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XRF and Raman Spectroscopic Study of Wall Polychromes in the Saltworks Castle in Wieliczka

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Abstract – **This study presents a comprehensive spectroscopic investigation of polychrome wall decorations recently uncovered in the Northern Wing of the Saltworks Castle in Wieliczka, Poland. Believed to date from the 16th to 19th centuries, these multi-layered wall paintings - remarkable for their secular context and heraldic motifs - were examined using X-ray fluorescence (XRF), Raman spectroscopy (RS), and Fourier-transform infrared spectroscopy (FTIR). The analysis focused on pigments and binders, confirming the use of 17th-century materials such as smalt, vermilion, malachite, lead-tin yellow, and protein-based binding media. The findings validate historical assumptions about the chronology and function of these rooms.**

I. INTRODUCTION

Studying the structural components, building materials, and plasterwork of heritage sites is essential for gaining a deeper understanding of historical architecture. Such analyses illuminate traditional construction techniques, offering crucial insights into the different phases of a building's development, as well as the properties and composition of the materials used - knowledge that is fundamental to conservation and restoration efforts. Continuous assessments of various materials, including mortars and plasters, also support the long-term monitoring of their condition and performance.

This study focuses on a series of polychrome wall paintings recently uncovered in the northern wing of the Wieliczka Saltworks Castle complex [1]. These extensive decorative schemes, comprising multiple layers, are believed to span from the 16th to the 19th centuries. The discovery is particularly significant due to the presence of heraldic symbols representing both the Polish-Lithuanian Commonwealth and the Vasa dynasty. The exceptional historical value of this find lies in the rare preservation of such a large, multi-period decorative ensemble in a non-religious setting in Poland.

The Wieliczka Saltworks Castle, once the administrative hub of the Wieliczka and Bochnia salt mines - together known as the Żupy Krakowskie enterprise - has a rich and layered history [1]. The architectural complex includes several distinct parts: the Middle Castle (13^{th} - 14th centuries), the Northern Castle (15th century), the Southern Castle (19^{th} - 20th centuries), and a 14th-century tower. Initially developed in the 13th century near a salt exploration shaft, the castle stands as an example of medieval military architecture, closely linked to the history of the state-controlled Cracow Saltworks. The site was administered by a royal appointee under the authority of the princes of Cracow and later the kings of Poland. A major phase of expansion and fortification occurred under King Casimir the Great in the 14th century, significantly contributing to the region's prosperity. Over more than 650 years, the castle has endured fires, wars, sieges, and other destructive events, the most devastating of which was the Soviet bombing in 1945 that severely damaged the central section. After this, the castle ceased to serve as the administrative center of the mines. Restoration of the Northern Wing was completed in 2024, and today, the revitalized castle houses the Kraków Saltworks Museum. In 2013, in recognition of its cultural and historical significance, the castle was inscribed on the UNESCO World Heritage List as an extension of the salt mines listing.

In 2022, decorative wall paintings spanning several historical periods were fully exposed for the first time in six rooms on the first floor of the Northern Castle. These polychromes, previously hidden beneath thick layers of secondary plaster, reflect the stylistic preferences of various eras and provide insight into the evolving functions of the rooms. Historically, the spaces served both administrative and residential purposes for high-ranking officials of the salt enterprise. Most of the well-preserved decorative layers date to the 19th century, while earlier layers have survived to a lesser extent, likely due to centuries of fire damage, renovations, and seismic activity from mining operations.

Initial stratigraphic investigations were conducted in the 1980s, confirming the presence of valuable painted layers. However, only limited exploratory work was undertaken at the time, which did not permit a comprehensive understanding of the extent of the polychrome decoration. The decision to fully uncover the artwork was not made until 2022. Following their exposure, extensive material analyses were performed. Wall samples were collected for pigment, binder, and stratigraphic analysis. Techniques used included X-ray fluorescence (XRF) spectroscopy and Raman spectroscopy (RS) for pigment identification, Fourier-transform infrared spectroscopy (FTIR) for binder analysis was also employed. These diagnostic analyses were conducted specifically in the first-floor rooms of the Northern Castle wing. The comprehensive analysis of the samples provided critical data on the techniques and materials used, as well as the chronology and stratification of the layers - particularly those bearing the coats of arms of the Polish-Lithuanian Commonwealth and the Vasa dynasty.

II. EXPERIMENTAL

The wall paintings are preserved only fragmentarily and exhibit a structurally complex and uneven surface. This publication focuses on the wall paintings believed to represent the oldest decorative layers, located in rooms 1.2 and 1.3 on the eastern side (see Figure 1).

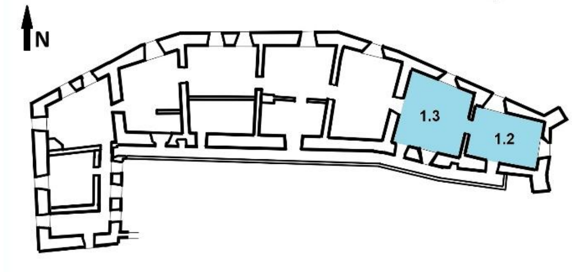

Fig. 1. Floor plan of the Northern Castle of Wieliczka Saltworks Castle.

Prior to sampling, a comprehensive visual inspection was conducted to assess the condition of the paintings. Based on this assessment, a targeted sampling plan was established, selecting the most representative areas according to their decorative schemes and stratigraphy. Priority was given to zones that exhibited relatively good preservation, ensuring that the collected material reflected a broad range of colors. Samples were collected manually using a scalpel to minimize damage to the historic surface. Elemental analysis of the painted surfaces was carried out using an ARTAX 800 spectrometer (Bruker, Berlin, Germany). This instrument features a rhodium (Rh) X-ray tube and polycapillary optics, providing a focused beam spot of approximately 65 µm. The X-ray generator was operated at 50 kV and 300 µA, with each measurement lasting 45 seconds. Integrated laser and camera systems allowed for precise beam alignment with the analysis points. Data acquisition and evaluation were performed using Spectra 5.3 software (Bruker, Berlin, Germany).

Micro-Raman spectroscopy was conducted to complement the identification of pigments and crystalline compounds. The analyses were performed using a Renishaw InVia spectrometer (Renishaw, Wotton-under-Edge, UK), equipped with a Leica DMLM confocal microscope and a Peltier-cooled CCD detector. Excitation was provided by a 785 nm diode laser, with a maximum power of ~200 mW at the excitation port. For the analyses, the laser power on the sample was reduced to approximately 1% in order to minimize the risk of thermal degradation. Spectra were acquired with integration times ranging from 1 to 30 s, typically accumulated over 10–100 scans to improve the signal-to-noise ratio. A Leica L50×/0.5 objective (working distance ~10.6 mm) was employed, resulting in a laser spot size of approximately 2 µm on the sample surface. Precise positioning was ensured by an automated motorized stage within the instrument's measuring chamber.

FTIR spectroscopy was employed to identify organic components, particularly binding media. Spectral data were collected using a Shimadzu IR Affinity-1 spectrometer (Shimadzu, Kyoto, Japan) equipped with a GladiATR module (Pike Technologies, Fitchburg, WI, USA) featuring a diamond crystal. Infrared spectra were recorded over the 4000–400 cm^{-1} range, at a resolution of 4 cm^{-1}, averaging 250 scans per sample. Data processing was conducted using IR Solution software (Shimadzu, Japan).

III. RESULTS AND DISCUSSION

Figure 2 shows the oldest preserved wall decoration (1.2,III) from Room 1.2. On the southern wall, a fragment of a heraldic composition is visible, featuring the coat of arms of the Polish-Lithuanian Commonwealth during the Vasa dynasty (1587–1668).

Fig. 2. Detail of the wall painting located in Room 1.2, depicting the coat of arms of the Polish-Lithuanian Commonwealth under the Vasa dynasty (southern wall), shown alongside a historical map titled Image of the *Wieliczka Salt Mine and the City of Wieliczka, created by Willem Hondius in 1645.*

The heraldic composition includes a crowned white eagle and the Lithuanian Pahonia, arranged in alternating fields. In the center, remnants of the Swedish royal coat of arms are visible - three grey crowns on blue - though other elements, such as the Folkung lion and the Vasa family's wheat sheaf, have not survived. Small remnants suggest the original decoration included a green cartouche and a golden crown. The shield layout corresponds to that in the royal Vasa chapel in Kraków (1664-1666), confirming its official character. Its presence in Wieliczka Castle - a secular site focused on salt production - is particularly rare, as polychrome wall paintings from the 16th and 17th centuries are typically preserved in religious buildings. The discovery of this official emblem in a secular context suggests that the castle served ceremonial functions and hosted royal visitors, such as Queen Maria Kazimiera in 1683. Thus, the discovery of this unique coat of arms painting not only enhances our understanding of the castle's status but also contributes significantly to Poland's cultural heritage.

In Room 1.3, the preserved fragmentary polychromy (1.3,IV) shown in Figure 3 was examined. It has been preliminarily dated to the 17th century. On the western wall, it forms an ornamental decoration in shades of green, red, ochre, blue, and grey, with the pattern accentuated in black. On the remaining walls, the painted layer is visible in smaller fragments. The dominant colours of this polychrome layer include red, blue, black, green, ochre, and grey.

Fig. 3. Detail of the wall painting located in Room 1.3.

The elemental composition identified through X-ray fluorescence spectroscopy (XRF) analysis is presented in Table 1. The following pigments were detected: calcium carbonate, tin-lead yellow, vermilion, minium, smalt, azurite, malachite, lead red [2]. The presence of mixture of lead red and lead white could not be excluded. Due to the limitations of the XRF technique, the presence of carbon black should be confirmed using other methods.

Table 1. Pigments identified in individual layers based on XRF studies.

Sample No.	Colour	Elements detected by XRF	Pigments
1.2, III,1	Red	S, Ca, Fe, Hg, Pb	Lead pigment (minium), vermilion
1.2, III,3	Blue	Si, K, Ca, Fe, Co, Ni, Cu, As, Hg, Pb, Bi	Cobalt pigment (smalt), copper pigment (azurite?)
1.2, III,5	Green	Ca, Fe, Cu, As, Pb	Copper pigment (malachite), lead white
1.2, III,6	Grey	Ca, Mn, Fe, Cu, Hg, Pb	Calcium carbonate, carbon black?
1.2, III,9	Green	Fe, Cu, Sn, Pb	Tin-lead yellow
1.3, IV,1	Red	Ca, Pb	Lead pigment (minium)
1.3, IV,2	Blue	K, Ca, Ti, Mn, Fe, Cu, As, Sr, Pb	Copper pigment (azurite)
1.3, IV,3	Black	K, Ca, Ti, Mn, Fe, Cu, As, Sr, Pb	Carbon black?
1.3,IV,4	Green	Ca, Mn, Fe, Cu, As, Pb	Copper pigment (malachite)
1.3,IV,6	Grey	Ca, Ti, Mn, Fe, Cu, As, Sr, Pb	Calcium carbonate, carbon black?

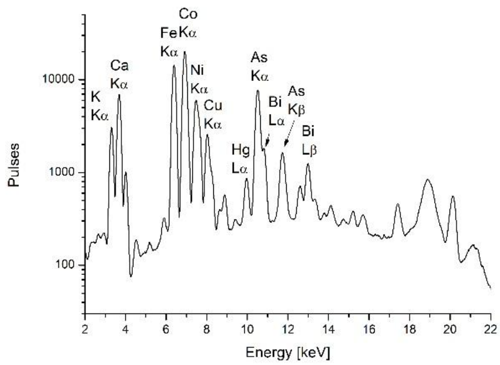

Fig. 4. XRF spectrum recorded from the blue section of the coat of arms located on the southern wall (painting decoration 1.2,III).

Figure 4 presents the XRF spectrum corresponding to the blue area (1.2,III,3) painted with smalt. Smalt is a type of finely ground blue glass that contains potassium (K), with its characteristic blue hue resulting from varying concentrations of cobalt (Co) ions. In addition to cobalt oxide - sometimes reaching levels of up to 70% - the composition may include other elements such as nickel (Ni), iron (Fe), arsenic (As), or bismuth (Bi), depending on the ore used [3]. This pigment was commonly produced in regions like Schneeberg and Saxony in Germany, as well as Bohemia. Its use has been widely documented in artistic works from the 15th century, with particular prevalence in the 16th and 17th centuries.

XRF results were further verified with Raman spectroscopy in the second stage of the study. For blue pigment Raman spectroscopy produces a very weak signal and finally only calcium carbonate was identified.

In the red area (1.2,III,1), cinnabar (HgS) was identified, with its spectrum shown in the Figure 5, characterized by bands visible at approximately 253, 286, and 343 cm^{-1}. Additionally, bands at 121, 391, and 550 cm^{-1} were observed and attributed to red lead (Pb_3O_4), while bands at 142 and 288 cm^{-1} indicated the presence of massicot (PbO) [4]. Vermilion, a bright red pigment historically derived from natural cinnabar or produced synthetically by combining mercury and sulfur. It has been widely used in various painting techniques throughout history, especially in wall painting, due to its high durability and resistance to both acidic and alkaline environments. Red lead, traditionally referred to as minium or Saturn red, is an artificially produced pigment, though it can also occur naturally. Employed since antiquity in both wall and panel painting, red lead is known for its vivid hue, although it may darken and acquire a brownish tint over time when used on murals.

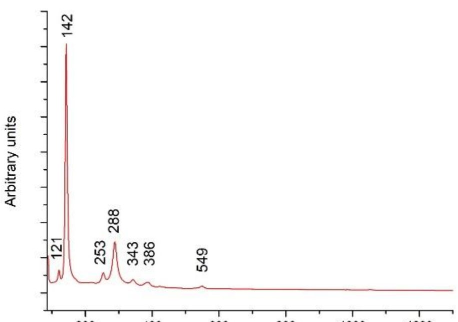

Fig. 5. Raman spectrum of the red area (1.2,III,1) of the coat of arms located on the southern wall.

In the dark green area, Raman spectroscopy analysis (Fig. 6) revealed bands at 144, 177, 267, 431, and 1089 cm^{-1}, which are characteristic of malachite ($CuCO_3 \cdot Cu(OH)_2$). As shown in Figure 7, further analysis of the same sample detected additional bands in other regions at 131, 174, 447, 482, 607, and 973 cm^{-1}, typical of langite ($Cu_4(SO_4)(OH)_6 \cdot 2H_2O$), as well as bands at 447, 865, and 973 cm^{-1} indicative of atacamite ($Cu_2Cl(OH)_3$). Moreover, the sample also exhibited bands at 211, 260, 462, 481, and 607 cm^{-1}, suggesting the presence of brochantite ($Cu_4(SO_4)(OH)_6$) [5]. Malachite, also known as "mountain green," is a green pigment of either natural or synthetic origin. Its use in painting dates back to pre-dynastic Egypt and has been documented in funerary artworks from the 4th Dynasty (circa 17th - 15th centuries BCE). While it appears less frequently in European painting and is mentioned less often than azurite, malachite stands out for its exceptional stability. Among copper-based green pigments, it is considered the most resistant to environmental and atmospheric degradation. Atacamite, clinoatacamite, langite, and brochantite are secondary copper minerals that can form through the alteration of primary copper carbonates such as malachite, especially under changing environmental conditions. These minerals were identified in a 17th-century polychrome painting, later concealed beneath a subsequent layer of plaster.

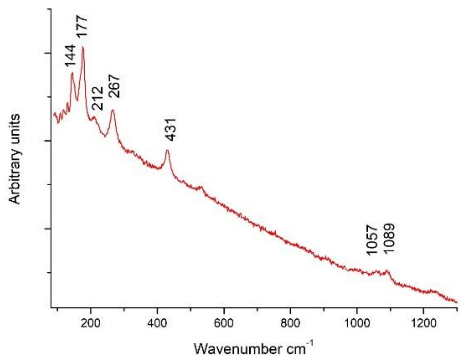

Fig. 6. Raman spectrum of the dark green area (1.2,III,5) of the coat of arms located on the southern wall.

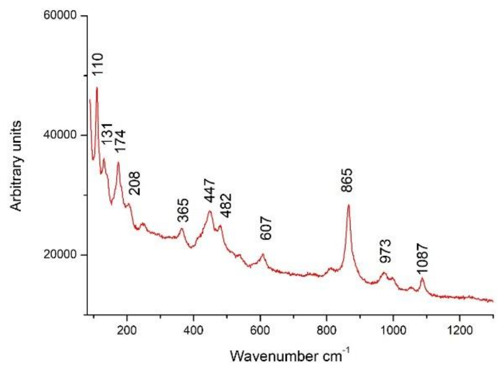

Fig. 7. Raman spectrum of the dark green area (1.2,III,5) of the coat of arms located on the southern wall.

While the presence of atacamite and clinoatacamite typically indicates chloride-induced transformation, in this case it could be related to the historical proximity of salt mines. Sulphate minerals such as langite and brochantite may have formed under the influence of sulphur compounds released, for example, through the burning of candles, common in enclosed spaces of the period. Alternatively, these minerals might not be degradation products at all but rather natural components of the original pigment, coexisting with malachite in the mineral deposit from which the pigment was sourced.

The sample identified as light green (1.2,III,9) confirmed the presence of tin-lead yellow [4]. Bands at 129, 196, 273, 292, 379, 456, and 525 cm⁻¹ were used to identify lead-tin yellow (Pb_2SnO_4) (Fig. 8). The light grey sample (1.2,III,6) showed the presence of carbon black and calcium carbonate.

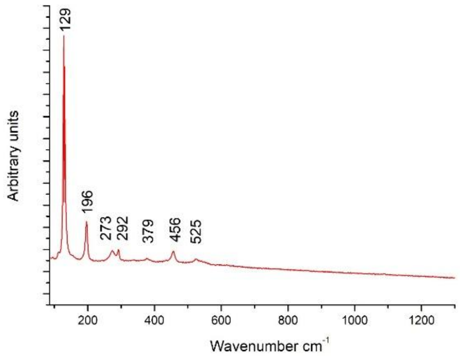

Fig. 8. Raman spectrum of the light green area (1.2,III,9) of the coat of arms located on the southern wall.

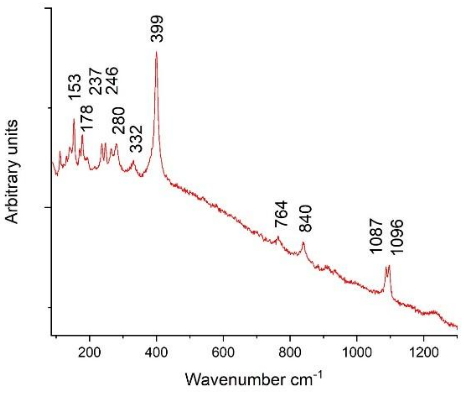

Fig. 9. Raman spectrum of the blue area (1.3,IV,2) of the layer with patronal and ornamental decoration.

In Room 1.3, samples taken from the layer with patronage and ornamental decoration revealed the presence of lead red, lead massicot, lead white, and calcium carbonate in the red areas (sample 1.3,IV,1). In the blue sample (1.3,IV,2), azurite and calcium carbonate were confirmed. Raman analysis recorded bands at 178, 246, 280, 332, 399, 764, 840, 1096 cm^{-1} characteristic of azurite (Fig. 9). The green sample (1.3,IV,4) showed malachite, along with langite, atacamite, clinoatacamite, azurite, and calcium carbonate. The grey sample (1.3,IV,6) revealed calcium carbonate and carbon black, while the black sample (1.3,IV,3) contained carbon black.

In both rooms, these pigments were used in the 17th century, which confirms the initial findings of conservators and art historians.

Analysis of the binders was performed using FTIR. Figure 10 presents the FTIR results for the oldest painted decoration of the coat of arms in Room 1.2. Spectrum revealed absorption bands characteristic of calcium carbonate (707, 870, 1396 cm⁻¹) and calcium oxalates (516, 777, 1323, 1640 cm⁻¹), suggesting the use of a protein-based binding medium. As widely reported in previous studies, oxalates typically form through the precipitation and crystallization of proteinaceous binders [6], especially under conditions of elevated humidity [7]. Consequently, their presence may indicate the application of a protein-containing material as a binding agent.

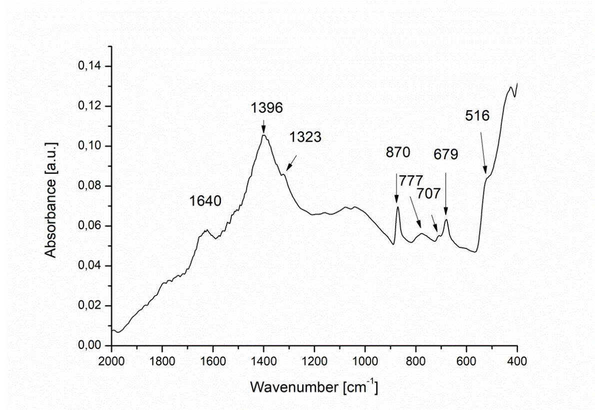

Fig. 10. FTIR spectra of yellow pigment in the oldest decoration (1.2,III).

A comparable result was obtained for the paint layer from Room 1.3. The FTIR spectrum revealed absorption bands at 521, 712, 872, 1040, and 1395 cm⁻¹, characteristic of calcium carbonate; at 773 and 1159 cm⁻¹, indicative of silica (quartz sand); at 521, 773, 1321, and 1621 cm⁻¹, associated with calcium oxalate; and at 748, 1040, 1159, 1395, 1462, and 1638 cm⁻¹, corresponding to an organic, proteinaceous compound. The detection of protein-based organic material is indicative of the use of tempera, animal glue, or casein-based painting techniques.

IV. CONCLUSIONS

This study focused on an in-depth examination of the pigmented plaster layers uncovered in the Saltwork Castle in Wieliczka. A broad diagnostic approach was applied, utilizing spectroscopic techniques such as XRF and Raman spectroscopy. The results confirmed earlier hypotheses proposed by art historians regarding the dating of the heraldic paintings found on the southern wall of room 1.2. Detailed pigment analysis indicated materials consistent with 17th-century painting practices, and the dating of layer IV in room 1.3 to the same century was also verified. These findings offer a solid foundation for conservators to assess the stratigraphy of wall layers in this historically significant site, which, until now, had not been investigated with such depth or interdisciplinary precision. The data provide valuable support for conservation documentation and contribute to broader research on the history of the castle. Moreover, the results enhance our understanding of the chronological development of painting techniques and workshop characteristics, which is essential for informed technical and aesthetic conservation efforts moving forward.

REFERENCES

[1] K.Ochniak-Dudek, "Saltworks Castle in Wieliczka: history and architecture", Studies and Materials for the History of Saltworks in Poland, 2012, vol.28, pp. 91-114.

[2] N.Eastaugh, V.Walsh, T.Chaplin, R.Siddall, "Pigment Compendium. A Dictionary and Optical Microscopy of Historical Pigments", Routledge Taylor and Francis, London, New York, 2013.

[3] Z.Zlámalová Cílová, M.Gelnar, S.Randáková, "Smalt production in the ore mountains : characterization of samples related to the production of blue pigment in Bohemia", Archaeometry, 2020, vol.62(6), pp. 1202-1215.

[4] I.M.Bell, R.J.H.Clark, P.J.S.Mallat, "Raman spectroscopic library of natural and synthetic pigments (pre- 1850 AD)", Spectrochim. Acta A, 1997, vol.53, pp. 2159-2179.

[5] R.L.Frost, "Raman spectroscopy of selected copper minerals of significance in corrosion", Spectrochim. Acta A, 2003, vol.59, pp. 1195-1204.

[6] M.Del Monte, C.Sabbioni, G.Zappia, "The origin of calcium oxalates on historical buildings, monuments and natural out-crops", Sci. Total. Environ., 1987, vol.67, pp. 17–39.

[7] E.Possenti, C.Colombo, M.Realini, C.L. Song, S.G.Azarian, (2021) "Insight into the effects of moisture and layer build-up on the formation of lead soaps using micro-ATR-FTIR spectroscopic imaging of complex painted stratigraphies", Anal. Bioanal. Chem., 2021, vol.413, pp. 455–467.