PERIODICO di MINERALOGIA
established in 1930

Dipartimento di Scienze della Terra
Sapienza Università di Roma

An International Journal of
Mineralogy, Crystallography, Geochemistry,
Ore Deposits, Petrology, Volcanology
and applied topics on Environment, Archaeometry and Cultural Heritage

A Raman microspectroscopy-based comparison of pigments applied in two gothic wall paintings in Slovenia

Maja Gutman Levstik [1,*], Ajda Mladenovič [1], Anabelle Križnar [2,3], Sabina Kramar [4]

[1] Institute for the Protection of the Cultural heritage of Slovenia, Conservation Centre, Restoration Centre, Poljanska 40, 1000 Ljubljana, Slovenia
[2] Department of Art History, Faculty of Arts, University of Ljubljana, Aškerčeva 2, 1000 Ljubljana, Slovenia
[3] Centro Nacional de Aceleradores (CNA), University of Seville, Av.da, Thomas A. Edison 7, 41092 Sevilla, Spain
[4] Slovenian National Building and Civil Engineering Institute, Dimičeva 12, 1000 Ljubljana, Slovenia

ARTICLE INFO

Submitted: March 2018
Accepted: December 2018
Available on line: February 2019

* Corresponding author:
maja.gutman@rescen.si

DOI: 10.2451/2019PM778

How to cite this article:
Levstik M.G. et al. (2019)
Period. Mineral. 88, 95-104

ABSTRACT

The present study deals with the characterisation of pigments used in two overlaid gothic wall paintings from the former 13th century Minorite church of St. Francis of Assisi (Koper, Slovenia), in order to define differences in the technologies used. Paint layer samples were analysed via Raman microspectroscopy, supported by SEM/EDS and FT-IR analysis, when necessary. The results revealed that the 14th century mural was painted mainly *a fresco* with final elements *a secco,* a technique typical of Italian mediaeval wall painting. In contrast, the 15th century painting was executed mostly *a secco*, a technique often applied in Northern Europe and the Alpine region. The differences between the two paintings are especially obvious in the pigments applied. While the earlier painting is characterised by azurite, carbon black, red and yellow ochres, lime white and green earth, the palette used for the younger painting is much broader. In addition to red and yellow ochres, carbon black and lime white, lead pigments such as lead white, red lead and lead-tin yellow type I were also determined, as well as a number of expensive pigments including cinnabar, azurite and malachite. Also found in the younger painting was the rare orange yellow pigment vanadinite. In both layers, azurite was applied *a secco* for the background area. Gilding was confirmed in both layers, carried out as application of gold leaves on red bole (in the earlier mural) and on mordant (on a younger, superimposed (overlaid painting), which is quite exclusive and rare for Slovene mediaeval painting. In the younger layer also a use of tin foil for secondary elements was discovered.

Keywords: wall paintings; pigments; Gothic; gilding; Raman microspectroscopy.

INTRODUCTION

The church of the Minorite monastery of St. Francis of Assisi in Koper (Slovenia) is considered one of the most important Gothic architectural monuments and the best preserved building constructed by mendicant orders in Slovenia. It was probably erected in the second half of the 13th century and represents a significant step in the architectural development of a characterised type of floor plan (Štefanac, 2013). Besides its architectural significance, during research undertaken in 2007 prior to the building's renovation in 2012-2014, an important discovery was made in a deep walled-in niche in the choir: two gothic wall paintings, one overlaying the other.

The lower, earlier wall painting was probably painted

in around 1320 (Košuta, 2016) and was later damaged by chiselling and hammering undertaken while preparing the surface for the new layer of render (Figure 1). The main figure depicts the Madonna Enthroned with the Child, flanked by two saints. On the sidewall of the niche, two additional saints and a medallion with the Lamb of God are still preserved. The idealised rendering of faces, the latter's almond-shaped eyes, green underpainting observed under the flesh tones, soft drapery folds and colour modelling together speak of strong Italian early Trecento influences, albeit with several byzantine elements related to the later Comnenian style, as developed in Rome before Giotto (Bomford et al., 1989; Poeschke, 2005). The wall painting carried out as a decoration of the tomb niche shows high artistic and technical skills. The sarcophagus, which must have once been placed on the shelf of the niche, belonged to a nobleman probably named Giovanni, according to both Saints next to the Virgin Mary: St. John the Baptist and St. John the Evangelist.

The second wall painting was painted in the third quarter of the 15th century (Košuta, 2016) and was applied on a thin layer of plaster that was, on its discovery, already partially detached from the surface (Figure 2). The scene of St. Francis´ Death, accompanied by friars and nuns, is set in a church interior, depicted in perspective. Its style also shows Italian influences, but of lower artistic quality, revealing elements characteristic of the Friuli region (Furlan, 1987; Poeschke, 2005). The discovery of both layers and their stylistic characterization was still not published; the stylistic definition was offered to the authors by one of the most relevant art historians for mural paining in Slovenia.

After a thorough study by the Cultural Heritage Commission of Slovenia, the decision was made to detach the overlaid 15th century painting, so that both artistically important layers could come to life. After the necessary conservation and restoration treatments, the younger mural was returned to the church and placed on the opposite side of the presbytery, in a special construction mirroring the original niche. The earlier wall painting was conserved and presented *in situ* (ICOMOS, 2003).

Until recently, gothic wall paintings in Slovenia have mostly been studied from an art-historical point of view (Stelè, 1972; Höfler, 1996-2004). Nevertheless, material analyses have for several years formed part of such research, combining different disciplines in order to

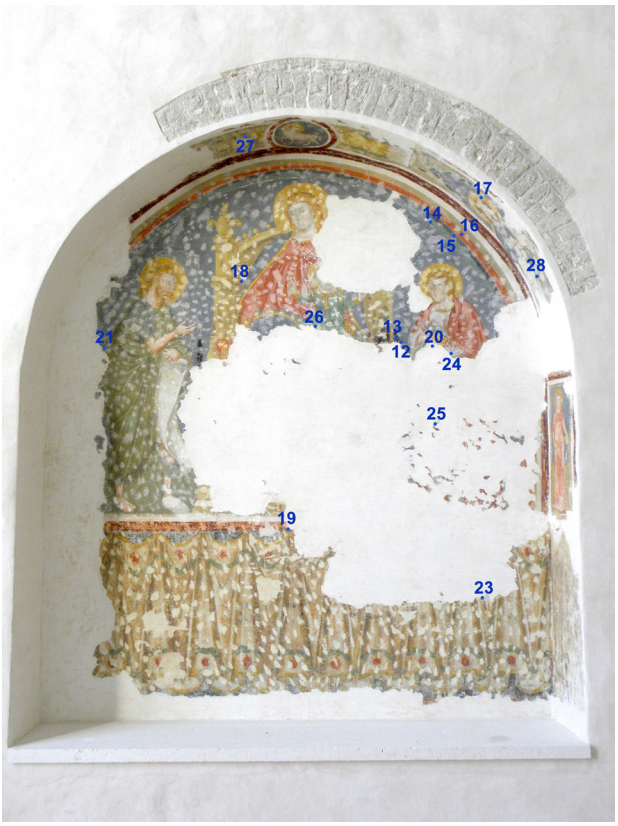

Figure 1. The earlier wall painting dating to the early 14th century.

Figure 2. The younger wall painting dating to the late 15th century.

assist conservators, restorers and art historians in both preserving the nation's Cultural Heritage and obtaining a wider knowledge of artistic production in the past (Križnar, 2006; Križnar et al., 2011; Križnar et al., 2011; Mladenovič et al., 2015). Both murals in Koper are of extreme importance in Slovene art-history due to their style, execution and contact with Italy, therefore they were selected for the material analysis. Among various analytical techniques possible, Raman microspectroscopy has been very helpful in characterising pigments (Burgio and Clark, 2001; Correia et al., 2007; Ospitali et al., 2008; De Santis et al., 2012), and was therefore selected as the principal method for the identification of pigments.

In this line, the principal objective of the present study was to obtain information regarding the painting techniques employed and materials applied in both painting layers, which would thus reveal differences in the execution of two wall paintings carried out a century apart. It was also of interest to determine whether they were executed using *a fresco*, *a secco* or in lime techniques, or if the artists combined two or even all three methods. Such knowledge regarding painting techniques, the possible application of lime-wash, selection of pigments and their mixture, as well as the construction of the paint layers, was also essential for appropriate conservation-restoration intervention.

EXPERIMENTAL

Materials

A total of 25 samples were extracted from different locations in both wall paintings, in order to obtain a complete colour palette, but at the same time always trying to minimise any damage. Information regarding the samples and their locations is given in Table 1 and shown in Figures 1 and 2.

Methods

In order to characterise the microstratigraphy of the paint layers, the first step involved examining polished cross-sections of the paint layers via optical microscopy using an Olympus BX-60 equipped with a digital camera (Olympus JVC3-CCD).

Raman spectra of the pigments were then obtained from the polished cross-sections of paint layers using a Horiba Jobin-Yvon LabRamHR800 spectrometer equipped with a high stability BX 40 optical microscope, a grating with 600 grooves per mm and an air-cooled CCD detector. Measurements were performed in the LabSpec 5 acquisition software program using a 785 nm laser excitation line with an output power of 31.4 mW and a Leica 100x objective, at a spectral resolution of about 1 cm^{-1}. Scanning times were determined for each sample separately, depending on the acceptable quality of the

Table 1. Investigated samples with painting techniques and pigments determined by Raman microspectroscopy and SEM/EDS.

Sample	Paint layer	Painting technique	Identified pigments
Early 14th century wall painting			
FAK12	blue	secco	azurite, yellow ochre (goethite)
FAK14	green	secco	green earth (celadonite)
FAK15	black	fresco	carbon black
FAK16	red	fresco	red ochre (hematite)
FAK17	gold		gold (bole)
	red	fresco	red ochre (hematite)
FAK18	orange	fresco	carbon black, red ochre (hematite)
FAK19	red	fresco	red ochre (hematite)
FAK21	green	secco	green earth (celadonite), red and yellow ochre (hematite and goethite), carbon black, lime white (calcite)
FAK23	brown	fresco	red ochre (hematite), lime white (calcite)
FAK24	violet	fresco	carbon black, yellow and red ochre (yellow and hematite)
FAK25	red	fresco	red ochre (hematite)
FAK26	green	secco	green earth (celadonite)
FAK27	blue	secco	carbon black, lime white (calcite)
	orange	fresco	yellow and red ochre (goethite and hematite)
FAK28	grey	fresco	red ochre (hematite)
Late 15th century wall painting			
FAK1	brown	secco	red ochre (hematite), magnetite
	red	secco	lead-tin yellow type I, red lead (minium)
FAK2	brown	fresco	carbon black, lime white (calcite)
FAK3	green	secco	malachite
FAK4	black	secco	carbon black
FAK5	green	secco	malachite
	black	secco	carbon black
FAK6	orange	secco	yellow and red ochre (goethite and hematite)
FAK7	yellow	secco	lead-tin yellow type I
	brown		tin foil
	blue	secco	azurite, yellow ochre (goethite)
FAK8	blue	secco	azurite, yellow ochre (goethite)
FAK9	gold		gold (mordant)
	yellow	secco	red lead (minium), lead white
	white	secco	lime white (calcite)
	yellow	secco	red and yellow ochre (hematite and goethite), vanadinite
FAK10	red	secco	cinnabar (cinnabarite)
	green	secco	malachite
FAK11	grey	secco	carbon black
	white	lime wash	lime white (calcite)
	black	fresco	carbon black

spectra obtained and also to ensure that the samples were not altered due to the heating produced by the laser. In general, the scanning time varied between 10 and 60 s. Spectra were acquired in the range of 100-1800 cm^{-1} with an accumulation number of 1. At least five measuring points were selected, taking into account every pigment. All spectra were analysed in LabSpec 5 and presented after baseline correction. In order to identify the pigments collected, various databases and references were used (Burgio and Clark, 2001; Ospitali et al., 2008; De Santis et al., 2012).

The chemical composition of the metal foil layers (FAK7, FAK9, FAK17) was additionally examined on the polished cross-sections of paint layers using a Scanning Electron Microscopy JEOL 5500 LV SEM equipped with an Energy Dispersive X-Ray spectrometer (EDS), in a low vacuum mode (between 10 and 15 Pa) at an accelerating voltage of 20 kV and working distance of 20 mm. X-ray spectra were optimised for quantification using the cobalt optimisation standard. Finally, the correction of EDS data was performed via the standard ZAF-correction procedure included in the INCA Energy software. Most pigment samples were not analysed by SEM-EDS, because Raman microspectroscopy results were conclusive enough.

Blue paint layer sample (FAK12) was additionally analysed with FT-IR microspectroscopy in order to determine the type of binder. Paint layer, collected with a fine needle under a stereomicroscope, was placed into a cell fitted with diamond windows and analysed using FT-IR microspectroscopy. Spectra were recorded with a spectral resolution of 4 cm^{-1} in the range of 4000-600 cm^{-1}; 32 signal-averaged scans of the samples were acquired.

RESULTS AND DISCUSSION

Pigments

Early 14th century mural painting

The colour palette of the earlier wall painting includes blue, green, black, grey, red, brown, violet and orange, derived from pigments such as azurite, carbon black, red and yellow ochre, lime white and green earth (Table 1). Besides, also gold was identified.

Azurite [$2CuCO_3 \cdot Cu(OH)_2$], which was characterised based on Raman bands at 112, 154, 180, 249, 280, 330, 400, 541, 764, 839, 1096, 1429, 1429, 1459 and 1578 cm^{-1}, was used for backgrounds and was applied *a secco* without underlayer (Thompson, 1956; Knoepfli et al., 1990; Mora et al., 2001), as observed on a cross-section (Figure 3). FT-IR confirmed the presence of a proteinaceous material. Goethite was also identified, mixed with azurite, as shown by Raman bands at 92, 247, 392 and 485 cm^{-1}. Goethite, haematite and other

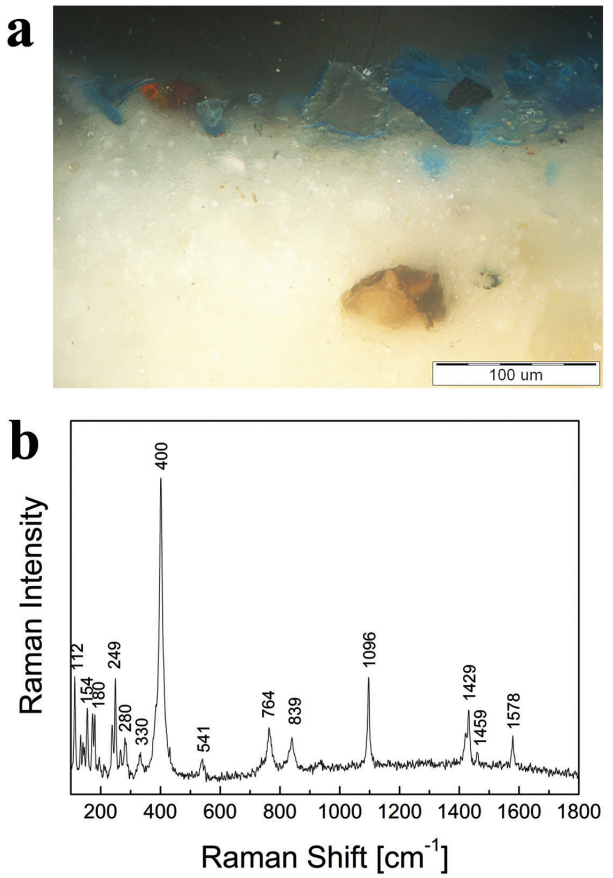

Figure 3. Blue paint layer with azurite (a) and Raman spectrum of azurite (b) - sample FAK12.

occurring minerals including cuprite, rutile and malachite, are commonly detected as impurities in azurite specimens used for pigments, rather than as deliberate additions by the artist (Aru et al., 2014). This is not surprising, since azurite is a naturally occurring mineral. However, as azurite was also occasionally combined with red pigments to produce purple hues (Howard, 2003), the mixing of azurite with yellow ochre cannot be excluded in this instance. Azurite was, despite its relatively high price, the most important blue pigment used in European paintings throughout the Middle Ages and Renaissance (Thompson, 1956; Howard, 2003), and was quite commonly employed in wall paintings in Slovenia during the mediaeval period, especially for the sky or blue clothing of saint figures (Križnar, 2006; Gutman et al., 2014). Due to its high price, the pigment was finely ground in order to reduce the required quantity, which resulted in a loss of colour intensity. For this reason, it was normally applied *a secco* over a grey (veneda) or brownish-red (morello) underlayer to enhance the intensity of the blue colour and minimise the amount of pigment used (Križnar et al., 2011). However, in this mural painting, no underlayer

was found, what is extraordinary. Recent analysis of other Slovenian mediaeval wall paintings has revealed that the large background areas, also painted with azurite, were executed in lime technique, without any underpainting (Gutman et al., 2014). In the studied wall painting, a large amount of blue pigment was used to paint a background, likely indicating this work was completed for a wealthy client. Nevertheless, the blue colour found in some areas of the earlier painting was obtained by mixing carbon black and lime white and painted *a secco* over a layer of red ochre, previously applied *a fresco* (sample FAK27).

Raman bands at 226, 246, 292, 411, 499, 612 and 1320 cm^{-1} ascribed to haematite (Fe_2O_3) indicate the use of red ochre, which was applied either *a secco* or *a fresco* for decorative elements and for the drapery of Virgin Mary and St. John the Evangelist. A brown or grey colour was also occasionally obtained by using this pigment mixed with carbon black, with the Raman bands at 1315 and 1601 cm^{-1}, which are attributed to the D (disordered) and G (graphitic) bands, respectively, indicating amorphous carbon (Reich and Thomsen, 2004; Tomasini et al., 2012). The violet colour of the drapery was obtained by adding yellow and carbon black to haematite.

The green paint layer was obtained either by the use of solely green earth, as revealed by the Raman bands at 169, 273, 393, 540, 701 cm^{-1} that identify the presence of celadonite $\{K(Mg,Fe^{2+})(Fe^{3+},Al)[Si_4O_{10}](OH)_2\}$, or by green earth mixed with red ochre, yellow ochre and carbon black (Figure 4) to obtain different tonalities. In both cases the paint was applied *a secco*. Pure green earth was used for the garment of Jesus and a decorative element above the head of a saint. Green earth, mixed with red and yellow ochre and carbon black, was applied for the garment of this saint.

The black colour used for decorative elements and applied *a fresco* was found to consist of carbon black, as identified by Raman bands at 1315 and 1601 cm^{-1}.

One very interesting discovery is the use of a gilding technique on the haloes of the saints, since gilding is rarely found in wall paintings in Slovenia and the present study is the first to document its use in gothic wall paintings. Recent analysis (2015) of a lavishly decorated early 16th century wall painting at the pilgrimage church of St. Primus and Felician, Kamnik, revealed the use of metal application on the haloes and gifts of the Magi, including gold leaf applied on a base of red ochre and mordant for the imitation of costly textiles. Gilding was also found on the baroque wall paintings in Kreljeva Palace, Koper, where a brass foil was used (Mladenovič et al., 2015). The use of gilding on wall paintings enjoyed its most significant development in Italy between the 13th and 14th centuries (Cavallo and Verda, 2009), which no doubt influenced the gold additions to the paintings in question. As confirmed

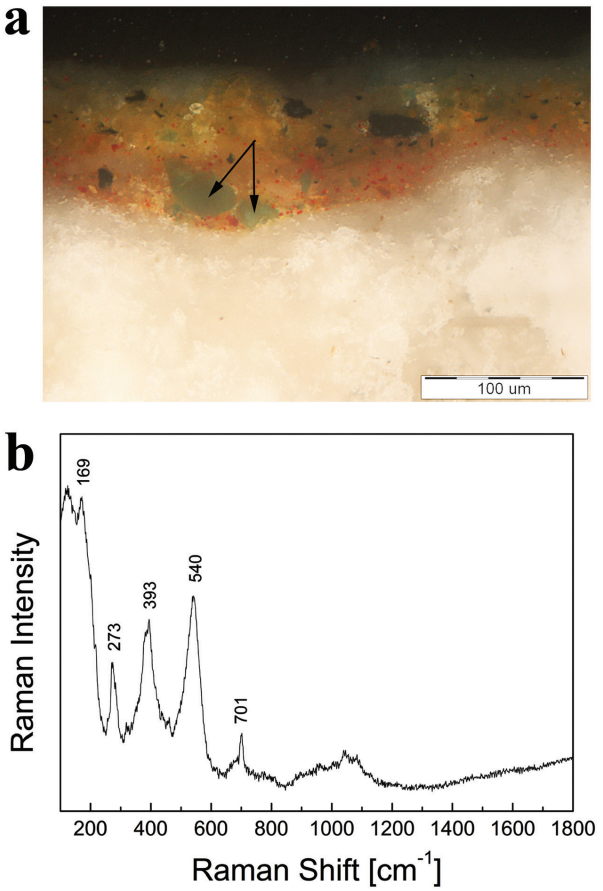

Figure 4. (a) Grains of green earth - sample FAK21. (b) Raman spectrum of celadonite.

by SEM/EDS analysis, gold leaves were applied over a layer of red ochre (bole), as shown in Figure 5, on a raised plaster decorated with radiant impressions, thus achieving an effect of splendour.

Late 15th century mural painting

The colour palette of the 15th century wall painting is much richer, including red, brown, green, black, orange, yellow, blue, white and grey colours, as well as gold. Besides common pigments such as red and yellow ochre, carbon black and lime white, both expensive (cinnabar, azurite and malachite) and rare (orange yellow vanadinite) pigments were also identified, as well as lead pigments such as lead white, red lead and lead-tin yellow type I.

As in the earlier painting, azurite was applied *a secco* for the background areas, with goethite also identified among the azurite grains.

Red pigments comprised red ochre, red lead and cinnabar. Red ochre was used either as a single pigment or mixed with yellow ochre (goethite) and applied *a secco* for brown or ochre layers. Magnetite (Fe_3O_4) was

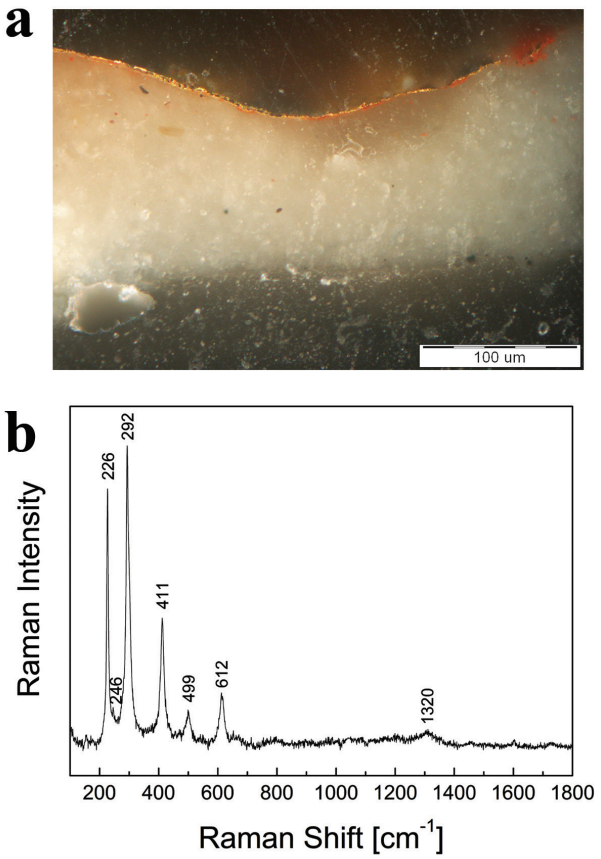

Figure 5. a) Gold leaf applied on a layer of red ochre, indicating bole gilding technique - sample FAK17. b) Raman spectrum of haematite, indicating red ochre.

occasionally identified (Raman band at 663 cm^{-1}) together with red ochre, representing an impurity.

Raman bands at 121, 152, 224, 314, 391, 480 and 550 cm^{-1} (Figure 6) revealed the presence of red lead (minium, Pb_3O_4). This pigment was in one case applied *a secco* together with lead-tin yellow type I (Pb_2SnO_4), thus forming a red paint layer under the brown one (sample FAK1). As shown in Figure 7, the lead-tin yellow type I pigment was identified by its main Raman bands at 130, 195, 275, 291, 455 and 550 cm^{-1}. This particular synthetic pigment, obtained as a mixture of lead monoxide, red lead or lead dioxide with tin dioxide (Pelosi et al., 2010), was in use between the 13th and 18th centuries, most commonly between the 15th and 17th centuries, and is rarely found in Slovenian mediaeval wall paintings (Križnar 2006; Gutman et al., 2014). Furthermore, this pigment was also identified overpainted on a tin foil (FAK7), the latter being characterised via SEM/EDS analysis evidencing the presence of tin (Sn). The combination of tin foil painted with bright lead-tin yellow pigment was used for decorative stars in the blue sky, imitating gold. Indeed, tin

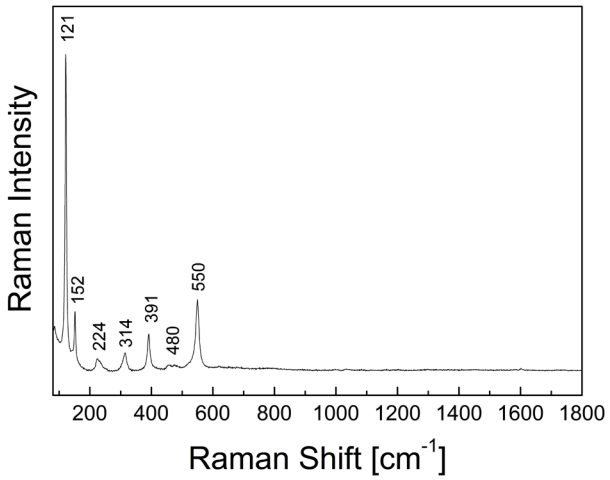

Figure 6. Raman spectrum of red lead - sample FAK1.

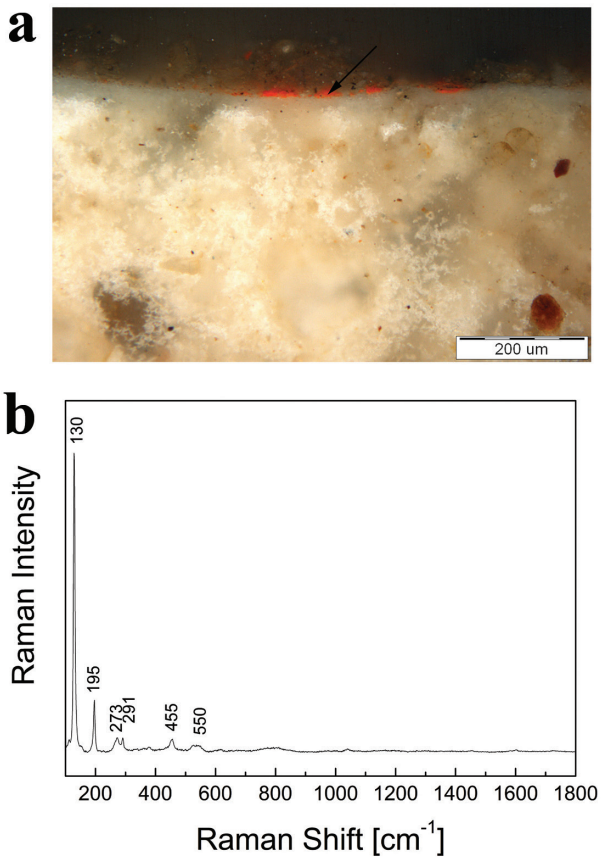

Figure 7. Raman spectrum of lead-tin yellow type I - sample FAK1.

foil was commonly used instead of expensive gold leaf, sometimes covered with a lead-tin yellow, organic yellow dye or purple layer, presumably to produce an intense lustrous colour (Schädler-Saub, 2000; Howard, 2003). However, such a find is rare in Slovenian wall paintings

and puts this mural in an exceptional position among the objects of our mediaeval Cultural Heritage.

In another case, red lead was used, mixed with lead white in gilding. Lead white, an inorganic pigment that can be either natural or synthetic, was here identified based on its Raman spectrum with a characteristic doublet at 1049 and 1053 cm^{-1}. This result is indicative of hydrocerussite ($2PbCO_3 \cdot Pb(OH)_2$) and can be distinguished from lead carbonate (cerussite, $PbCO_3$), which has a single band at around 1050 cm^{-1} (Correia et al., 2007). It is unclear whether lead white was used as an original pigment or is only residue of production of red lead pigment. The gilding was used for the flat drawn halo of Saint Francis, where gold leaves were adhered onto a layer of lead pigments (mordant-gilded).

Cinnabar was identified based on Raman bands at 253, 287 and 343 cm^{-1} and was applied on a green background (Figure 8). According to the Raman bands at 148, 178, 263, 431 and 1090 cm^{-1}, the green layer consists of malachite. Among the three red pigments typically present in mediaeval wall paintings, cinnabar was less common since it was very expensive due to its rare finding in the nature (Thompson, 1956; Križnar et al., 2011) and often used only for small details or mixed with other pigments (Gutman et al., 2014). Its adulteration with red ochre or red lead was quite common in Roman and mediaeval times due to its high price, particularly when used in wall paintings (Perardi et al., 2003). Natural cinnabar was clearly especially popular in the 13th and 14th centuries (Gutman et al., 2014), after which it was replaced by the synthetic and much cheaper vermilion. For this reason it was not frequently found in later wall paintings, as confirmed by those in Slovenia (Križnar, 2006). Although it can be very difficult to distinguish between natural cinnabar and synthetic vermilion due to their identical chemical compositions, analysis of the morphology of the pigment grains shown in the SEM image of sample FAK10 reveals an angular form rather than a uniform shape. This suggests that the artist applied a natural pigment, obtained from the crushed mineral (Eastaugh et al., 2008), thus confirming its use in the 15th century and suggesting a wealthy client.

Interestingly, vanadinite [lead vanadate, $Pb_5(VO_4)_3Cl$] was recognised based on Raman bands at 322, 355, 794, 826 cm^{-1} (Figure 9), mixed with red and yellow ochre. Since vanadinite is such a rare pigment in wall paintings, we applied additional analysis by SEM-EDS, which confirm the presence of Pb, V and Cl. The application of this red-orange-yellow pigment that is otherwise infrequently used for painting purposes on stelae and pottery (Eastaugh et al., 2008), is, according to the authors' knowledge, not known from wall paintings. Again, another unique feature of this mural in Koper,

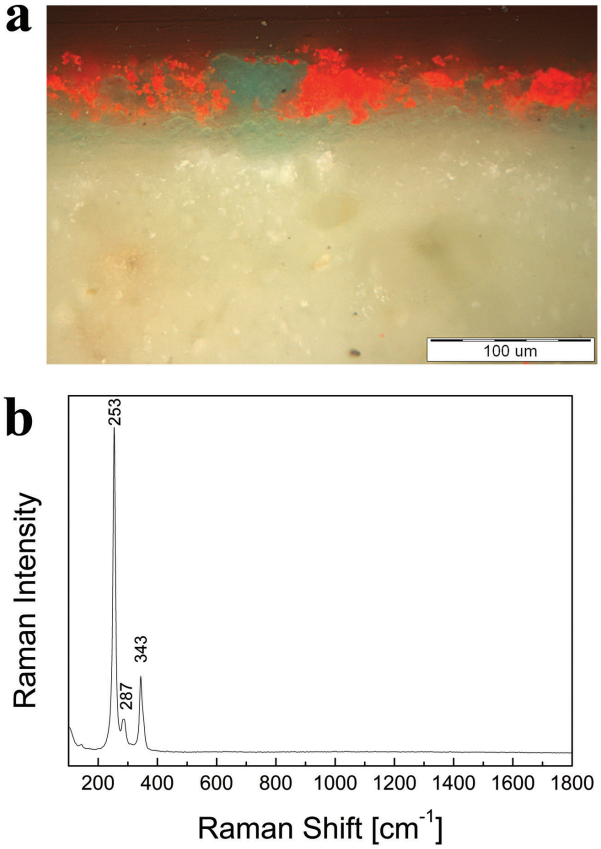

Figure 8. (a) Paint layer with cinnabar applied over malachite - sample FAK10. (b) Raman spectrum of cinnabar.

found by Raman microspectroscopy.

The green paint layer was formed by malachite applied *a secco* either directly on the render or underlain by a carbon black *a fresco* layer (Figure 10). Malachite is found quite frequently in Slovenian mediaeval wall paintings, but is not as common as green earth (Križnar et al., 2011) as it was rather expensive, being typically painted *a secco* over a grey or reddish-brownish underpainting (Križnar, 2006). Such coloured underlayers were employed to both increase the covering power and enhance the colour of the green pigments (Howard, 2003). Whereas grey underpainting is a characteristic underlayer for azurite or malachite in wall paintings north of the Alps, where it is known as veneda and is described as early as the 13th century by Theophilus, in Italy the use of a brown-red underpaint, morellone, is more common (Knoepfli et al., 1990; Mora et al., 2001; Križnar, 2006; Križnar et al., 2011).

Lime white was used for white paint layers, as well as for colour modelling applied on yellow underpainting as a base for flesh tones (FAK9) and the grey layer (FAK11).

Painting techniques

Mediaeval wall paintings in Slovenia are generally

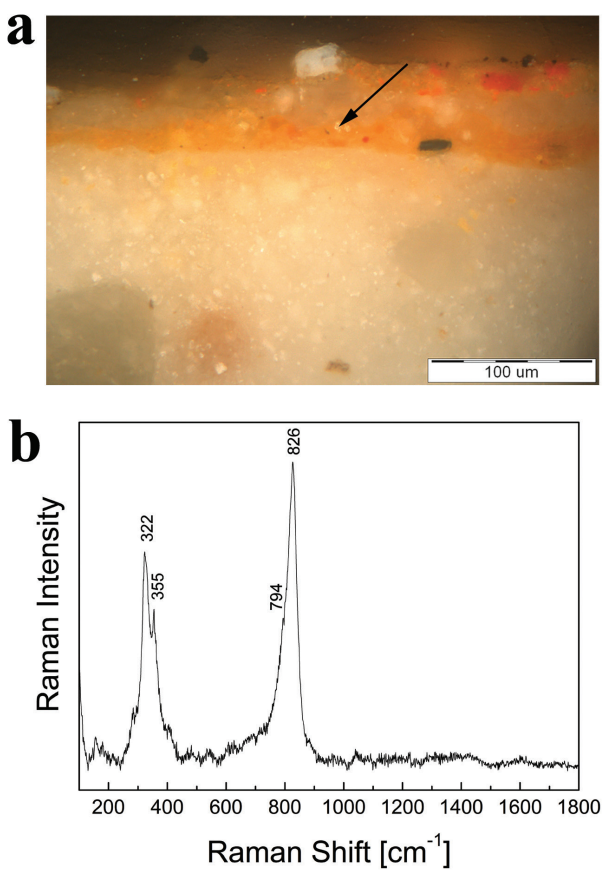

Figure 9. Yellow orange paint layer with vanadinite - sample FAK9. a) Optical microscopy, reflective light. b) Raman spectrum of vanadinite.

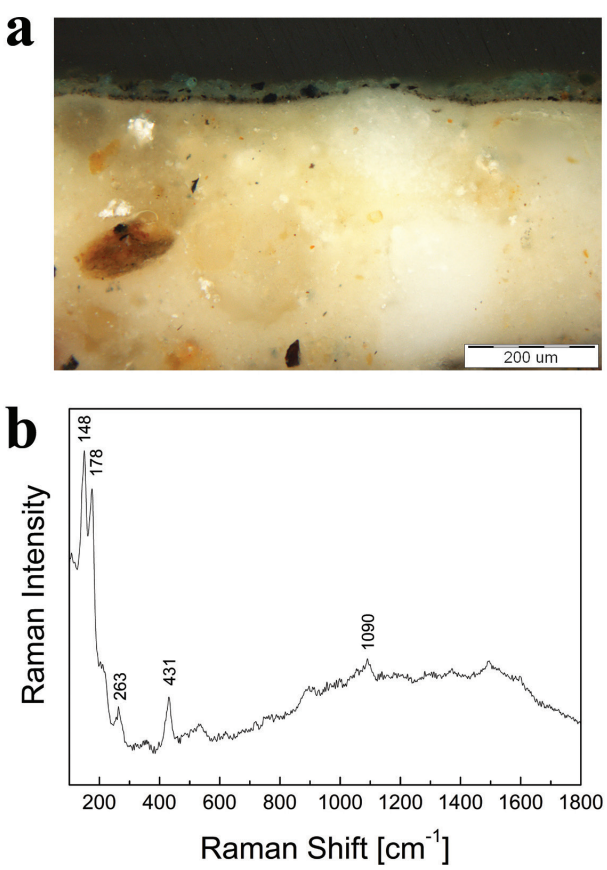

Figure 10. a) Green paint layer with grey underpainting, known as veneda - sample FAK5. b) Raman spectrum of malachite.

characterised not only by their diverse stylistic tendencies, developed at the crossroads between Italy and Northern Europe, but also by their execution using a combination of the *a fresco*, *a secco* and lime techniques (Križnar, 2006; Gutman et al., 2014). *A fresco* painting is made on a fresh plaster and the lime from the support functions as the principal binder for the pigments. It is usually painted on smaller portions of plaster, giornattas, in order to use the humidity of the support. Only the final details are usually finished already on a dry support, using organic binders with pigments. When the plaster is dry, pigments must be mixed with binding media, normally an organic one, and applied on the wall. The colour layers are not so resistant and tend to detach, what is characteristic for this *a secco* technique. Lime technique is, in a way, a simplified fresco painting, but the colour layers are painted on a layer of fresh lime-wash, also applied in smaller portions. It is not so resistant as *a fresco* painting, because with time, lime layer tends to detach from the wall (Thompson, 1956; Knoepfli et al., 1990; Mora et al., 2001; Križnar, 2006). *A fresco* is principally related to Italian painting, while the lime technique is more common in Northern Europe and in the Alpine region (Knoepfli et al., 1990; Mora et al., 2001). Nevertheless, in Slovene mediaeval mural painting, *a secco* is found mostly as an auxiliary technique applied in combination with the other two (Križnar, 2006).

The results obtained from the present research revealed that the older wall painting from the early 14th century was painted mainly on fresh mortar, *a fresco*, with final elements added *a secco*, a procedure characteristic of Italian wall painting (Knoepfli et al., 1990; Serchi, 1999; Mora el al., 2001). The technical execution of this wall painting therefore confirms the stylistic characterisation pointed out by art historians, which is an important correlation between style and technique. Also, generally, colours were applied in a single layer, usually thicker as observed on cross-section (Figure 3). Application of one to two layers is characteristic for *a fresco* painting due to the limited binding strength of the lime from the plaster, which can offer binding through carbonatisation only to those layers that are the closest to the support. Two layers were found only for the application of a blue paint layer over orange underpainting. Considering further the high quality execution observed in figure design, soft colour

transitions and precise brushstrokes, the artist probably came from Italy.

On the contrary, the younger painting dating from the late 15th century was executed principally in *a secco* technique, which is more common in Northern Europe (Križnar, 2006; Mora et al., 2001). Stratigraphic analysis of this painting showed that also in this mural mostly a single paint layer was applied, however, in some areas up to three colour layers were discovered (Figure 9). These can be thinner or thicker, as seen under the optical microscope. Such execution on one hand confirms the northern painting tradition that is also well known in the region of Friuli (again, correlation with the art-historical stylistic definition), but on the other hand also reveals an artist/ workshop of, most likely, provincial and local provenience, as observed in its weaker technical dexterity.

CONCLUSIONS

Two layers of wall paintings were discovered in one of the most important Gothic mediaeval churches in Slovenia, one dating from the first half of the 14th century and the other, overlaying the first, from the late 15th century. The younger wall painting was successfully detached and samples from both murals were analysed using different laboratory techniques in order to characterise the materials applied.

Raman microspectroscopy enabled the identification of a wide range of pigments, all inorganic, natural as well as synthetic. In both wall paintings, azurite was used for colouring the background. However, whereas the earlier painting is characterised by the use of carbon black, red and yellow ochre, lime white and green earth, the younger wall painting includes malachite, vanadinite, cinnabar (probably natural mineral), lead pigments and especially lead-tin yellow type I.

Another difference between the two paintings is associated with the employed gilding technique. Although in both layers gold leaves were used for the haloes of the saints, bole was used in the earlier and mordant in the younger wall painting. In the latter, tin foil was also applied as false gilding for less important decorative elements such as stars.

Analysis of stratigraphic sections helped to identify painting techniques, with the results confirming the use of two principal mural painting procedures, *a fresco* and *a secco*. The comparison of both murals confirmed the earlier art-historical characterization that the 14th century wall painting is strongly influenced by the Italian pre-Giotto painting of the Trecento, with a principal painting technique of fresco buono and details finished *a secco*. The 15th century painting is in execution much closer to the North-European tradition, with the *a secco* painting technique allowing a wider and more complex pigment palette. In addition, grey underpainting known as veneda was recognised in both mural paintings. The present study represents an important addition to the knowledge base regarding the variety of mediaeval wall painting in Slovenia, which is stylistically and technically situated at the crossroads between Italian and North-European artistic currents.

By providing information regarding the painting techniques applied, the present study helped the restorers with the selection of materials used during the intervention process. No degradation of (for instance) lead pigments or cinnabarite was identified, as extensive deterioration was most probably prevented when the wall paintings were covered with plaster and thus protected from environmental influences.

ACKNOWLEDGEMENTS

This work was financially supported by the Municipality of Koper within the framework of the conservation restoration project "Minorite church of St. Francis of Assisi" and Slovenian Research Agency Programme Group P2-0237. The authors would like to thank Prof. Janez Höfler, specialist in Slovenian mediaeval wall paintings, for his contribution to the stylistic characterisation of both wall paintings.

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