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Analysis of the Materials and Painting Techniques Used in Medieval Mural Paintings in Slovenia up to 1380

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Introduction

Scientific analytical methods are becoming increasingly more important for a truly comprehensive understanding and better-grounded interpretation of visual works of art. Until recently, the study of artworks had been narrowly focusing on stylistic classification, on resolving open questions of iconography and on establishing stylistic links between particular mural cycles using the traditional means of stylistic analysis, since these are the principal tasks of art history. But not all information can be gathered by this approach only, considering that artists also expressed themselves through their selection of materials and the mastering of painting techniques, which in turn affects the modelling (which is softer or rougher as a result), as well as the subsequent conservation of the artwork in later centuries. Therefore, art historians need to collaborate with natural scientists, principally chemists, physicists, geologists, biologists as well as with conservators and restorers in order to fully understand a given monument not only in terms of its artistic form but also in terms of its material structure and execution technique. Such an interdisciplinary approach can inform intervention procedures and enable a perdurable conservation of monuments.

The present project focuses on mediaeval mural paintings in Slovenia to 1380. Over 60 mural cycles have been systematically studied including from a material and technical perspective and in close collaboration with art historians and restorers. The murals included in this study can be found throughout the territory of present-day Slovenia. During the late Middle Ages, this geographical area was – along with the neighbouring territories – criss-crossed by busy supraregional trade routes and became as a result a paradigm example for studying cultural exchange between the continental European North and the Mediterranean South. This exchange is also reflected in painting style and in painting techniques. Most of the murals have been previously studied by Slovene and foreign art historians,[1] but there are several new discoveries that have not been investigated yet. All mural paintings up to 1380 (old and new discoveries alike) have been now re-evaluated and had material analysis carried out on them. Before this, only a few material studies had been made in Slovenia to date,[2] which makes this research even more pertinent.

Objectives

The present research project, which is still ongoing, has two primary objectives. First, it aims to significantly supplement the results of earlier art-historical research and, secondly and more importantly, it seeks to identify by scientific methods the painting materials and techniques used by individual late mediaeval mural painters and their workshops. The material analyses focus primarily on: (a) the characterization of supports (plasters), including their composition (binders and aggregates), impurity, consistency, varieties of sand (colour, granulation), the number of layers and the application of *giornatas*; (b) the use of lime-wash; (c) the identification of selected pigments and their possible degradation; (d) the identification of binders; (e) the sequence of colour layers; (f) the colour modelling; (g) the painting process from the preparatory work (under-drawings, incisions, pouncing, under-paintings) to the final colour modelling (shades, highlights); and the painting technique (*a fresco, a secco*, lime technique or combined). A comparison of obtained results enable us to recognize an artistic process or technique, a characteristic brushstroke, helping to identify an artist or a link to a workshop, and thus supporting or rejecting specific art-historical hypotheses.

1 STELE 1935; STELE 1969; RADOCSAY 1977; PROKOPP 1983; HÖFLER 1985; ŽELEZNIK 1993; HÖFLER 1996; ZIMMERMANN 1996; HÖFLER 1997; VODNIK 1998; HÖFLER 2001; HÖFLER 2004; BALAŽIC 2008.

2 POHL 1966; PIRNAT 1972; MOLE 1984–1987; BOGOVČIČ 1995; NEMEC 1995; KRIŽNAR 2006.

Analytical Methods and Techniques

After a precise visual examination of the paintings *in situ*, non-invasive techniques are applied where possible, such as digital microscopy (DM), ultraviolet fluorescence (UVF), VIS spectrophotometry and portable X-ray fluorescence (XRF). However, in many cases the paintings are too high and thus inaccessible with the equipment, and the interior of the churches is generally too bright for UVF. Therefore, small samples of ca. 2–4 mm^3 must be extracted from several areas of interest (as few as possible), including support, pigments or colour layers. Different laboratory techniques can be used, among which the most common ones are optical microscopy (OM), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), stationary X-Ray Fluorescence Spectroscopy (XRF), X-ray powder diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR) and Raman Spectroscopy. Samples are therefore prepared according to the analytical procedure implemented; raw samples can be studied by OM, SEM-EDX, XRF or Raman, but they are mostly embedded in resin to elaborate cross-sections (analysed by OM, SEM-EDX or Raman) or prepared as KBr pellets (FTIR), while plasters are crushed into powder (XRD).

UVF reveals later interventions, based on the characteristic fluorescence of specific materials under UV light that can distinguish between older and newer materials.[3] VIS spectrophotometry, applied in reflectance mode for the study of mural painting, helps us to identify and classify colours using surface measurements that can quantify visible effects depending on the colouring materials used, i.e. pigments.[4] XRF offers an elemental analysis of the irradiated point, characterizing the chemical elements and in turn the materials applied (pigments, support). The results are, however, limited, since it detects only elements with a higher atomic number such as those above 14 (Z>14), which means that only inorganic materials can be identified using this method. Further, different materials characterised by the same chemical element such as copper greens or lead pigments, cannot be distinguished.[5] OM is the basic technique for the analysis of paint layers. Through different magnification under reflected light it enables us to recognise the composition of the support (plaster), the sequence of colour layers and thus the painting procedure, and also to identify certain pigments according to their characteristic granulometry as well as possible pigment changes; it can even discern the painting techniques used.[6] SEM offers much higher magnification of the sample studied compared to OM, and is generally used in combination with EDX for elemental analysis. Black-and-white SEM images enable us to visualize the morphology

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3 DE LA RIE 1982; MATTEINI, MOLES 1984, pp. 171–177; ALDROVANDI, PICCOLO 2003, pp. 67–84; STUART 2007; CONSENTINO 2015.

4 BACCI 1995; OLTROGGE 2008; ARTIOLI 2010, pp. 46–47; *Spectroscopy* 2021, pp. 103–131.

5 MATTEINI, MOLES 1984, pp. 133–139; APPOLONIA, VOLPIN 1999, pp. 30–33; SECCARONI, MOIOLI 2004; ARTIOLI 2010, pp. 34–37; *Analytical Chemistry* 2017, pp. 77–128.

6 MATTEINI, MOLES 1984, pp. 37–55; APPOLONIA, VOLPIN 1999, pp. 20–27; ARTIOLI 2010, pp. 64–66.

of the sample and distinguish between light and heavy elements present in the material. The high magnification helps at selecting specific areas or individual particles for chemical analysis, offering very precise results.[7] The XRD technique is generally used for plaster characterization in the study of mural paintings. It identifies compounds (minerals, phases) and can give us a good insight into a plaster composition (binder, aggregate types) and weathering products.[8] FTIR and Raman are two of the most frequently used molecular techniques in art that are also suitable for the identification of organic materials such as colorants or binders. Both methods use different physical processes such as absorption, emission and vibration for identification of molecular structure of the analysed material.[9] Recently, the emphasis has been on non-invasive techniques which do not require sample extraction. Therefore, most of the equipment required for the above techniques, including XRF, XRD, FTIR and Raman among others, have been developed as mobile units in order to be to use them *in situ*.[10] Nevertheless, high quality results, especially for FTIR and Raman, are difficult to obtain outside the laboratory due to various non-controllable factors. No portable equipment was available for this research.

For extracted samples prepared according to the analytical technique, OM, XRD and Raman were primarily used. FTIR and SEM-EDX were applied only on certain selected samples. Other techniques will be added if necessary. The optical microscopy of cross-sections was performed in visible (VIS) and ultraviolet (UV) light to obtain information on the stratigraphy of the selected samples. Cross-sections were examined with an Olympus BX-60 microscope and SC50 (Olympus) digital camera in reflected light at 50x to 200x magnification. XRD was selected for plaster characterization. Cross-sections and raw samples were analysed using a Raman spectrometer LabRAM HR800 (Horiba Jobin-Yvon) connected to an Olympus BXFM microscope, with a 785 nm wavelength laser and CCD detector in the range between 80 cm^{-1} and 1800 cm^{-1} at a spectral resolution of 1 cm^{-1}. Calibration was performed using Si crystal. The time and filter were adapted to each sample. The phase composition of the raw plaster samples was determined using a PANalytical Empyrean X-ray diffractometer (Malvern Panalytical, Malvern, UK) equipped with CuKa radiation and a PIXcel 1D detector. The samples were ground to a particle size of less than 63 μm. They were put in zero diffraction plate. The samples were measured at 45 kV at a current of 40 mA, in the range of 4 to 70° 2q, at a step size of 0.013° 2q with a scan step time of 68s. The analysis of X-ray diffraction patterns was performed with the X'Pert High Score Plus diffraction software v. 4.9 from PANalytical using PAN IICSD v. 3.4 powder diffraction files. Some selected

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7 MATTEINI, MOLES 1984, pp. 75–86; APPOLONIA, VOLPIN 1999, pp. 38–41; ARTIOLI 2010, pp. 66–68; *Spectroscopy* 2021, pp. 71–102.

8 MATTEINI, MOLES 1984, pp. 125–132; APPOLONIA, VOLPIN 1999, pp. 33–38; ARTIOLI 2010, pp. 50–52; *Analytical Chemistry* 2017, pp. 77–128; *Spectroscopy* 2021, pp. 161–207.

9 MATTEINI, MOLES 1984, pp. 107–110; *Analytical Chemistry* 2017, pp. 129–211; *Spectroscopy* 2021, pp. 45–69.

10 *Analytical Chemistry* 2017, pp. 41–75.

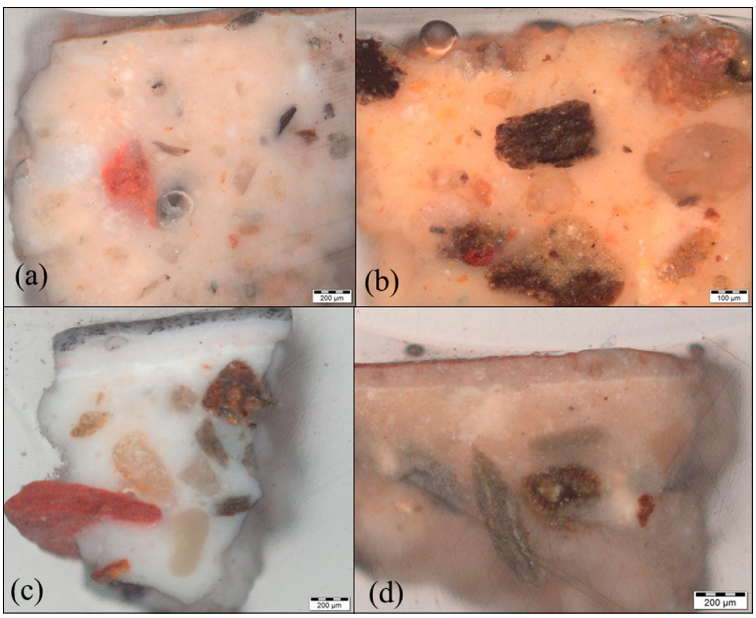
raw samples were analysed by FTIR with a Spectrum 100 spectrometer connected to a Spectrum Spotlight 200 (PerkinElmer) microscope. Layers were separated with a scalpel and in some cases solvents of different polarity were used to extract materials form the mixtures. All samples were analysed in transmission mode, compressed in a diamond anvil cell. Spectra were scanned using a MCT detector in the range between 4000 cm^{-1} and 600 cm^{-1} with a spectral resolution of 4 cm^{-1}, averaging 32 scans for each spectrum. For SEM-EDX analysis, the stratigraphic sections had been previously metallized with a thin layer of gold (Au) and then studied with a JEOL JSM 5400 SEM instrument coupled to an Oxford Link EDX analyser with a Si(Li) detector, Be window, at 20 kV.

The combination of all these techniques provides more reliable (and fully verifiable) data concerning the composition of plasters, their impurity and consistency, the possible use of lime-wash, the selection of pigments and binders, as well as offering other important insights into the painting techniques used by a number of late-mediaeval artists – in particular with respect to painting on fresh mortar (*a fresco*), lime-technique (painting on a fresh layer of lime-white), painting *a secco*, or (the most common practice) a combination of these. Such scientific results combined with the stylistic characterization of artworks enables a deeper understanding of an artist/workshop and can even establish authorship or workshop connections between mural cycles. This project represents ongoing research and not all analyses have been carried out yet (such as SEM-EDX), while FTIR has been used only in a few selected samples so far.

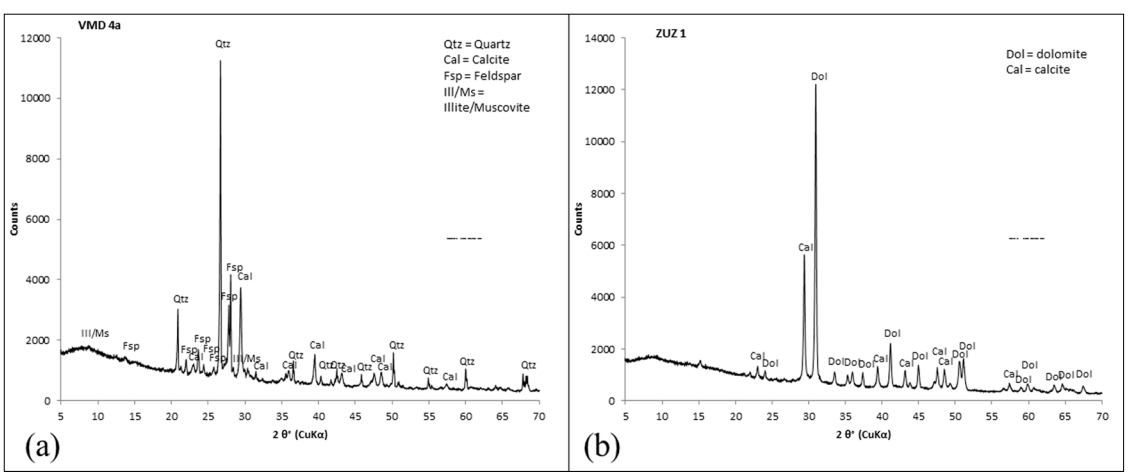
Painting Materials and Techniques

1. Plaster

Plaster is generally made as a mixture of lime as a binder and of sand as aggregate. Images made by optical microscope (OM) reveal different aggregate granulation and colour, which varies from light, almost transparent, to intense red and almost black, indicating different mineralogical-petrographic and chemical compositions (Fig. 1). Mostly, the aggregate grains have an angular form, however in some cases they can be rounded. They can also vary in their sphericity, for instance being elongated or isometric. Rounded grains can indicate a river or lake provenance of the aggregate, since the water smooths the angular forms. For a good painting surface, the sand must be thoroughly cleaned; if it is not, its impurities can cause damage over time, affecting also the painting surface. As for the binder, a slaked lime ($Ca(OH)_2$) is used, which should be properly cleaned and rested before its use, if not, white lime lumps can form, which can be observed under an optical microscope. Depending on the sand and binder type or possible mineral additives, the plaster can have whiter or darker tonality. Mineralogical composition was determined mainly using an XRD that identified the principal materials in a plasters, such as calcite, dolomite and quartz, while in some plasters also feldspars, illite/muscovite or plagioclases were detected. Their



1. Microphotographs of plaster samples and colour layers using optical microscopy in reflected light from the following locations: (a) St Peter's church in Ribičje, (b) St Thomas's church in Štomaž pod Štjakom, (c) St James's church above Potoče, and (d) the church of Our Lady on the Rock in Vuzenica. All plasters consist of lime and sand. The samples (c) and (d) reveal a thin layer of limewash under the colour layer (© Institute for the Protection of Cultural Heritage of Slovenia, Restoration Centre, Ljubljana (IPCHS, RC), Scientific department).



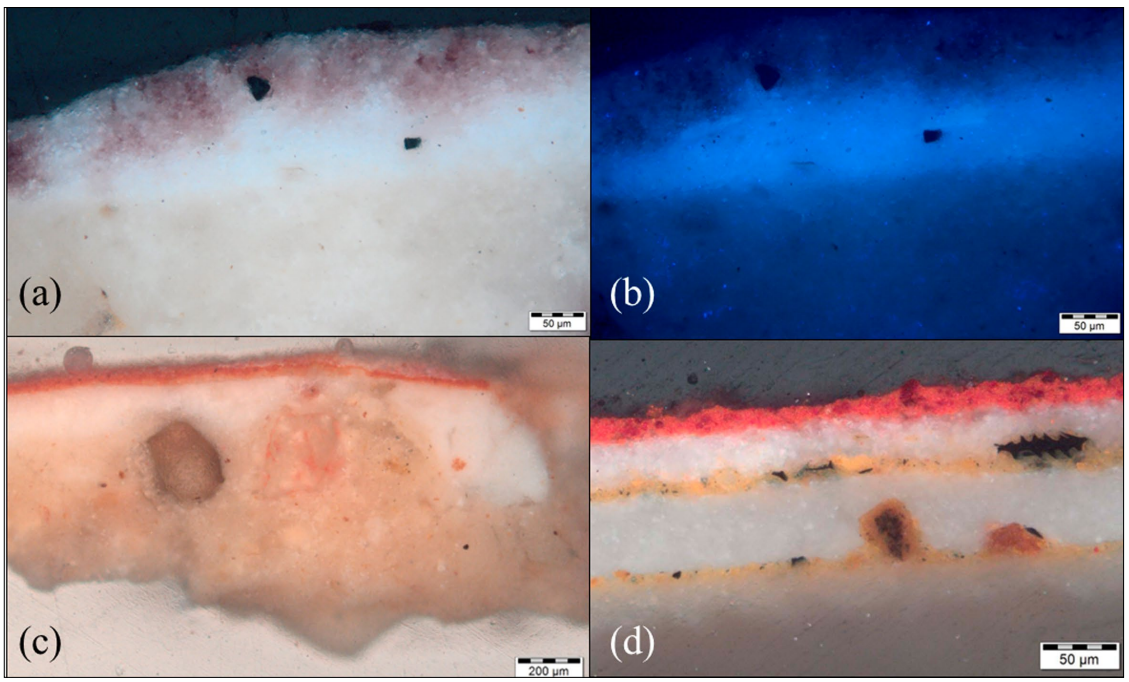
2. XRD patterns reveal different plaster compositions, as observed on two samples: (a) plaster made of lime and sand with mineral additives, the church of Our Lady on the Rock in Vuzenica; (b) plaster made of lime and crushed calcite, St Nicholas's church in Žužemberk (© Slovenian National Building and Civil Engineering Institute, Ljubljana, Materials Department, Laboratory for cements, mortars and ceramics).

3. Microphotographs of plaster samples and colour layers using optical microscopy in reflected light from the following locations: (a) St Thomas's church in Velike Poljane, (b) St Thomas's church in Gorenja Straža, and (c) St Michael's church in Biljana. All plasters are white and consist of lime and crushed calcite (© IPCHS, RC, Scientific department).

relative quantity varies from mural to mural, and the main interest lies in the quantity of calcite, i.e. binder. The lowest quality of plaster with a low amount of binder (calcite) and predominant silicate aggregate (mostly quartz) was found in the murals in in the church of Our Lady on the Rock in Vuzenica (Fig. 2a), resulting in bad consistency of these plasters which tend to pulverize, also affecting the colour layers.

In rare cases, instead of sand, a crushed coarse-grained calcite (calcite) was used for Slovene medieval mural paintings (as is indicated by the angularity of the grains), sometimes with the addition of transparent quartz grains, resulting in a bright, white plaster (Fig. 3). Such plaster is a perfect support for painting on a fresh mortar (*a fresco)*, since it generally includes little or no impurities, while the binder and the aggregate are chemically almost the same. It is a typical support for Italian Trecento *a fresco* painting,[11] which could indicate the Italian origin of the artist or a material influence. The analysis discovered such composition in the church of St Thomas in Velike Poljane, in the church of St Thomas in Gorenja Straža, on the northern interior wall of the church of St Michael in Biljana, in the church of St Oswald in Zgornje Jezersko, in the church of St Nicholas in Žužemberk (Fig. 2b), and in the cloister of Stična monastery (in a coat of arms and votive image). For the most part, the presence of dolomite in these plasters is quite high; part of it could also be present as dolomitic lime, not only in the aggregate. No other materials such as brick or straw was found in any of the mural paintings to 1380 studied so far. These additives could have been used to strengthen the plaster and make it more resistant. For *a fresco* technique, the plaster

[11] *Reclams Handbuch* 1990, p. 31; MORA, MORA, PHILIPPOT 2001, pp. 146–149; PECCHIONI, FRATINI, CANTISANI 2008, pp. 143–145, 148. Already Cennino Cennini in his treatise *Il libro dell'arte* (III, 66) speaks about the quality of the plaster for mural painting: BROECKE 2015, pp. 98–101.



4. Microphotographs of plaster samples and colour layers using optical microscopy in reflected (a, c, d) and UV (b) light from the following locations: (a, b) St Thomas's church in Štomaž pod Štjakom, (c) the church of Our Lady on the Rock in Vuzenica, and (d) St James's church above Potoče. A layer of limewash is clearly visible between the plaster and the colour layers (a, b, c) or between the colour layers (d) (© IPCHS, RC, Scientific department).

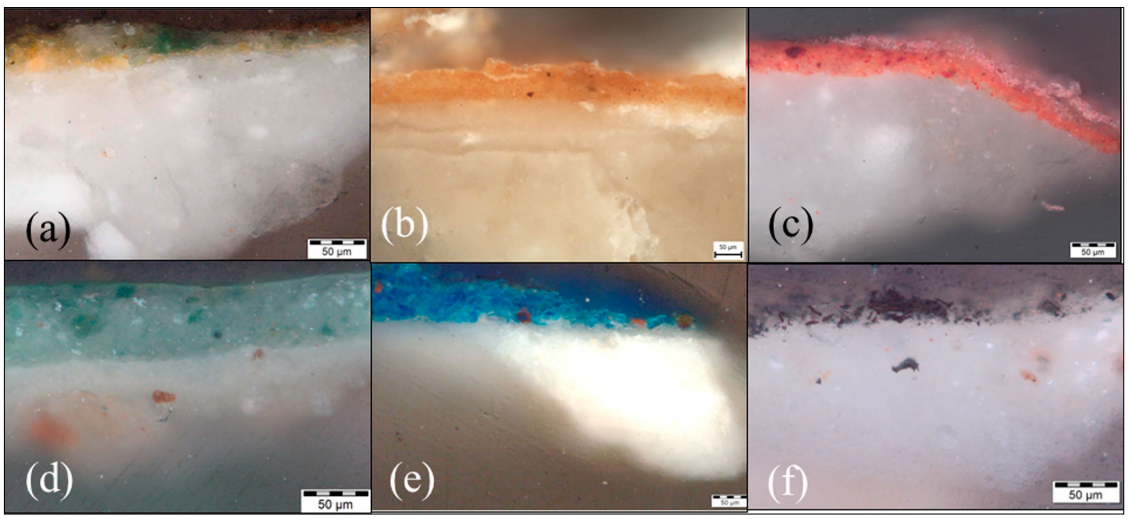
was generally applied as *pontantae*[12] or *giornatae;*[13] only rarely, however, we can distinguish them, mainly due to the fragmentary state of the murals.[14]

In some cases, cross-sections reveal a layer of lime-wash between the plaster and the colour layers (Fig. 4). This technique is more common for Central- and North-European painting and

12 *Pontata* is a long horizontal application of fresh plaster that can run along the entire length of the wall and includes several scenes. It is more common for Romanesque and early Gothic painting. See *Reclams Handbuch* 1990, p. 64; MORA, MORA, PHILIPPOT 2001, p. 149; KRIŽNAR 2006, p. 23.

13 *Giornata* is a smaller portion of a fresh plaster to be painted in one day, generally in 3–5 hours as long as it takes to the plaster to dry. It can have a rectangular shape of covering the entire scene, or it can be divided into individual figures or groups. See *Reclams Handbuch* 1990, p. 64; MORA, MORA, PHILIPPOT 2001, p. 14; KRIŽNAR 2006, p. 39. Already Cennini (III, 66) writes about *giornatas*: BROECKE 2015, pp. 98, 101.

14 We can distinguish plaster portions in very few cases, such as, for example, in the murals of the triumphal arch and the presbytery triumphal wall in the church of Our Lady on the Rock in Vuzenica and on the exterior western wall of the church of St Nicholas in Žužemberk.



5. Microphotographs of plaster samples and colour layers using optical microscopy in reflected light show various pigments: (a) yellow earth (goethite) and green earth, St Ulrich's church in Tolmin, (b) orange earth, St Oswald's church in Leskovec nad Višnjo Goro, (c) red earth (heamatite), cloister, Stična monastery (coat of arms); (d) green earth, St Thomas's church in Štomaž pod Štjakom, (e) azurite, St Pancras in Stari trg pri Slovenj Gradcu, and (f) carbon black, St Helen's church in Gradišče pri Divači (© IPCHS, RC, Scientific department).

can be used as primary or auxiliary technique.[15] In our research, we found that it was mostly used as auxiliary technique to freshen up the already dry plaster, though it was applied as the principal painting technique on the oldest paintings of the triumphal arch and the eastern part of the south wall of the church of St Nicholas in Pangrč Grm. In the church of St James above Potoče, a white layer of lime was found also between some colour layers (Fig. 4d).

2. Pigments

The pigment palette is mostly limited to natural inorganic pigments, such as lime white, yellow, orange and red earths (identified by Raman as goethite and haematite) (Fig. 5a–c), green earth (Fig. 5a, d) and in few cases also minerals as malachite and azurite (Fig. 5e). To obtain a black colour, organic pigments were selected, mostly lamp or carbon black (Fig. 5f). All these pigments are suitable for *a fresco* or lime technique, as they are stable in humid and alkaline environment.[16]

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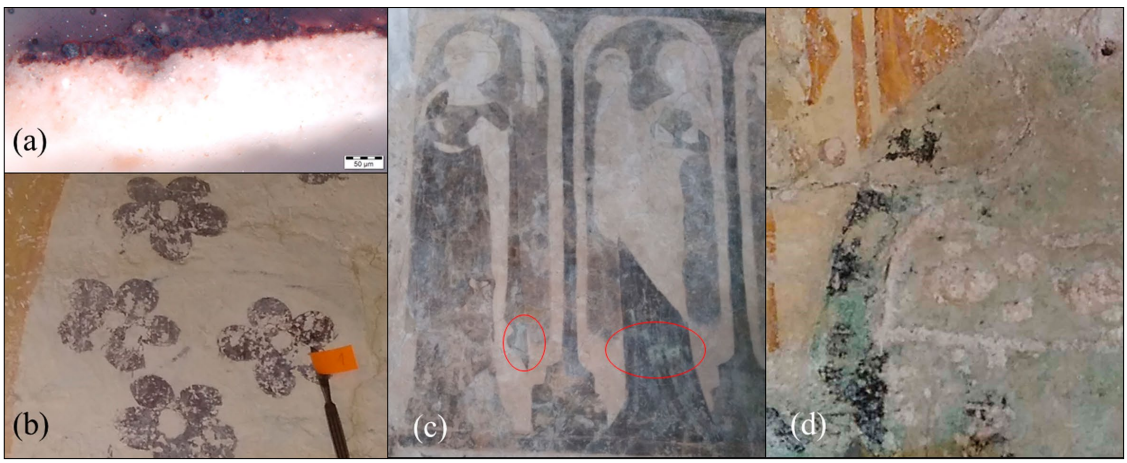
15 *Reclams Handbuch* 1990, pp. 71–73; MORA, MORA, PHILIPPOT 2001, pp. 140. The first mention of lime technique can be found already in the mediaeval text by the monk Theophilus, *Schedula diversarum artium* (I, 15): THEOPHILUS PRESBYTER 1979, pp. 23, 24.

16 *Reclams Handbuch* 1990, pp. 41–50; MORA, MORA, PHILIPPOT 2001, pp. 69–84; KRIŽNAR 2006, pp. 30–54; *Artists' Pigments* 2012; BROECKE 2015, pp. 56–94.

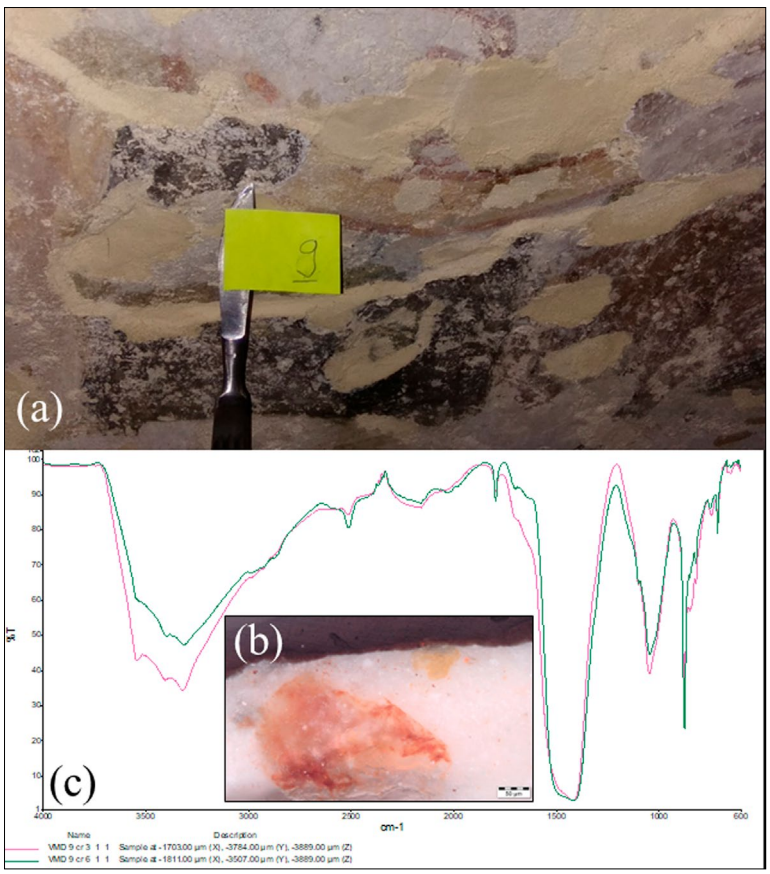


6. Colour darkening due to pigment degradation, observed on the sample microphotograph (a) and in situ (b, c, d) in the following locations: (a, b) Pb pigment (?), St Peter's church in Ribičje, (c) Pb and/or Cu pigments, St James's church in Ormož (central nave), and (d) malachite, St Nicholas's church in Žužemberk (St. Erasmus) ((a) © IPCHS, RC, Scientific department; (b-d) photos: Anabelle Križnar).

In a few cases, lead pigments were detected, mostly on the basis of their black appearance on the wall as a result of chemical degradation forming black plattnerite (PbO_2) or lead sulphate ($PbSO_4$). This could happen due to oxidizing agents in the atmosphere or due to microbiological activity.[17] Such an example can be found on the presbytery wall of the church of St Peter in Ribičje (Fig. 6a). Raman analysis confirmed the formation of platternite. An interesting case are the paintings that cover the upper layer of the triumphal arch and the presbytery triumphal wall in the church of Our Lady on the Rock in Vuzenica, that have blackened in many areas of the draperies (Fig. 7a) or even faces, which points towards a hypothesis of lead-pigment degradation. However, no conclusive results have been obtained so far. FTIR can confirm the use of lead white pigment only in one sample (Fig. 7b, c), while in the other samples only silicates (earths) have been detected. Raman did not produce any conclusive results. Darkening can be observed also for green malachite and/or blue azurite. When exposed to heat in an alkali environment (such as fresco painting), black copper oxides can form as tenorite (CuO).[18] A clear example of it is, again, the mural in Ormož (Fig. 6c), where the transition from green/blue to black can be observed even with the naked eye. The darkening of green malachite is strongly present also on St Erasmus's coat in Žužemberk (Fig. 6d).

17 COCCATO, MOENS, VANDENABEELE 2017, pp. 17–19.

18 COCCATO, MOENS, VANDENABEELE 2017, pp. 12–14.

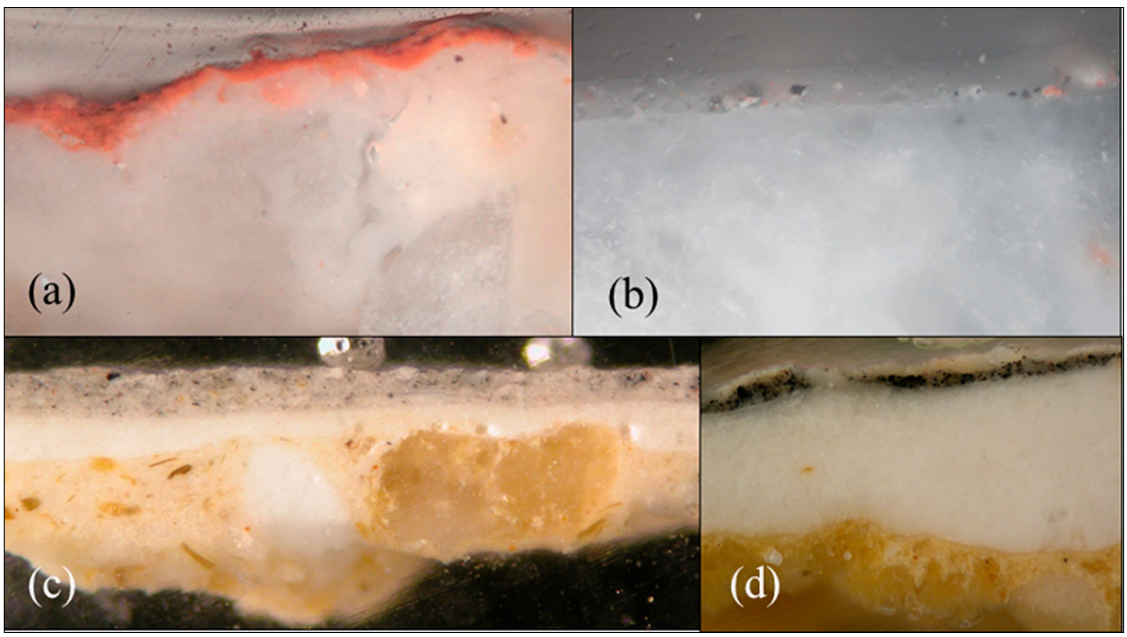


7. Colour darkening due to pigment degradation, observed on (a) the saint's figure, triumphal arch, church of Our Lady on the Rock in Vuzenica, (b) the dark colour layer on the sample microphotograph taken from the marked location (reflected light), (c) the FTIR spectrum of the analysed sample, indicating possible lead white together with calcite, silicates, potential acrylic or natural resin, gypsum, and calcium oxalate ((a) photo: Anabelle Križnar; (b, c) © IPCHS, RC, Scientific department).

3. Painting technique

The study of cross-sections under an optical microscope can reveal the painting technique used by the artist: *a fresco*, *a secco*, lime technique or, what is generally the case, the combination of two or three of them.[19] This can be determined through the form of the contact between the support and colour layer(s) which can be smooth and blurred (indicating painting on a fresh support) or straight and defined (painting on a dry surface), and a layer of lime-wash can be easily identified. Thus, according to the cross-section findings, the high presence of calcite in most of the painting layers identified by Raman Spectroscopy and the predominance of calcite in most plasters as shown by XRD results indicate that the principal painting technique was *a fresco* with pigments applied on a humid mortar. The cross-sections reveal a smooth transition between the support and colour layers (Fig. 8a), due to the carbonatization process through which the lime in the plaster moves up to the

19 Microscopic Analysis 2018.



8. Microphotographs of plaster samples and colour layers using optical microscopy in reflective light reveal various painting techniques: (a) a fresco, St Michael's church in Biljana, (b) a secco, St Thomas's church in Gorenja Straža, (c) auxiliary lime technique, St Agnes's church in Brdinje pri Kotljah, (d) principal lime technique, St Nicholas's church in Pangrč Grm (the older layer) ((a, b) © IPCHS, RC, Scientific department; (c, d) photos: Anabelle Križnar).

surface, involving pigment grains and thus serving as binder.[20] When the plaster had dried too much and the lime could no longer serve as a binder, *a fresco* painting was combined with *a secco* and sometimes with lime technique, the latter mostly as auxiliary procedures. Painting on a dry plaster can be clearly distinguished in cross-sections as a very clear line between the plaster and the colour layer since the lime is not transiting anymore (Fig. 8b). In this technique, the pigments must be applied mixed with an organic binder, egg yolk, casein, or animal glue.[21] Organic materials have not yet been analysed. The ration of *a secco* to *a fresco* painting depends on the size of the *giornata* and, of course, on the dexterity of the painter and how quickly he can work. Painting on a dry surface was mostly used for the final details or for backgrounds and secondary figures. In some cases, the plaster was refreshed with one or several layers of lime wash, which can be also clearly distinguished on cross-sections as a white layer between the plaster and colour layers (Fig. 8c) or between colours (Fig. 4d). Only in Pangrč Grm was the lime technique used as the principal one, creating a thick white support of lime wash which peals from the wall together with colour layers (Fig. 8d).

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20 *Reclams Handbuch* 1990, pp. 32, 61–62; MORA, MORA, PHILIPPOT 2001, pp. 63–64; PECCHIONI, FRATINI, CANTISANI 2008, pp. 32–40.

21 *Reclams Handbuch* 1990, pp. 51–58.

Painting Procedures

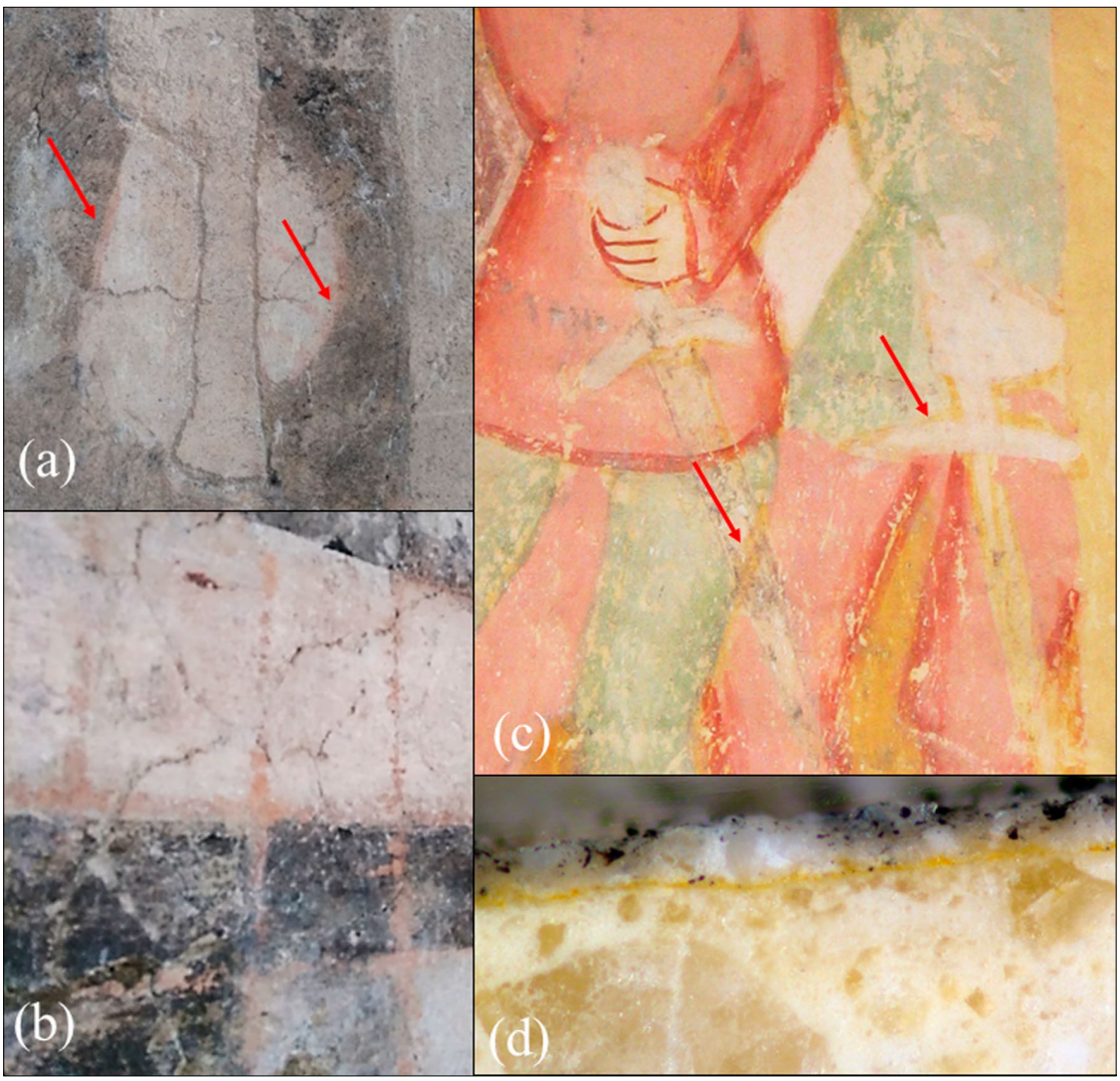
Painting procedures reveal an artist's way of working and can characterize them, thus helping in the authentication of a painting. These procedures include preparatory drawings, incisions, pouncing, underpaintings, modelling, and final details.

Preparatory drawing carried out on the lower plaster layer (*arriccio*) is known as *sinopia*, and that on the upper plaster layer (*intonaco*) as underpainting.[22] *Sinopia*, generally traced in red colour, can be only seen where the upper plaster layer has fallen off, therefore only in rare cases. We must bear in mind, though, that many painters did not use it, especially if they were working only on one layer of plaster; it is a painting procedure more common in Italian art. In our research, we have found *sinopia*, for example, in the church of St Francis of Assisi in Koper, on the oldest 14th century scene representing the *Madonna and child*, where the lower part of the mural is damaged. A thin red line is visible, as shown in Fig. 9. An underdrawing can be distinguished more easily, especially where the colour layers have fallen off or where the final contour does not cover it completely. Artists could use different colours: yellow, pink, red, black, though only rarely green.[23] On murals up to 1380, yellow, red, and black have been found (Fig. 10). A ruler could have been used to trace auxiliary straight lines (scene bordures, architectural elements), though in most cases

9. A red line of sinopia, drawn on arriccio in a red ellipse. St Francis of Assisi church in Koper (Photo: Anabelle Križnar).

22 *Reclams Handbuch* 1990, pp. 79–84; KRIŽNAR 2006, pp. 26–27; BROECKE 2015, pp. 97–98, 100–101.

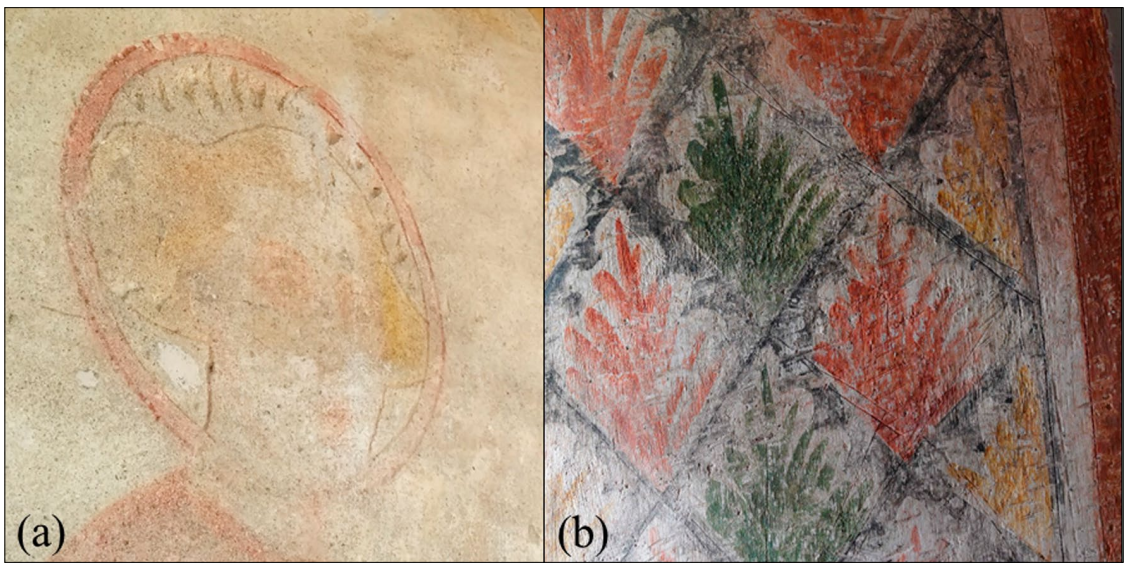
23 *Reclams Handbuch* 1990, pp. 83–84.



10. (a) A red underdrawing and (b) straight red lines traced with a wet rope, both from St James's church in Ormož (the central nave). (c) Yellow underdrawing observed on figures and swords, also revealed on the (d) sample microphotograph (reflected light), St Nicholas's church in Pangrč Grm (the younger layer) (Photos: Anabelle Križnar).

artists chose to use a rope, impregnated in red colour and pressed on the wall.[24] A characteristic point-like line marked by the rope can be clearly distinguished in several murals, as we can see on the paintings in the main nave of the church of St James in Ormož (Fig. 10b). Sometimes, the underdrawing can also be discovered by means of cross-sections, revealing a thin colour layer

24 *Reclams Handbuch* 1990, pp. 76–78.



11. (a) Deep incisions and pouncings for the halos and head contours, St Trinity church in Knežja Njiva. (b) Straight, thin and shallow incisions, traced with a sharp object and a ruler; many mistakes can be observed, St Ulrich's church in Tolmin (Photos: Anabelle Križnar).

in yellow (Fig. 10d), red or black under the principal colour layer, especially if the sample was extracted from the area of a contour, where such underdrawing can be expected. Sinopia and underdrawing are generally well preserved since they are done on fresh plaster.

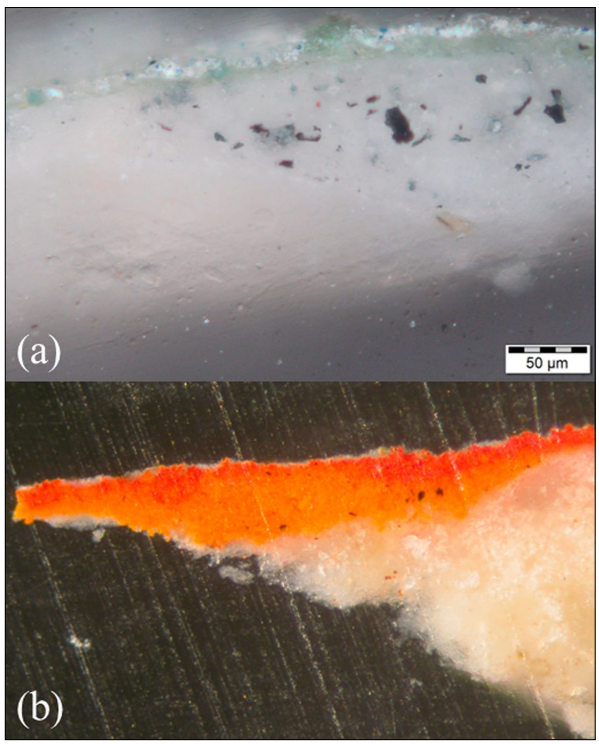
Incisions and pouncing are made into a fresh mortar as well, leaving thin or wide, shallow, or deep lines or forms. They are very common in Slovene medieval murals and used principally for saints' heads and halos (Fig. 11a), but also for other, mostly decorative elements such as crowns, belts, swords, or even entire figures, especially when transferred from a pattern, or for straight lines when rope was not used (Fig. 11b).

Underpaintings are uniform colour layers applied under another colour to give it a desired, generally more intense or darker tonality.[25] For the most part, expensive pigments such as blue azurite or green malachite were underlaid in order to use less pigment and still obtain a deep colour hue. The underpainting could be grey, known as *veneda*,[26] or dark red, known as *morello*.[27] The first one was generally common in the painting North of the Alps and the second in Italian Trecento

25 *Reclams Handbuch* 1990, pp. 89–96.

26 The terminology was first employed already by Theophilus in his treatise for a mixture of black pigment and lime, suggesting that a painter underlays malachite or azurite with it (I, 6, 15, 16): THEOPHILUS PRESBYTER 1979, pp. 18, 23, 25.

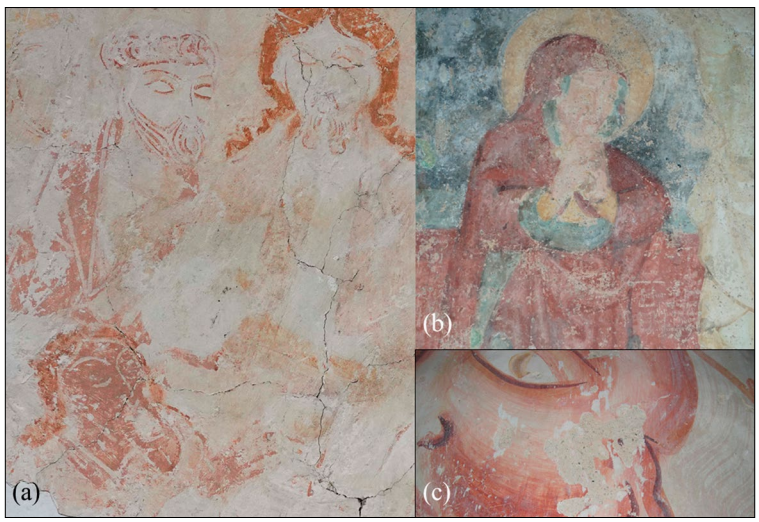
27 Cennini in his treatise (III, 83) writes about a reddish underlayer, made as a mixture of black pigment with red ochre and suggest using it under blue azurite: BROECKE 2015, pp. 119–121.



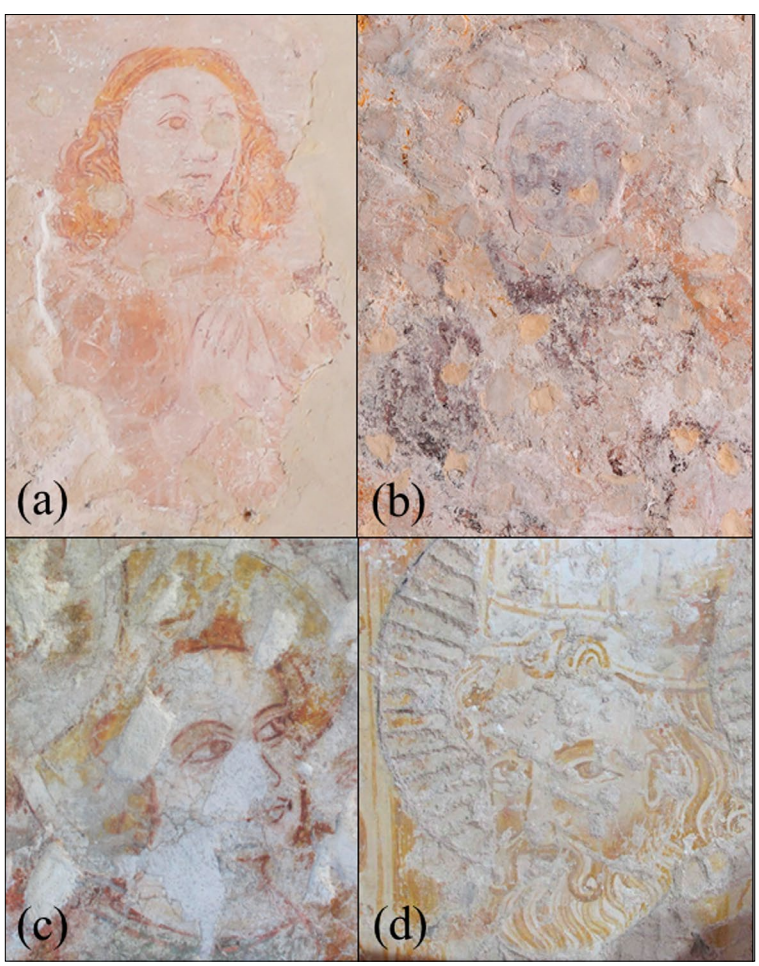
12. Sample microphotographs of plasters and colour layers using optical microscopy in reflective light reveal underpaintings: (a) grey under green malachite, cloister, Stična monastery (Votive scene), (b) orange minium under red cinnabar, St George's church in Ptuj ((a) © IPCHS, RC, Scientific department; (b) photo: Anabelle Križnar).

painting. We find both in Slovene territory, thus confirming the area as a meeting point of northern and southern painting techniques as well as place of collaboration of artists of various provenances. Sometimes, these underpaintings can be discerned even with the naked eye through the upper painting layer, if it is very thin, or on areas where the colour has fallen off. Mostly, though, it can be revealed through cross sections by observing a thicker grey (Fig. 12a) or reddish colour layer between the plaster and the upper colour layer. *Veneda* and *morello* used to be applied *a fresco*, malachite and azurite *a secco*. Both pigments could have also been applied directly on the plaster (Fig. 5e), which is often the case in pre-1380 murals. Other pigments could have been applied as underpaintings as well, such as yellow earth under green or minium under cinnabar (Fig. 12b), however, it is rarely found.

Colour modelling reveals the dexterity of a painter through his brushstroke and colour transitions. The brushstroke can be wide and coarse or thin and precise, resulting in rough or smooth transitions between shades and highlights, creating plane surfaces or round volumes. The oldest paintings are rather flat with predominant line (Fig. 13a), while the more recent ones already show soft modelling and a combination of wide and thin brushes (Fig. 13 b, c). In mural painting up to 1380, the line takes precedence over the colour, observed as strong contours that delimitate an object or figure. We can study in this way the form of the head and hair, eyes, nose, lips, hands and fingers, feet, if the figures are barefoot, and drapery folds. The accuracy of the final contour with the underdrawing, when visible, can also be compared. Such study allows us in many cases to determine if several scenes were carried out by the same painter or not. Such are the cases in Vuzenica and Žužemberk, where the specific form of the faces as well as the very characteristic shading (for example, eyelids in Žužemberk) allow us to attribute it to the same hand or close circle. Therefore, the figures on



13. Colour modelling: (a) flat, with a predominant contour, St Oswald's church in Leskovec nad Višnjo Goro; (b, c) creating volumes with a soft transition between light and dark tones, St Thomas's church in Štomaž pod Štjakom (© Research Centre of the Slovenian Academy of Sciences and Arts, France Stele Institute of Art History, Ljubljana (ZRC SAZU, UIFS), photos: Andrej Furlan).



14. Colour modelling can contribute to the characterisation and authentication of an artist, comparing the manner of face forms and shading: (a, b) faces of the donor on the chancel triumphal wall and the saint on the triumphal arch, the church of Our Lady on the Rock in Vuzenica. (c, d) Faces of the saint on the Storm scene on the exterior western wall and St Erasmus on the interior nave triumphal wall, St Nicholas's church in Žužemberk ((a, b) © ZRC SAZU, UIFS, photos: Andrej Furlan; (c, d) photos: Anabelle Križnar).

the upper layer on the triumphal arch and interior presbytery wall in Vuzenica (Fig. 14a, b) must have been painted by the same master or a very close disciple. Similarly, the figure of *St Erasmus* on the interior wall and the figures in the *Storm scene* on the western outside wall of Žužemberk church (Fig. 13c, d) are the work of the same workshop, though probably not by the same painter, portraying *St Erasmus* with a much better and softer modelling and showing his flesh-tone with brighter colour palette.

Conclusions

This still ongoing research involves the analysis of plasters, pigments, painting techniques and painting procedures of Slovene murals up to 1380. Paintings were first studied *in situ*, then small samples of support and colour layers were analysed using different analytical techniques (OM, SEM-EDX, XRF, XRD, Raman spectroscopy and FTIR). We still do not have all the results, but those obtained so far enable us to characterize plasters as a mixture of lime and aggregate: the latter is composed mostly of silicates, but in some cases crushed calcite was also used. The pigments are mostly natural inorganic: lime white, yellow, red and green earths, rarely malachite and azurite, while the blacks are organic, mostly carbon or lamp one. In several cases, lead pigments were also applied, but due to their degradation, they have turned black. Black areas can be found also in some areas of azurite or malachite, while we often find degradation from blue azurite to green (para)tacamite. The principal painting technique is *a fresco* combined with *a secco*. The proportion of the dry-painted parts varies, depending on the mural cycle and the dexterity of the artist. Lime technique was sometimes applied as auxiliary technique under colour layers. Only in Pangrč Grm was it used as the principal painting technique. The study of painting procedures has revealed *sinopia* only on one mural, while underdrawings have been easier to discern and were traced with yellow, red or black colour. Incisions and pouncing are very common but can vary in the depth and width of the line/form. For straight lines, mostly a rope soaked in red colour was pressed against the wall. Underpaintings were rarely found under malachite, azurite and, in just one case (Ptuj) they were found under cinnabar. In modelling, the line takes precedence over the colour, therefore we find mostly flat figures and objects. However, in later murals, greater volume and a softer modelling can be appreciated. This is, of course, also dependent on the quality of the artist. The material and technical study of mural paintings can thus make an important contribution to our understanding of an artwork or an artist, as well as informing conservation-restoration work.

Literature

ALDROVANDI, PICOLO 2003
Alfredo ALDROVANDI, Marcello PICOLO, *Metodi di documentazione e indagini non invasive sui dipinti*, Padova 2003.

Analytical Chemistry 2017
Analytical Chemistry for Cultural Heritage (ed. Rocco Mazzeo), Berlin 2017.

APPOLONIA, VOLPIN 1999
Lorenzo APPOLONIA, Stefano VOLPIN, *Le analisi di laboratorio applicate ai beni artistici policromi*, Padova 1999.

ARTIOLI 2010
Gilberto ARTIOLI, *Scientific Methods and Cultural Heritage. An Introduction to the Application of Materials Science to Archaeometry and Conservation Science*, Oxford-New York 2010.

Artists' Pigments 2012
Artists' Pigments. A Handbook of Their History and Characteristics, 1–4 (eds. Robert L. Feller, Ashok Roy, Elisabeth West FitzHugh, Barbara Hepburn Berrie), Washington 2012[2].

BACCI 1995
Mauro BACCI, Fibre Optics Applications to Works of Art, *Sensors and Actuators. B: Chemical*, 29/1–3, 1995, pp. 190–196.

BALAŽIC 2008
Janez BALAŽIC, *Stensko slikarstvo v dobi Luksemburžanov v zahodnem panonskem prostoru*, Ljubljana 2008 (unpublished doctoral dissertation).

BOGOVČIČ 1995
Ivan BOGOVČIČ, Gotsko stensko slikarstvo. O nastanku, ogroženosti, restavriranju/Gothic Mural Painting. The Development, Endangerment, Restoration, *Gotika v Sloveniji. Nastanek, ogroženost, reševanje likovne dediščine/The Origin, Endangerment, and Preservation of Art* (ed. Ivan Bogovčič), Ljubljana 1995, pp. 14–21.

BROECKE 2015
Lara BROECKE, *Cennino Cennini's Il libro dell'arte. A New English Translation and Commentary with Italian Transcription*, London 2015.

COCCATO, MOENS, VANDENABEELE 2017
Alessia COCCATO, Luc MOENS, Peter VANDENABEELE, On the Stability of Mediaeval Inorganic Pigments. A Literature Review of the Effect of Climate, Material Selection, Biological Activity, Analysis and Conservation Treatments, *Heritage Science*, 5/1, 2017, pp. 1–25.

CONSENTINO 2015
Antonio CONSENTINO, Practical Notes on Ultraviolet Technical Photography for Art Examination, *Conservar Património*, 21/6, 2015, pp. 53-62.

DE LA RIE 1982
Etienne René DE LA RIE, Fluorescence of Paint and Varnish Layers, 1–3, *Studies in Conservation*, 27, 1982,

pp. 1–7, 65–69, 102–108.

HÖFLER 1985
Janez HÖFLER, *Stensko slikarstvo na Slovenskem med Janezom Ljubljanskim in Mojstrom sv. Andreja iz Krašc*, Ljubljana 1985.

HÖFLER 1996
Janez HÖFLER, *Srednjeveške freske v Sloveniji. 1: Gorenjska*, Ljubljana 1996.

HÖFLER 1997
Janez HÖFLER, *Srednjeveške freske v Sloveniji. 2: Primorska*, Ljubljana 1997.

HÖFLER 2001
Janez HÖFLER, *Srednjeveške freske v Sloveniji. 3: Okolica Ljubljane z Notranjsko, Dolenjsko in Belo krajino*, Ljubljana 2001.

HÖFLER 2004
Janez HÖFLER, *Srednjeveške freske v Sloveniji. 4: Vzhodna Slovenija*, Ljubljana 2004.

KRIŽNAR 2006
Anabelle KRIŽNAR, *Slog in tehnika srednjeveškega stenskega slikarstva na Slovenskem*, Ljubljana 2006.

MATTEINI, MOLES 1984
Mauro MATTEINI, Archangelo MOLES, *Scienza e restauro. Metodi di indagine*, Firenze 1984.

Microscopic Analysis 2018
Microscopic Analysis of Wall Painting Techniques. Laboratory Replicas and Romanesque Case Studies in Southern Switzerland, *Studies in Conservation*, 63/6, 2018, pp. 326–341.

MOLE 1984–1987
Izidor MOLE, Poskus analize tehnologije gotskih fresk (I–IV), *Varstvo spomenikov*, 26, 1984, pp. 89–99; 27, 1985, pp. 121–135; 28, 1986, pp. 189–208; 29, 1987, pp. 123–136.

MORA, MORA, PHILIPPOT 2001
Paolo MORA, Laura MORA, Paul PHILIPPOT, *La conservazione delle pitture murali*, Bologna 2001[2].

NEMEC 1995
Ivo NEMEC, Gotika v Sloveniji. O materialih/Slovene Gothic Materials, *Gotika v Sloveniji. Nastanek, ogroženost, reševanje likovne dediščine/The Origin, Endangerment, and Preservation of Art* (ed. Ivan Bogovčič), Ljubljana 1995, pp. 35–41.

OLTROGGE 2008
Doris OLTROGGE, *The Use of VIS Spectroscopy in Non Destructive Paint Analysis. Potential and Limits of the Method for 19th and Early-20th-Century Paintings*, Köln 2008.

PECCHIONI, FRATINI, CANTISANI 2008
Elena PECCHIONI, Fabio FRATINI, Emma CANTISANI, *Le malte antiche e moderne tra tradizione ed innovazione*, Bologna 2008.

PIRNAT 1972
Miha PIRNAT, Tehnike stenskega slikarstva na Slovenskem, *Varstvo spomenikov*, 16, 1972, pp. 51–56.

POHL 1966
Emil POHL, Raziskava slikarske tehnike na stenskih slikah v Pangrč Grmu, *Varstvo spomenikov*, 10, 1966, pp. 103–109.

PROKOPP 1983
Maria PROKOPP, *Italian Trecento Influence on Murals in East Central Europe, Particularly Hungary*, Budapest 1983.

RADOCSAY 1977
Dénes RADOCSAY, *Wandgemälde im mittelalterlichen Ungarn*, Budapest 1977.

Reclams Handbuch 1990
Reclams Handbuch der künstlerichen Techniken. 2: Wandmalerei, Mosaik, Stuttgart 1990.

SECCARONI, MOIOLI 2004
Claudio SECCARONI, Pietro MOIOLI, *Fluorescenza X. Prontuario per l'analisi XRF portatile applicata a superfici policrome*, Firenze 2004.

Spectroscopy 2021
Spectroscopy, Diffraction and Tomography in Art and Heritage Science (eds. Mieke Adriaens, Mark Dowsett), Amsterdam 2021.

STELE 1935
France STELE, *Monumenta Artis Slovenicae. 1: Srednjeveško stensko slikarstvo*, Ljubljana 1935.

STELE 1969
France STELE, *Slikarstvo v Sloveniji od 12. do 16. stoletja*, Ljubljana 1969.

STUART 2007
Barbara H. STUART, *Analytical Techniques in Materials Conservation*, Chichester 2007.

THEOPHILUS PRESBYTER 1979
THEOPHILUS PRESBYTER, *On Divers Arts. The Foremost Medieval Treatise on Painting, Glassmaking and Metalwork* (eds. John Greenfield Hawthorne, Cyril Stanley Smith), New York 1979.

VODNIK 1998
Alenka VODNIK, *Tekstilni vzorci v srednjeveškem stenskem slikarstvu na Slovenskem*, Ljubljana 1998 (Razprave Filozofske fakultete).

ZIMMERMANN 1996
Tanja ZIMMERMANN, *Stensko slikarstvo poznega 13. in 14. stoletja na Slovenskem*, Ljubljana 1996 (unpublished doctoral dissertation).

ŽELEZNIK 1993
Adela ŽELEZNIK, *La pittura postvitalesca in Friuli*, *Carinzia e Slovenia*, Trieste 1993 (unpublished typescript).

Anabelle Križnar, Katja Kavkler, Sabina Dolenec

Analiza materialov in slikarskih tehnik srednjeveškega stenskega slikarstva v Sloveniji do leta 1380

Povzetek

Sodoben pristop k preučevanju umetniških del zahteva tudi raziskovanje materialov in postopkov, ki so jih uporabljali umetniki pri njihovem ustvarjanju. Na področju stenskega slikarstva to vključuje znanje o uporabljenih pigmentih, razlikovanje med slikanjem na svež in na suh omet, apneno ali mešano tehniko in študij slikarskega postopka od pripravljalne risbe do končnega modeliranja. Te informacije skupaj z umetnostnozgodovinsko študijo omogočajo popoln vpogled v umetniško delo in umetnikov način ustvarjanja, kar omogoča boljšo primerjavo med različnimi deli, umetniki ali delavnicami. Osnovni pristop je analiza materiala, ki je lahko neinvazivna ali invazivna; slednja temelji na odvzemu majhnih vzorcev, ki se nato analizirajo z različnimi laboratorijskimi tehnikami, kot so optična mikroskopija (OM), skenirna elektronska mikroskopija z energijsko disperzno rentgensko spektroskopijo (SEM-EDX), rentgenska fluorescenca (XRF), rentgenska difrakcija (XRD) ali ramanska spektroskopija, ki so najpogostejše. Doslej je bilo raziskanih več kot 40 izbranih srednjeveških fresk po vsej Sloveniji, ki so potrdile ozko, praviloma naravno paleto anorganskih pigmentov, primernih za fresko poslikavo, v redkih primerih so bili najdeni tudi svinčevi pigmenti, ki pa so večinoma potemneli. Glavna slikarska tehnika je freska, večinoma v kombinaciji s *secco* ali apneno tehniko, slednja je v nekaterih primerih tudi glavna. Postopek slikanja se od poslikave do poslikave razlikuje in razkriva umetnike različnih slikarskih in tehničnih spretnosti. Delo še vedno poteka.