CHARACTERIZATION OF PAINTED BEEHIVE PANELS: SLOVENIAN UNIQUE FOLK ART CREATIVITY**

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Painted beehive panels are representative examples of folk art specific and unique to Slovenia. Although without precedence in European ethnographic art, not much attention has been given in the past to the artists' materials involved in the creation of these paintings. This study, which included three different panels (dating from the beginning of the 19th to the second half of the 20th centuries), was focused on material characterization using Raman and Fourier-transform infrared spectrometer (FTIR) spectroscopy (non-, minimally invasive and invasive). The analyses showed that many of the examined paint layers were composed of historically commonly available colouring agents, although less traditional ones were also detected on individual panels. Additionally, the research suggests that lipids are the main or even the sole component of the paints' binder. This evidence corresponds fairly well with written texts of the 20th century.

KEYWORDS: PAINTED BEEHIVE PANELS, SLOVENIA, 19TH AND 20TH CENTURIES, MATERIAL CHARACTERIZATION, MICROSCOPY, SPECTROSCOPY, NON-INVASIVE

INTRODUCTION

The expression 'painted beehive panels' refers to the painted rectangular wooden boards of smaller dimensions (usually about 1.4 cm thick, 12–15 cm high, with the most frequent ratio between height and width of 1:2.3) (Makarovič and Rogelj Škafar 2000). These panels, generally painted in vivid colours, mostly depict figurative motifs of religious, numerous secular and even fictional images, and were designed to be affixed to the frontal planes of wooden beehives which were stacked into apiaries exposed outdoors. Principally, they were generated between the mid-18th and the early 20th centuries. The commencement and development of painted beehive panels is stated as unique for, and confined solely to, specific regions of Slovenia (Makarovič and Rogelj Škafar 2000). These exclusively Slovene cultural objects are classified under folk art insomuch as the paintings were made predominantly by (professional or self-thought) provincial painters of the lower, rural classes for community/clients of equal social status (mostly village beekeepers and farmers). The painting style of the panels is usually subordinated to the restricted size of the support and the clarity of the depicted narrative. Many paintings are thus executed in a flat rendered style, lacking volume and a sense of perspective. Individual figures/objects are

frequently 'framed' with mostly darker contours and juxtaposed in the foreground; shapes are filled with colour, modelled coarsely or not at all; and the background is usually undefined, painted as a block of a relatively uniform colour. Written texts and past research have focused mainly on historical, art historical, ethnographical, sociological, iconographical and other aspects of these paintings, but not much has been dedicated to their technological and material characteristics. Texts from the first half of the 20th century (Vurnik 1929; Bukovec 1942) mention several possible material properties: the presence of a white, chalk-containing ground layer or a white preparatory paint layer applied on a wooden support, followed by a drawing and paint layers; the use of oil or tempera paints, often home produced; the use of poppy seed oil, pure linseed oil, mastic resin, egg white and egg-varnish tempera as possible binders of the paints; the use of pigments which were considered durable at the time (listed as earth pigments, sooth black, vine black, cinnabar, Schweinfurt (emerald) green, ultramarine, etc.); and a final coating of bleached linseed oil, possibly mixed with a resin (mastic). These characteristics were ascribed especially to the older panels made before 1880—according to Bukovec (1942), they must have been technically superior since their preservation state is considerably better than that of panels made after 1880 (according to the text, other types of paints (regrettably not specified) were used after that date, which has contributed to the lesser stability of the latter panels). On the other hand, contemporary researchers (Makarovič and Rogelj Škafar 2000) state that the paintings were always painted in oil. The first paint layer is supposed to be applied directly onto the wooden support and across the entire frontal plane. It represents the background of the painted motif. The underdrawing and the paint layers of the composition followed after the complete drying of the first stratum; apart from durable mineral pigments, only (local) linseed oil and turpentine are supposed to be used for the paints of the older panels. They too mention the use of industrially produced paints towards the end of the 19th century and poorer condition of the panels painted in such manner. However, before the latest research, the present authors were not aware of any published professional or scientific paper that would analytically corroborate the material properties and support or contradict the above-mentioned statements about the technology of painted beehive panels. The first material study was recently performed by the authors on one selected beehive panel (a panel depicting 'A fight over a pair of men's trousers'), confirming oil as a binder and several pigments and other particulate materials, such as cinnabar/vermillion, Fe oxide, Pb oxide, Fe hydroxide, C-based black, Prussian blue, ultramarine, lead white, Ca carbonate, Ba sulphate, anatase, and possibly chrome yellow and Emerald green (Retko *et al.* 2020). The study presented the first step in a wider technical study of beehive panels' materials and possible subsequent conservation treatments on this type of cultural heritage.

The determination of the material composition of a cultural heritage object is of great importance because it benefits a broader understanding of the created work as such, its technical, artistic, historical and other contexts, values and importance. On the other hand, it can also give information about its current preservation state, knowledge about and prediction of its degradation, not to mention providing guidelines for safer and more appropriate conservation–restoration treatments.

In this study, the main objective was to define the material composition of three painted beehive panels owned by the Slovene Ethnographic Museum due to the lack of in-depth analytical studies regarding the material composition of painted beehive panels in general. The panels were chosen randomly, although with an emphasis on the different dates of their creation (between the first half of the 19th and the second half of the 20th centuries, and some decades apart) in order to investigate possible time-dependent technological characteristics. For that purpose, Raman and

infrared spectroscopic techniques in different manners (e.g., non-invasive, invasive) were used. Furthermore, the objective was also to compare the identified materials composing individual panels, and the analytical results with the theories about painted beehive panels' technology.

MATERIAL AND ANALYTICAL METHODS

Brief description of the paintings and investigation strategy

Three investigated panels, marked as PK1, PK3 and PK4, are briefly described in Table 1; their images with the locations of the performed analyses are shown in Figure 1. Besides the general data and scarce catalogue descriptions of PK1 and PK3 (Makarovič and Rogelj Škafar 2000), there is no available information about the production and history of these panels. The majority of the analyses were performed in a non-invasive manner by means of non-invasive reflection Fourier-transform infrared spectrometer (FTIR) (locations labelled as A) and Raman spectroscopy (labelled as R). In addition, analysis in a minimally invasive manner was performed on PK1 using transflection FTIR spectroscopy (labelled as TRF) in order to investigate further the material composition of the upper most layer. Moreover, minute samples of about 1 mm^2 (containing strata from the support's surface to the upper most layer) were removed from the frontal planes of all panels with a scalpel in order to investigate their stratigraphic construction and material composition (one sample from PK1, one from PK3 and three from PK4 are included in this study). Half of an individual sample's bulk was set aside for transmission FTIR analysis; the other half was prepared as a cross-section.

The locations of the measurements and removed samples (the latter marked as PKx–y, where PKx is the label of the panel and y the number of the sample) are presented in Figure 1.

Ultraviolet (UV)-induced visible fluorescence examination

Panels were examined under UV radiation emitted from UV-A fluorescent bulbs Osram L 36 W/73 (Osram GmbH, Germany). UV-induced visible fluorescence photography was performed with a Canon EOS 350D camera with an EF-S18–55 mm f/3.5–5.6 II lens.

Reflection FTIR spectroscopy

Non-invasive FTIR analyses of the panels' surfaces were carried out with a portable Alpha-R spectrometer (Bruker Optics GmbH, Germany). The pseudo-absorption spectra ($A' = \log (1/R)$,

Table 1   *Descriptions of the selected painted beehive panels*

Label	Title	Date	Dimensions (cm)
PK1	Unidentified scene of military violence	1836	12.8 × 25.4 × 1.4
PK3	The Holy spirit as a dove	Beginning of the 20th century*	14.7 × 30.9 × 1.6
PK4	Landscape motif	2nd half of the 20th century*	13.4 × 28.3 × 1.2

Note:
*Based on a personal communication with Dr Bojana Rogelj Škafar, Folk Art and Pictorial Sources Collection, Slovene Ethnographic Museum.

Figure 1   *Selected painted beehive panels in visible (left) and ultraviolet (UV) radiation (right) of (a) PK1, (b) PK3 and (c) PK4, with marked locations of non-invasive reflection Fourier-transform infrared spectrometer (FTIR) (marked as A), non-invasive Raman measurements (marked as R), minimally invasive micro-transflection FTIR (marked as TRF) and with marked sampling locations on PK1 (PK1-1), PK3 (PK3-1) and PK4 (PK4-1, PK4-3 and PK4-4).*

where R = reflectance) were collected in reflection mode between 7500 and 400 cm^{-1} at a 4 cm^{-1} spectral resolution. A total of 160 scans per sample were averaged, and for the background measurement, a gold mirror was used. An integrated video camera controlled and monitored the sampling area. Processing of the FTIR data was implemented using Bruker OPUS software.

Preparation of the cross-sections of the samples

Samples intended for cross-sections were embedded in a transparent two-part co-polymer resin (methyl methacrylate and unsaturated polyester resin copolymer) Kristal PS (Samson Kamnik d.o.o., Slovenia). Grinding and polishing of the cast samples were performed with silicone carbide abrasive papers and paraffin oil, and the samples thus prepared were cleaned in petroleum ether in an ultrasonic bath.

Optical microscopy of the cross-sections

The cross-sections of the samples were examined by means of an Olympus BX 60 microscope connected to an Olympus SC-50 video camera using visible and UV radiation, the latter emitted from an Hg bulb USH-1030 L (Ushio Inc., Japan).

Transmission and transflection FTIR spectroscopy

FTIR transmission and transflection spectra were recorded using a Perkin Elmer Spectrum100 FTIR spectrophotometer coupled to a Spotlight FTIR microscope equipped with an N-cooled Hg-Cd telluride (MCT) detector. The samples investigated by FTIR transmission mode were placed between the windows of a diamond anvil cell and examined under the microscope.

For transflection mode, a diamond-coated sampling stick was employed for micro-samplings from painted beehive panels as well as the sample holder under the micro-FTIR spectrophotometer. Transflection FTIR spectra were acquired with an aperture of 100×100 μm^2. The background spectrum was obtained on the clean diamond stick.

On the cultural heritage objects, where sampling is limited, transflection FTIR spectroscopy represents an efficient alternative to conventional transmission FTIR. Its performance allows very precise sampling and is considered as micro-invasive even though sampling is usually not visible to the naked eye. The collected transflection spectra are due to similarity with transmission spectral profiles and are very easy to interpret. For more about the micro-transflection technique, see Rosi *et al.* (2017).

The transmission and transflection FTIR spectra were collected in the range between 4000 and 600 cm^{-1} by recording a total of 64 spectral scans accumulated and with 4 cm^{-1} spectral resolution.

Raman spectroscopy

The spectra of the painted panel surfaces and of cross-sections of the samples were recorded using 785 and 514 nm laser excitation lines with a Horiba Jobin Yvon LabRAMHR800 Raman spectrometer coupled to an Olympus BXFM optical microscope. The spectra were recorded using ×50 LWD objective lens and/or ×100 objective lens and a 600 grooves/mm grating. A multi-channel, air-cooled charge-coupled display (CCD) detector was used. The experimental parameters (time of exposure, accumulation, power at the sample, etc.) were adjusted according to the specifics of the samples. In most cases, when using 785 nm, the exposure time was set between 5 and 25 s and consisted of two scans, and power was set to between about 2 and about 20 mW. Usually, when using 514 nm, the exposure time was set to between 1 and 10 s and consisted of 1–10 scans, and power was set to between about 0.3 and about 3 mW. However, in some cases, lower power was used and longer exposure times or even more accumulations selected. The majority of the analyses using Raman spectroscopy were performed non-invasively. In such cases, a panel was placed directly under the objective and the spectra were then collected using the x50 LWD objective from the locations of the interest. The analysis was also performed on the cross-sections of the samples in order to obtain information on stratigraphic composition. The spectral interpretation and identification of the materials were performed in comparison with the institute's own spectral database and the literature (Bell *et al.* 1997; Burgio and Clark 2001).

RESULTS AND DISCUSSION

In the following sections, a detailed material composition of each painted beehive panel (PK1, PK3 and PK4) is reported in Table 2 according to the results collected by Raman and infrared (FTIR) spectroscopy in different manners (non-invasive, minimally invasive and invasive). The locations of the analyses in addition to the removed paint samples are denoted in Figure 1. The most interesting or analytically challenging findings are then discussed in the text dedicated to the analytical investigation. For example, the material composition of the green-painted

Table 2 *Identified materials on selected painted beehive panels in relation to the location and the technique used for the identification*

	PK1	PK3	PK4
Colouring agents (pigments, fillers, etc.)			
Pb carbonate (lead white)	R4–R7, R9–R11, R13, R16, R19–R21, A3, PK1-1	R7, R8, R15, R16, PK3-1	
Pb sulphate	R6, R7, R11, R21	R8, R11, R12, PK3-1	
Ba sulphate	R4, R12, R13, PK1-1	PK3-1	A1, A2, A5, A6, R8–R11, R15, R17, R18, R20, R21, PK4-1, PK4-3, PK4-4
Ca carbonate	R7, R22	PK3-1	A1, A2, A5, A6, R12-R14, R16, R18, R19, PK4-1, PK4-3, PK4-4
Zn oxide (zinc white)			PK4-1
Pb oxide (massicot)		R2, R3, R5, R11, R12	
Fe hydroxide (likely goethite type)	R19		
Pb chromate (chrome yellow)			R8, R9, PK4-3, PK4-4
Fe(III) oxide (likely hematite type)	R3, R17, R18, R23		R22
Hg sulphide (cinnabar/vermilion)	R1, R3–R5, R11, R15, R20	R6, R7, R9, R10, R13, R14, R17, PK3-1	
Monoazo red pigment—pigment red 3 (Toluidine red)			PK4-1, PK4-3, PK4-4
S-containing Na alumino-silicate (ultramarine)			R1–R5, PK4-1, PK4-4
Fe(III) hexacyanoferrate (II) (Prussian blue)	R14, A6	A1–A3, R1, R4, R18–R21, PK3-1	PK4-4
Cu acetate arsenite (Emerald green)	PK1-1, R25		
Cu arsenite (Schelle's green)	PK1-1		
C-based black	R2, R5, R8, R19–R22, R24, PK1-2	R4, R5, PK3-1	R6, R7, PK4-4
Organic components (components of binders, protective layers, etc.)			
Lipids	A1–A3, A5, A6, TRF1	A1–A3, A5, PK3-1	A1, A2, A4-A6, PK4-1, PK4-3, PK4-4
Triterpenic resin	A1, A2, A5, A6, TRF1, TRF2, PK1-1	A1–A3, A5, PK3-1	PK4-1
Beeswax	A4, TRF2	PK3-1	
Oxalates	TRF, F_c	F_c	PK4-4, A, F_c
Carboxylates (Cu, Zn)	TRF (Cu), F_c (Cu)	F_c (Pb)	PK4-3, PK4-4 (Zn), A4 (Zn)
(Organic) components on the rear of the panel			
Beeswax	A4	A4	

Note: R, Raman spectroscopy; A, reflection Fourier-transform infrared spectrometer (FTIR) spectroscopy; TRF: transflection FTIR; PK*x*–*y*, Raman or FTIR spectroscopy on the removed sample.

background is presented in the case of PK1; the investigation of the cross-section in relation to the position of the blue background paint on panel PK3; and the identification of zinc soaps as well as specific colouring agents in certain painted areas and in red foundation paint on PK4. In the cases of PK1 and PK4, the use of a non-invasive approach is presented at the outset, which is then supported and complemented with the results obtained on the removed samples. The spectral results of many colouring agents and/or organic materials (i.e., binders and coatings) reported in Table 2, which are usually very easily identified by Raman and FTIR spectroscopy, are therefore not shown. In the following—technological—part, predictions and conclusions on the art technology of the panels are presented based on the results obtained by UV-induced visible fluorescence examination and vibrational spectroscopy.

Painted beehive panel 'Unidentified scene of military violence': PK1

Analytical investigation   Analytically, one of the most interesting parts of the PK1 panel's pictorial field is the green colour of the painted background. Non-invasive Raman spectroscopy on these areas showed limitations as the strong fluorescence signal overrode weak Raman scattering, even though different exciting wavelengths were used to identify colouring materials. The
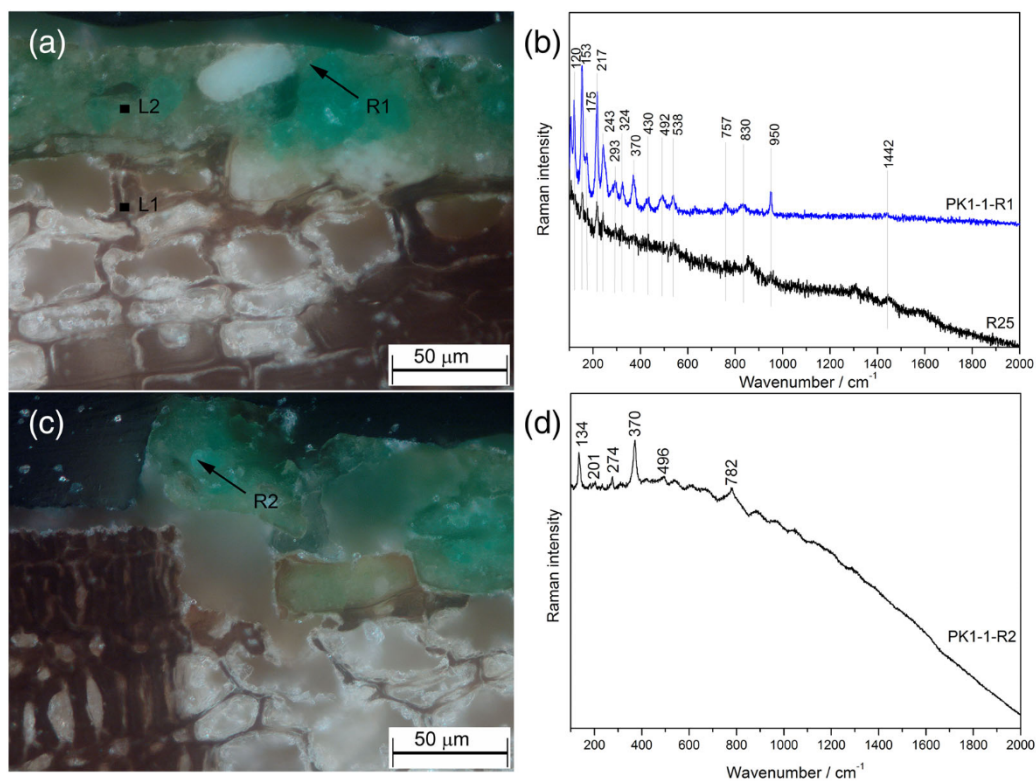

Figure 2   *(a, c) Optical micrographs of sample PK1-1 taken from the painted beehive panel PK1 (for the location, see Fig.1) with marked locations of Raman analysis (R1, R2) and marked paint layers (L1, L2). (b) Raman spectrum obtained directly on the panel (black spectrum, location R25 in Fig.1) and Raman spectrum (blue spectrum) obtained on the cross-section of sample PK1-1 at the location marked as R1 in (a); $\lambda_0 = 785$ nm. (d) Raman spectrum obtained on the cross-section of sample PK1-1 at the location marked as R2; $\lambda_0 = 785$ nm.*

spectrum with a weak signal-to-noise ratio was collected on the green background paint (location R25, spectrum presented in Fig. 2), based on which the presence of pigment Emerald green was assumed. For a more detailed study, sample PK1-1 (sampling location close to R25) was investigated. The sample consists of only two layers: the surface of the wooden support followed by a green paint layer (visible on the micrograms of the sample's cross-section in Fig. 2, a, c); the upper most transparent layer, otherwise visible on the loose, unembedded portion of the sample, most likely dissolved during the preparation of the cross-section (a gap between the sample's surface and the casting resin is visible on the micrograms in Figure 2, a, c). Point analysis by Raman microscopy on the green layer of the cross-section (Fig. 2, b) confirmed the presence of Emerald green based on the bands at about 120, 153, 175, 217, 243, 293, 324, 370, 430, 492, 538, 757, 830, 950 and 1442 cm^{-1}. Additionally, on the left part of the sample (Fig. 2, c), at the location marked as R2, another green pigment, namely Scheele's green, was detected based on the bands at about 134, 201, 274, 370, 496 and 782 cm^{-1}.

The green colour of the painted background was also investigated by means of total-reflection FTIR spectroscopy. Collected total-reflection FTIR spectrum (the area marked A1 in Fig. 1, a) is illustrated in Figure 3 (a). Sharp bands placed at 1470 and 1391 cm^{-1} corresponding to methyl and methylene groups bending vibrations of a natural resin, and the peculiar out-of-plane bending vibration of the exomethylene groups in lower mid-IR region at 898 cm^{-1} suggest the presence of triterpenic resin, possibly dammar (Invernizzi *et al.* 2018). Furthermore, the derivative-like bands in the CH stretching region in the reflection FTIR spectrum as well as the strong signal of carbonyl stretching vibration at 1742 cm^{-1} (Fig. 3, a) indicate the presence of lipids. Additional confirmation for the presence of a lipid component is evident in the near-IR range of reflection FTIR spectrum, where a typical doublet of $\nu + \delta$ CH is placed at 4330 and 4259 cm^{-1}. The remaining bands in the near-IR range belong to the wooden support.

In addition, the same green area of PK1 was examined by micro-transflection and transmission FTIR spectroscopy (Fig. 1, a: the location is marked as TRF1 (transflection mode) and on the removed sample PK1-1 (transmission mode)). The transflection spectrum collected from that area is presented in Figure 3 (b) (blue spectrum) and contains characteristic bands of triterpenic resin and lipids. Beside the signals of the latter materials, the transflection FTIR spectrum reveals a sharp band of asymmetric stretching vibration of (-COO^{-}) group placed at 1593 cm^{-1} which indicates the presence of Cu carboxylate (Otero *et al.* 2014). Moreover, the absorption band at
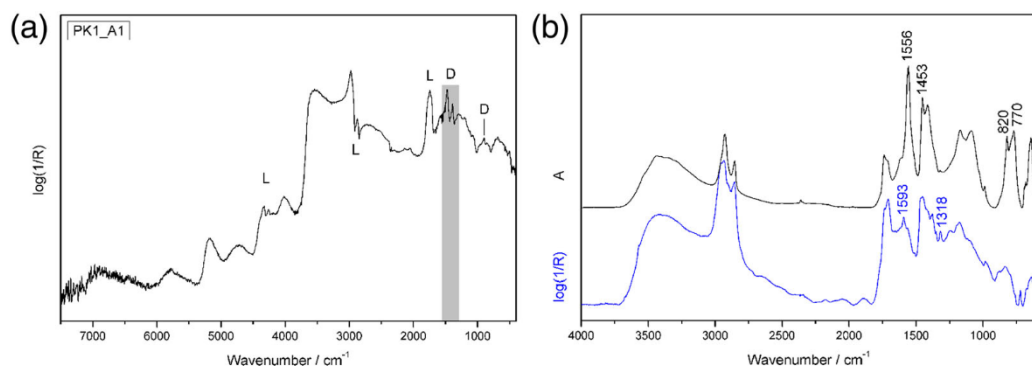

Figure 3 *(a) Reflection Fourier-transform infrared spectrometer (FTIR) spectrum obtained at location A1 on the painted beehive panel PK1, identifying lipids (L) and triterpenic dammar resin (D). (b) FTIR spectra in transmission (black line) and transflection (blue line) modes of green paint present on the green area TRF1.*

1318 cm^{-1}, which is present also in the spectrum obtained in transflection mode on the area marked as TRF2 (spectrum not included), confirms the presence of metal oxalates (Monico *et al*. 2013). Furthermore, the corresponding transmission FTIR spectrum (Fig. 3, b: black spectrum) obtained on the green paint layer of sample PK1-1 revealed the presence of pigment Emerald green based on the presence of strong vibrations of arsenate group placed at 820 and 760 cm^{-1} and symmetric and asymmetric vibrations of acetate group placed at 1556 and 1452 cm^{-1}, respectively (Holakooei *et al*. 2018). These results showed the importance of the application of infrared spectroscopy in different modes; while non-invasive reflection FTIR enabled the detection of triterpenic resin and lipids—transflection FTIR complemented those results with detection of Cu carboxylate. Sampling with a diamond stick allowed for a more precise selection of the materials present in the topmost layer. Therefore, in the transflection FTIR spectrum (Fig. 3, b: blue line), the spectral contribution of the triterpenic resin is more clearly distinguished from the signals of the oil, which is present in the underlying layers. The results of infrared spectroscopy in transmission mode with the identification of Emerald green led to an even more detailed result on paint composition and supported the results of Raman spectroscopy.

Investigation of the technology   Different analytical techniques revealed the presence of Emerald green and Scheele's green within the green-painted background. It is impossible to interpret correctly why the two pigments would be simultaneously present in the same paint layer (intentionally/unintentionally, put into a mixture by the author/vendor/manufacturer, etc.). One plausible interpretation is perhaps the use of Emerald green made by a sulphate method where a small amount of Scheele's green is said to be added in the process of Emerald green preparation (West Fitzhugh 1997). Sections, painted white, proved to contain mostly lead white. Cinnabar/vermilion was determined on red-painted areas, whereas darker red contours indicate the presence of Fe oxide and possibly cinnabar/vermilion. No yellow pigment could be detected on yellow hues of the soldier's trousers, although the analysis determined the paints contain lead white. Lead white, cinnabar/vermillion, Fe hydroxide pigments and C-based black were detected on some of the brown-painted segments of the panel. Prussian blue proved to be the main component of the painted blue dress, and a C-based black pigment of some black-painted portions. Lead white, cinnabar/vermilion and C-based black were detected within parts of greyish skin tones. Ca carbonate might be present as an impurity or perhaps as an extender/filler or a natural component of other pigments as it was found only within two-point analyses on areas painted in ochre and brownish hues. Ba sulphate could perhaps represent a paint filler or an extender. Little is known about the availability of paints and colouring agents in Slovenia in the first half of the 19th century, specifically in relation to (unknown) provincial painters or workshops. Regarding beehive panels, it is presumed that the majority of paints were 'home-produced' with materials available locally, therefore relatively innovative mixtures, such as ones with deliberate addition of barites or blanc fixe, are somewhat questionable. Nevertheless, in Europe Ba sulphate started to be extensively used in paints in the early 19th century, for example, as an adulterant for lead white (Feller 1986), therefore interpreting it as a filler/extender/adulterant within the paints of the panel PK1 might not be preposterous, also in connection with Emerald green, which was historically often mixed with other inorganic materials to produce less expensive versions or different shades of the pigment. Pb sulphate was detected within regions of different colours and hues of which all share the presence of lead white. According to the known data of Pb sulphate (fairly limited) use as a white pigment (Eastaugh *et al*. 2008), it is questionable that the material would be employed deliberately on a Slovene folk art painting from the third decade of the 19th century. It is also very unlikely the substance would represent an impurity due to modern methods of lead white production (Tumosa and

Mecklenburg 2005), although lead white production methods in Slovenia are yet to be investigated. The analysis also did not show the presence of specific pigments, for example, Pb chromate pigments where Pb sulphate is often present (Feller 1986; Eastaugh *et al.* 2008). The appearance of Pb sulphate on the painting therefore needs further study. IR spectroscopy analysis of the painted surface showed the presence of lipids and a natural resin, possibly dammar. Although dammar resin has been known in Germany at least since 1829 (Lucanus 1942; Feller 1966), its use as an original protective coating or a paint additive on a Slovene painted beehive panel from 1836 and destined for outdoor exposure is questionable. UV-induced visible fluorescence examination showed a continuous fluorescence over the painted surface (Fig. 1), likely due to a film-forming material such as a varnish. It is presumed the coating is non-original, since the fluorescence extends over the areas with paint losses as well, and might be the source of the triterpenic resin, and possibly beeswax determined in TRF 2 (e.g., matt dammar varnish containing beeswax). Apart from dammar, a possible interpretation of the identified triterpenic resin would be mastic. So far, known mentions of mastic resins appear only in some of the 20th-century notes of the leading Slovene restorer and impressionist painter M. Sternen (1870–1949), who was also Bukovec' source for the information regarding mastic's possible use on the painted beehive panels (Bukovec 1942). Since we hold no other data regarding the use of mastic in Slovenia in the 19th and 20th centuries, and conservation treatments of the 20th century appear to have employed mostly dammar resins, we presume the resin identified might belong to dammars. The lipids could represent a paint binder or a paint binder component, which would be in accordance with theories stating that these panels were usually done in an oil-painting technique. However, oil impregnation, either original or of a possible restoration procedure done in the past, could be an equally credible source of the characterized material. Transmission FTIR analysis performed on the sample detected lipids within all the paint layers, and thus supports the interpretation of an oil adhesive in the paints.

Painted beehive panel 'The Holy Spirit as a dove': PK3

Analytical investigation   According to Makarovič and Rogelj-Škafar (2000) and visual examinations of several beehive panel paintings in the Slovene Ethnographic Museum, the first paint
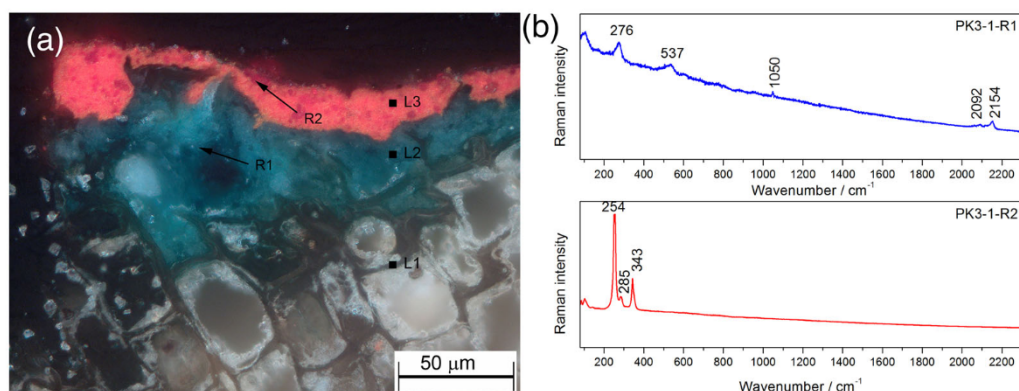

Figure 4   *(a) Optical micrograph of sample PK3-1 taken from the painted beehive panel PK3 (for the location, see Fig.1) with marked locations of Raman analysis (R1, R2) and marked paint layers (L1–L3). (b) Raman spectra obtained on R1, identifying Prussian blue and lead white; and R2, identifying cinnabar/vermillion; $\lambda_0 = 785$ nm.*

layer of many panels might be laid directly on and across the entire frontal plane of a wooden board, and also serving as a background for a painted motif. In order to investigate the possible presence of such background paint and to characterize more than one layer in detail, the cross-section of sample PK3-1 (Fig. 4, a) was taken from a red-painted flower. It shows two paint layers: red over blue (Fig. 4, a). First the blue layer seems to be applied directly to the wooden support. Due to a clear margin between the two paint layers, the blue must have been completely dry before the application of the red one. Using Raman spectroscopy (Fig. 4, b), it was determined that the blue lower layer was composed of Prussian blue (Raman bands at about 276, 537, 2092 and 2154 cm^{-1}) and lead white (Raman band at about 1050 cm^{-1}). In the upper red layer, the presence of cinnabar/vermilion was verified (Raman bands at about 254, 285 and 343 cm^{-1}) and additional pigment particles were observed. Due to certain physical properties (e.g., particles' shape and colour visible in cross-section under UV radiation) and the interfering signal of fluorescence in the Raman spectra, the presence of a red lake pigment is suggested, though additional research should be carried out in future for the complete confirmation.

Investigation of the technology   Among the three investigated panels, panel PK 3 is the most damaged since almost all the paint on its lower half is missing. As such, it also shows the simplest use of colours. Nevertheless, several material identifications and some insights into the technology of the painting were possible. Non-invasive analyses suggested the blue pictorial background consists of Prussian blue; in one-point analysis Pb oxide (possibly massicot) was also detected. On the other hand, the blue lower layer of sample PK3-1, which might represent the same blue background, shows a mixture of Prussian blue and lead white. The data are not sufficient enough to conclude if both the investigated blue areas are indeed part of the same layer, for example, the blue background which was perhaps uniformly laid over the entire frontal plane of the panel as the first layer. However, since the blue layer lies under the red of a painted flower and acts as a separate layer (which was sufficiently dry before the application of the latter), the chance is it might be a part of the background. Further analyses, such as hyper-spectral imaging, would be necessary to verify such a statement since the panel is too damaged to sustain additional sample withdrawal. The green foliage too consists of predominantly Prussian blue; only a few point analyses of the green leaves showed the presence of Pb oxide (massicot) and C-based black, as well as cinnabar/vermilion, although the latter had been detected only on the areas in close proximity to the red painted sections, and might not be the integral part of the darker green paint. Consequently, the question regarding green paint composition arises: Is the green foliage composed of Prussian blue and massicot and possibly some C-based black and cinnabar/vermillion? Or does the majority of these pigments play only a minor role, and perhaps some green pigment (e.g., chrome green) could be present but not able to be detected by non-invasive analysis only? Since the sampling of these areas could not be performed, the questions remain for future investigations. The non-invasive analyses of red-painted sections showed the presence of cinnabar/vermilion exclusively, although the red paint might be a mixture of at least two red pigments (the other possibly a red lake), as was observed by microscopy and an analysis performed on the cross-section. The presence of lead white and possibly Pb sulphate and Pb oxide (massicot) was detected within the whitish highlights non-invasively as well, although we cannot conclude whether or not all were deliberately set in a pigment mixture.

  Especially on the upper third of the panel, local surface fluorescence is visible under UV radiation, which might indicate the presence of a coating, for example, a dammar varnish, since a triterpenic resin was detected with FTIR spectroscopy techniques (possible identification of dammar in some of the point analysis with reflection FTIR). The presumed coating is currently

considered part of a past conservation treatment since the FTIR analyses detected the resin on the areas with paint losses as well, and verified its absence in the lower part of the paint bulk of PK3-1. On the cross-section of PK3-1 there is no indication of a final transparent coating, though the sample was taken from an area that does not show surface fluorescence visible on the upper part of the panel, which additionally speaks for the possible presence of a non-original varnish which might have been applied only locally. The resin detected in the upper paint bulk of PK3-1 might be a contamination, although possible deliberate addition of the resin in the red paint of the flowers needs to be investigated further. Lipids were detected almost within all point analyses performed on the painted surface and in the paint bulk of PK3-1, and are thus considered the main binding material of the paints used.

Painted beehive panel 'Landscape motif': PK4

Analytical investigation   Investigation of the ochre and white painted areas (the church tower in the middle of the panel (A1) and a white cloud on the right side (A4)) revealed the presence of Zn oxalate and Zn carboxylate by total-reflection FTIR spectroscopy (Fig. 5, a). Derivative-like and/or reststrahlen bands placed at 1633, 1360, 1320, 824 and 498 cm^{-1} are characteristic signals of Zn oxalate (Monico *et al.* 2013). The reststrahlen spectral feature with a minimum at 1540 cm^{-1} belongs to the asymmetric stretching vibration group v_{AS} (-COO$^-$) of the Zn carboxylate. Its symmetric stretching vibration v_S (-COO$^-$) is in total-reflection spectrum placed at 1398 cm^{-1} (Casadio *et al.* 2019). As already proven non-invasively, Zn carboxylate was detected by means of transmission FTIR spectroscopy as well on the yellow layer of samples PK4-3 and PK4-4. In addition to the characteristic band at 1540 cm^{-1}, the broadened signal with a maximum at 1583 cm^{-1} indicates the non-crystalline zinc soaps and/or formation of ionomer-like structures in oil paint binding media where Zn ions are bound to carboxylate moieties (Fig. 5, b) (Casadio *et al.* 2019). The mentioned metal carboxylate could be formed as a consequence of a reaction between pigment zinc white (which was also found in the paints, e.g., in the blue layer of sample PK4-1) and the lipid binder.

Furthermore, the results obtained on the removed sample PK4-4 by means of Raman and IR spectroscopy are shown in Figure 6. Figure 6 (a) depicts the optical micrograph of the cross-section of sample PK4-4. The sample was taken from the bottom edge of the panel painted
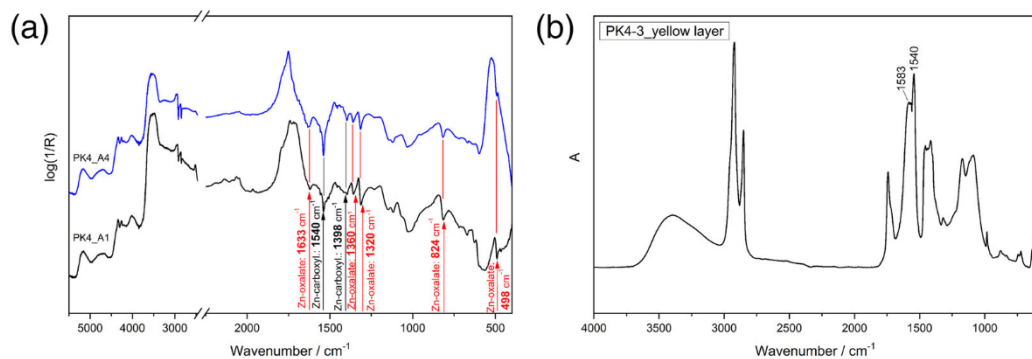

Figure 5   *(a) Total-reflection Fourier-transform infrared spectrometer (FTIR) spectra collected on area PK4_A1 (black line) and PK4_A4 (blue line), with marked signals of Zn oxalate and Zn carboxylate. (b) Transmission FTIR spectrum collected on the yellow layer of sample PK4-3.*
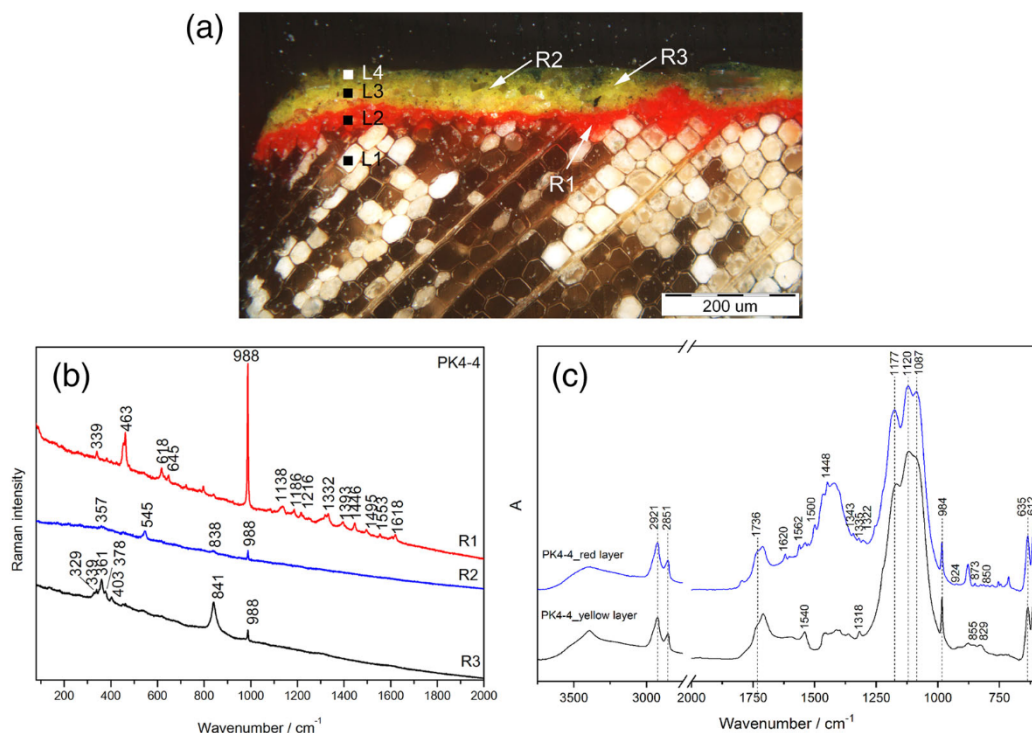
Figure 6   *(a) Optical micrograph of sample PK4-4 (taken from the painted beehive panel PK4; for the location, see Fig.1c) with marked locations of Raman analyses (R1–R3) and marked paint layers (L1–L4). (b) Raman spectra obtained on locations R1, identifying PR3 and BaSO₄; R2, identifying ultramarine, BaSO₄ and chrome yellow; and R3, identifying chrome yellow; $\lambda_0 = 785$ nm. (c) Transmission FTIR spectra collected on the red (blue line) and yellow paint layers (black line) of sample PK4-4.*

in yellowish and greenish hues. The sample consists of three paint layers: a red applied directly to the wooden support, followed by a yellow with a clear border between them (and thus it was presumed that the red layer was completely dry before the application of the next) and an upper green, incorporated in the yellow one (the green was probably painted on the still wet lower yellow paint). Using Raman and transmission FTIR spectroscopy, synthetic organic pigment PR3 (pigment red 3-β-naphthol, monoazo pigment) was identified in the first red paint layer. In the Raman spectrum, it was detected according to the Raman bands placed at about 339, 1138, 1186, 1216, 1332, 1393, 1446, 1495, 1553 and 1618 cm^{-1} (Scherrer *et al*. 2009) (in addition to Ba sulphate (about 463, 618, 645 and 988 cm^{-1})). In the IR spectrum, collected in the transmission mode, PR3 was identified based on IR bands at 1620, 1562, 1500, 1448, 1343, 1335, 1322, 924, 873 and 850 cm^{-1} (Vila and García 2012). Furthermore, in the yellow/green layer ultramarine (Raman band at about 545 cm^{-1}), Ba sulphate (Raman band at about 988 cm^{-1}) and chrome yellow (Raman band at about 357 and 838 cm^{-1}) were found (Fig. 5, b). The presence of chrome yellow was also confirmed at location R3 (Raman bands at about 329, 339, 361, 378, 403 and 841 cm^{-1}), where Ba sulphate was additionally detected based on the band at about 988 cm^{-1} (Fig. 6, b). FTIR analysis of the yellow layer (Fig. 6, c) showed the presence of chrome yellow (855 and 829 cm^{-1}), oxalate (1318 cm^{-1}), Ba sulphate (1177, 1120, 1087, 984, 635 and 612 cm^{-1}), Zn carboxylate (1540 cm^{-1}) and an oil component (2921, 2851 and 1736 cm^{-1}).

Investigation of the technology   Amongst the analysed painted beehive panels, painting PK4 shows the minimum amount of damage. On several smaller parts, a partial or complete loss of the paint film was observed, which uncovers a lower red paint layer or the wooden support. Dried paint runs (probably due to an excessive film build) of the same red colour are visible along the support's edges as well. Based on the visual examination of the painting and the characteristics of the cross-sections, it could be indicated that the red layer, containing PR3 and Ba sulphate as a probable filler, acted as a ground or an underpaint layer, and was most likely applied across the entire frontal plane of the wooden board. Although we currently consider the bottom red paint mainly as a preparatory layer, the painter actually made scarce use of it for the motif and left it uncovered to represent the colour of the roofs of the castle in the background. In contrast, the final paint film of the red roofs in the front picture plane shows orange fluorescence under UV radiation and signs of wrinkling, perhaps due to the considerable amount of a binder used for the final red glaze and/or specific pigments which might inhibit the drying process of the paint (e.g., red lakes). Except for the Ca carbonate and Ba sulphate, no red colouring agent was detected on any of the latter red-coloured areas. The possible use of red lakes in the final red stratum needs to be investigated further. Additionally, the fluorescence emission within Raman analyses prevented the determination of the pigments used in white-painted sections of the panel. Nevertheless, Zn oxide was detected on the cross-section of sample PK4-1 by Raman spectroscopy, and Zn carboxylates and oxalates on many other painted areas and within paint layers by FTIR analyses. However, these results do not necessarily speak of zinc white being the only possible white colouring agent on the panel. A difficulty also lies in the interpretation of the composition of green-coloured paints. Different sections of green paints show the presence of Prussian blue, ultramarine, Fe oxide, C-based black, chrome yellow and Ba sulphate, though the results from point-to-point analyses are too inconsistent to conclude the exact pigment or pigment mixtures used. Ba sulphate was detected in areas containing chrome yellow and/or Zn carboxylates, in the red paints (the uncovered underpaint and top glazes) and the green paints, whereas Ca carbonate was principally ascertained in connection with the red paints (the uncovered underpaint and top glazes alike). Both materials are currently considered as fillers, extenders or adulterants of the employed paints or colouring agents. The analysis also showed that the blue paints were predominantly composed of ultramarine, while yellow and orange paints were of chrome yellow. Lipids were detected in all the measurements with reflection FTIR, and in all the paint layers of all the samples analysed with transmission FTIR. This result (along with the presence of carboxylates) indicates that the paints probably involved an oil binder. Triterpenic resin was detected only within one sample where it was impossible to determine its stratigraphic position. Since there is no indication of a final varnish layer on the cross-sections and the coating could not be verified by UV-induced visible fluorescence inspection as well, the detection of the resin on this panel needs further study.

Comparison of the technology of the selected panels   Invasive analyses made certain insights into the construction/composition of the panels. The older writings indicate that the wooden support could have been covered with white, chalk-containing ground layer before an underdrawing and paint applications (Vurnik 1929; Bukovec 1942), but there are reasons to doubt such presumptions. White backgrounds indeed exist on painted beehive panels; however, visual observations of many panels stored in the Slovene Ethnographic Museum indicate they are part of the painting composition and do not act as traditionally employed preparatory layers typical for fine art easel/panel paintings of certain historical periods. No such traditional white ground was verified on any of the panels in this study, neither by means of visual inspection nor by samples'

cross-sections microscopy. Samples' cross-sections show the direct application of paint on the wooden boards. Makarovič and Rogelj Škafar (2000) stated that the wood of the beehive panels was simply 'painted over with an oil paint that would form the background colour of the finished picture'. In this research, due to the limited number of collected samples, it cannot be said with any certainty that the first layers of PK1 and PK3 are indeed the paint of the background colour applied cross the entire frontal plane. Such conclusions are usually based on a greater number of investigated cross-sections, but more extensive sampling is ethically questionable on objects of such a small size, especially when heavily damaged, as is the case with PK3. However, on panel PK1, a green colour, similar to the green background paint, can be observed visually almost all over the picture plane as a subjacent layer visible through some of the upper paint layers and/or on damaged areas, but on such the paint composition (Emerald and Scheele's green) could not be verified and compared by non-invasive analysis only. On panel PK3 was Prussian blue identified in the bare bluish background colour non-invasively and as a part of the first layer of one taken sample, although the analysis of the latter showed the presence of lead white which the first did not. Therefore, no indisputable conclusions regarding the possible presence of the blue background layer below the rest of the painted composition can be made. Panel PK4 is somewhat an exception to the rule. Although the panel does not exhibit a traditional (white) ground layer, the visual inspection of the panel and cross-section microscopy confirmed a red foundation layer composed of toluidine red (PR 3) as the main colouring agent. This paint film does not play a role in the composition's background colour (which is supposed to be typical for older panels and possibly present on PK1 and PK3); the red layer seems to act above all as a preparatory or a ground layer, although it was somewhat exploited for the painted composition: for the red roofs of the depicted buildings.

On average, and according to the very limited number of samples' cross-sections withdrawn from all three panels, the number of paint layers is scarce, from one layer on plainly painted areas (e.g., backgrounds) or two or at most three on areas of painted motifs (e.g., the contours of figurative compositions). A similar number of layers (two to three) is also shown in the cross-sections of PK4, which was worked out much more freely and less meticulously, although still naïvely. The painter of PK4 probably painted the majority of the composition above the red foundation paint film (which was allowed to dry before carrying out the landscape) in an *alla prima* painting technique, meaning that the paints were most likely laid down directly, without letting the subjacent layers of paints dry before the application of the ones on top, and probably in a single session. Such an approach seems different from those employed on the older two panels of which all paint layers were probably sufficiently dry before the application of the following ones. In average, the paint layers on the panels are fairly thin, ranging from $\leq 10\,\mu m$ to around $40\,\mu m$. IR spectroscopy showed the presence of lipids on all panels, in all point analyses with reflection FTIR, as well as with transflection FTIR on PK1. Although Bukovec (1942) discussed the use of oil among the possible binders, he also mentioned the painters applying bleached linseed oil over a completed painting (according to Bukovec, surely mixed with a resin (mastic) since linseed oil by itself tends to 'disintegrate' too quickly). Notwithstanding that such an interpretation would be possible according to the organic materials found within this research with reflection FTIR, the transmission FTIR on different stratigraphically positioned paint layers on different panels indicates the lipids are a component (presumably an exclusive one) of the paint binders of all panels. However, on panels PK1 and PK3, IR spectroscopy indeed detected triterpenic resin, which might belong to dammars, whereas its potential presence on PK4 needs further verification. Based on the inspection of the panels under UV radiation and FTIR analyses, the resin on PK1 and PK3 is currently considered a component of a protective coating possibly

applied during a past conservation campaign. It is not yet known when dammar resin came into use in Slovenia. Personal discussions with museum conservators corroborated that past conservation treatments throughout the 20th century often employed an application of beeswax and/or dammar varnish. However, the earliest published mention of dammar varnish in Slovenia found thus far by the authors is from 1888–89 in an advertisement for Brothers Eberl, paint and varnish manufacturers and housepainters (Hribar 1889), and dammar varnish might have been available on the market and used for varnishing paintings before that date.

CONCLUSIONS

The analyses of the painted beehive panels PK1 (of 1836), PK3 (beginning of the 20th century) and PK4 (second half of the 20th century) indicate the relatively simple use of pigments or pigment mixtures, although certain colouring agents, additives or natural impurities not able to be detected by the analytical instruments employed in this research could be additionally present (e.g., lake pigments). Analyses with non-invasive and invasive analytical techniques show the use of fairly common materials according to the panels' creation dates. Prussian blue and C-based black were detected on all three panels; cinnabar/vermillion and lead white on all except PK4; Fe oxide pigments on two panels (PK1, PK4); and ultramarine on one (PK4). Fe oxide hydroxide pigment occurred only on panel PK1; and Pb oxide (massicot) only on PK3. The most recent of the panels additionally exhibited the presence of zinc white, chrome yellow and toluidine red. On the oldest panel, Emerald green and Scheele's green were also confirmed. Pigments in paint layers of basic colour tones seem to be used almost pure or mixed with, for example, a certain white pigment to achieve lighter hues, or adulterated with only a few additional colouring agents for specific tones, or with fillers/extenders (most likely added during the pigments' or paints' manufacture) such as barite. The latter was detected on all panels, usually in connection with specific pigments where the addition of Ba sulphate is expected. Since lipids were located in the majority of the paint layers and most likely represent the main or even sole component of the paint binder, an oil painting technique was probably employed for the execution of all three panels. Triterpenic resin was detected on the panels as well. Although mastic resin (as a paint binder or additive of an original surface coating) was noted by Bukovec (1942), in the case of PK1 and PK3, the triterpenic resin probably belonged to a non-original varnish that might be of a dammar type. Nonetheless, an additional investigation is in order in the case of PK3 in order to distinguish unquestionably the distinct type of the identified triterpenic resins (mastic or dammar). The possible presence of the resin on PK4 needs further investigation as well. In addition, beeswax was found on panel PK1, where it might be part of a surface coating (e.g., matt dammar varnish), whereas on PK3 its presence is not yet comprehended.

The possible presence of a white, chalk-containing ground layer, mentioned in the older texts (Vurnik 1929; Bukovec 1942), was not verified by this study. The first paint layer of panels PK1 and PK3 most likely corresponds to the concepts of Makarovič and Rogelj Škafar (2000): the foundation layer seems to be a pigmented oil paint laid directly into the wooden support that simultaneously acts as a composition's background, though the latter statement was not analytically corroborated for PK1 (non-invasive techniques did not enable the identification of the green pigment also used on the background colour visible at other locations of the panel), and needs to be further investigated for the Prussian blue-containing background of PK3. Panel PK4, however, does show a red preparatory layer (containing pigment toluidine red, possibly bound with oil) which was scarcely employed for the painting's composition as well, although not for its background.

From an analytical point of view, the most complex and/or difficult to interpret were the green paints of all three panels. The results of non-invasive analyses of green areas did not give proper or sufficient enough results for the exact determination of the main green colouring agents or potential blue and yellow pigment mixtures. Minimally invasive or invasive analyses, on the other hand, confirmed the presence of Emerald green and Scheele's green on PK1. We showed micro-transflection offers a great alternative when the collected reflection FTIR is distorted and when Raman spectroscopy fails due to fluorescence interference. It was especially useful in the characterization of triterpenic resin, carboxylates, oxalates and beeswax. The use of non-invasive analytical techniques is crucial especially in cases where sampling is very limited. A lot of information about the beehive panel paintings was gained non-invasively from the surface analysis. However, the sampling, although very limited, and the use of invasive methods gave further insights into the layering structure of the panels.

PEER REVIEW

The peer review history for this article is available at https://publons.com/publon/10.1111/arcm.12657.

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