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HAND-HELD XRF FOR THE PRELIMINARY SCREENING OF EARLY ROMANESQUE FRESCOES IN SLOVAKIA

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ABSTRACT

Within the investigation of historical paintings, portable X-ray fluorescence (XRF) can successfully be used for a non-invasive screening that involves basically describe inorganic pigments and locate repaints, retouches and surface alterations. In combination with imaging techniques, e.g., IR-reflectography, such a screening could effectively reduce further sampling and select areas important for detailed investigations.

In a case of paintings, the description of layer stratigraphy and painting technique is limited when using only non-invasive tools. Elements located in underpainting and ground layers are usually found as accompanying in whole measured area.

Within our study, hand-held XRF was used for the screening of a cycle of Early Romanesque frescoes in the single nave church of St. George at Kostoľany pod Tribečom, Slovakia. After the first stage of the pre-restoration research coming out from non-invasive measurements and microanalysis of very limited amount of samples, we were able to distinguish the relics of full-area 19th century re-paints by zinc and barite whites and also partly re-established the original colouring of paintings based namely on the detailed screening of Cu and Pb. Copper-based pigments were almost totally washed-out from the painting and the original green and blue colours turned to yellow and light grey, respectively. Low concentrations of Cu can now be detected only by portable XRF when integrating the measured area of ca 2mm^2 or more. Blackened parts containing lead was finally interpreted as conversion of red lead (Pb_3O_4) to plattnerite (PbO_2) and cerussite ($PbCO_3$).

INTRODUCTION

Unique wall paintings at Kostoľany pod Tribečom, Slovakia, were uncovered in the sixties of the 20th century. Archaeological, construction-historic, art-historic and restorer research were taken out within the reconstruction of the church in fifties of 20th century [2, 5, 7]. It was found out that the single nave church with rectangular presbytery was not built later than in the 1st half of the 11th century. The wall paintings, probably painted shortly after the church was built, were badly damaged during a thousand years of their existence. According to literature, they had been several times over-painted. In the 16th century the church burned out and it had not been repaired for a long time so rainwater poured in and most of the top cycle of paitings fell off.

After the last building reconstruction in fifties of 20th century, the wall paintings were further faded, damaged by varying humidity and smudged by candle smoke, because of their insufficient preservation and unfavourable climatic conditions. The relative humidity inside the church, still regularly used for services, is high even during dry periods of the year and fluctuation in temperature plays an important role as well.

Within the first stage of our investigation, visual inspection of the frescoes was combined with imaging techniques (UV luminiscence, IR reflectography) and non-invasive analytical measurements. In limited amount, microsamples were then taken to describe the layer stratigraphy in areas of the most importance. The aim of the work presented here was to distinguish original paints and re-paints and to describe the alteration processes causing numerous colour changes of frescoes.

METHODS

Portable X-ray Fluorescence

Non-invasive *in situ* investigation of paintings was performed by hand-held EDXRF spectrometer X-MET 3000 TXR (Oxford Instruments). It consists of an X-ray tube equipped with a Rh anode (40 kV), and a high resolution SiPIN diode detector with Peltier cooling allowing a typical resolution of 230-250 eV.

Measurements were performed in the working distance of ca 2-3 mm from the object and typical counting time was 60 s. The method of fundamental parameters [3] was used to calculate concentrations of elements heavier than potassium (Z>19).

Light Microscopy

Microsamples of colour layers were embedded in polyester resin, polished in the cross-section and observed by the Olympus BX-60 light microscope in reflected normal and UVA light of the wavelength range of 330-380 nm. Materials colour and luminiscence in UV were used to describe the layer stratigraphy. Characteristic light green luminiscence of the zinc white (ZnO) was used to indicate the 19th century re-paints.

Electron Microscopy and Microanalysis (SEM/EDX)

Selected cross-sections were investigated by the scanning electron microscope Philips XL30 CP. Robinson detector of back-scattered electrons was used under the constant pressure conditions (0.5 mbar) without the necessity of surface metallization. When using the voltage of 25kV, the penetration depth of electron beam did not exceed 5 micrometers. Energy-dispersive spectrometer EDAX with compact Sapphire Si(Li) detecting unit and light elements performance technology (LEAP+) was used allowing a detection of elements heavier than Be (Z>4) at resolution of 135eV. Standardless quantification using ZAF correction (Genesis Spectrum SEM Quant ZAF, version 3.60) was applied to calculate the elemental composition; the typical counting time was 60 s.

Powder X-ray Microdiffraction (Micro-pXRD)

Diffraction patterns of colour layers on fragments or their cross-sections were collected with a PANalytical X´PertPRO diffractometer equipped with a conventional X-ray tube (CoKα radiation, 40 kV, 30 mA, point focus), an X-ray monocapillary with diameter of 0.1 mm, and a multichannel detector X'Celerator with an anti-scatter shield. A sample holder for single crystal XRD measurement was adopted by adding z-(vertical) axis adjustment (Huber 1005 goniometer head). The beam diameter on the sample was ca 0.15 mm on average.

Diffractograms were taken between 4 and 80° 2Θ with 0.0167° step and 2200 s counting time per step that produces total counting time of about 23 hours. XRD patterns were not pre-treated before interpretation as no background correction was needed.

Qualitative analysis was performed with HighScore software package (PANalytical, The Netherlands, version 1.0d), Diffrac-Plus software package (Bruker AXS, Germany, version 8.0) and JCPDS PDF-2 database [4].

RESULTS AND DISCUSSION

The wall paintings can be subdivided onto three major parts – the southern and northern walls and the presbytery. On both walls, only intermediate cycle of scenes is preserved in extent giving any iconographic meaning. Other ones, lower and upper, are partly or completely destroyed due to building reconstructions and water soaking onto the walls. In the presbytery, overpaintings on a new plaster are superimposed on original layers in part of the decoration. They can probably be dated to the Gothic period. Visually, all the frescoes are faded, namely on the northern wall, and their colour composition include red, yellow, white, grey and brown-black. The question, if these colours represent the original ones, was answered by non-invasive screening of elements by portable XRF.

In whites and greys we found namely Ca, which, according to previous expectations proved then by measurements of samples, come from the calcium carbonate. The black pigment in greys is the charcoal black (not visible by XRF when measuring in the air). Iron is, as also expected, the major element of yellows and reds, indicating here the presence of earthy pigments. Ca and Fe were more or less present in all the measurements.

The screening of Pb, Cu, Zn and Ba was much more interesting. The presence of Zn and locally also Ba indicated thin repaints and retouches by zinc (and/or barium) whites carried out not earlier than at 19th century (Fig. 1). On figures 2-4 the relative concentration of zinc exceeding 10 wt. % is indicated by light green colour of the measured spots. It is clear that these repaints are more abundant on the southern wall.

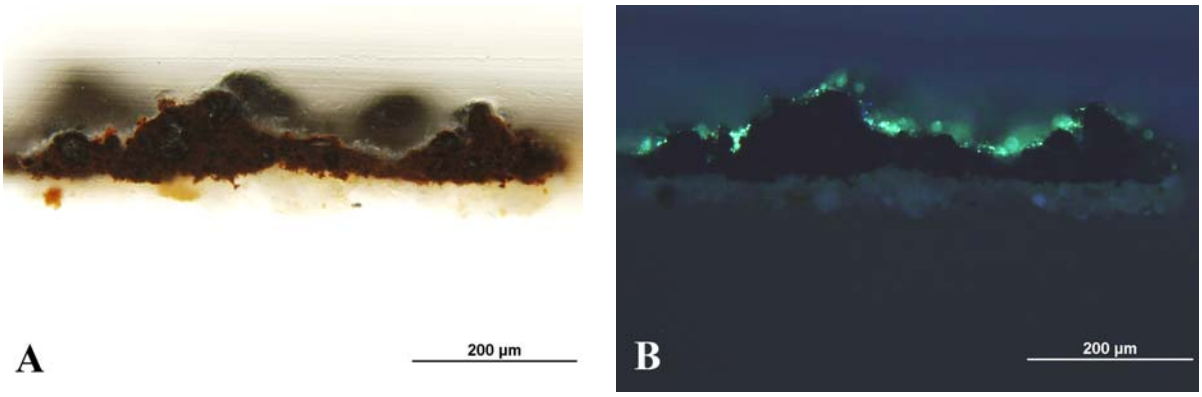

Figure 1. Cross-section of the microsample in normal (A) and UVA (B) light showing darkening of the red lead (transformation to plattnerite) in the original colour layer. On the top of the fragment thin retouches by the zinc white (ZnO) are indicated by the light green UV luminiscence

The lead-containing pigments were present in variable amounts – in the brown-black parts of paintings, the lead concentration exceeded usually 90 wt.% (indicated by orange spots on figures 2-4), and in other parts, the lead was admixed only in much lower concentrations somewhere exceeded 10 wt.% (white spots on figures 2-4). The brown-black parts containing only lead clearly indicated the effect of darkening of lead-based pigments mentioned already by Cennino Cennini for the red lead [1], or later also for the lead white as an effect of e.g. microbial activity [6]. For the confirmation, samples of the black parts of paintings were analysed by SEM/EDX and micro-pXRD. It was found that the brown-black layer contains predominantly plattnerite (PbO_2), accompanied by cerussite ($PbCO_3$) and lead magnesium carbonate - $PbMg(CO_3)_2$. This could indicate that the lead white (cerussite) converted to plattnerite, because no red lead (Pb_3O_4) was found. But, as we found earlier, strong oxidizing agents (like NaHClO) are necessary to enable this conversion. On the other hand, red lead is mentioned very frequently as spontaneously unstable.

To simulate the alteration process in the wall painting, we mixed the red lead with the aqueous solution containing Mg^{2+} and CO_3^{2-} ions, which are mobilized from the dolomitic plaster of the Kostoľany church. After 3 months of reaction, darkened product contained plattnerite, cerussite, lead magnesium carbonate - $PbMg(CO_3)_2$, and unconsumed red lead. Thus we approved that the brown-black was originally orange, all the red lead has been converted to the mixture of plattnerite and cerussite under normal conditions of varying humidity. The presence of dissolved carbonate and magnesium ions caused the crystallisation of $PbMg(CO_3)_2$. No lead white was necessary to be added. We can imagine easily, that on the face of the Virgin Mary (Fig. 5), black contours of the neck, lips etc., could originally been rather orange than white. In other parts of paintings, the content of the lead is connected exclusively to the presence of the lead white but, because of much lower concentrations, present probably only in retouching. The lead white undoubtedly used as pigment in the colour layer is only visible in Gothic overpaintings where it is found in the incarnate (Fig. 4).

The screening of copper gives the most interesting maps. Although the green and blue colours are completely missing in all the paintings and only very uncertain bluish or greenish shades can be observed in some parts of the scenes, the relative concentration of copper measured by portable XRF reached in some places several or even tens weight percents. For comparison, SEM/EDX was able to measure much less or even no concentration of Cu in microsamples taken from areas pre-selected by XRF. Because of very low concentrations, often under the detection limit of SEM/EDX it was not possible to identify exactly the copper-based pigment, no green or blue grains were found under the microscope. The only method being able to register these remains of copper in the colour layer was the portable XRF, because of collecting the energies from much larger area of painting (ca 2 mm^2) than SEM/EDX. The only way how to reconstruct the original colour was to observe if the increased concentrations of Cu give any logical image from the iconographic point of view. Concentrations exceeding 10 wt. % are indicated by blue spots in figures 2-4.

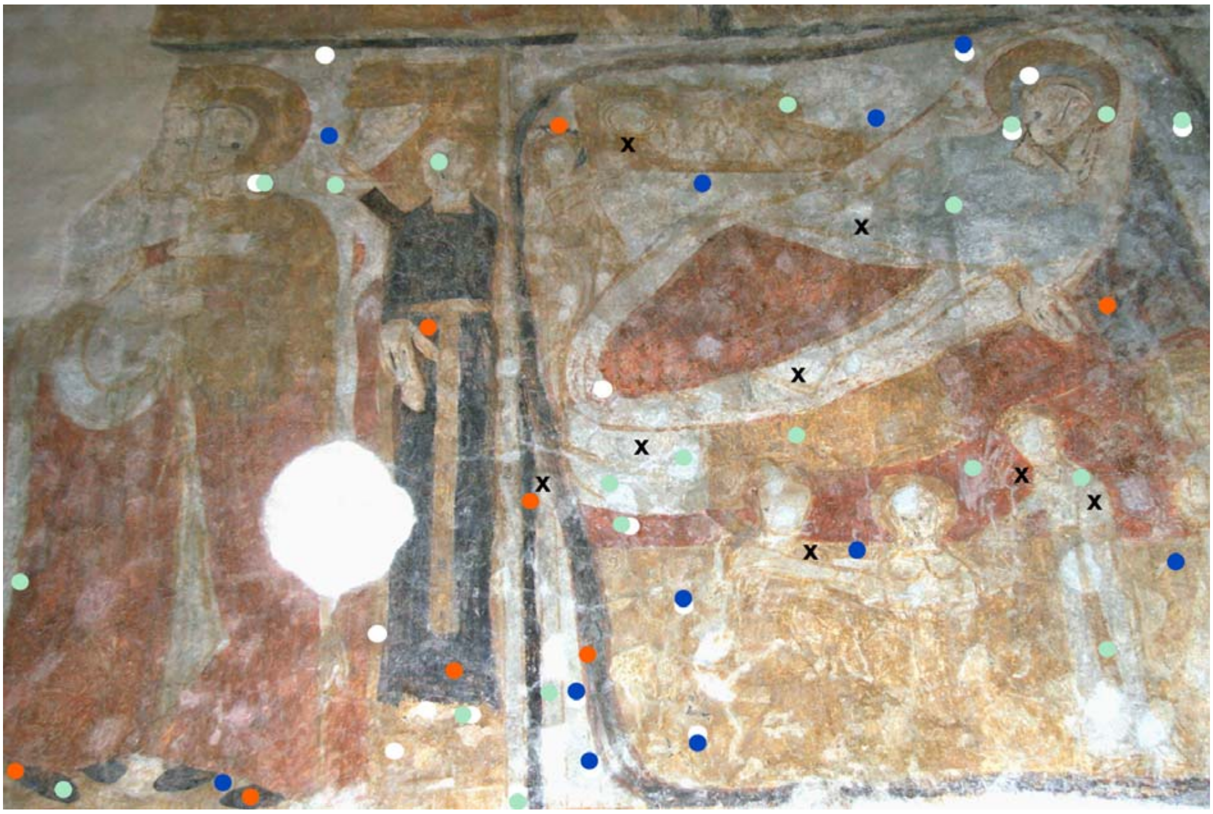

Figure 2. Increased concentrations of selected elements on the southern wall measured by portable XRF (blue points > 10 wt.% of Cu, light green points > 10 wt.% of Zn, white points > 10 wt.% of Pb, orange points > 90 wt.% of Pb, x – none or only very low concentration of all the selected elements)

Figure 3. Increased concentrations of selected elements on the northern wall measured by portable XRF (blue points > 10 wt.% of Cu, light green points > 10 wt.% of Zn, white points > 10 wt.% of Pb, orange points > 90 wt.% of Pb, x – none or only very low concentration of all the selected elements)

Figure 4. Increased concentrations of selected elements in the presbytary measured by portable XRF (blue points > 10 wt.% of Cu, white points > 10 wt.% of Pb, orange points > 90 wt.% of Pb, x – none or only very low concentration of all the selected elements)
In the Gothic overpainting in the right down corner of the figure the lead white is used in colour layer exclusively in the incarnate, while in the original painting, its concentration is varying only because of local re-paints or retouches. No darkening of the lead white is visible.

Figure 5. Thin contours of the Virgin Mary's face painted by the red lead, now converted to brown-black plattnerite

On the southern wall (Fig.2), the background of all the panels can be divided to three horizontal strips with red one in the middle. The copper was undoubtedly found only as a part of the upper and lower strip of the background and was not used for painting of any clothes of figures. In the upper strip, now light grey, we could expect originally blue colour of the sky. In the lower strip, now yellow, we could expect originally brown colour of the earth. According to copper, the yellow of the background can be distinguished from the yellow used for clothes of figures.

On the northern wall, especially in the scene of "Adoration of the star" (Fig. 3), the copper was found not only in the background (similarly to the southern wall) but also in some clothes. Thus we can conclude that the first magus from the left was originally dressed in greenish trousers and the white coat, the second in white trousers and the yellow coat, and finally the third one in yellow trousers and probably green or blue coat.

These findings illustrate very well the conditions causing almost complete wash-out of copper salts from the wall paintings. It indicates that not only climatic conditions, but with a high probability also inappropriate methods of cleaning lead finally to the damage of original colouring of the frescoes.

CONCLUSIONS

Based on non-invasive measurements by portable XRF, the original colouring of badly damaged and faded Early Romanesque wall paintings at Kostoľany pod Tribečom, Slovakia, was virtually re-established. By the screening of relic concentrations of copper, originally blue sky in the background or green parts of clothes have been indicated in a logic iconographic sense. Almost complete washing-out of copper-based pigments as well as complete conversion of the red lead into brown-black plattnerite indicate not only effects of unfavourable climatic conditions but also a long-term lack of interest in one of the oldest well-preserved wall paintings in Slovakia and Central Europe in general.

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BIBLIOGRAPHY

1. Cennino C., Il Libro dell' Arte The Craftsman's Handbook e Thompson Jr., D.V., translator, Dover Publications, New York, 1978, 1437.
2. Habovštiak A.: Archaeological research at Kostoľany pod Tribečom, Monumentorum tutela 2 (1967), 43-77 (in Slovak)
3. He F, Vanespen TJ.: General approach for quantitative energy dispersive X-ray fluorescence analysis based on Fundamentals parameters. Anal Chem. 63(20) (1991) 2237-2244
4. JCPDS PDF-2 database, International Centre for Diffraction Data, Newtown Square, PA, U.S.A. release 54, 2004.
5. Krása J.: Wall paintings in the St. George's church at Kostoľany pod Tribečom, Monumentorum tutela 2 (1967), 115-127 (in Slovak)
6. Lyalikova N.N., Petushkova Y.P. Role of microorganisms in the weathering of minerals in building stone of historical buildings. Geomicrobiology Journal 9(2-3) 1991, 91-101
7. Maříková-Kubková J.: Wall paintings in the St. George's church at Kostoľany pod Tribečom, Technologia Artis 2006 (2006), 85-92 (in Czech)

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