 8H_2O$], an iron phosphate hydrate known as "blue ochre" [14]. Green earths or terres vertes are pigments derived from the minerals celadonite ($K[Mg,Fe^{2+}]Fe^{3+}[Si_4O_{10}][OH]_2$) and glauconite ($[K,Na][Mg,Fe^{2+},Fe^{3+}][Fe^{3+},Al]\ [Si,Al]_4O_{10}[OH]_2$) [15].

When the stone surface shows degradation processes, calcium sulphate is present and this compound could be identified by FTIR spectrum, through the following bands: O-H stretching vibrations in the range 3700–3200 cm^{-1}, stretching vibrations of SiO_4^{3-} in the range 1140–1120 cm^{-1} and the bending vibrations of the same groups in the range: 700–550 cm^{-1}. The strong bands are observed at 3405 and 3546 cm^{-1}, the stretching vibration has a strong doublet band at 1117 and 1140 cm^{-1} and the bending vibrations of the SO_4 tetrahedron shown at 669 and 604 cm^{-1} [16, 17]. All paint layers demonstrate the presence of salt efflorescence. For celadonite, there are some specific OH bands at 3601, 3556 and 3533 cm^{-1} (Fig. 2).

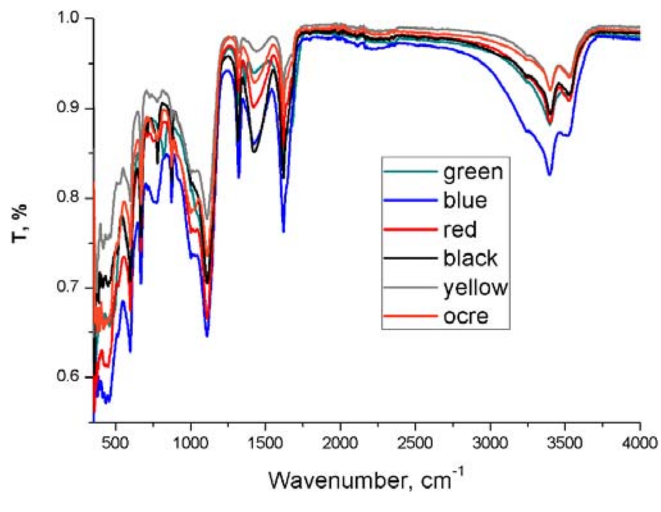


Fig. 2 – (Color online). FTIR spectra of the investigated pigments.

In the investigated samples, calcium and magnesium carbonate were detected, identified by CO_3 asymmetric stretching band (splitted in two bands at 1421–1481 cm^{-1} area (specific for calcite), the absorption band from 800 cm^{-1}, 850 and 680 cm^{-1} assigned to bending vibrations, band from 1120 cm^{-1}, with a detailed reprezentation for the area 400–1500 cm^{-1}. The Raman experiments were performed directly on the samples prelevated in very small quantities from the Corvins' Castle (pieces of wall paintings) – Fig. 3. Two visible diode lasers are available in this apparatus: 785 nm and 1064 nm. The literature also reports the effectiveness of Raman spectroscopy to identify the artworks [18].

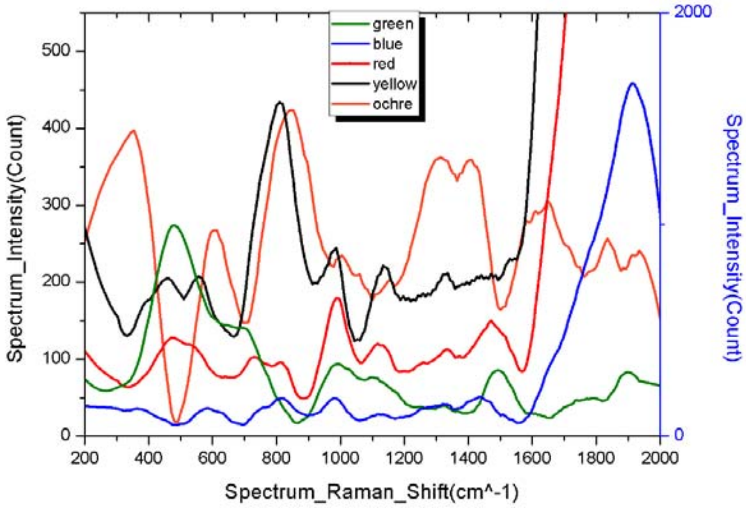


Fig. 3 – (Color online). Raman spectra for the pigments prelevated from Loggia Matia (except the black one).

The pigments found in the samples are analyzed by Raman spectra in the 200–2000 cm^{-1} region, as follows: **The white colour** of the wall sample, contain gypsum for the base layer, which displayed a single band at 1006 cm^{-1} and calcite ($CaCO_3$) identified in by the bands at 1090, 713 and 278 cm^{-1}. Also, TiO_2 was identified in various white areas of the paint displaying bands at 607, 442 and 258 cm^{-1} [19].

The green pigments could be a mixture of orpiment (As_2S_3), with bands at 355 cm^{-1}, and medium intensity ones at 292 and 382 cm^{-1}, and different basic copper sulphates emerald green ($Cu(C_2H_3O_2) \cdot 3Cu(AsO_2)_2$). Bands at 416 cm^{-1} are assigned to brochantite ($Cu_4(SO_4)(OH)_6$), while the bands at 593 cm^{-1} are due to langite ($Cu_4(SO_4)(OH)_6 \cdot 2H_2O$) [19]. Certainly, celadonite is present here, as FTIR detected above.

Blue pigment. The Raman examination of the blue pigments revealed Ultramarine blue ($Na_7Al_6Si_6O_{24}(S_n^-)$) (band at 546 cm^{-1} with its shoulder at 585 cm^{-1}) coexisting with malachite ($CuCO_3 \cdot Cu(OH)_2$) and azurite ($2CuCO_3 \cdot Cu(OH)_2$). Also, natural indigo ($C_{16}H_{10}N_2O_2$), in samples, characterized by some bands at 250, 545, 599 and 1582 cm^{-1} [20].

Red pigment. Hematite in majority-identified by the bands from 612 cm^{-1}, celadonite and glauconite.

Yellow pigment. Chrome yellow ($2PbSO_4 \cdot PbCrO_4$ or $PbCrO_4$) [18, 19] (839 cm^{-1}), coexisting with bands of orpiment (As_2S_3), and also goethite (FeO(OH)), with bands at 297, 395 and 1113 cm^{-1}.

Ochre color corresponds to an iron (III) oxide chromophore (Fe_2O_3 plus clay and silica), is explained by the strong Raman band observed at 287 cm^{-1} [21–23]. The bands at 662 and 614 cm^{-1} could be ascribed to magnetite ($FeO \cdot Fe_2O_3$), and also, red lead (Pb_3O_4) could be present.

All these results could be very well correlated with elementary analysis of the present elements detected by EDS (Figs. 4, 5).

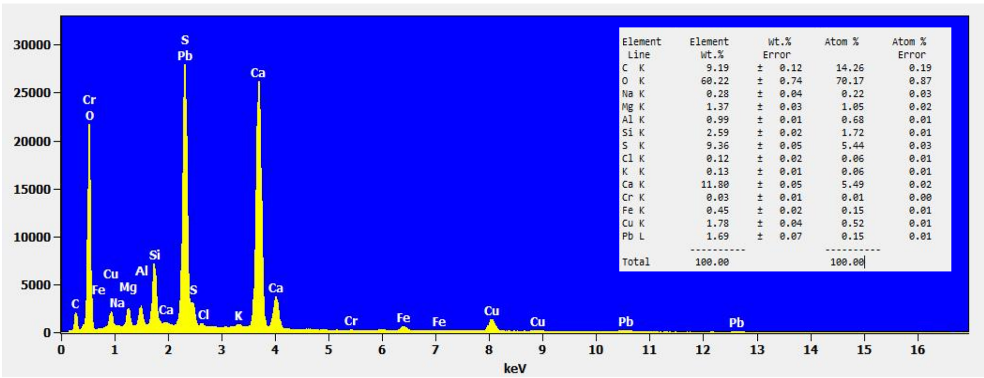


Fig. 4 – (Color online). The EDS example for green pigments.

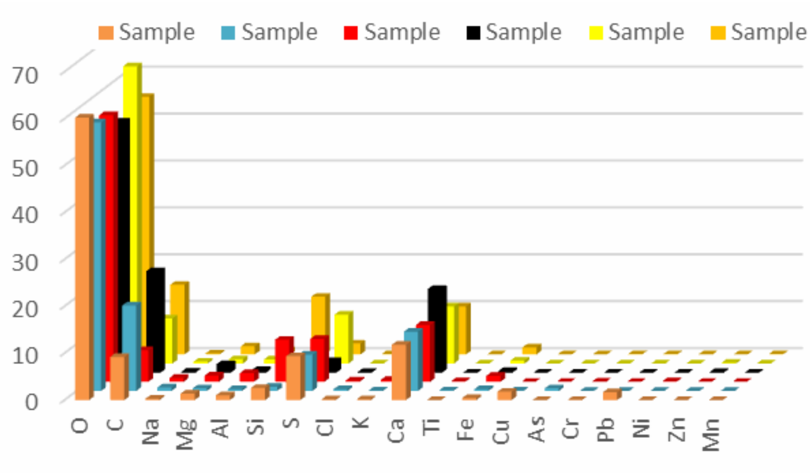


Fig. 5 – (Color online). The graphical representation of elements (by EDS) from the studied pigments.

In antiquity the number of mineral pigments is very high, for example, hematite (reddish, orange, purple, and brown), goethite (yellow), lepidocrocite (brown), calcite (white), dolomite (white), celadonite (green), malachite (green), and quartz (translucent and white). In XRD diagrams, the above-mentioned minerals have been identified, and another, too, as follows: all pigment bearing layers (green, blue, red and yellow) contain *calcite* which derives from the lime binding matrix in the paint, and also gypsum, derived from the degradation processes supported by this mural paint [24]. The artistic palette is composed of mineral pigments: goethite, hematite, azurite and two species of earth green pigments which are celadonite and glauconite, cerussite [25]. The black pigment could be of animal origin (bone or ivory black) – Fig. 6.

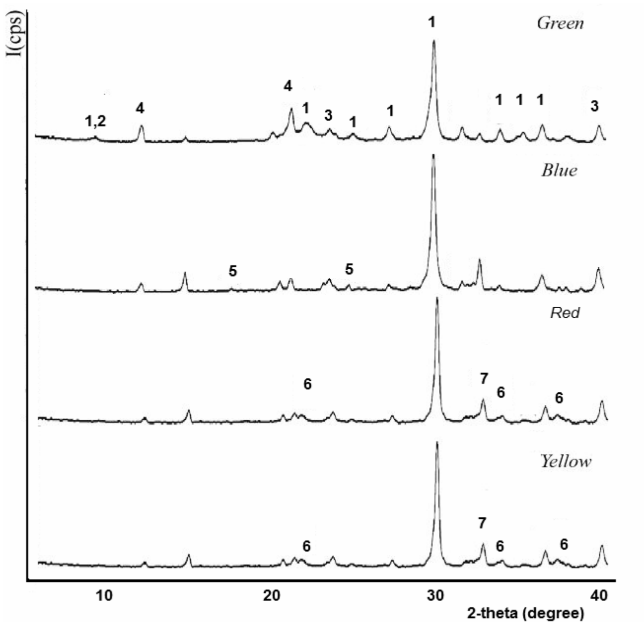
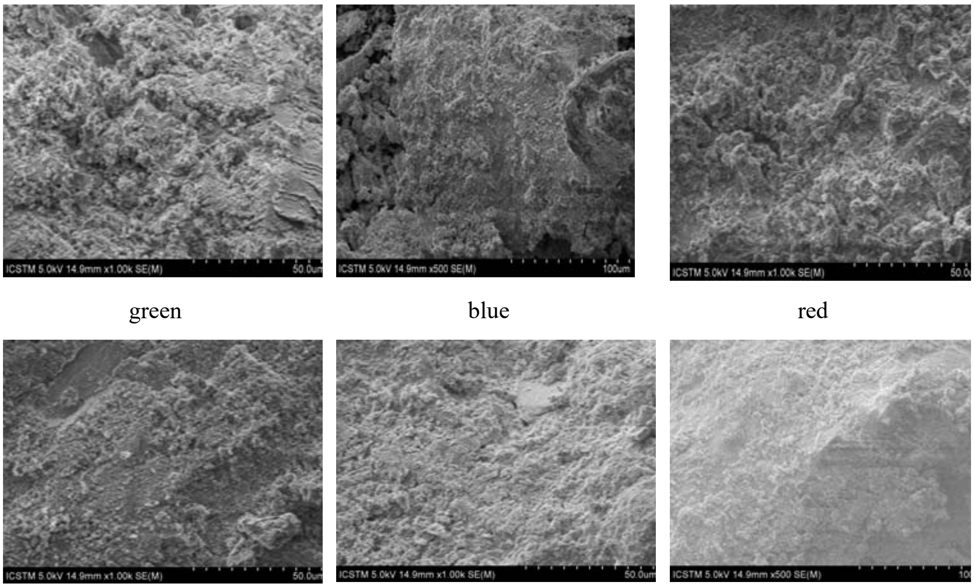


Fig. 6 – XRD diagram sor the identified pigments (1 = celadonite; 2 = glauconite; 3 = calcite; 4 = gypsum; 5 = azurite; 6 = goethite; 7 = haematite).

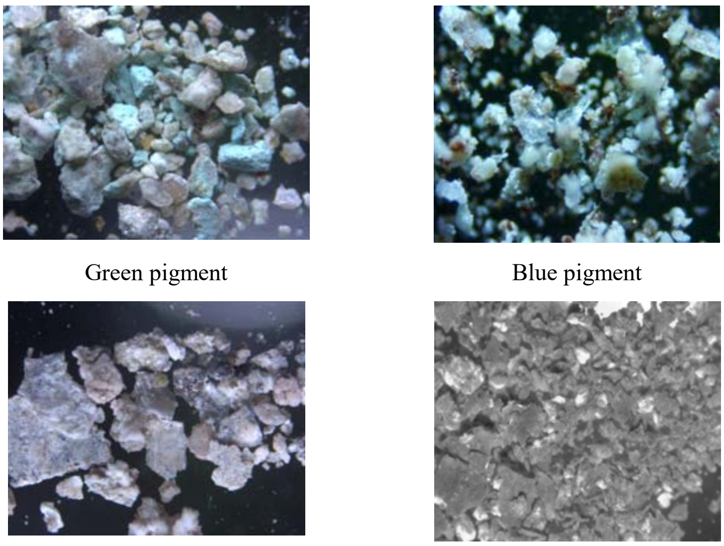
Single point analysis using SEM-EDS revealed ubiquitous Ca in the coating (as binder and aggregate), attributed to calcite (Fig. 7). Silicon was detected in the most abundant, largest, and irregularly shaped particles with a broad grain size distribution (~10–100 µm), suggesting the presence of quartz as an aggregate. Fewer amounts of smaller particles (<10–50 µm) also identified as aggregates were made of Mg and interpreted as dolomite. Scarce acicular crystals composed of Al, Si, Mg, and K were identified. In the SEM images, scarce angular grains of variable crystal size below ~15 µm in diameter were seen. The analyses identified Fe and Ti, attributed to hematite (Fe_2O_3) and rutile (TiO_2), respectively [26]. These particles, not easily observed with OM due to their small crystal size, but were clearly identified in the SEM-EDS images (Figs. 7, 8).



green blue red

black yellow ochre

Fig. 7 – SEM images of the studied pigments.



Green pigment Blue pigment

Red pigment Black pigment

Fig. 8 – (Color online). The OM images of the main pigments identified at Loggia Matia.

In CIEL*a*b* measurements, L* defines lightness and its values range from 0 to 100, a* and b* represent, respectively, red/green and yellow/blue tone axes (Fig. 9). Due to the repeated conservation/restoration procedures applied to these mural paints, was very difficult to strictly select a single color. This could be the reason of overlapping the colors for all the investigated pigments, which has been observed for different supports [27, 28].

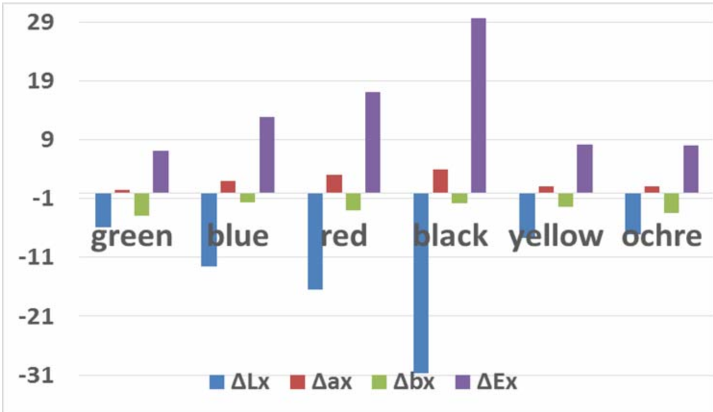


Fig. 9 – (Color online). Cromatic parameters of the pigments identified at mural paint.

4. CONCLUSIONS

In this paper has been treated the structural, morphological and compositional aspects of the pigments prelevated from the Matia's loggia of Corvins' Castle, in order to collect informations about the manufacturing and weathering/deterioration processes of this mural paint. A complex collection of analytical techniques: optical microscopy, scanning electron microscopy with energy-dispersive spectrometry (SEM-EDS), X-ray diffraction (XRD), optical microscopy (OM), in relationship with FTIR and Raman spectrometry and with chromatic parametershave, in order to identify the major constituents of these pigments. The major constituents and their provenance have been identified and discussed in correlation with local raw materials and traditional prepared compounds.

Acknowlegements. This study was supported by the grant 51PCCDI/2018, from UEFISCDI-MEN.

REFERENCES

1. C.C. Roman, S. Tincu, *Notes on the religious complex of the Corvins' Castle, Hunedoara*, Terra Sebvs. Acta Mvsei Sabesiensis **1**, 153–157 (2009).
2. C. Bogdan, *Contribuţii arheologice la cunoaşterea evoluţiei Castelului Corvineştilor de la Hunedoara*, BMI **XXXIX**(2), 18–25 (1970).

3. C.C. Roman, *Cronica Cercetărilor Arheologice din România,* CIMEC – Institutul de Memorie Culturală, Bucureşti **86**, 101–105 (2001).
4. C.C. Roman, *Cronica Cercetărilor Arheologice din România*, CIMEC – Institutul de Memorie Culturală, Bucureşti **92**, 144–145 (2003).
5. I. Bodochi, *Castelul Corvinilor în secolul al XVII-lea (1),* Corviniana **XII**, 207–232 (2008).
6. P. F. Sugar, P. Hanák and T. Frank, *A History of Hungary*, Indiana University Press, 1994.
7. R. M. Ion, L. Iancu, D. Carutiu-Turcanu, V. Schroder, S. Tincu, C. Roman, N. Ion, I. A. Bucurica, S. Teodorescu, I. D. Dulama, R. M. Stirbescu and A. Gheboianu, *Traditional building materials and modern restoration products identified at the painted Matia-fresco Loggia, Corvins' Castle, Romania,* Geophysical Research Abstracts **20**, 5198 (2018).
8. R.M. Ion, L. Iancu, R.M. Grigorescu, D. Carutiu-Turcanu, S Tincu, N. Ion, I.A. Bucurica, S. Teodorescu, I.D. Dulama, R.M. Stirbescu, A. Gheboianu and M.L. Ion, *Arhaeometric Concepts and Methods of Intervention on Historical Monument Buildings. The Case of the Corvins' Castle,* IOP Conf. Series: Mat. Sci. Eng. **374**, 012073 (2018).
9. R.M. Ion, L. Iancu, R.M. Grigorescu, S. Tincu, G. Vasilievici, N. Ion, I.A. Bucurica, S. Teodorescu, I. D. Dulama, R. M. Stirbescu, C. Radulescu and M. L. Ion, *Arhaeometric investigations on ceramic materials FROM Hunedoara – THE COURT AREA,* Journal of Science and Arts **18**, 471–480 (2018).
10. G. Artioli, *Scientific Methods and Cultural Heritage*, New York, Oxford University Press, 2010; Moropoulou, A. Bakolas and K. Bisbikou, *Investigation of the technology of historic mortars,* J.Cult. Heritag. **1** (1) 45–58 (2000); DOI: 10.1016/S1296-2074(99)00118-1.
11. R.M. Ion, *Materiale de Istorie şi Muzeografie* **XXX**, 80–98, Editura MMB, Bucureşti, 2016.
12. M. Steiger, E.A. Charola and K. Sterflinger, *Weathering and deterioration. In Stone in Architecture*, Springer: Berlin/Heidelberg, Germany, 2011.
13. R. Siddall, *Mineral Pigments in Archaeology: Their Analysis and the Range of Available Materials*, Minerals **8**, 201 (2018). DOI: 10.3390/min8050201.
14. Putnis, B. Winkler and L. Fernandez-Diaz, *In situ IR spectroscopic and thermogravimetric study of the dehydration of gypsum,* Mineralogical Magazine **54**, 123–128 (1990). DOI: 10.1180/minmag.1990.054.374.14
    P. Adriano, A.S. Silva, R. Veiga, J. Mirao and A. Candeias, *Microscopic characterisation of old mortars from the Santa Maria Church in Évora,* Materials Characterization. **60** (7), 610 – 620 (2009). DOI: 10.1016/j.matchar.2008.11.008
15. S. Akyuz, T. Akyuz, S. Basaran, C. Bolcal and A. Gulec, *FT-IR and micro-Raman spectroscopic study of decorated potteries from VI and VII century BC, excavated in ancient Ainos – Turkey*, J. Molec. Struct. **834**, 150–158 (2007).
16. C. Genestar and C. Pons, *Earth pigments in painting: characterisation and differentiation by means of FTIR spectroscopy and SEM-EDS microanalysis,* Anal. Bioanal. Chem. **382**, 269–274 (2005). DOI: 10.1007/s00216-005-3085-8
17. M.R. Derrick, D. Stulik and J. M. Landry, *Infrared Spectroscopy in Conservation Science*, Los Angeles, The Getty Institute, 1999.
18. C. Cardell, I. Guerra, J. Romero-Pastor, G. Cultrone and A. Rodriguez-Navarro, *Innovative Analytical Methodology Combining Micro-X-Ray Diffraction, Scanning Electron Microscopy-Based Mineral Maps, and Diffuse Reflectance Infrared Fourier Transform Spectroscopy to Characterize Archeological Artifacts,* Anal. Chem. **81**, 604–611 (2009); DOI: 10.1021/ac8022444.
19. K. Castro, A. Sarmiento, I. Martinez-Arkarazo, J. M. Madariaga and L. A. Fernandez, *Green Copper Pigments Biodegradation in Cultural Heritage: From Malachite to Moolooite, Thermodynamic Modeling, X-Ray Fluorescence, and Raman evidence*, Anal. Chem. **80**, 4103–4110 (2008). DOI: 10.1021/Ac800255w.
20. L. Burgio and R. Clark, *Library of FT-Raman Spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman Spectra of Pigments with Visible excitation*, Spectrochim. Acta A **57**, 1491–1521 (2001).

21. D. L. A. De Faria, S. V. Silva and M. T. J. De Oliveira, *Raman microspectroscopy of some iron oxides and oxyhydroxides*, Raman Spectrosc. **28**(11), 873–878 (1997). DOI: 10.1002.
22. F. Casadio, C. Daher and L. Bellot-Gurlet, *Raman Spectroscopy of cultural heritage Materials: Overview of Applications and New Frontiers in Instrumentation, Sampling Modalities, and Data Processing*, in R. Mazzeo (ed.), *Analytical Chemistry for Cultural Heritage*, Berlin, Springer, 2017, 161–212.
23. D. Bersani, P.P. Lottici, S. Virgenti, A. Mora, F. Ospitali, E. Salvioli-Mariani, M. Catarsi and C. Pedrelli, *Micro-Raman and SEM-EDS investigation of medieval pottery.* In: Raman in art and archaeology Conference, Modena, Book of abstracts **45** (2009).
24. G. D. Smith and R.J.H. Clark, *Raman microscopy in art history and conservation science,* Reviews in Conservation **2**, 96–104 (2001).
25. R.M. Ion, T. Nyokong, N. Nwahara, I.R Suica-Bunghez, L. Iancu, S. Teodorescu, I. D. Dulama, R.M. Stirbescu, A. Gheboianu and R.M. Grigorescu, *Wood preservation with gold hydroxyapatite system,* Heritage Science **6**, 1–12 (2018).
26. N. Eastaugh, V. Walsh, T. Chaplin and R. Siddall, P*igment compendium: A Dictionary of Historical Pigments;* Elsevier Butterworth-Heinemann: Oxford, 2004.
27. JIS Z8729:2004. Color specification-CIELAB and CIELUV color spaces.
28. Nazdar Ink Technologies. Available online: https://www.nazdar.com/en-us/News-events/ArtMID/4165/ArticleID/224