Zavod za varstvo
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Research institute

H2020 WIDESPREAD-2-Teaming; #739574

InnoRenew CoE Renewable Materials and Healthy Environments Research and Innovation Centre of Excellence

WP 6.1 Advanced materials for cultural heritage storage

Case-study investigation task

Report on analytical material characterisation of selected beehive panel paintings from the collection of Slovene Ethnographic Museum

Ljubljana, May 2020

GENERAL DATA :

HERITAGE LOCATION:	Ljubljana / Metelkova 2 / Slovene Ethnographic Museum (HRN 9667)
TYPE OF HERITAGE / TITEL:	movable - painted beehive panels / *Unidentified scene of military violence*, *A fight over a pair of men's trousers*, *The Holy spirit as a dove*, *Landscape motif*
AUTHOR / DATE:	unknown authors / 1836, 1882, Begining of the 20th Century, 2nd half of the 20th Century
TECHNIQUE / MATERIAL / DIMENSIONS:	presumably oil on wood /approx. 12,8 x 25,4 x 1,4 cm, 13 x 32,5 x 1,5 cm, 14,7 x 30,9 x 1,6 cm, 13,4 x 28,3 x 1,2 cm
OWNER:	Slovene Ethnographic Museum
PROJECT:	H2020 WIDESPREAD-2-Teaming; #739574, InnoRenew CoE Renewable Materials and Healthy Environments Research and Innovation Centre of Excellence, WP6.1-Advanced materials for cultural heritage storage
TASK WP6.1 LEADER:	dr. Polonca Ropret, Research Institute, Conservation Centre, Institute for the Protection of Cultural Heritage of Slovenia
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1 ABSTRACT

This report is part of the start-up project WP6.1-Advanced materials for cultural heritage storage of EU project InnoRenew CoE (H2020 WIDESPREAD-2-Teaming; #739574). It focuses on material characterisation of start-up project's case study – selected beehive panel paintings from the collection of Slovene Ethnographic Museum (SEM) – in order to obtain data for model samples preparation involved in the experimental task of the project, dealing with sensing techniques and sensor development for detection of mould activity in museum storage rooms, and development of novel packaging materials/systems for museum objects storage.

Four different panels were included in the study: PK1 – Unindentified scene of military violence (sln. *Neugotovljiv prizor vaškega nasilja*), 1836; PK2 – A fight over a pair of men's trousers (sln. *Boj za moške hlače*), 1882; PK3 – The Holy spirit as a dove (sln. *Sv. Duh v podobi goloba*), begining of the 20th Century; PK4 – Landscape motif (sln. *Motiv pokrajine*), 2nd half of the 20th Century. Preliminary analyses on selected painted beehive panels in order to obtain information on material composition were performed. Surfaces of all four panels (frontal and back planes) were investigated non-invasively by means of Raman spectroscopy and reflection FTIR spectroscopy. Invasive analysis were performed on few taken samples from the painted areas of each of the panel, employing Raman spectroscopy and transmission FTIR spectroscopy. Transflection FTIR spectroscopy was additionaly performed on PK1. The results obtained gave indentification of materials employed in panel paintings' original construction (detection of pigments and binders of paint layers), degradation products of materials present within the paintings' compositions, and materials possibly added to the paintings later in history (e.g. varnishes, coatings applied in conservation campaigns). The results are presented in the following chapters of the report in detail.

2 EXPERIMENTAL

2.1 Sample preparation

Majority of the analysis were performed in non-invasive manner. For more detailed study, micro-samples were removed from the panels. In such case, analysis were performed either directly on the sample without prior manipulation or on the cross-sections of the samples.

Preparation of the cross-sections of the samples: removed samples were embedded in a casting resin, and then ground and polished.

2.2 TECHNIQUES AND METHODS

2.2.1 Optical microscopy

The cross sections of the micro samples were examined by means of an Olympus BX 60 microscope, which was connected to a JVC 3-CCD video camera using visible or ultraviolet light.

2.2.2 Fourier Transform Infrared (FTIR) spectroscopy

2.2.2.1 Perkin Elmer Spectrum 100 FTIR spectrophotometer

FTIR transmission spectra were recorded using a Perkin Elmer Spectrum100 FTIR spectrophotometer coupled to a Spotlight FTIR microscope equipped with nitrogen cooled mercury-cadmium telluride (MCT) detector. The samples taken from the beehive panels were placed between the windows of a diamond anvil cell and examined under microscope with aperture of 60 × 60 µm. The spectra were collected in the range between 4000 and 600 cm^{-1}, at 4 cm^{-1} spectral resolution and with an average of 64 spectral scans accumulated.

2.2.2.2 Alpha-R FTIR spectrometer (Bruker Optics)

Non-invasive FTIR analysis of samples' surface was carried out with portable Alpha-R spectrometer (Bruker Optics GmbH, Germany). The spectra were collected in reflection mode between 7500 and 400 cm-1, at 4 cm-1 spectral resolution. One hundred and sixty scans per sample were averaged and for the background measurement, 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.

2.2.3 Raman spectroscopy

The spectra of the samples were recorded using a 785 nm 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 long working distance objective lens and/or ×100 objective lens and a 600 grooves/mm grating. A multi-channel, air-cooled CCD detector was used. Experimental parameters

(time of exposure, accumulation, power at the sample etc.) were adjusted according to the specifics of the samples. Spectra identificiation was performed by comparsion to the literature[1,2,3,4] or to in-house built spectral database.

Majority of the analyses by the means of Raman spectroscopy were performed non-invasively. In such case, a panel was placed directly under the objective and then the spectra were collected using the x50 long working distance objective from the places of the interest. Furthermore, from two panels (PK2 and PK4) micro-samples were also removed. In such case, analysis was performed on the cross-sections of the samples in order to obtain information on stratigrafy.

[1] Burgio, L. & Clark, R. J. . Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman spectra of pigments with visible excitation. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **57,** 1491–1521 (2001).

[2] Bell, I. M., Clark, R. J. H. & Gibbs, P. J. Raman spectroscopic library of natural and synthetic pigments (pre- ≈ 1850 AD). *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **53,** 2159–2179 (1997).

[3] Correia, A. M., Clark, R. J. H., Ribeiro, M. I. M. & Duarte, M. L. T. S. Pigment study by Raman microscopy of 23 paintings by the Portuguese artist Henrique Pous ao. **1,** 1390–1405 (2007).

[4] Burgio, L., Clark, R. J. H. & Firth, S. Raman spectroscopy as a means for the identification of plattnerite (PbO2), of lead pigments and of their degradation products. *Analyst* **126,** 222–227 (2001)

3 DESCRIPTION OF THE PAINTED BEEHIVE PANELS

3.1 GENERAL DATA ON THE BEEHIVE PANEL PAINTINGS TECHNOLOGY

The term "beehive panel paintings" (or "painted beehive panels") refers to the painted rectangular wooden boards of smaller dimensions, affixed to the frontal planes of wooden beehives, stacked into an apiary, generated mostly between the mid-18th and the early 20th Century. Commencement and development of beehive panel painting is stated as unique for and confined solely to specific regions of Slovenia. 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 the community/clients of equal social status (mostly village bee-keepers). Written texts and research in the past focused mainly on historical, art historical, ethnographical, sociological, iconographical and other aspects of these paintings, but not much was dedicated to the insights of their technological/material characteristics.

In 1929 custodian S. Vurnik[5] published a study on painted beehive panels which also includes some data regarding painting technology. According to him, larger part of the panels is made of lime wood, sometimes spruce, seldom from maple trees but hardly ever from hardwood species. He assesses the support was finely smoothed and sometimes covered with white paint or chalk containing coating, followed by a drawing, still visible on some of the panels, and then painted. Based on Vurnik's judgment and enquiries, the paints used were some sort of tempera, often "home-produced"; he believes the provincial painters of the 18th Century adopted the method of paint preparation from the "bourgeois" painters, who, in his opinion, grounded pigments with egg white or oil, although the former did not use complicated colour mixtures (at times, red and blue on white ground with black contoured shapes were the only colours employed, in addition, green, yellow and brown rounded up the common colour scale).

An interesting insight into the beehive panels' painting technique was written by A. Bukovec[6] in the 1st half of the 20th Century. He mentions a (white) basic colour on which "coloured" paint was applied – a good ground layer, made from white chalk instead of lead white, was in his opinion of crucial importance for the preservation of beehive panels and paintings on general. After the drying of the preparatory coating, a drawing of the composition was made. Like Vurnik, Bukovec too reports the drawings are still visible on some of the beehive panels. He also mentions a painter who had been using stencils for such underdrawings. He writes about remarkably preserved older beehive panels (in comparison to the ones

[5] Vurnik, Stanko (1929). Slovenske panjske končnice. Etnolog (Ljubljana), letnik 3, str. 157-178. URN:NBN:SI:doc-4BFEVI0K from http://www.dlib.si

[6] Bukovec, Avgust (1990). Naše panjske končnice. Slovenski čebelar, letnik 92, številka 1, 92, št. 1 (1990) - št. 9 (1990). URN:NBN:SI:DOC-XQVOMB2S from http://www.dlib.si

made after 1880) which presumably owned their good condition to the oil adhesive quality (probable use of purified linseed oil, perhaps even poppy seed oil or even use of a resin such as mastic). Another factor of stability of these older panels was, according to Bukovec, the employment of durable pigments that he also lists: golden ochre, Indian red, soot or vine black, cinnabar, green earth, Paris green and ultramarine; he reports that cobalt blue was certainly not used due to its costs, although it was the most durable among the blues. He also emphasizes the painters did not only paint in oil but utilised emulsion paints made of egg and varnish. Bukovec goes on about painters applying bleached linseed oil over a completed painting, surly mixed with a resin (mastic) since linseed oil by its own tends to "disintegrate" too quickly in his opinion. Further on he speaks about importance of wood quality and proclaims that the best surviving panels were made from lime or exceptionally compact spruce wood. He says he examined many of the paintings made before 1870 and can corroborate that they were indeed made of above mentioned colours/paints exclusively. Bukovec was not a painter himself – in his writing he also expresses gratitude to the one of the leading Slovene impressionist painters and a chief restorer of the time, M. Sternen, for all the information regarding painting technology. It can be presumed the information he received and summarised were amalgamated presumptions, facts and even misrepresentations about general painting technology of previous centuries blended with the painting practice from the first half of the 20th Century (some of the data Bukovec might have also perceived incorrectly), and not necessarily the "truth" about painted beehive panels.

More recent literature[7] sheds light on the beehive paintings' technology seemingly more accurately. Makarovič mentions the picture support was usually planed and well smoothed softwood board (although hardwood species could be used as well), about 14 mm thick, 12-15 cm high, with most frequent ratio between height and width of 1:2.3. At least till the end of the 19th Century, the colour layers are said to be done exclusively in oil painting technique, i.e. paints made of local linseed oil, earth pigments and turpentine. The paints are supposed to be "home-made in the post-Baroque, rural craft painting tradition" and applied layer by layer, usually in thin applications, after allowing a previous layer to dry completely. In general, there were probably no isolation and preparatory layers, characteristic of traditional fine art panel and easel painting construction methods. Presumably, the first layer, applied directly to the wooden support, was relatively uniformly laid-on monochrome oil paint, often of a vivid colour (white as well), which usually represents the background of the painted motif.

Panels, created over their general, century and a half lasting history, differ in style according to the level of painters' skill, mastery of the craft, painting method/technique, chosen motif, and the date of their creation. However, in most cases, they share a common feature: the style being subordinated to the restricted size of the support and the clarity of the depicted narrative. Majority of the paintings are executed in flat rendering style, lacking volume and sense of perspective, individual figures/objects of

[7] Makarović, G., Rogelj Škafar, B.: Poslikane panjske končnice : zbirka Slovenskega etnografskega muzeja = Painted beehive panels : the collection of the Slovene Ethnographic Museum. Ljubljana: Slovenski etnografski muzej, 2000, p. 20-21.

the painted compositions “framed” with darker contours and juxtaposed in the foreground, the shapes filled with colour, modelled coarsely or not at all, the background surrounding undefined, painted as a block of relatively uniform colour.

With painters, proficiently skilled in their craft, the technical and stylistic characteristics of these paintings are regarded intentional. Stylistic simplicity was probably necessary for the picturesque panels, juxtaposed as vivid, multi-coloured mosaic tiles, positioned on frontal plane of an apiary, to be visually perceived from a distance (and through the clouds of swarming bees). Considering the apiaries were exposed to the external environment, thinner applications of oil colours would be fairly logical choice among traditionally available paints. However, the authors of this study are not aware of any published professional or scientific paper analytically corroborating above mentioned material characteristics of the painted beehive panels.

3.2 DESCRIPTION OF THE FOUR BEEHIVE PANEL PAINTINGS (SLOVENE ETHNOGRAPHIC MUSEUM COLLECTION) SELECTED FOR ANALYTICAL RESEARCH

Four different painted beehive panels owned by Slovene Ethnographic Museum were selected for this study. The images and brief description are gathered in Figure 1 and Table 1.

a) PK1

b) PK2

c) PK3 d) PK4

Figure 1. Selected painted beehive panels; a)PK-1, b)PK-2, c)PK-3, d) PK-4 in visible light (upper image) and in UV-light (bottom image).

Table 1: Description of the selected painted beehive panels.

Working code	**Title**	**Date**	**Inventory Number**	**Dimensions** **h(cm) x w(cm) x d(cm)**
PK1	Unindentified scene of military violence (sln. *Neugotovljiv prizor vaškega nasilja*)	1836	EM 15782	approx. 12,8 x 25,4 x 1,4 cm
	Cathalogue Description: “ 734 Inv. no. 15782 / old. inv. no. of the National Museum: 10319/a / 12.5 x 15.5 cm / date: 1836. The panel was bought from M.Babič, Ljubljana, in 1933. The number ‘2’ in the centre of the panel indicates that it is a picture from a narrative series, painted on several panels. Work in the craft painting tradition of Leopold Sloj’s workshop in Kranj.” [8]			
PK2	A fight over a pair of men’s trousers (sln. *Boj za moške hlače*)	1882	s.n.	approx. 13 x 32,5 x 1,5 cm
	Cathalogue Description: / (the panel is not recorded in the catalogue)			
PK3	The Holy spirit as a dove (sln. *Sv. Duh v*	Begining of the	EM 15779	approx. 14,7 x 30,9 x 1,6 cm

[8] Makarović, G., Rogelj Škafar, B.: *Poslikane panjske končnice : zbirka Slovenskega etnografskega muzeja = Painted beehive panels : the collection of the Slovene Ethnographic Museum.* Ljubljana: Slovenski etnografski muzej, 2000, p. 352.

	podobi goloba)	20th Century[9]		
	Cathalogue Description: "731 Inv. no. 15779 / old inv. no. of the National Museum: 11682 / 14.5 x 30.5 cm. The panel was part of the Grebenc Collection; his written commentary reads 'Panel no. 4; made in Zgornja Šiška, found in Goričane'."[10]			
PK4	Landscape motif (sln. *Motiv pokrajine*)	2nd half of the 20th Century[11]	s.n.	approx. 13,4 x 28,3 x 1,2 cm
	Cathalogue Description: / (the panel is not recorded in the catalogue)			

[9] Data provided by dr. Bojana Rogelj Škafar (Folk art and pictorial sources collection curator at Slovene Etnographic Museum).

[10] Makarović, G., Rogelj Škafar, B.: *Poslikane panjske končnice : zbirka Slovenskega etnografskega muzeja = Painted beehive panels : the collection of the Slovene Ethnographic Museum.* Ljubljana: Slovenski etnografski muzej, 2000, p. 351.

[11] Data provided by dr. Bojana Rogelj Škafar (Folk art and pictorial sources collection curator at Slovene Etnographic Museum).

4 RESULTS and DISCUSSION

4.1 PK1

4.1.1 Marked locations of performed analysis

Figure 2: Marked locations of Raman analysis.

Figure 3: Marked locations of reflection and transflection FTIR analysis.

Figure 4: Marked locations of sample removal. Samples are marked as PK1-1, PK1-2.

LABEL	TYPE	MICROLOCATION	PURPOSE
PK1-1	sample of paint layers on wooden support; sample consists of all stratigrafically present picture layers at the microlocation (residues of wooden support and paint layers on top)	female figure (first figure from the left); woman's blue dress; right side of woman's chest - near the armpit of woman's right arm; blue paint close to the damaged area (missing paint layers revealing wooden support on the left side of the panel)	RAMAN, FTIR
PK1-2	sample of paint layers on wooden support; sample consists of all stratigrafically present picture layers at the microlocation	green paint of the green wall (green painted background) in the upper part of the panel, left of the mirror, close to the damaged areas revealing wooden support	RAMAN, FTIR

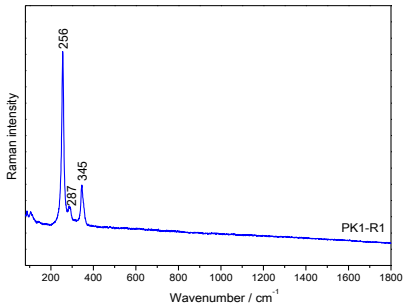
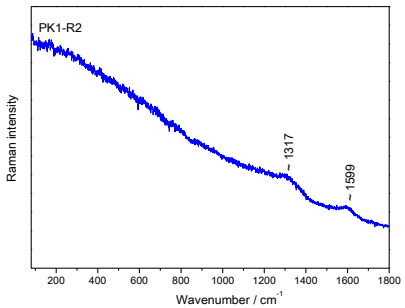
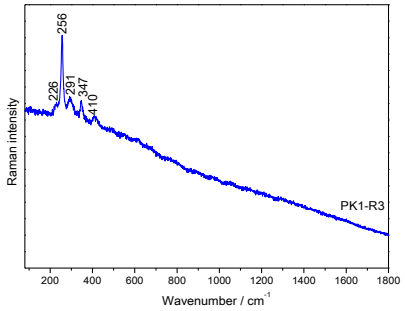
4.1.2 Raman spectroscopy

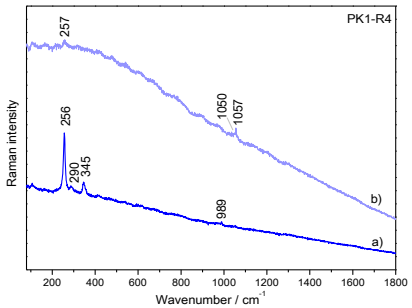
4.1.2.1 Non-invasive analysis

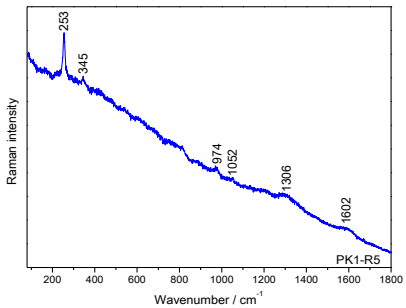
Raman spectra, obtained at different locations on painted beehive panel marked as PK1, are presented in Table 2. Additionally, material identification on different locations based on the obtained spectra is also provided.

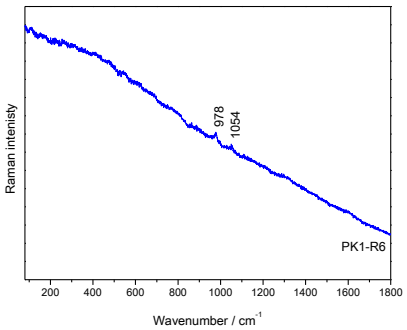
The locations of the obtained spectra from which no material could be identified are given in Figure 9 at the end of the report – said spectra are omitted from this report.

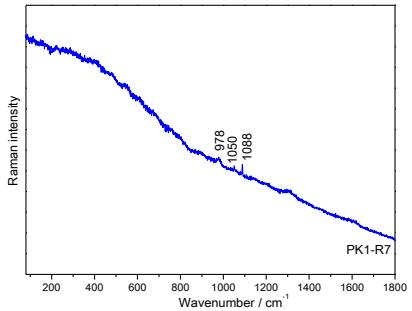
Table 2: Raman spectra obtained on different locations of beehive panel marked as PK1 with identification.

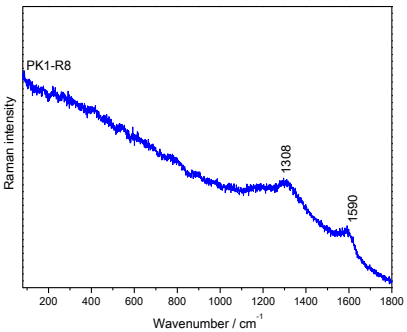
a) PK1-R1	b) PK1-R2	c) PK1-R3
		
Identified material: **cinnabar/vermilion** (256, 287, 345 cm^{-1}).	Identified material: **carbon-based black** (broad bands at ~ 1317, ~1599 cm^{-1})	Identified material: **cinnabar/vermilion** (256, 291, 347 cm^{-1}), possibly also iron oxide (likely haematite type – bands at 226, 291, 410 cm^{-1}).

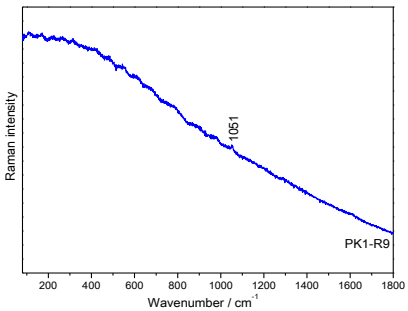
<table>
<tr><td>d) PK1-R4</td><td>e) PK1-R5</td><td>f) PK1-R6</td></tr>
<tr><td> 

Identified material: cinnabar/vermilion (257 and 256, 290, 345 cm^{-1}), lead white (1050, 1057 cm^{-1}), possibly barium sulphate (989 cm^{-1}).</td><td> 

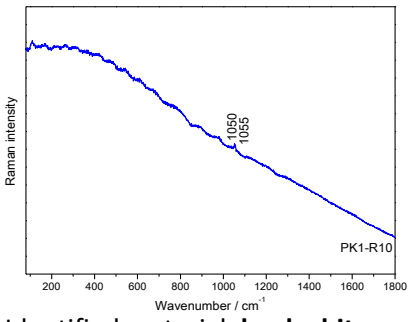
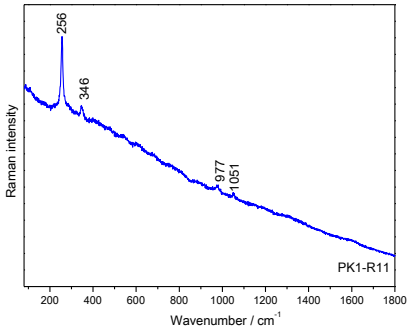
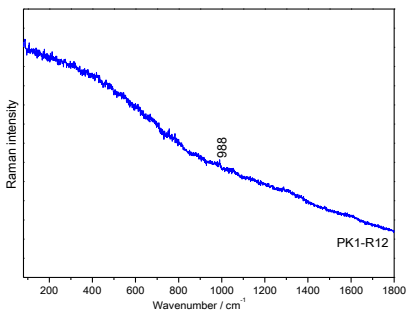
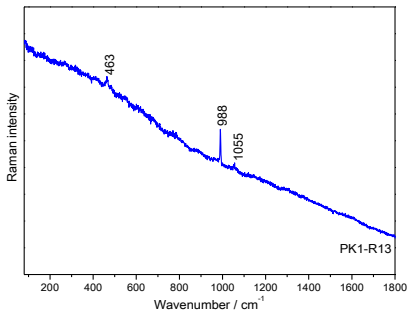
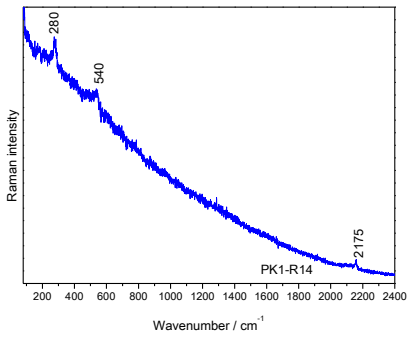
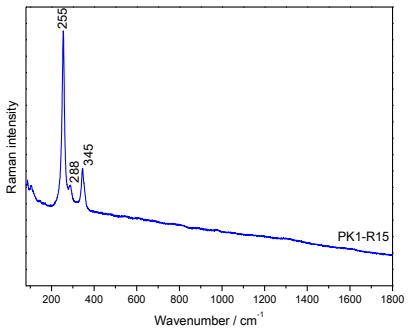
Identified material: cinnabar/vermilion (253, 345 cm^{-1}), lead white (1052 cm^{-1}), carbon-based black (~1306, 1602 cm^{-1}), possibly lead sulphate (974 cm^{-1}).</td><td> 

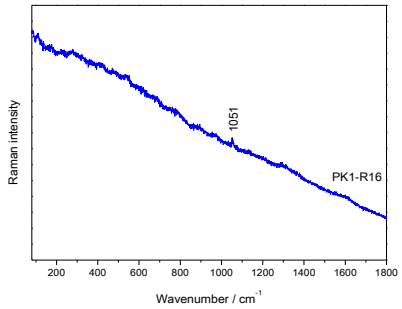
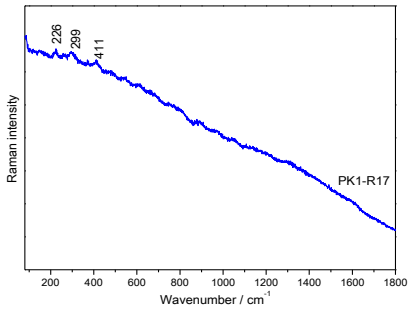
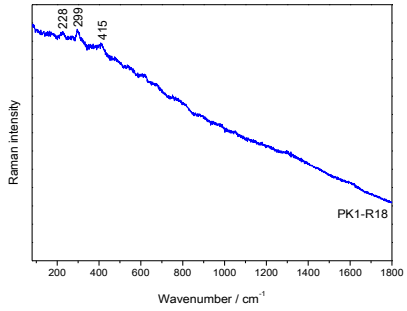
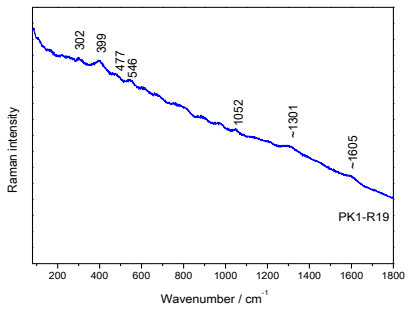
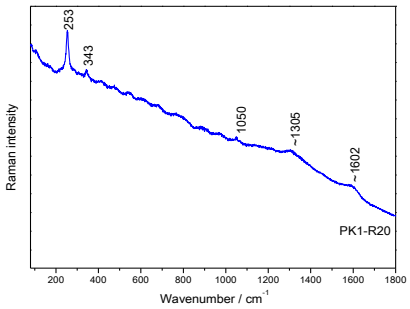
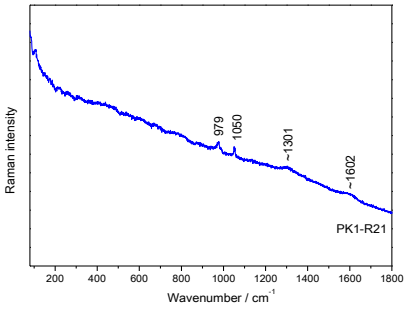
Identified material: lead white (1054 cm^{-1}), possibly lead sulphate (978 cm^{-1}).</td></tr>
<tr><td>g) PK1-R7</td><td>h) PK1-R8</td><td>i) PK1-R9</td></tr>
<tr><td> 

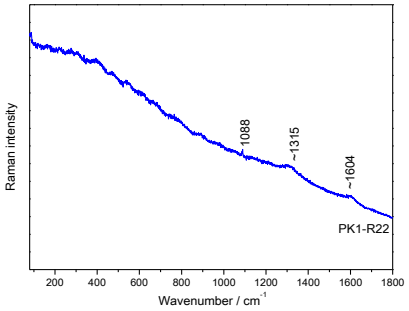
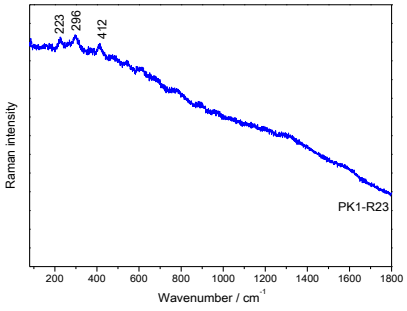
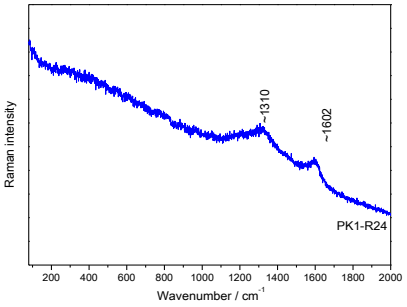
Identified material: lead white (1050 cm^{-1}), calcium carbonate (1088 cm^{-1}), possibly lead sulphate (978 cm^{-1}).</td><td> 

Identified material: carbon-based black (~1308, 1590 cm^{-1}).</td><td> 

Identified material: lead white (1051 cm^{-1}).</td></tr>
</table>

j) PK1-R10	k) PK1-R11	l) PK1-R12
 Identified material: **lead white** (1050, 1055 cm^{-1}).	 Identified material: **cinnabar/vermilion** (256, 346 cm^{-1}), **lead white** (1051 cm^{-1}), possibly lead sulphate (977 cm^{-1}).	 Identified material: most likely barium sulphate (988 cm^{-1}).
m) PK1-R13	n) PK1-R14	o) PK1-R15
 Identified material: **barium sulphate** (463, 988 cm^{-1}), **lead white** (1055 cm^{-1}).	 Identified material: **Prussian blue** (255, 288, 345 cm^{-1}).	 Identified material: **cinnabar/vermilion** (255, 288, 345 cm^{-1}).

p) PK1-R16	q) PK1-R17	r) PK1-R18
 Identified material: **lead white** (1051 cm^{-1}).	 Identified material: **iron oxide** (likely haematite type – bands at 226, 299, 411 cm^{-1}).	 Identified material: **iron oxide** (likely haematite type – bands at 228, 299, 415 cm^{-1}).
s) PK1-R19	**t) PK1-R20**	**u) PK1-R21**
 Identified material: **iron hydroxide** (likely goethite type – bands at 302, 399, 477, 546 cm^{-1}), **lead white** (1052 cm^{-1}), **carbon-based black** (~1301, 1605 cm^{-1}).	 Identified material: **cinnabar/vermilion** (253, 343 cm^{-1}), **lead white** (1050 cm^{-1}), **carbon-based black** (~1305, 1602 cm^{-1}).	 Identified material: **lead white** (1050 cm^{-1}), **lead sulphate** (979 cm^{-1}), **carbon-based black** (~1305, 1602 cm^{-1}).

v) PK1-R22	w) PK1-R23	x) PK1-R24
		
Identified material: **calcium carbonate** (1088 cm^{-1}), **carbon-based black** (~1315, 1604 cm^{-1}).	Identified material: **iron oxide** (likely haematite type – bands at 223, 296, 412 cm^{-1}).	Identified material: **carbon-based black** (~1310, 1602 cm^{-1}).

4.1.2.2 Investigation of cross-sections of the removed samples

a) Sample PK1-1

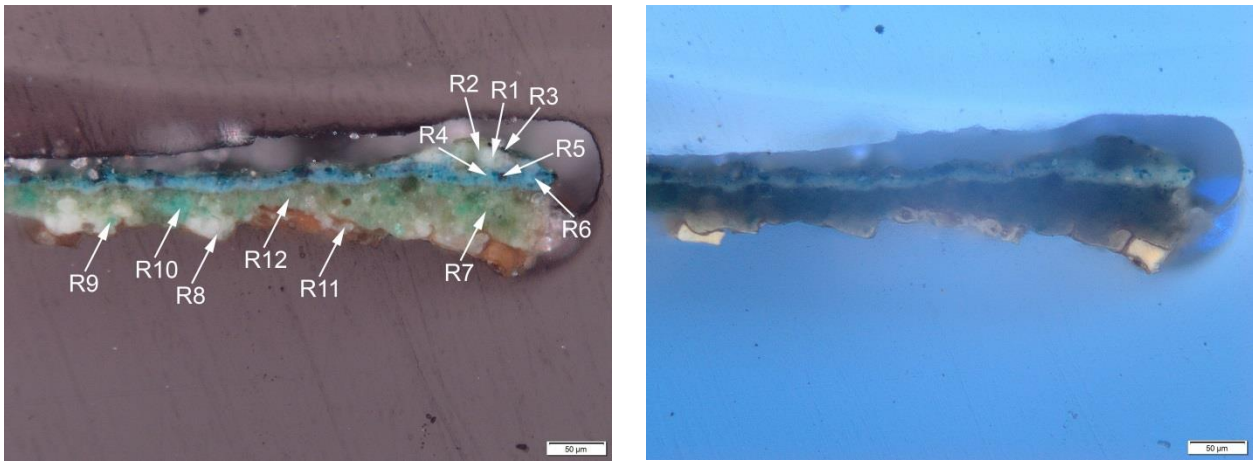
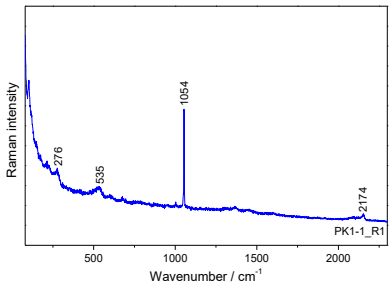
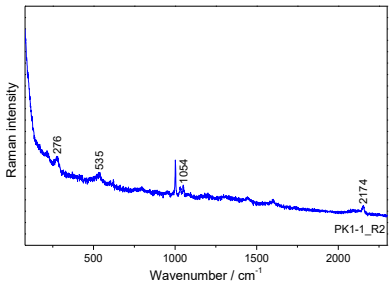
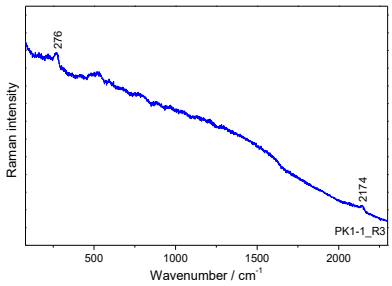
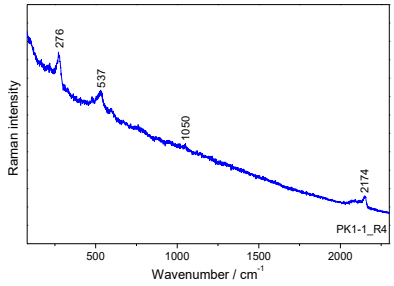
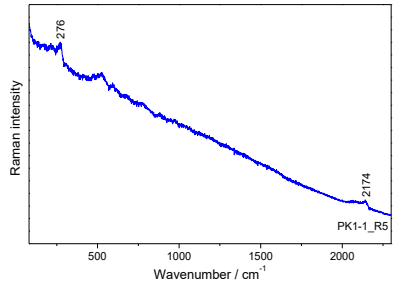
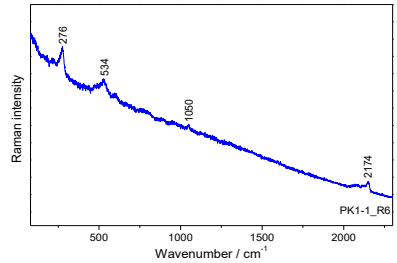
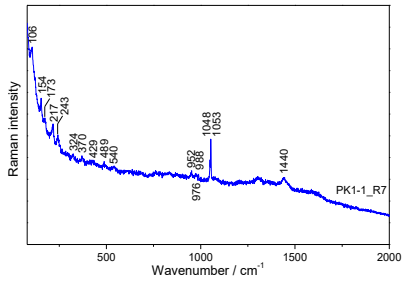
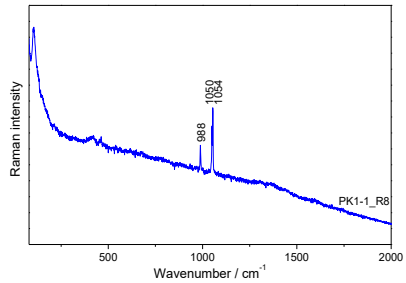
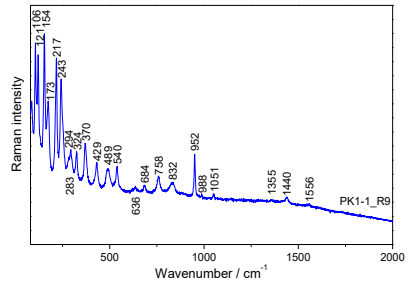
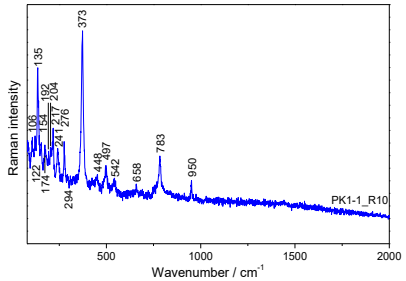
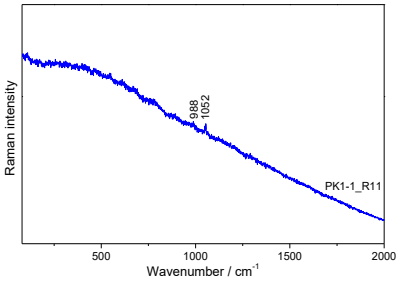
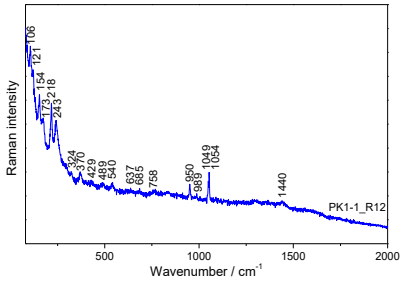


Figure 5: Optical images of cross-section of the sample PK1-1 in visible (left image) with marked locations of Raman analysis (R1 - R12) and UV-light (right image).

Table 3: Raman spectra obtained on different locations of cross section of the sample PK1-1 with identification.

a) PK1-1-R1	b) PK1-1-R2	c) PK1-1-R3
 Identified material: **lead white** (1054 cm^{-1}), **prussian blue** (276, 535, 2174 cm^{-1}).	 Identified material: **lead white** (1054 cm^{-1}), **prussian blue** (276, 535, 2174 cm^{-1}).	 Identified material: **prussian blue** (276, 2174 cm^{-1}).

d) PK1-1-R4	e) PK1-1-R5	f) PK1-1-R6
 Identified material: **lead white** (1050 cm^{-1}), **prussian blue** (276, 537, 2174 cm^{-1}).	 Identified material: **prussian blue** (276, 2174 cm^{-1}).	 Identified material: **lead white** (1050 cm^{-1}), **prussian blue** (276, 534, 2174 cm^{-1}).
g) PK1-1-R7	h) PK1-1-R8	i) PK1-1-R9
 Identified material: **emerald green** (106, 154, 173, 217, 243, 324, 370, 429, 489, 540, 952, 1440 cm^{-1}), **lead white** (1048, 1053 cm^{-1}), **barium sulphate** (988 cm^{-1}), **lead sulphate** (976 cm^{-1}).	 Identified material: **lead white** (1050, 1054 cm^{-1}), **barium sulphate** (988 cm^{-1}).	 Identified material: Identified material: **emerald green** (106, 121, 154, 173, 217, 243, 324, 370, 429, 489, 540, 636, 684, 758, 952, 1355, 1440, 1556 cm^{-1}), **lead white** (1048, 1053 cm^{-1}), **barium sulphate** (988 cm^{-1}).

j) PK1-1-R10	k) PK1-1-R11	l) PK1-1-R12
		
Identified material: **emerald green** (106, 122, 154, 174, 217, 241, 294, 542, 950 cm^{-1}), **scheele's green** (135, 192, 204, 276, 373, 448, 497, 658, 783 cm^{-1}).	Identified material: **lead white** (1052 cm^{-1}), **barium sulphate** (988 cm^{-1}).	Identified material: **emerald green** (106, 121, 154, 173, 218, 243, 324, 370, 429, 489, 540, 637, 695, 758, 950, 1440, 542, 950 cm^{-1}), **barium sulphate** (989 cm^{-1}), **lead white** (1049, 1054 cm^{-1}).

b) Sample PK1-2

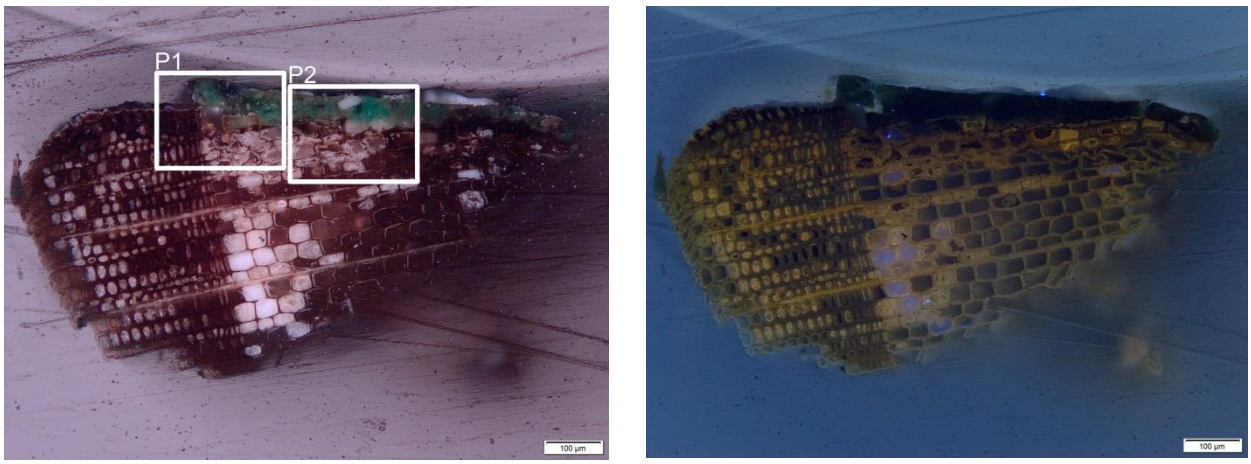


Figure 6: Optical images of cross-section of the sample PK1-2 in visible (left image) with marked general regions of Raman analysis and UV-light (right image).

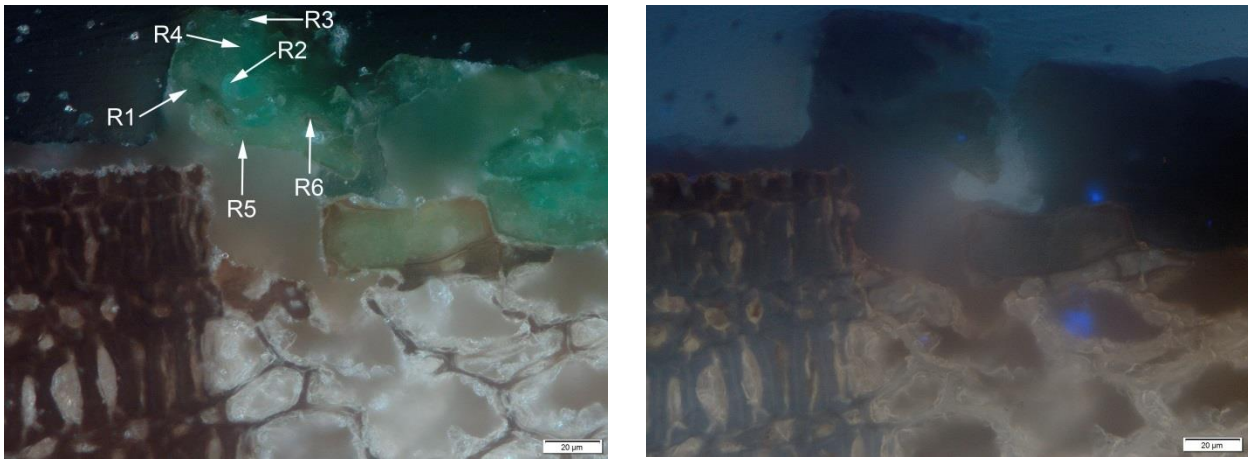


Figure 7: Optical images of region P1 of cross-section of the sample PK1-2 in visible (left image) with marked locations of Raman analysis (R1 – R6) and UV-light (right image).

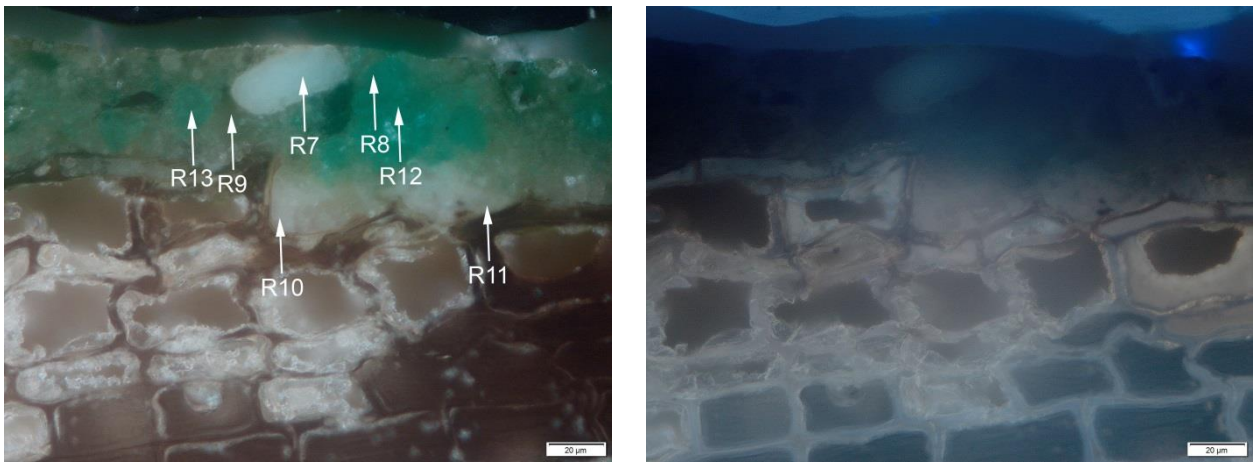
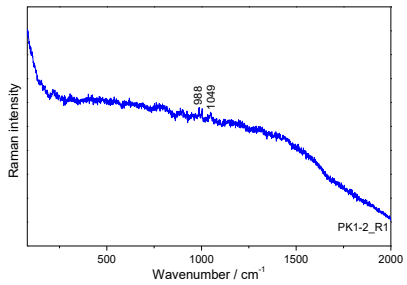
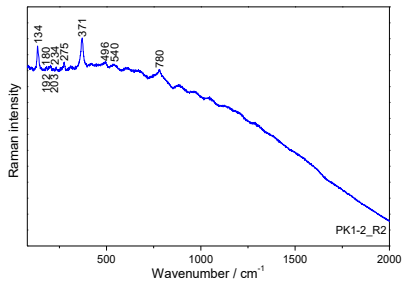
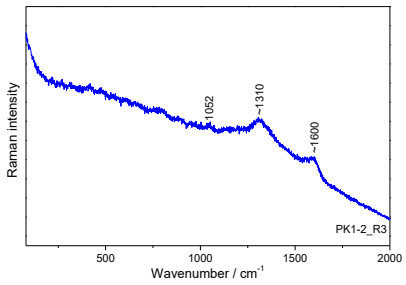
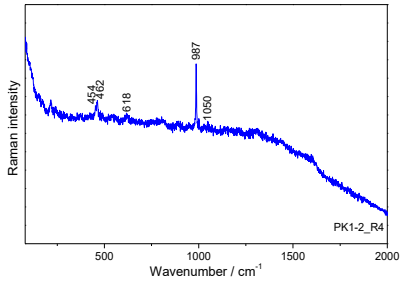
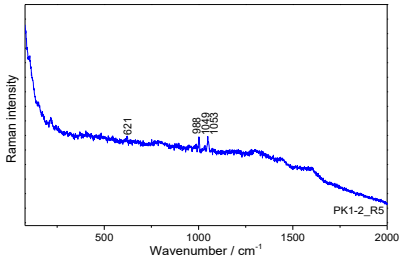


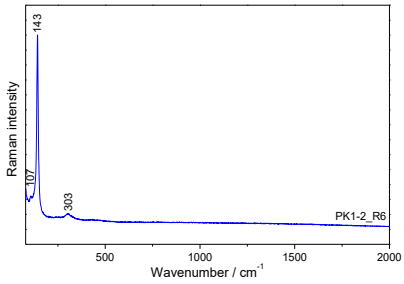
Figure 8: Optical images of region P2 of cross-section of the sample PK1-2 in visible (left image) with marked locations of Raman analysis (R7 – R13) and UV-light (right image).

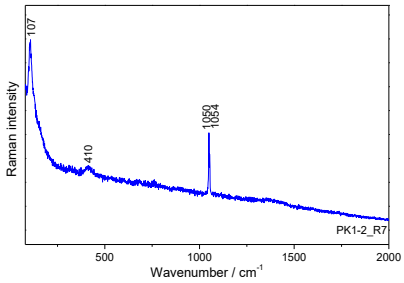
Table 4: Raman spectra obtained on different locations of cross section of the sample PK1-2 with identification.

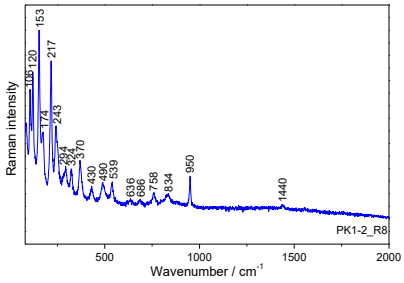
a) PK1-2-R1	b) PK1-2-R2	c) PK1-2-R3
		
Identified material: **lead white** (1049 cm^{-1}), **barium sulphate** (988 cm^{-1}).	Identified material: **Scheele's green** (134, 180, 192, 204, 234, 275, 371, 496, 540, 780 cm^{-1}).	Identified material: **lead white** (1052 cm^{-1}), **carbon black** (1310, 1600 cm^{-1}).

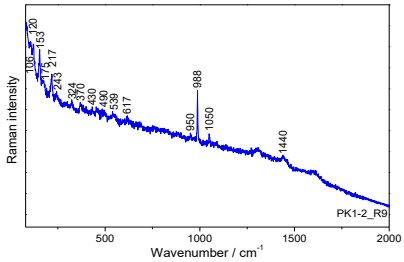
<table>
<tr><td>d) PK1-2-R4</td><td>e) PK1-2-R5</td><td>f) PK1-2-R6</td></tr>
<tr><td> 

Identified material: barium sulphate (453, 462, 618, 987 cm^{-1}), lead white (1050 cm^{-1}).</td><td> 

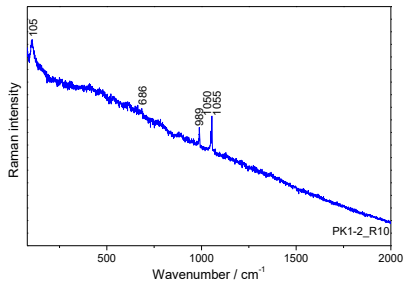
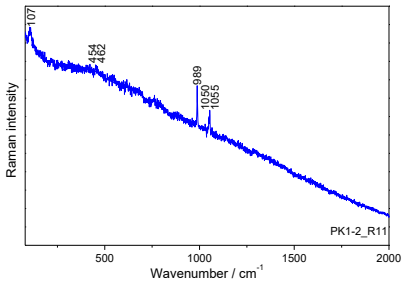
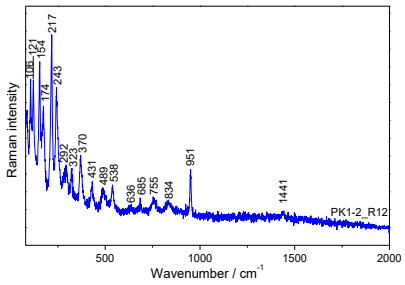
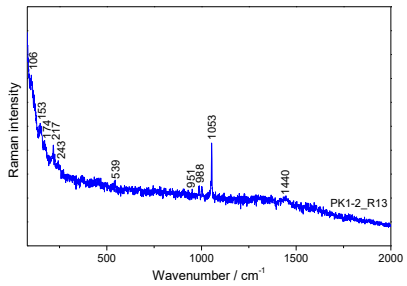
Identified material: barium sulphate (621, 988 cm^{-1}), lead white (1049, 1053 cm^{-1}).</td><td> 

Identified material: possibly lead oxide (Massicot)??</td></tr>
<tr><td>g) PK1-2-R7</td><td>h) PK1-2-R8</td><td>i) PK1-2-R9</td></tr>
<tr><td> 

Identified material: lead white (107, 410, 1050, 1054 cm^{-1}).</td><td> 

Identified material: emerald green (106, 120, 153, 174, 217, 243, 294, 324, 370, 430, 490, 539, 636, 686, 758, 834, 950, 1440 cm^{-1}).</td><td> 

Identified material: emerald green (106, 120, 153, 175, 217, 243, 324, 370, 430, 490, 539, 617, 950, 1440 cm^{-1}), barium sulphate (988 cm^{-1}), lead white (1050 cm^{-1}).</td></tr>
</table>

j) PK1-2-R10	k) PK1-2-R11	l) PK1-2-R12
 Identified material: **lead white** (105, 686, 1050, 1055 cm^{-1}), **barium sulphate** (989 cm^{-1}).	 Identified material: **lead white** (107, 1050, 1055 cm^{-1}), **barium sulphate** (454, 462, 989 cm^{-1}).	 Identified material: **emerald green** (106, 121, 154, 174, 217, 243, 292, 323, 370, 431, 489, 538, 636, 685, 755, 834, 951, 1441 cm^{-1}).
m) PK1-2-R13		
 Identified material: **emerald green** (106, 153, 174, 217, 243, 539, 951, 1440 cm^{-1}), **barium sulphate** (988 cm^{-1}), **lead white** (1053 cm^{-1}).		

4.1.2.3 Other locations

In this chapter, the additional locations of Raman measurments are marked, but the signal was obscured by the fluorescence.

Figure 9: Locations of noninvasive Raman measurments of beehive panel marked as PK1, where material identification was not possible due to fluorescence

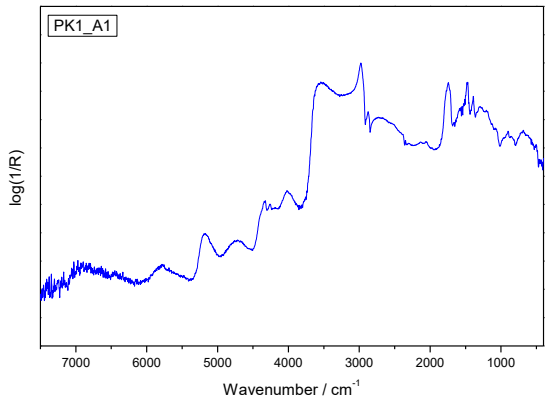
Table 5: Description of Raman spectroscopy measurment locations on beehive panel marked as PK1, where no material identification was possible

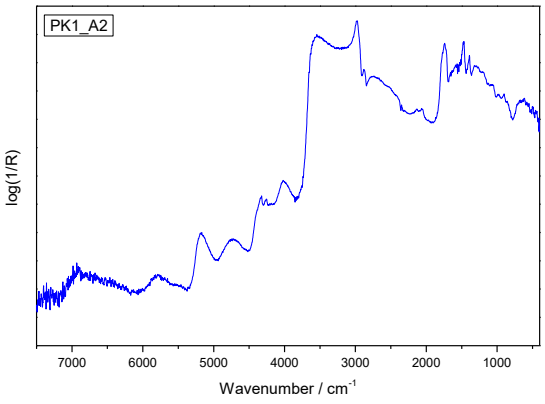
Label of analysis	Colour	Description	Laser wavelength [nm]
fl1	dark brown/violet	mirror (upper middle part of the panel); mirror's frame; upper right side	514
fl2	green	green wall (background); upper edge of the panel, left from the mirror	514
fl3	green	green wall (background); above the painted date	514
fl4	dark brown/violet	table; right back table leg; dark contour on the left side of the table leg	785
fl5	yellow	brown door (right side of the panel);	785

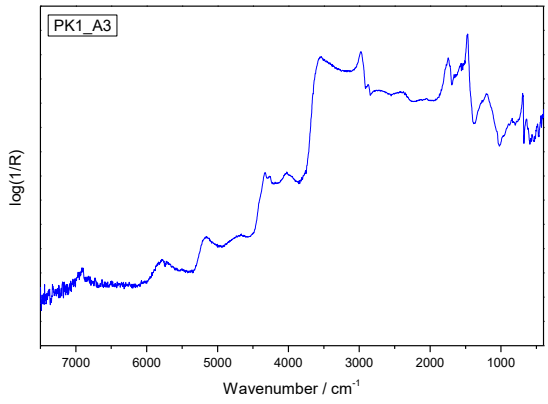
		door's upper area; yellow horizontal line	
fl6	dark brown/violet	dark vertical contour on the left edge of the white wall	785

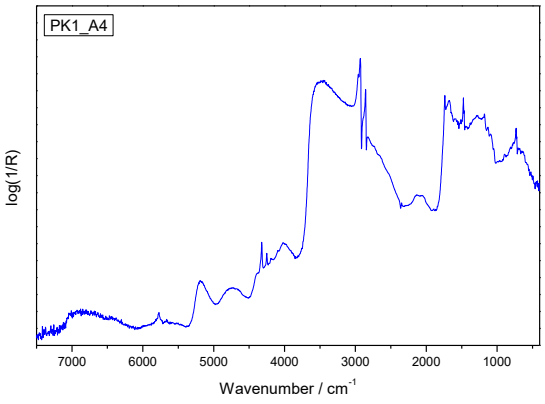
4.1.3 Reflection FTIR spectroscopy

Table 6: Reflection infrared spectra obtained on different locations of beehive panel marked as PK1 with identification.

<table>
<tr><td>a) PK1-A1</td><td>b) PK1-A2</td></tr>
<tr><td> 

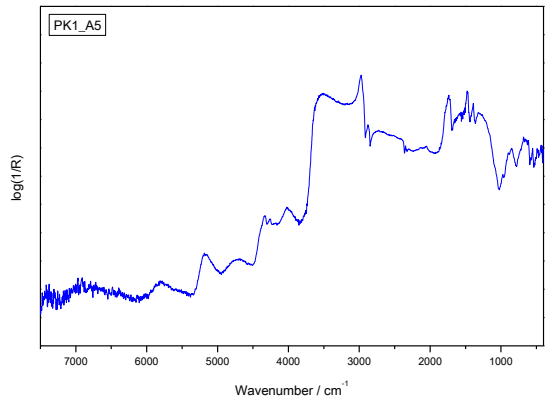
Identified material: lipids, triterpenic resin (dammar)</td><td> 

Identified material: lipids, triterpenic resin (dammar)</td></tr>
<tr><td>c) PK1-A3</td><td>d) PK1-A4</td></tr>
<tr><td> 

Identified material: lipids, basic lead carbonate</td><td> 

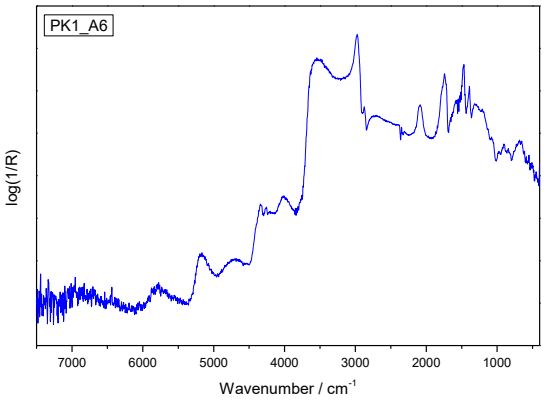
Identified material: beeswax, wood</td></tr>
</table>

e) PK1-A5



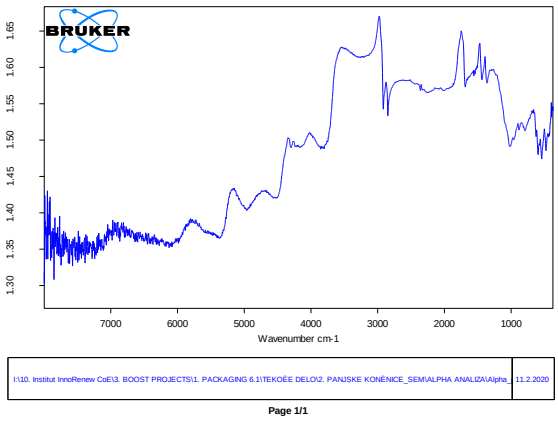
Identified material: **lipids, triterpenic resin (dammar), unidentified bands**

f) PK1-A6



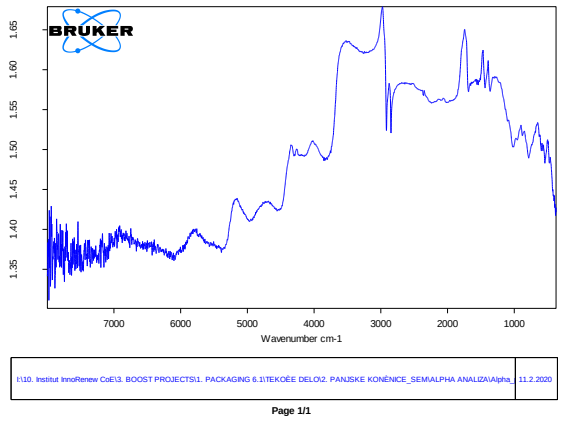
Identified material:**lipids, Prussian blue, triterpenic resin (dammar)**

g) PK1-A7



Identified material: **lipids, triterpenic resin (dammar), unidentified bands**

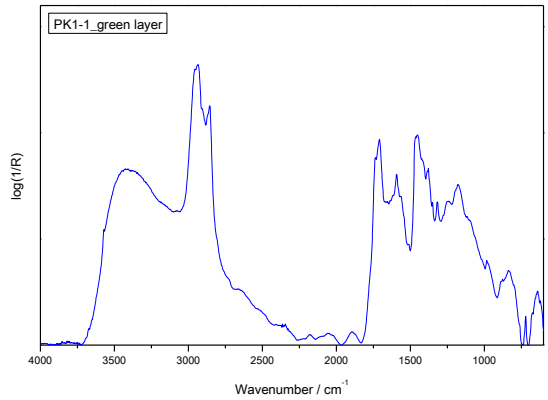
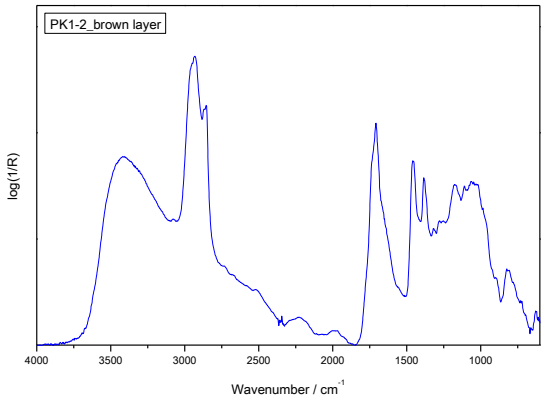
h) PK1-A8



Identified material: **lipids, triterpenic resin (dammar), unidentified bands**

4.1.4 Transflection FTIR spectroscopy

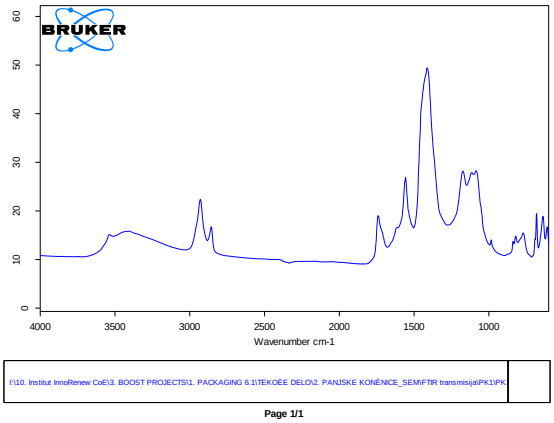
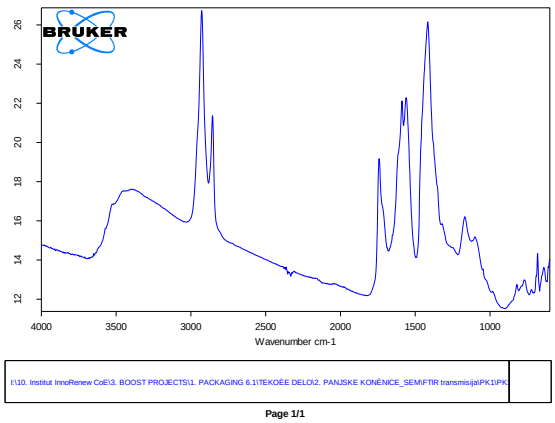
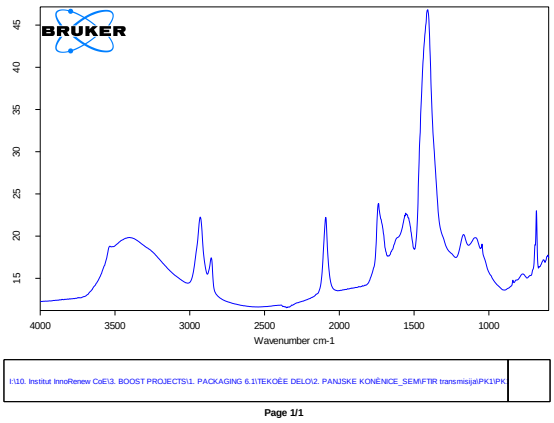
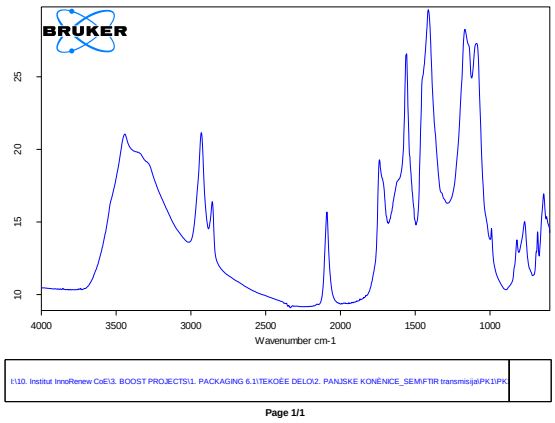
Table 7: Tranflection spectra obtained on different locations of beehive panel marked as PK1 with identification.

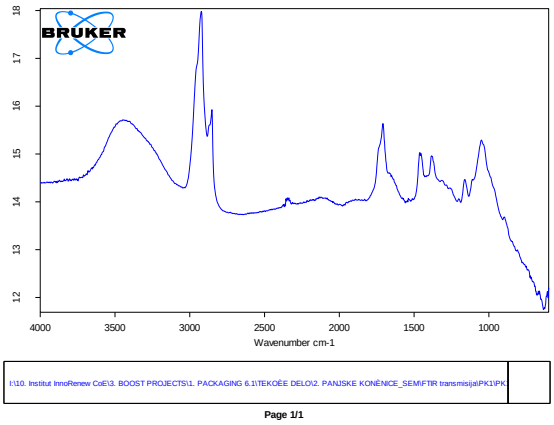
a) PK1- TRF1  Identified material: **Triterpenoid resin, copper carboxylate (Emerald green), oxalate, lipids**	b) PK1-TRF2  Identified material: **Triterpenoid resin, oxalate, beeswax**

4.1.5 Transmission FTIR spectroscopy

a) Sample PK1-1

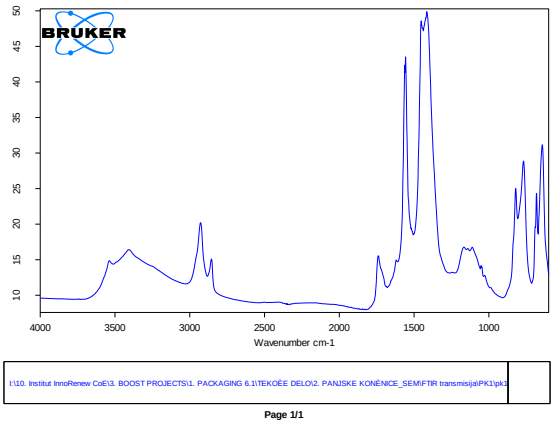
Table 8: Transmission spectra obtained on different layers of sample marked as PK1-1 with identification.

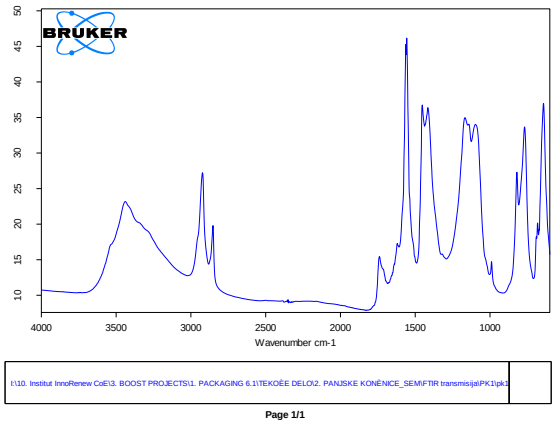
a) PK1-1_layer1_green	b) PK1-1_layer1_green (seen as transparent under the microscope)
	
Identified material: **Lead white, emerald green, barium sulphate,** lipids	Identified material: **lead white, lipids, copper carboxylate, oxalate, emerald green.**
c) PK1-1_layer2_blue_1	d) PK1-1_layer2_blue_2
	
Identified material: **Prussian blue, lead white, emerald green**, lipids	Identified material: **Prussian blue, lead white, emerald green, barium sulphate**, lipids

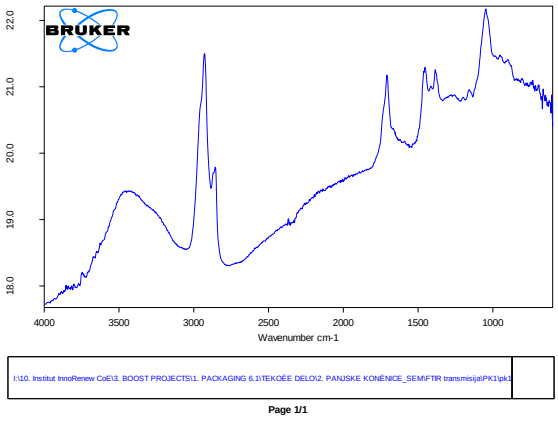
e) PK1-1_layer3_transparent	
 Identified material: **triterpenic resin**, unidentified bands	

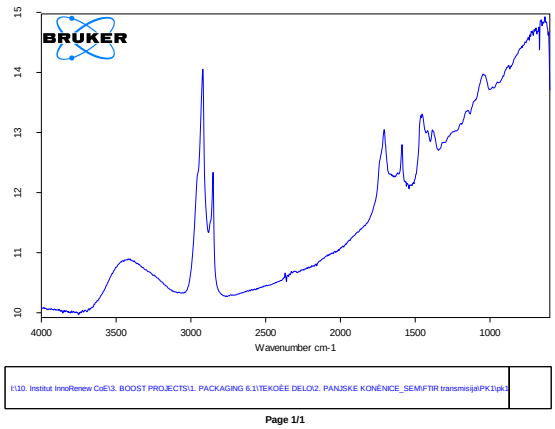
b) Sample PK1-2

Table 9: Transmission spectra obtained on different layers of sample marked as PK1-2 with identification.

<table>
<tr><td>a) PK1-2_layer1_green_1</td><td>b) PK1-2_layer1_green_2</td></tr>
<tr><td> 

Identified material: lead white, emerald green, barium sulphate.</td><td> 

Identified material: lead white, emerald green, barium sulphate.</td></tr>
<tr><td>c) PK1-2_layer2_transparent_1</td><td>d) PK1-2_layer2_transparent_2</td></tr>
<tr><td> 

Identified material: triterpenic resin, 1050??.</td><td> 

Identified material: triterpenic resin, copper carboxylate.</td></tr>
</table>

4.1.6 Gathered results

Label of analysis	Surface paint colour/material	Location description	Identified material
R1	red	soldier (third figure from the left); soldier's red jacket; chest; soldier's left chest side	cinnabar/vermilion
R2	black/dark red	soldier (third figure from the left); soldier's red jacket; painted contour of soldier's left armpit	carbon-based black
R3	dark red	soldier (third figure from the left); soldier's red jacket; painted contour of soldier's left elbow	cinnabar/vermilion, iron oxide
R4	white	soldier (third figure from the left); soldier's red jacket; chest; 2nd button from above	cinnabar/vermilion, lead white, barium sulphate (?)
A4	brown	wood at the back of the panel	lipids, beeswax, wood
R5	greyish	soldier (third figure from the left); soldier's right hand	cinnabar/vermilion, lead white, carbon-based black, lead sulphate (?)
R6	light yellowish	soldier (third figure from the left); soldier's yellowish trousers; soldier's left thigh	lead white, lead sulphate (?)
R7	ochre	soldier (third figure from the left); soldier's yellowish trousers; soldier's right thigh; shadow on inner side of the thigh	lead white, calcium carbonate, lead sulphate (?)
A7			lipids, tritepenic resin, unidentified bands
R8	dark grey	soldier (third figure from the left); soldier's black boots; soldier's right boot; upper part of the boot	carbon-based black
R9	white	kneeling male figure (middle figure); white garment; figure's back	lead white
R10	white	kneeling male figure (middle figure); white garment; figure's back	lead white
A5			lipids, tritepenic resin
R11	greyish ochre	kneeling mail figure (middle figure); figure's hair	cinnabar/vermilion, lead white, lead sulphate (?)
R12	green	green wall (background); above the painted date (left from the mirror)	barium sulphate (?)
A1			lipids, triterpenic resin

PK1-2			Scheele's green, copper carboxylate (emerald green), lead white, barium sulphate, triterpenic resin
TRF1	green		triterpenoid resin, copper carboxylate (Emerald green), oxalate, lipids
R13	green	green wall (background); above the painted date (left from the mirror)	barium sulphate, lead white
A2			lipids, triterpenic resin
R14	blue	female figure (first figure from the left); blue dress; woman's left hand; wristband of the sleeve	Prussian blue
A6			lipids, Prussian blue, triterpenic resin
PK1-1			lead white, Prussian blue, copper carboxylate (emerald green), Scheele's green, barium sulphate, lead sulphate, lipids, oxalate, triterpenic resin
R15	dark red	book on the table; right side of the book; right side of the textblock	cinnabar/vermilion
R16	white	mirror (upper middle part of the panel);painted reflection on the middle right side	lead white
R17	dark brown/violet	table; right back table leg; dark contour on the left side of the table leg	iron oxide
R18	reddish brown	table; right back table leg; reddish brown shadow	iron oxide
R19	ochre	table; right back table leg; basic ochre colour	iron hydroxide, lead white, carbon-based black
A8			lipids, tritepenic resin, unidentified bands
R20	greyish ochre	female figure (first figure from the left); hair	cinnabar/vermilion, lead white, carbon-based black
R21	greyish white	white wall (right side of the panel); left edge	lead white, lead sulphate, carbon-based black
A3			lipids, basic lead carbonate
R22	dark ochre/brown	brown door (right side of the panel); upper left side; basic dark ochre/brown colour	calcium carbonate, carbon-based black
R23	dark red	soldier (third figure from the left); soldier's red jacket; painted contour of soldier's right elbow, positioned on green	iron oxide

		background	
R24	dark brown	kneeling male figure (middle figure); garment; dark contour between shirt and trousers (possibly belt)	carbon-based black
TRF2	dark ochre/brown	Brown floor (beside soldier's left boot)	triterpenoid resin, oxalate, beeswax

4.2 PK2

4.2.1 Marked locations of performed analysis

Figure 10: Marked locations of Raman analysis.

Figure 11: Marked locations of reflection FTIR analysis.

Figure 12: Marked locations of sample removal. Samples are marked as PK2-1, PK2-2, PK2-2b, PK2-3, PK2-4.

Table 10: Description of the removed samples

LABEL	TYPE	MICROLOCATION	PURPOSE
PK2-1	sample of paint layers on wooden support; sample consists of all stratigrafically present picture layers at the microlocation	female figure; fourth figure from the left; woman's skirt; dark blue contour at the bottom of woman's skirt; right side of the contour line	RAMAN, FTIR
PK2-2	sample of paint layers on wooden support; sample consists of all stratigrafically present picture layers at the microlocation	left side of the panel; upper edge of the panel; green treetop on the left side of the tree	RAMAN, FTIR
PK2-3	sample of paint layers on wooden support; sample consists of all stratigrafically present picture layers at the microlocation	female figure; fifth figure from the left; woman's dress; light green apron; right bottom part of the apron	RAMAN, FTIR
PK2-4	sample of paint layers on wooden support;	female figure; third figure from the left; woman's face; cheek; residues of skin tone	RAMAN,

LABEL	TYPE	MICROLOCATION	PURPOSE
	sample consists of all stratigrafically present picture layers at the microlocation	colour on greenish or bluish underpaint layer	FTIR, GC-MS

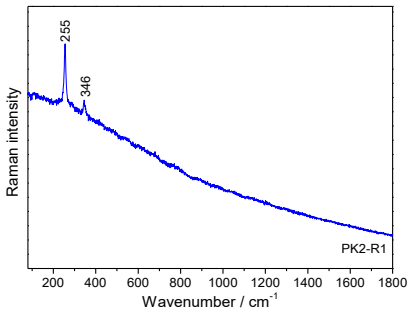
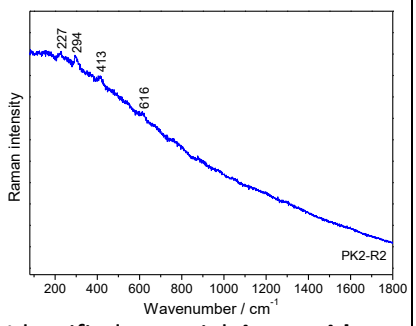
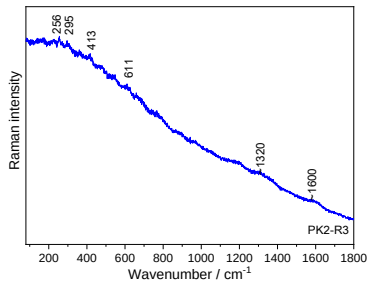
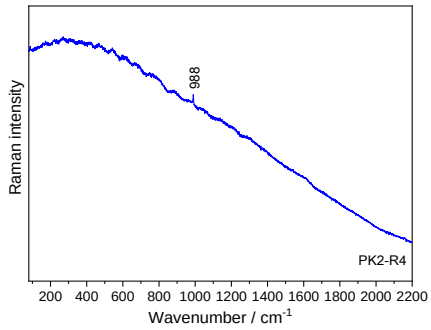
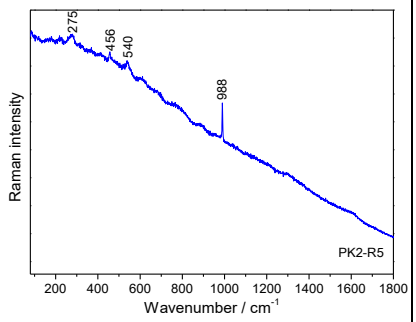
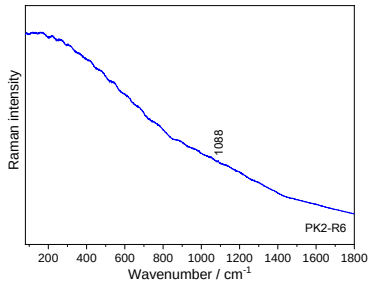
4.2.2 Raman spectroscopy

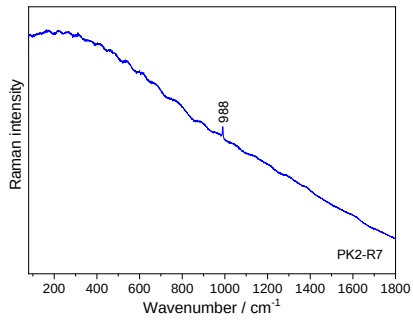
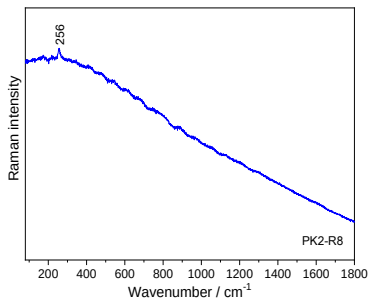
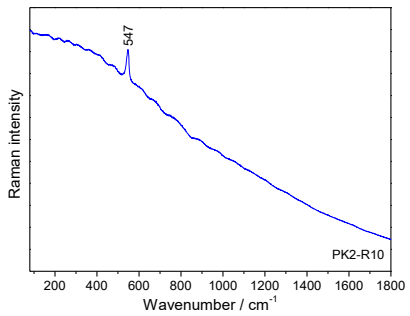
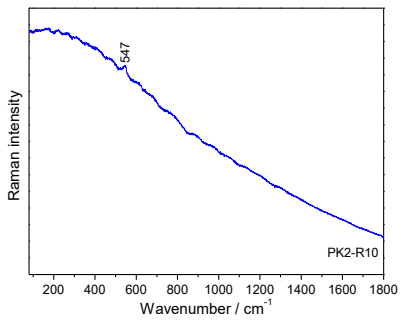
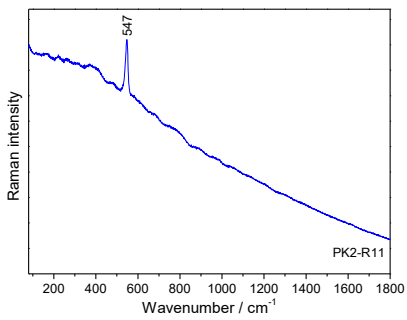
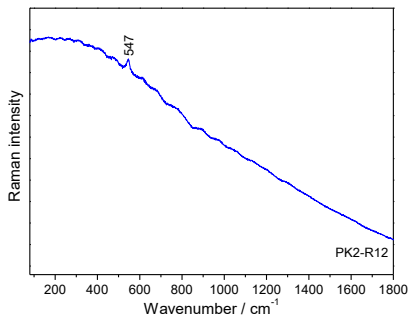
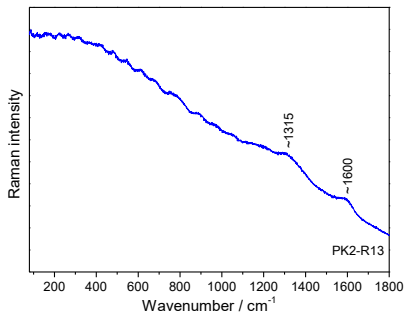
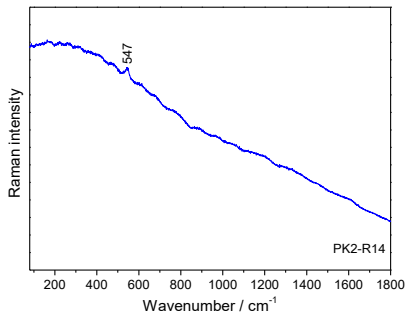
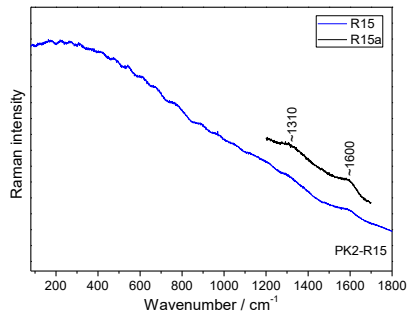
4.2.2.1 Non-invasive analysis

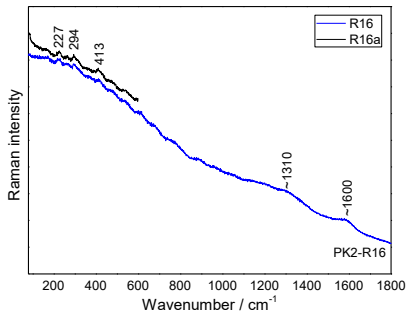
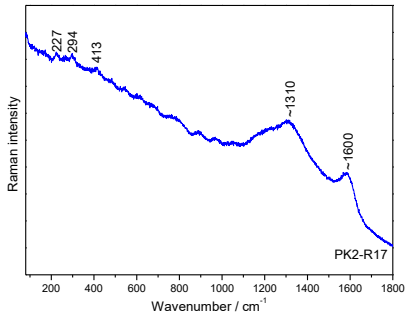
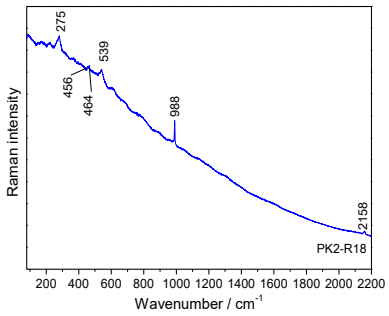
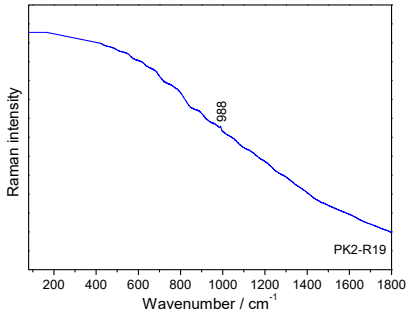
Raman spectra obtained at different locations on painted beehive panel marked as PK2 are presented on Table 11. Additionally, material identification based on the obtained spectra is gathered in.

The locations of the obtained spectra from which no material could be identified are given in Figure 21 at the end of the report–said spectra are omitted from this section.

Table 11: Raman spectra obtained on different locations of beehive panel marked as PK2 with identification.

a) PK2-R1	b) PK2-R2	c) PK2-R3
 Identified material: **cinnabar/vermilion** (256, 345 cm^{-1}).	 Identified material: **iron oxide** (likely haematite type – bands at 227, 294, 413, 616 cm^{-1}).	 Identified material: **cinnabar/vermilion** (256 cm^{-1}), **iron oxide** (likely haematite type – bands at 295, 413, 611 cm^{-1}), **carbon-based black** (broad bands at ~1320 and ~1600 cm^{-1}).
d) PK2-R4	e) PK2-R5	f) PK2-R6
 Identified material: **barium**	 Identified material: **prussian blue** (275, 540 cm^{-1}), **barium**	 Identified material: possibly calcium carbonate (1088 cm^{-1}).

sulphate (988 cm^{-1}).	**sulphate** (456, 988 cm^{-1}).	
g) PK2-R7	h) PK2-R8	i) PK2-R9
 Identified material: **barium sulphate** (988 cm^{-1}).	 Identified material: possibly cinnabar/vermilion (256 cm^{-1}).	 Identified material: **ultramarine** (547 cm^{-1}).
j) PK2-R10	k) PK2-R11	l) PK2-R12
 Identified material: **ultramarine** (547cm^{-1}).	 Identified material: **ultramarine** (547 cm^{-1}).	 Identified material: **ultramarine** (547 cm^{-1}).
m) PK2-R13	n) PK2-R14	o) PK2-R15
 Identified material: **carbon-based**	 Identified material: **ultramarine**	 Identified material: **carbon-**

black (~1315, ~1600 cm^{-1}).	(547 cm^{-1}).	**based black** (~1310, ~1600 cm^{-1}).
p) PK2-R16	q) PK2-R17	r) PK2-R18
 Identified material: **iron oxide** (likely haematite type – bands at 227, 294, 413 cm^{-1}), **carbon-based black** (~1310, ~1600 cm^{-1}).	 Identified material: **iron oxide** (likely haematite type – bands at 227, 294, 413 cm^{-1}), **carbon-based black** (~1310. ~1600 cm^{-1}).	 Identified material: **prussian blue** (275, 540, 2156 cm^{-1}), **barium sulphate** (456, 464, 988 cm^{-1}).
s) PK2-R19		
 Identified material: **barium sulphate** (988 cm^{-1}).		

4.2.2.2 Investigation of cross-sections of the removed samples

a) Sample PK2-1

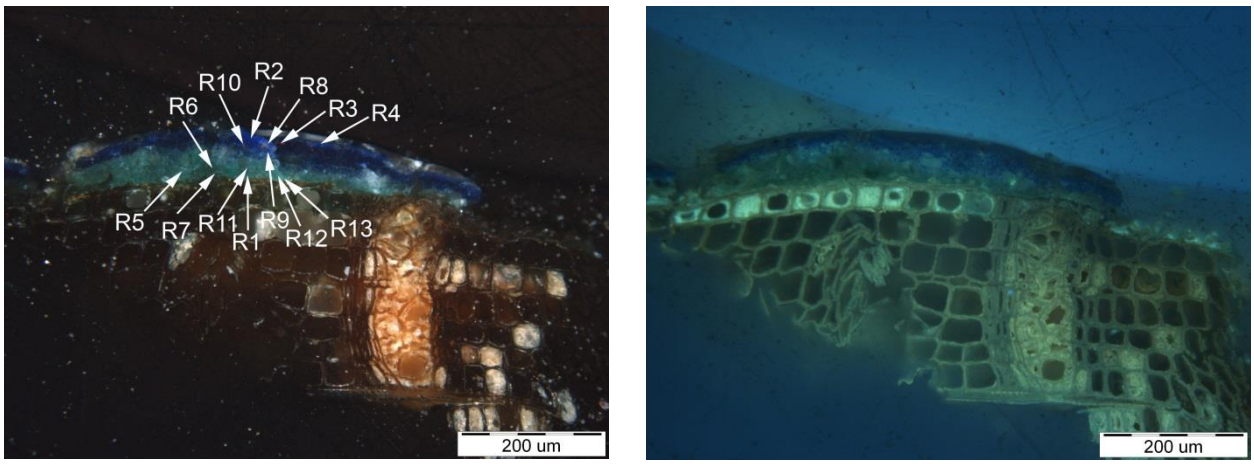
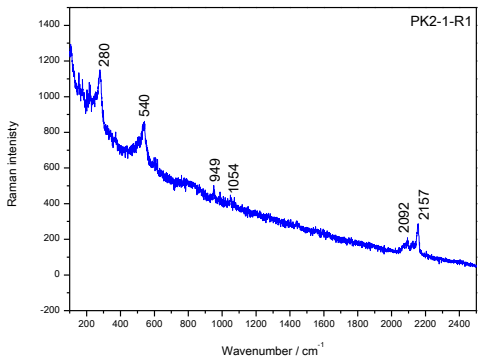
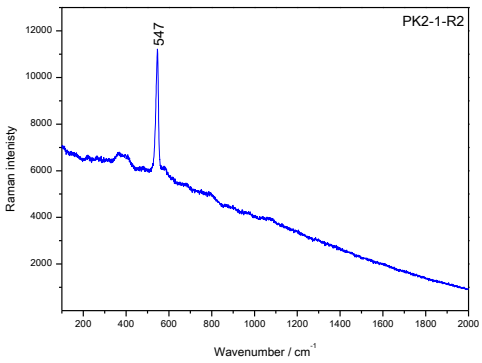
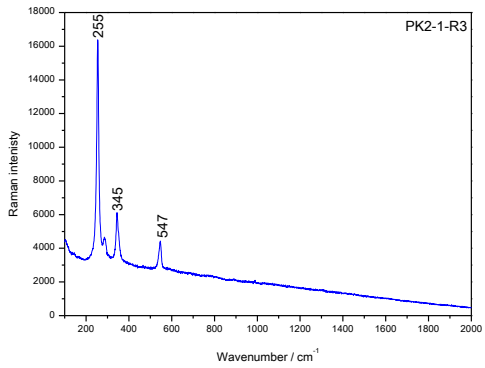


Figure 13: Optical images of cross-section of the sample PK2-1 in visible (left image) with marked locations of Raman analysis (R1 - R13).and UV-light (right image).

Table 12: Raman spectra obtained on different locations of cross section of the sample PK2-1 with identification.

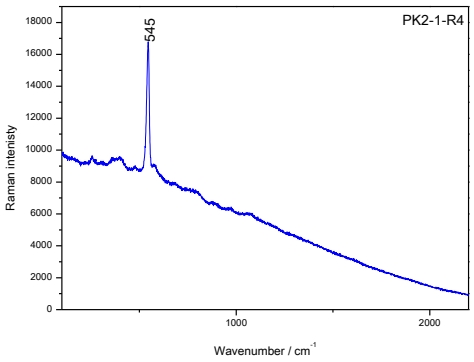
a) Table 13: PK2-1-R1	b) PK2-1-R2
	
Identified material: **Prussian blue** (280, 540, 2092, 2157 cm^{-1}), lead carbonate (**lead white,** 1054 cm^{-1}), unidentified band: 949 cm^{-1}.	Identified material: **ultramarine** (547 cm^{-1}).

c) PK2-1-R3



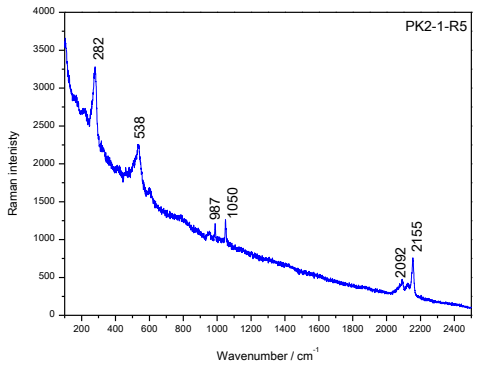
Identified material: **cinnabar** (255, 345 cm^{-1})**, ultramarine** (547cm^{-1})**.**

d) PK2-1-R4



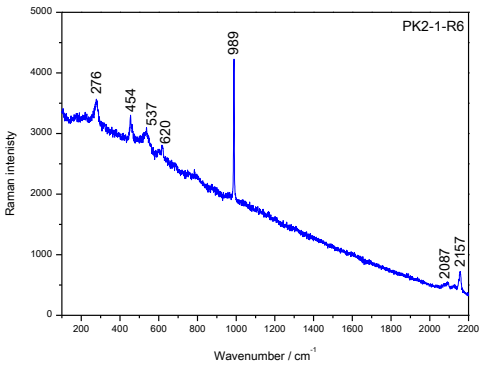
Identified material: **ultramarine** (547 cm^{-1}).

e) PK2-1-R5



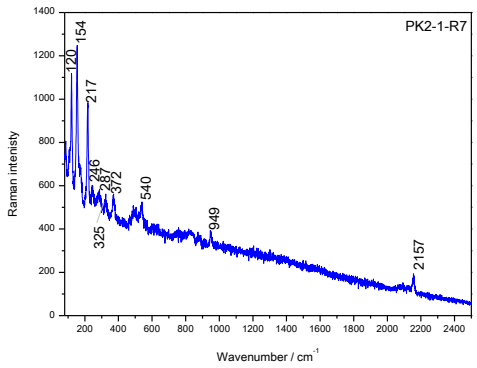
Identified material: **Prussian blue** (282, 538, 2092, 2156cm^{-1})**,** lead carbonate (**lead white**, 1050 cm^{-1})**, barium sulphate** (987 cm^{-1})**.**

f) PK2-1-R6



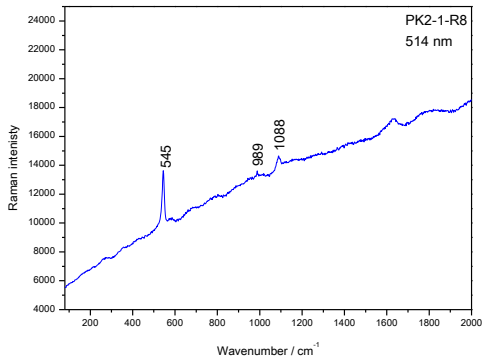
Identified material: **Prussian blue** (276, 537, 2087, 2157 cm^{-1})**, barium sulphate** (454, 620, 989 cm^{-1})**.**

g) PK2-1-R7



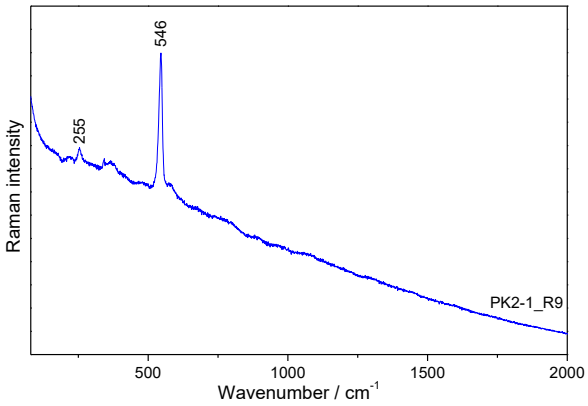
Identified material: **Prussian blue** (287, 540, 2157 cm^{-1})**,** unidentified bands: 120, 154, 217, 246, 325, 372, 949 cm^{-1} : possibly Emerald green**.**

h) PK2-1-R8



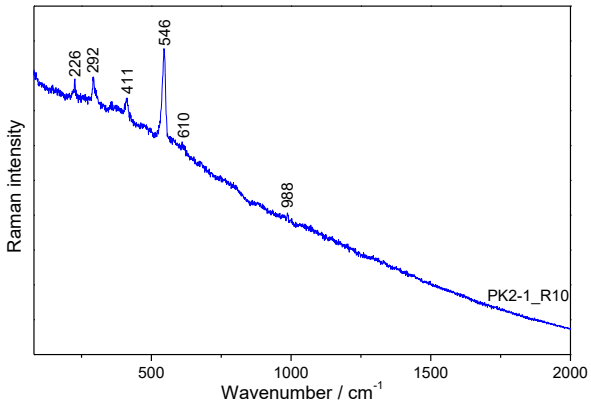
Identified material: **ultramarine** (545 cm^{-1}), barium sulphate (988 cm^{-1}), **calcium carbonate** (calcite type – band at 1088 cm^{-1}).

i) PK2-1-R9



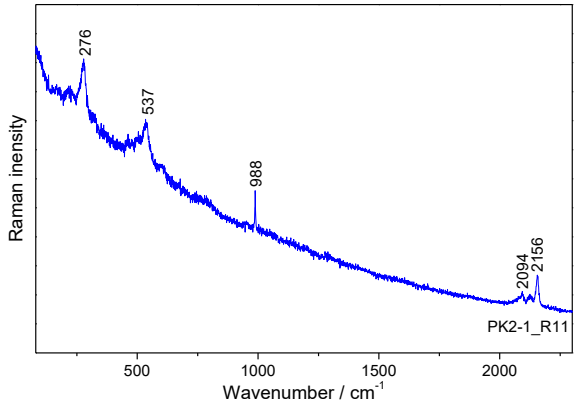
Identified material: **ultramarine** (255, 546 cm^{-1})

j) PK2-1-R10



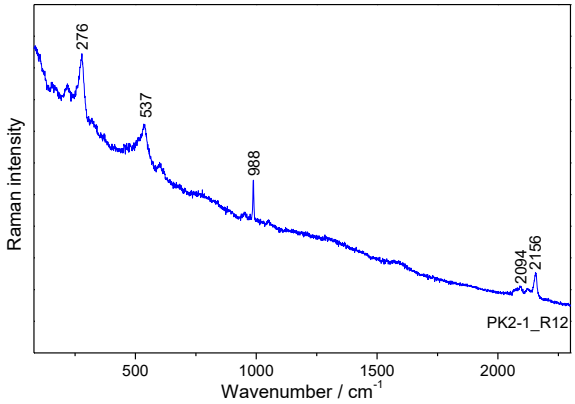
Identified material: **iron oxide** (likely haematite type – bands at 226, 292, 411 cm^{-1}), **ultramarine** (546 cm^{-1}), **barium sulphate** (988 cm^{-1}).

k) PK2-1-R11



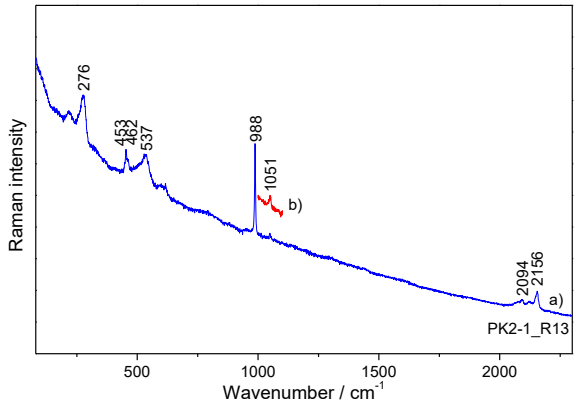
Identified material: **prussian blue** (276, 537, 2094, 2156 cm^{-1}), **barium sulphate** (988 cm^{-1}).

l) PK2-1-R12



Identified material: **Prussian blue** (276, 537, 2094, 2156 cm^{-1}), **barium sulphate** (988 cm^{-1}).

m) PK2-1-R13



Identified material: **prussian blue** (276, 537, 2094, 2156 cm^{-1}), **barium sulphate** (453, 462, 988 cm^{-1}), **lead white** (1051 cm^{-1}).

b) Sample PK2-2

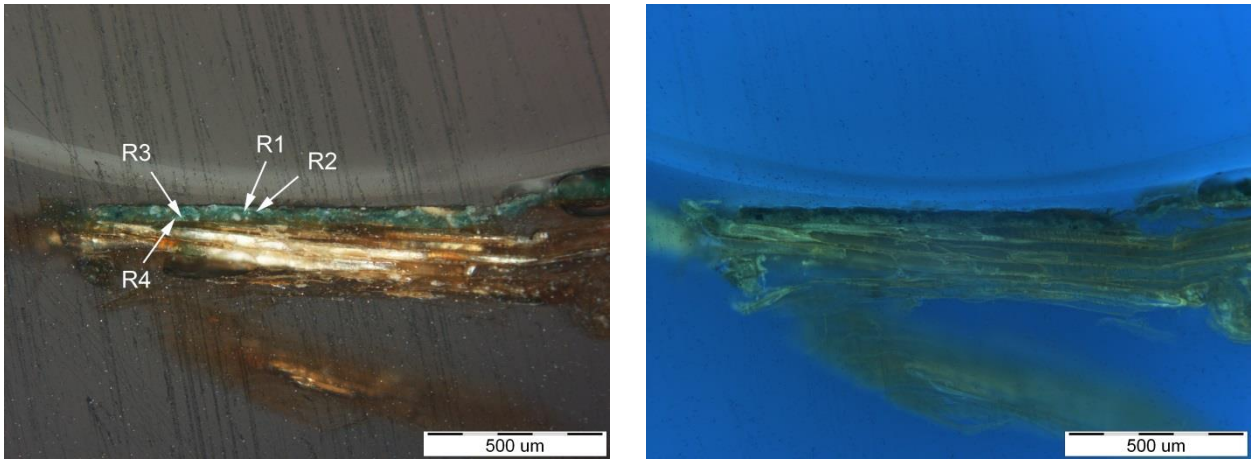
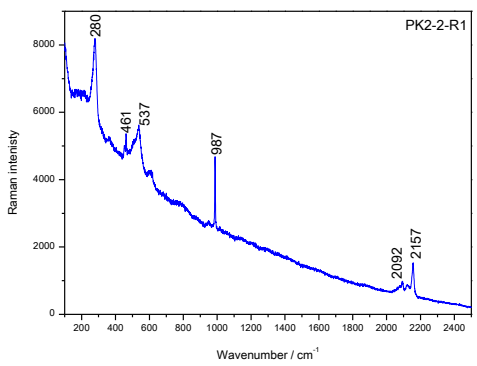
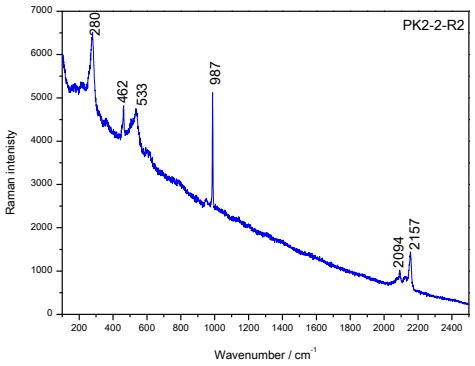
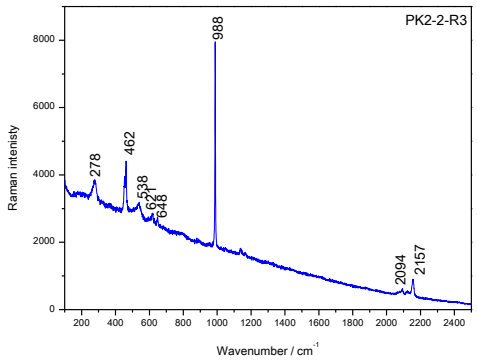
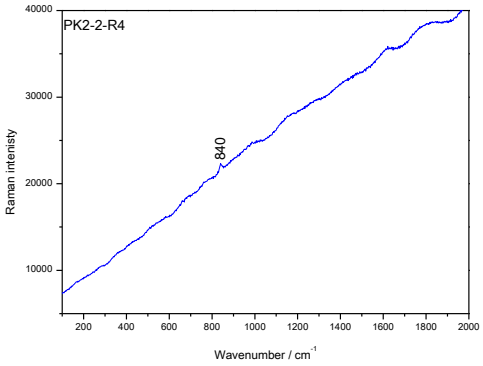


Figure 14: Optical images of cross-section of the sample PK2-2 in visible (left image) with marked locations of Raman analysis (R1 – R4) and UV-light (right image).

Table 14: Raman spectra obtained on different locations of cross section of the sample PK2-2 with identification.

a) PK2-2-R1	b) PK2-2-R2
 Identified material: **Prussian blue** (280, 537, 2092, 2157 cm^{-1}), **barium sulphate** (461, 987 cm^{-1})**.**	 Identified material: **Prussian blue** (280, 533, 2094, 2157 cm^{-1})**, barium sulphate** (462, 987 cm^{-1}).

c) PK2-2-R3	d) PK2-2-R4
	
Identified material: **Prussian blue** (278, 538, 648, 2094, 2157 cm^{-1})**, barium sulphate** (462, 621, 988 cm^{-1})**.**	Identified material: most likely lead(II) chromate (chrome yellow; 840 cm^{-1}).

c) Sample PK2-2b

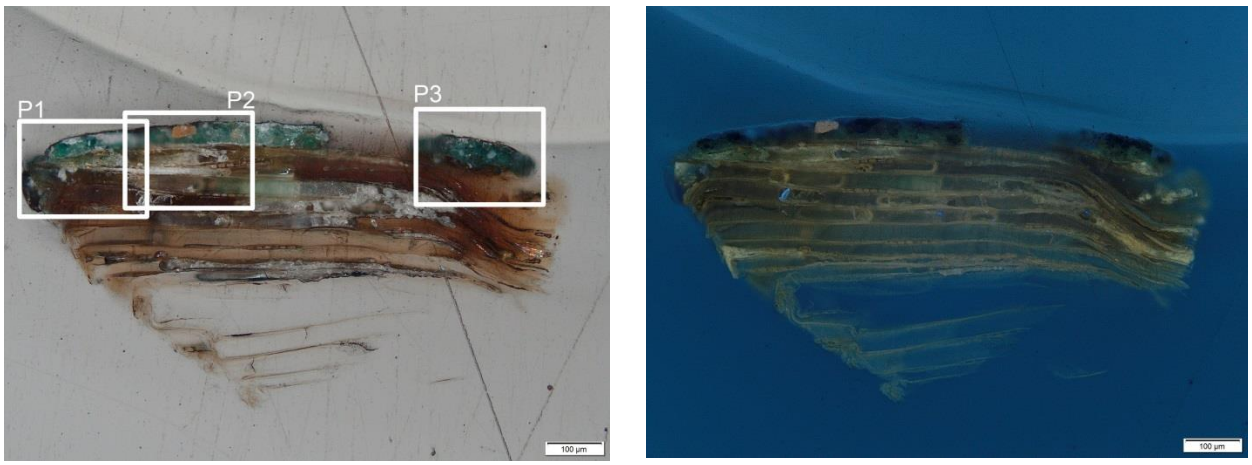


Figure 15: Optical images of cross-section of the sample PK2-2b in visible (left image) with marked general regions of Raman analysis and UV-light (right image).

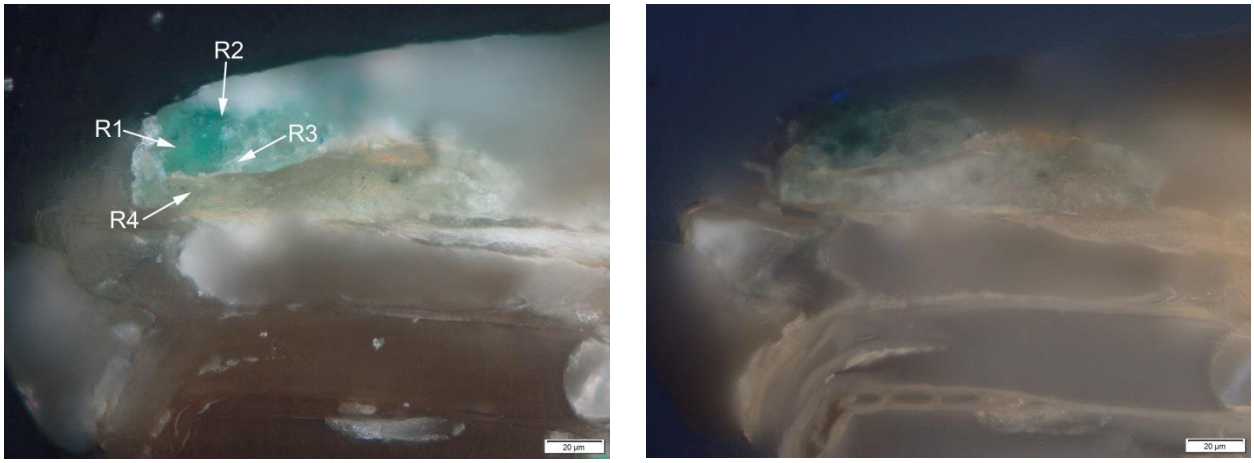


Figure 16: Optical images of region P1 of cross-section of the sample PK2-2b in visible (left image) with marked locations of Raman analysis (R1 – R4) and UV-light (right image).

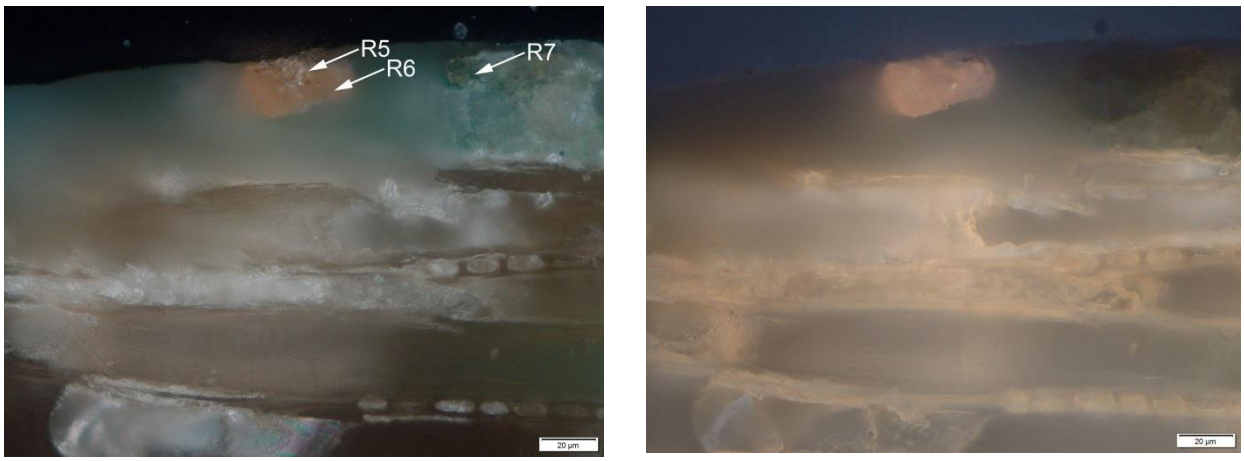


Figure 17: Optical images of region P2 of cross-section of the sample PK2-2b in visible (left image) with marked locations of Raman analysis (R5 – R7) and UV-light (right image).

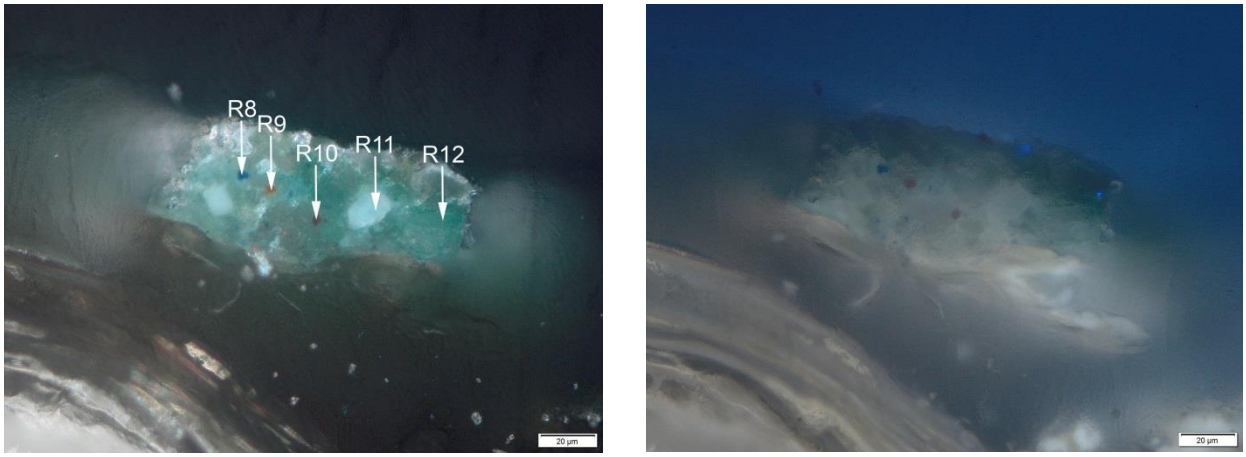
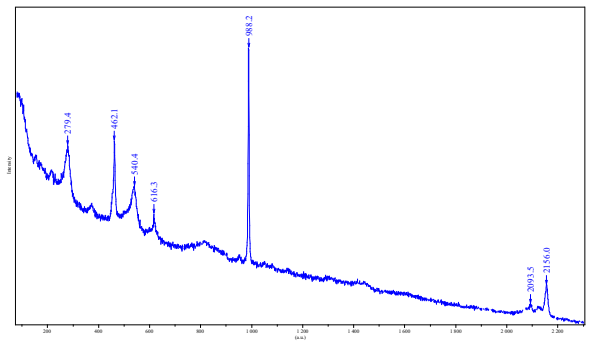
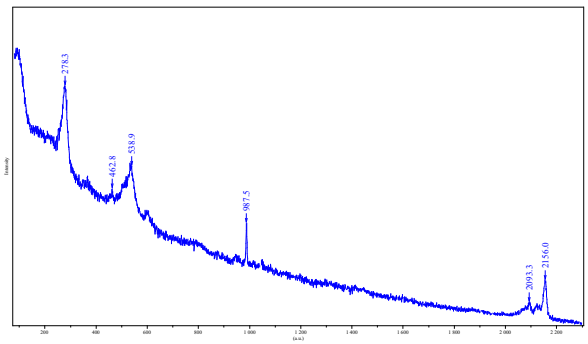
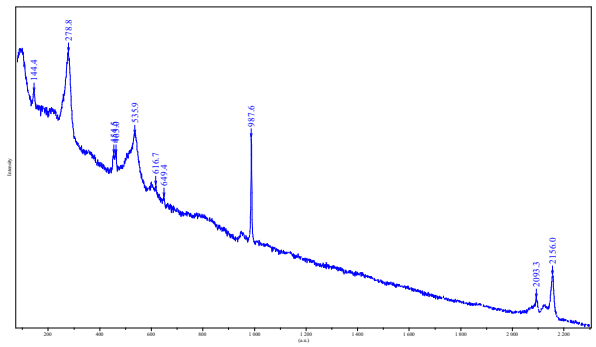
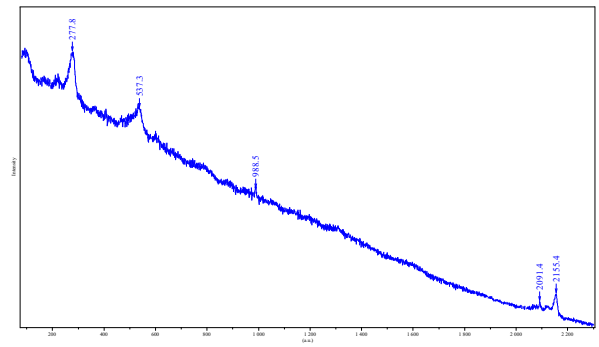
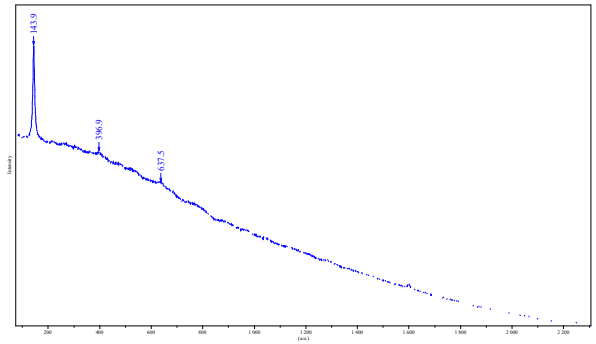
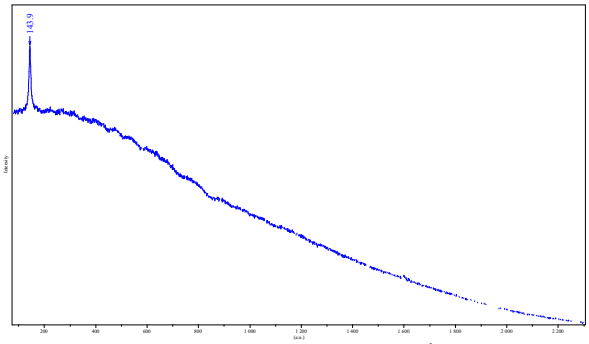
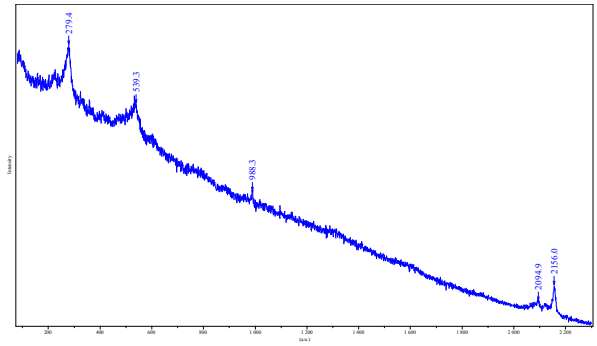
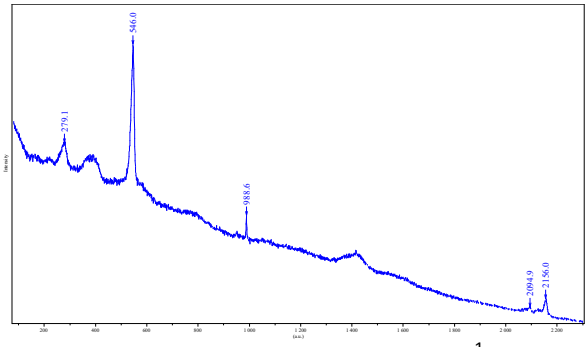


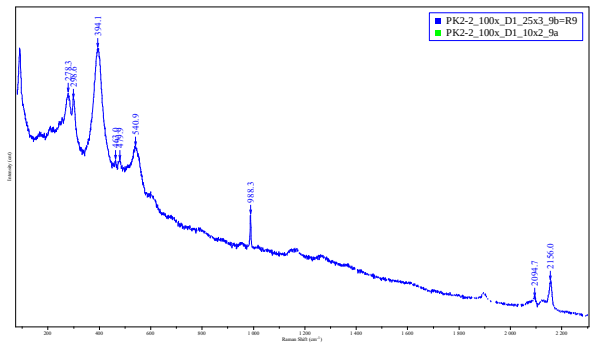
Figure 18: Optical images of region P3 of cross-section of the sample PK2-2b in visible (left image) with marked locations of Raman analysis (R8 – R12) and UV-light (right image).

Table 15:Raman spectra obtained on different locations of cross section of the sample PK2-2b with identification.

a) PK2-2b-R1	b) PK2-2b-R2
	
Identified material: **prussian blue** (279, 540, 2093, 2156 cm^{-1}), **barium sulphate** (462, 616, 988 cm^{-1}),	Identified material: **prussian blue** (278, 539, 2093, 2156 cm^{-1}), **barium sulphate** (463, 988 cm^{-1}).
c) PK2-2b-R3	**d) PK2-2b-R4**
	
Identified material: **prussian blue** (279, 536, 2093, 2156 cm^{-1}), **barium sulphate** (455, 463, 617, 649, 988 cm^{-1}), **anatase** (144 cm^{-1}).	Identified material: **prussian blue** (278, 537, 2091, 2155 cm^{-1}), **barium sulphate** (989 cm^{-1}).

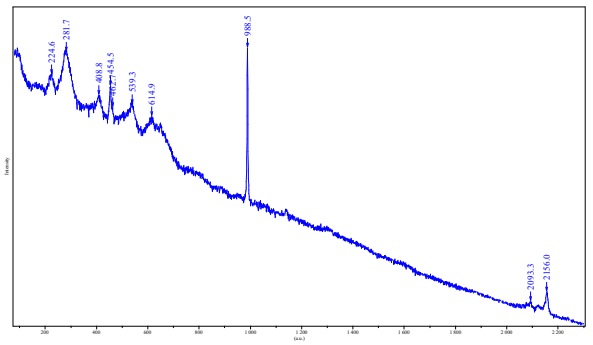
e) PK2-2b-R5	f) PK2-2b-R6
	
Identified material: **anatase** (144, 397, 638 cm^{-1}).	Identified material: **anatase** (144 cm^{-1}).
g) PK2-2b-R7	h) PK2-2b-R8
	
Identified material: **prussian blue** (279, 539, 2095, 2156 cm^{-1}), **barium sulphate** (988 cm^{-1}).	Identified material: **ultramarine** (546 cm^{-1}), **prussian blue** (279, 2095, 2156 cm^{-1}), **barium sulphate** (989 cm^{-1}).

i) PK2-2b-R9



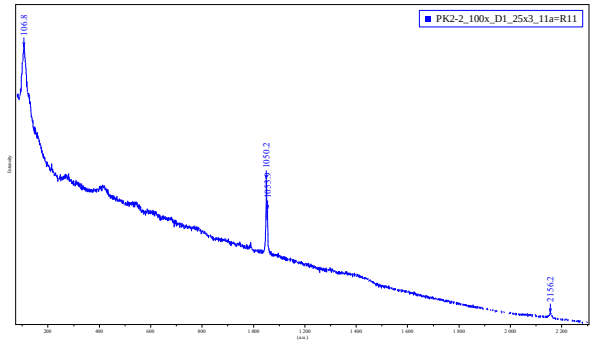
Identified material: **prussian blue** (278, 541, 2095, 2156 cm^{-1}), **barium sulphate** (463, 988 cm^{-1}), **iron hydroxide** (likely goethite type – bands at 299, 394, 480 cm^{-1}).

j) PK2-2b-R10



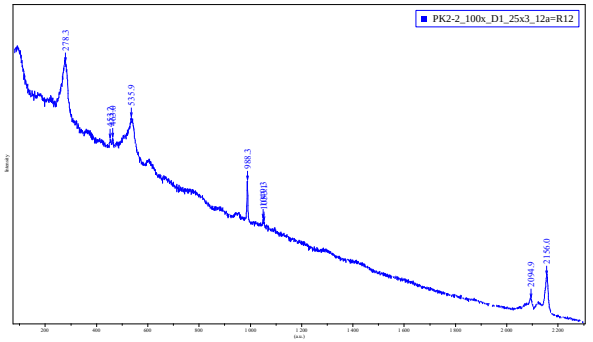
Identified material: **prussian blue** (282, 539, 2093, 2156 cm^{-1}), **barium sulphate** (454, 463, 988 cm^{-1}), **iron oxide** (likely haematite type – bands at 225, 409, 615 cm^{-1}).

k) PK2-2b-R11



Identified material: **lead white** (107, 1050, 1054 cm^{-1}), **prussian blue** (2156 cm^{-1}).

l) PK2-2b-R12



Identified material: **prussian blue** (278, 536, 2095, 2156 cm^{-1}), **barium sulphate** (453, 463, 988 cm^{-1}), **lead white** (1049, 1053 cm^{-1}).

d) Sample PK2-3

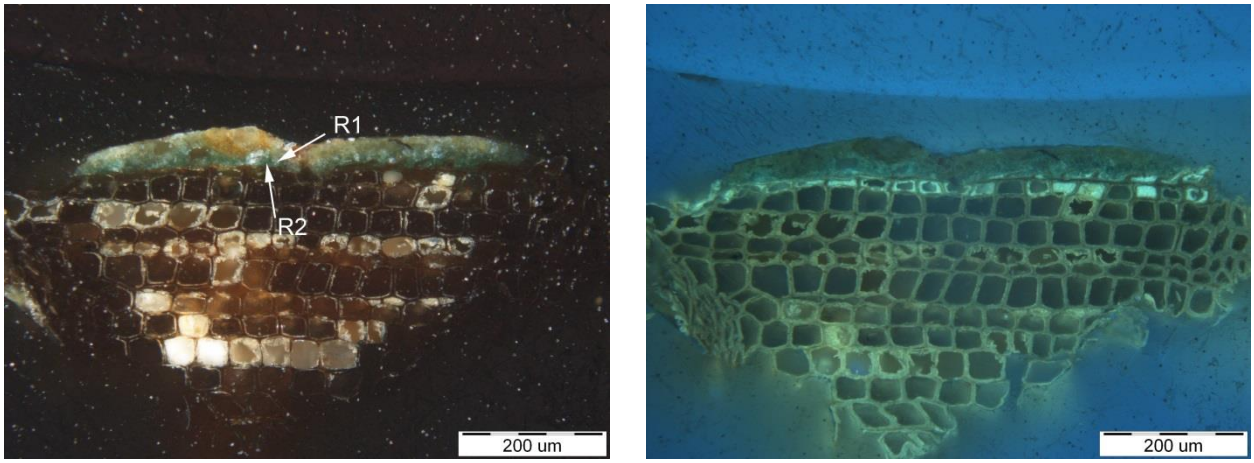
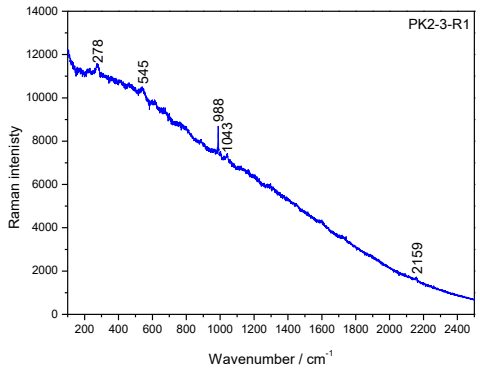
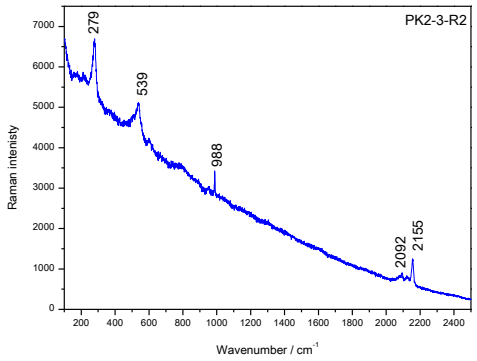


Figure 19: Optical images of cross-section of the sample PK2-3 in visible (left image) and UV-light (right image) with marked locations of Raman analysis (R1, R2).

Table 16: Raman spectra obtained on different locations of cross section of the sample PK2-3 with identification.

a) PK2-3-R1	b) PK2-3-R2
 Identified material: **Prussian blue** (278, 545, 2159 cm^{-1}), **barium sulphate** (988 cm^{-1})**,** posibbly also lead white.	 Identified material: **Prussian blue** (279, 539, 2092, 2155 cm^{-1})**, barium sulphate** (988 cm^{-1}).

e) Sample PK2-4

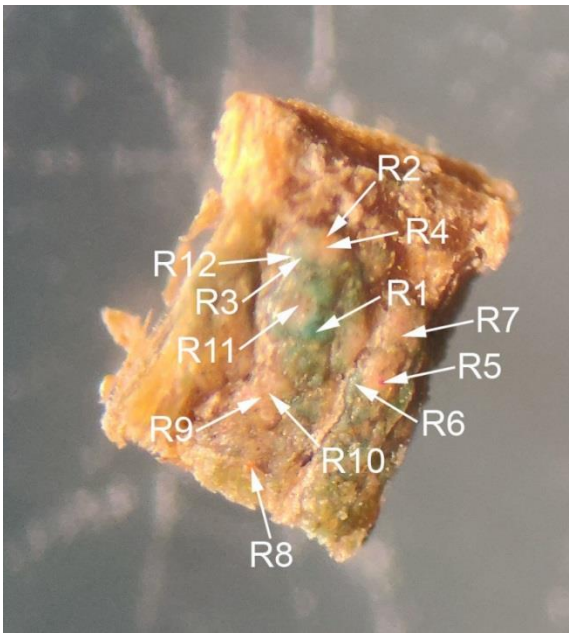
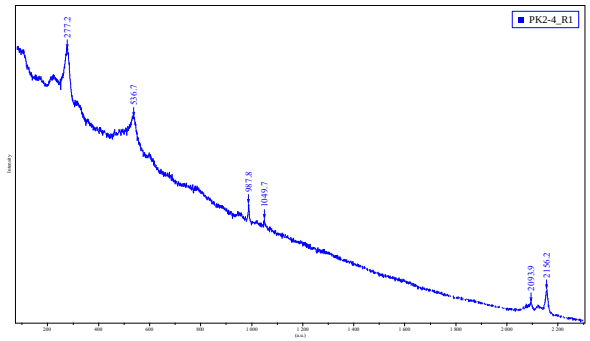
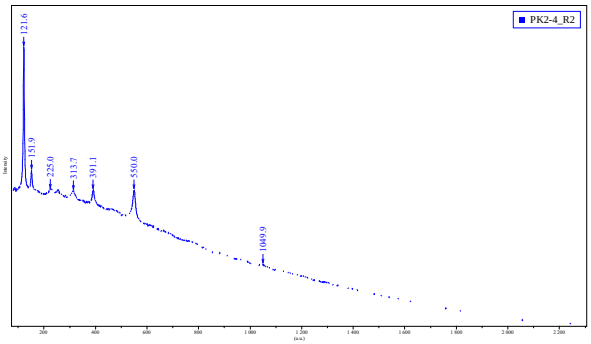
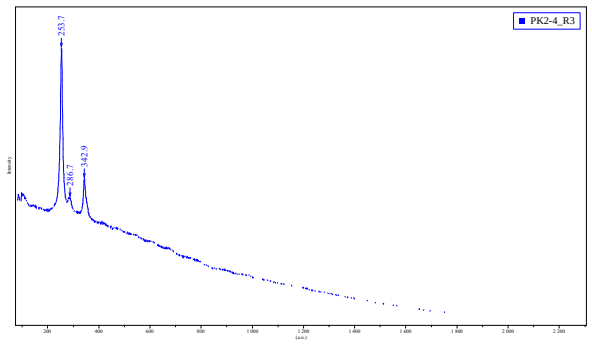
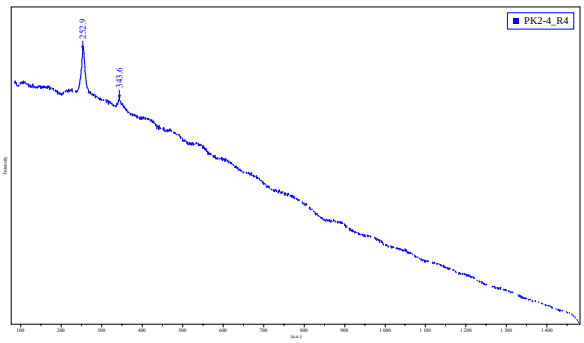
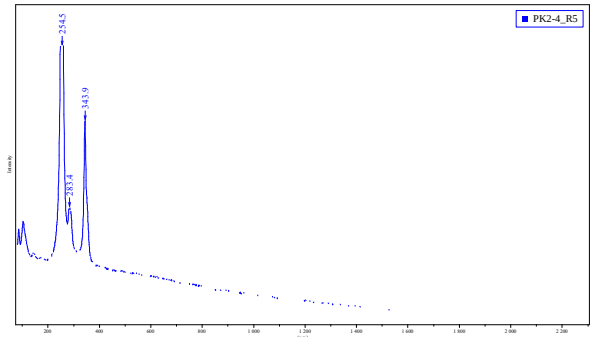
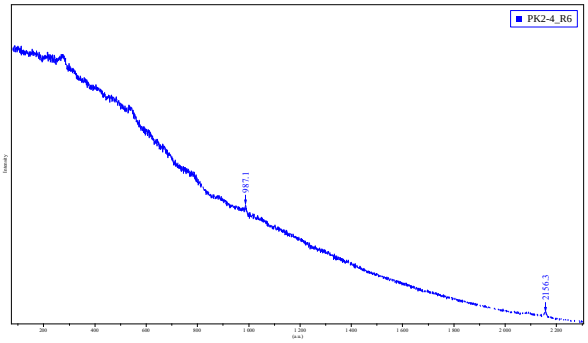
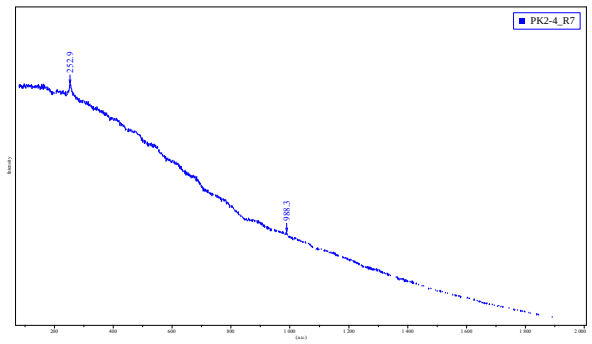
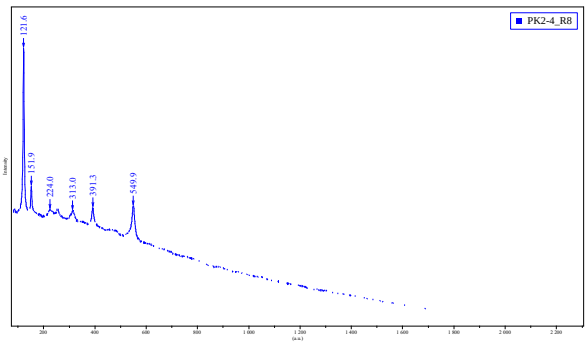
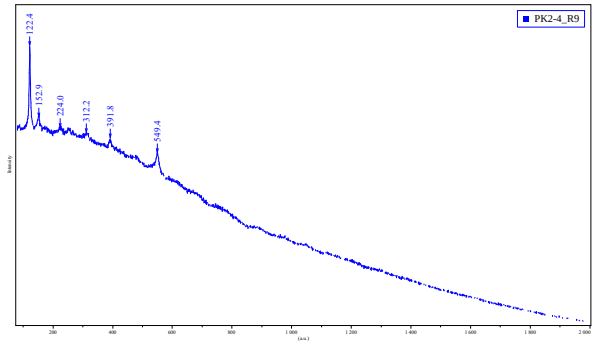
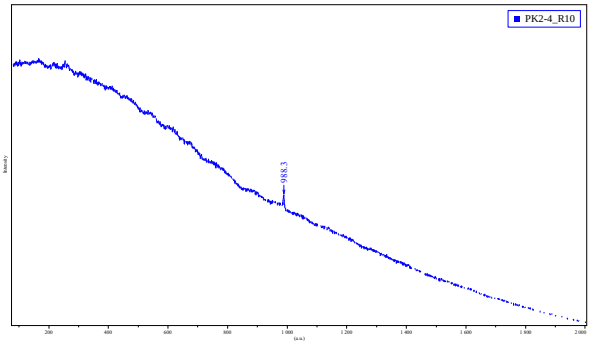


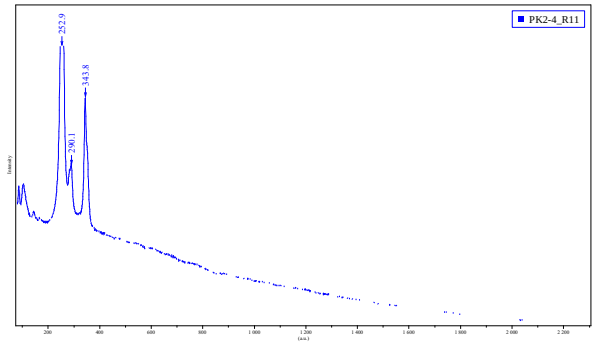
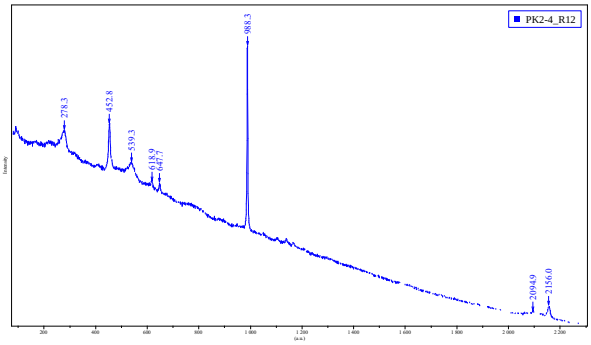
Figure 20: Optical images of the sample PK2-4 in visible light with marked locations of Raman analysis (R1 - R12).

Table 17: Raman spectra obtained on different locations of the sample PK2-4 with identification.

a) PK2-4-R1	b) PK2-4-R2
 Identified material: **prussian blue** (277, 537, 2094, 2156 cm^{-1}), **barium sulphate** (463, 988 cm^{-1}), **lead white** (1050 cm^{-1}).	 Identified material: **lead (II, IV) oxide** (minium – bands at 122, 152, 225, 314, 391, 550 cm^{-1}), **lead white** (1050 cm^{-1}).

c) PK2-4-R3	d) PK2-4-R4
	
Identified material: **cinnabar/vermilion** (254, 287, 343 cm^{-1}).	Identified material: **cinnabar/vermilion** (253, 344 cm^{-1}).
e) PK2-4-R5	**f) PK2-4-R6**
	
Identified material: **cinnabar/vermilion** (255, 283, 344 cm^{-1}).	Identified material: **prussian blue** (2156 cm^{-1}), **barium sulphate** (987 cm^{-1}).

g) PK2-4-R7	h) PK2-4-R8
	
Identified material: **cinnabar/vermilion** (253 cm^{-1}), **barium sulphate** (988 cm^{-1}).	Identified material: **lead (II, IV) oxide** (minium – bands at 122, 152, 224, 313, 391, 550 cm^{-1}).
i) PK2-4-R9	j) PK2-4-R10
	
Identified material: **lead (II, IV) oxide** (minium – bands at 122, 153, 224, 312, 392, 549 cm^{-1}).	Identified material: **barium sulphate** (988 cm^{-1}).

k) PK2-4-R11	l) PK2-4-R12
	
Identified material: **cinnabar/vermilion** (253, 290, 344 cm^{-1}).	Identified material: **prussian blue** (278, 539, 2095, 2156 cm^{-1}), **barium sulphate** (453, 619, 648, 988 cm^{-1}).

4.2.2.3 Other locations

In this chapter, the additional location of Raman measurments are marked, but the signal was obscured by the fluorescence.

Figure 21: Locations of noninvasive Raman measurments of beehive panel marked as PK2, where material identification was not possible due to fluorescence

Table 18: Description of Raman spectroscopy measurment locations on beehive panel marked as PK2, where no material identification was possible

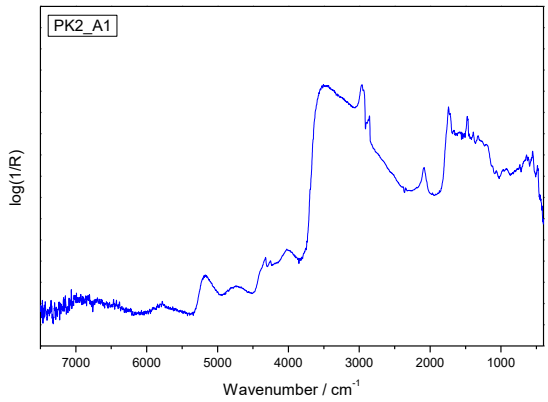
Label of analysis	Colour	Description	Laser wavelength [nm]
fl1	green	tree on the left side of the panel; green treetop on the right side of the tree, near the upper edge of the panel	514
fl2	light green	female figure; fifth figure from the left; women's dress; light green apron; central part of the apron	514
fl3	reddish-brown	male figure; first figure from the left; man's right leg; boot; contour of the boot on the left-hand side	785
fl4	green and reddish-brown	male figure; first figure from the left; man's right leg; boot; contour of the botto part of the trousers under the knee; green paint (possibly underpainting or background colour) with remains of reddish-brown contour	785

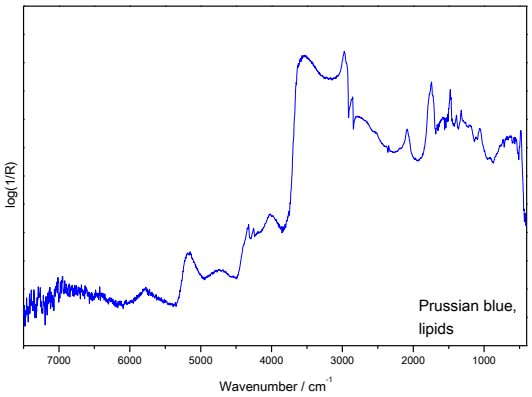
fl5	brownish-green	male figure; first figure from the left; bag; lower right part of the bag; inner colour of the bag; brownish-green paint (paint in upper stratigraphical layer or paint in lower stratigraphical layer (possibly background colour) or both)	785
fl6	black	left edge of the panel; painted black border	785
fl7	white-yellowish	male figure; first figure from the left; man's white-yellowish shirt; right bottom part of the shirt, above the knee of man's left leg; wood, possible remains of white-yellowih paint, green underpaint or backround colour and reddish-brown contour of a fold	785
fl8	green	tree on the left side of the panel; green treetop on the right side of the tree, near the upper edge of the panel	785
fl9	blue	skirt contour	785
fl10	black	signature	785
fl11	green	tree on the left side of the panel; green treetop on the right side of the tree, near the upper edge of the panel	785
fl12	white-yellowish	male figure; first figure from the left; man's white-yellowish shirt; sleeve of man's right upper arm; right side of the upper arm	785
fl13	white-yellowish	female figure; third figure from the left; woman's white-yellowish shirt; sleeve of woman's right upper arm near the elbow	785
fl14	white	female figure; fifth figure from the left; bundle on woman's back; central part of the bag	785
fl15	white	female figure; fifth figure from the left; bundle on woman's back; lower left part of the bag	785
fl16	white-yellowish	male figure; first figure from the left; man's white-yellowish shirt; sleeve of man's right upper arm; right side of the upper arm	785
fl17	light green	female figure; fifth figure from the left; women's dress; light green apron; right bottom part of the apron	785

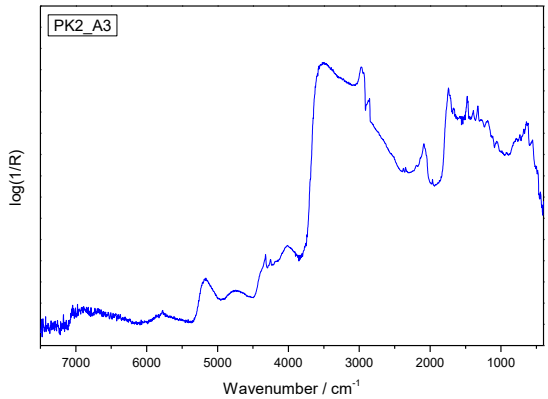
fl18	light green	female figure; fifth figure from the left; women's dress; light green apron; right bottom part of the apron	785
fl19	ochre-brown	tree on the right side of the panel; trunk of the tree; middle part of the trunk; inner ochre-brown paint	785

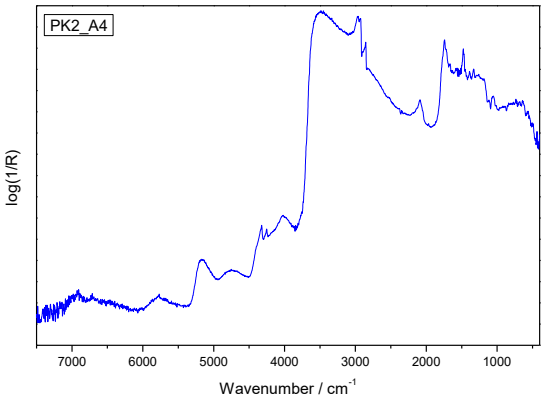
4.2.3 Reflection FTIR spectroscopy

Table 19: Reflection infrared spectra obtained on different locations of beehive panel marked as PK2 with identification.

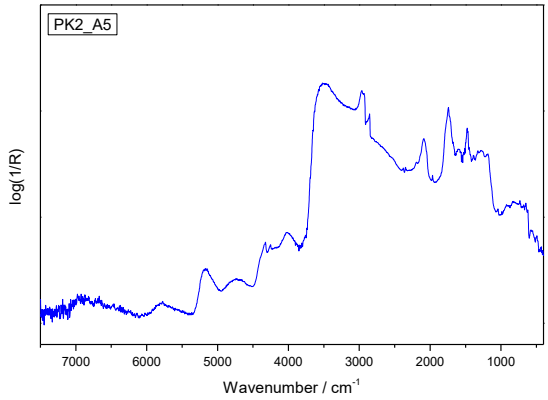
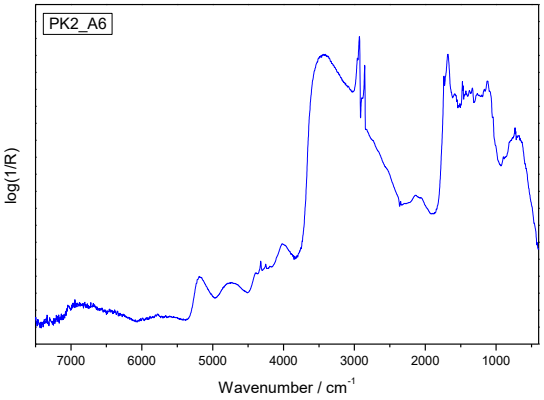
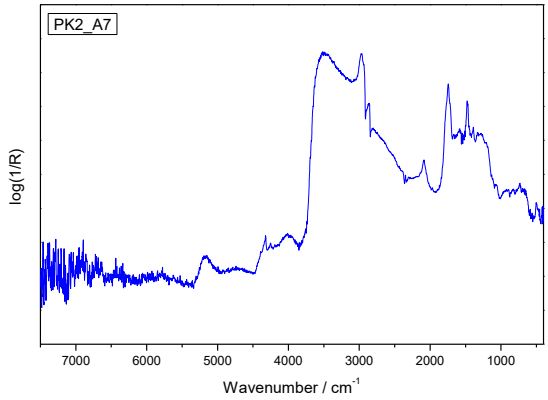
<table>
<tr><td>a) PK2-A1</td><td>b) PK2-A2</td></tr>
<tr><td> 

Identified material: lipids, Prussian blue, barium sulphate, triterpenoid resin, oxalate, beeswax</td><td> 

Identified material: lipids, Prussian blue, triterpenoid resin, oxalate, beeswax</td></tr>
<tr><td>c) PK2-A3</td><td>d) PK2-A4</td></tr>
<tr><td> 

Identified material: lipids, Prussian blue, barium sulphate, oxalate, triterpenoid resin,</td><td> 

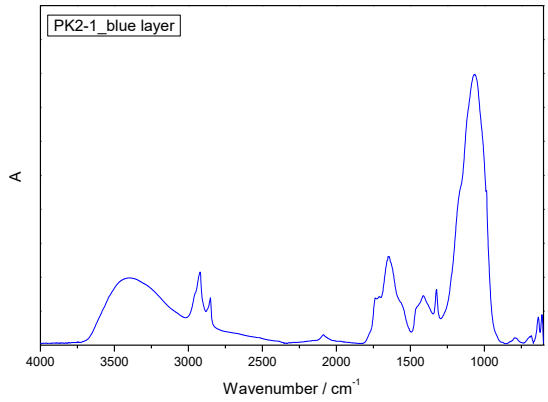
Identified material: lipids, Prussian blue, barium sulphate, triterpenoid resin, oxalate, beeswax in traces</td></tr>
</table>

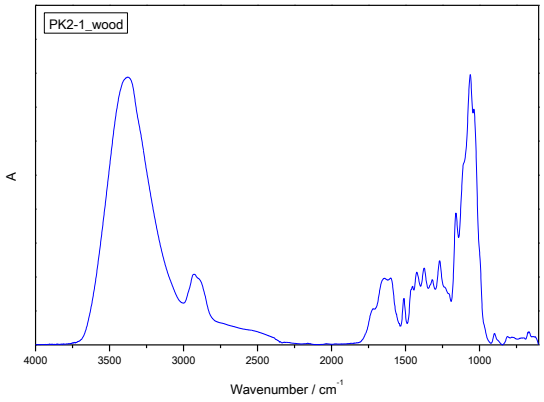
beeswax in traces	
e) PK2-A5	f) PK2-A6
 Identified material: **lipids, Prussian blue, barium sulphate, beeswax, triterpenic resin**	 Identified material:**lipids, wood components** (hemicellulose, lignin,cellulose)[1,2]**, beeswax**
g) PK2-A7	
 Identified material: **lipids, prussian blue, barium sulphate, triterpenic resin, beeswax**	

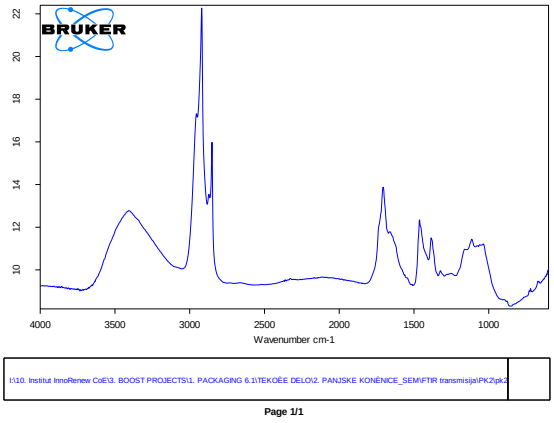
4.2.4 Transmission FTIR spectroscopy

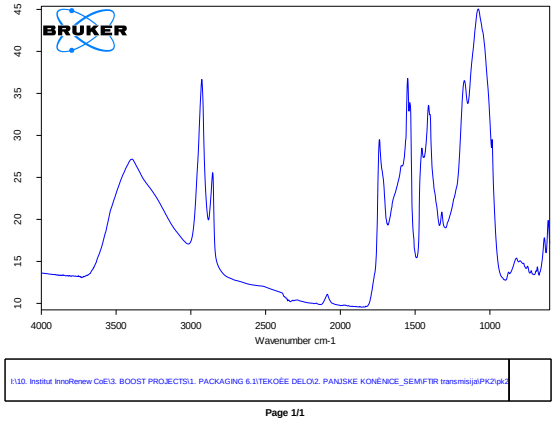
a) Sample PK2-1

Table 20: Transmission spectra obtained on different layers of sample marked as PK2-1 with identification.

<table>
<tr><td>a) PK2-1_blue layer</td><td>b) PK2-1_wood</td></tr>
<tr><td> 

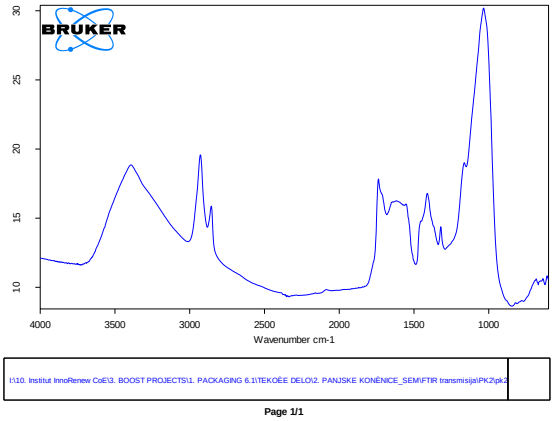
Identified material: Prussian blue, barium sulphate, oxalate, lipids</td><td> 

Identified material: Wood components (hemicellulose, lignin,cellulose)[1,2]</td></tr>
<tr><td>c) PK2-1_blue layer_1 (seen as transparent under the microscope)</td><td>d) PK2-1_bluelayer_2</td></tr>
<tr><td> 

Identified material: triterpenic resin, oxalate.</td><td> 

Identified material: prussian blue, oxalate, barium sulphate, lipids, carboxylates</td></tr>
</table>

e) PK2-1_bluelayer_3

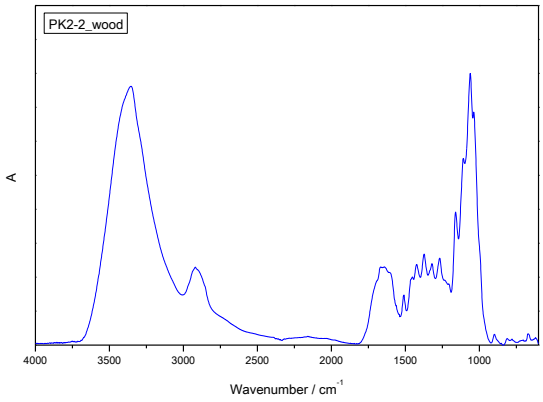


Identified material: **prussian blue, oxalate**.

b) Sample PK2-2

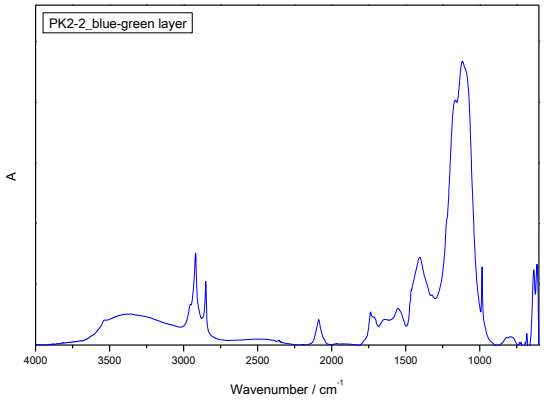
Table 21: Transmission spectra obtained on different layers of sample marked as PK2-2 with identification.

f) PK2-2_wood



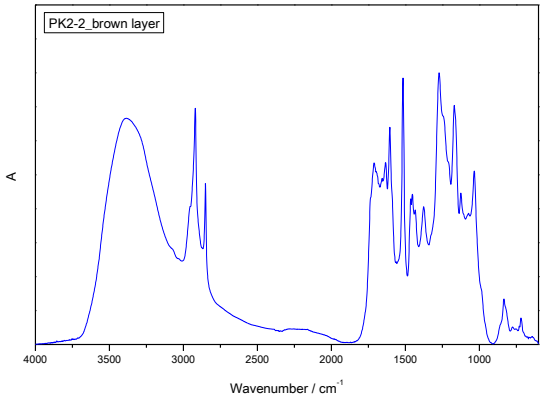
Identified material: **Wood components** (hemicellulose, lignin,cellulose)

g) PK2-2_blue-green layer



Identified material: **Prussian blue, barium sulphate, lipids, oxalate, beeswax, lead white**

h) PK2-2_brown layer

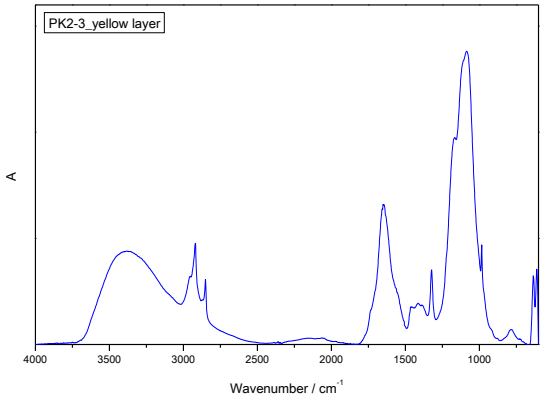


Identified material: **carnauba wax, non identified bands**

c) Sample PK2-3

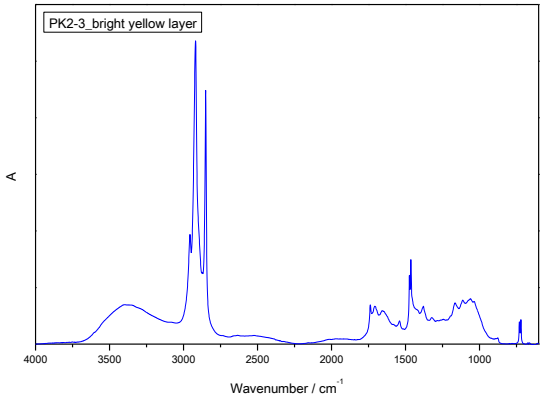
Table 22: Transmission spectra obtained on different layers of sample marked as PK2-3 with identification.

a) PK2-3_yellow layer



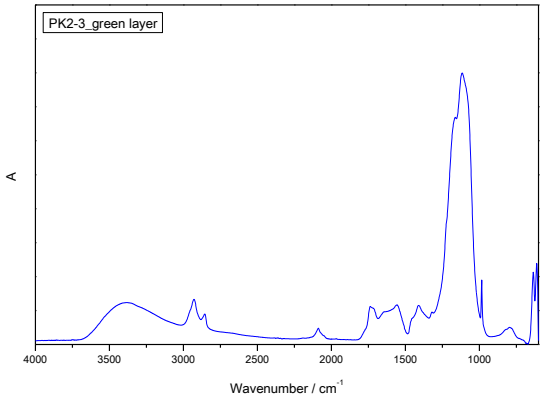
Identified material: **Barium sulphate, oxalate**

b) PK2-3_bright yellow layer



Identified material: **beeswax, triterpenoid resin, carboxylate, oxalate**

c) PK2-3_green layer



d) Identified material: **barium sulphate, prussian blue, lipids, oxalate**

4.2.5 Gathered results

Label of analysis	Surface paint colour/material	Location description	Identified material
R1	red	female figure; second figure from the left; woman's right shoulder; red scarf	cinnabar/vermilion
A1	red	female figure; fifth figure from the left; woman's red skirt; left bottom part of the red skirt	lipids, Prussian blue, barium sulphate, triterpenoid resin, oxalate, beeswax
R2	reddish-brown	female figure; third figure from the left; woman's hair	iron oxide (Fe_2O_3)
R3	reddish-brown	female figure; third figure from the left; woman's face; contour of lower jaw	iron oxide (Fe_2O_3), cinnabar/vermilion, carbon-based black
PK2-4	undetermined colour (damaged upper colour layer, greeinsh tinge possible from the underlayer)	female figure; third figure from the left; woman's face; cheek; residues of skin tone colour on greenish or bluish underpaint layer	prussian blue, barium sulphate, lead white, lead(II, IV) oxide (minium), cinnabar/vermilion
R4	green	upper left side of the panel; green treetop on the left side of the tree, close to man's hat	barium sulphate
A4	light colour (whitish/yellowish/greenish)	male figure; first figure from the left; man's white-yellowish shirt; sleeve of man's right upper arm; right side of the upper arm; either painted shadow or greenish underpainting (possibly background colour) positioned under the paint layer of the sleeve	lipids, Prussian blue, barium sulphate, triterpenoid resin, oxalate, beeswax in traces
R5	green	tree on the left side of the panel; green treetop on the left side of the tree, close to man's hat	barium sulphate, prussian blue,
A5		tree on the left side of the panel; green treetop on the right side of the tree, near the upper edge of the panel	lipids, Prussian blue, barium sulphate, beeswax, triterpenic resin
PK2-2		tree on left side of the panel; upper edge of the panel; green treetop on the left side of the tree	prussian blue, barium sulphate, lead (II) chromate (chrome yellow, ?), wood component, lipids, oxalate, beeswax, lead

			white, carnauba wax
PK2-2b			Prussian blue, barium sulphate, anatase, ultramarine, iron hydroxide (goethite type), iron oxide (haematite type), lead white, quartz?, carnauba wax
R6	white-yellowish	female figure; fortht figure from the left; woman's left leg; white-yellowish colour of socks or pants between the skirt and the shoe	calcium carbonate (?)
A6	wood	back of the panel; wood	lipids, wood components (hemicellulose, lignin,cellulose), beeswax
R7	light green	female figure; fifth figure from the left; women's dress; light green apron; upper part of the apron	barium sulphate
A7	reddish-brown	female figure; fifth figure from the left; woman's hair	lipids, prussian blue, barium sulphate, triterpenic resin, beeswax
R8	ochre-brown	tree on the right side of the panel; left branch of the tree; inner ochre-brown paint	cinnabar/vermilion (?)
R9	blue	female figure; second figure from the left; woman's skirt; blue contour (hem) on the bottom of woman's skirt; left side of the contour line	ultramarine
R10	blue	female figure; second figure from the left; woman's skirt; blue contour (hem) on the bottom of woman's skirt; left side of the contour line	ultramarine
R11	dark blue	female figure; fourth figure from the left; woman's skirt; dark blue contour (hem) at the bottom of woman's skirt; right side of the contour line	ultramarine
A2			lipids, Prussian blue, triterpenoid resin, oxalate, beeswax
PK2-1			ultramarine, prussian blue, cinnabar, barium sulphate, calcium carbonate (calcite type), iron oxide (haematite type), Emerald green (as impurity?) lead white, oxalate, lipids, carboxylates, wood component, triterpenic resin
R12	dark blue	female figure; fourth figure from the left; woman's skirt; dark blue contour (hem) at the bottom of woman's skirt;	ultramarine

		middle part of the contour line	
R13	black	left edge of the panel; painted black border	carbon-based black
R14	blue	female figure; second figure from the left; woman's skirt; blue contour of a fold on the upper part of woman's skirt	ultramarine
R15	black	date (1882); upper part of no. 2	carbon-based black
R16	reddish-brown	trousers between the third and the fourth female figure; above the women's hands; right side of the braces	iron oxide (Fe_2O_3), carbon-based black
R17	reddish brown	trousers between the third and the fourth female figure; above the women's hands; right side of the braces	iron oxide (Fe_2O_3), carbon-based black
R18	green	tree on the right side of the panel; green treetop on the left side of the tree, above the head of the fifth figure from the left	barium sulphate, prussian blue
R19	light green	female figure; fifth figure from the left; woman's dress; light green apron; upper part of the apron	barium sulphate
A3		female figure; fifth figure from the left; woman's dress; light green apron; right bottom part of the apron	lipids, Prussian blue, barium sulphate, oxalate, triterpenoid resin, beeswax in traces
PK2-3		female figure; fifth figure from the left; woman's dress; light green apron; right bottom part of the apron	prussian blue, barium sulphate, lead white (???), oxalate, beeswax, triterpenic resin, carboxylate, oxalate, lipids

4.3 PK3

4.3.1 Marked locations of performed analysis

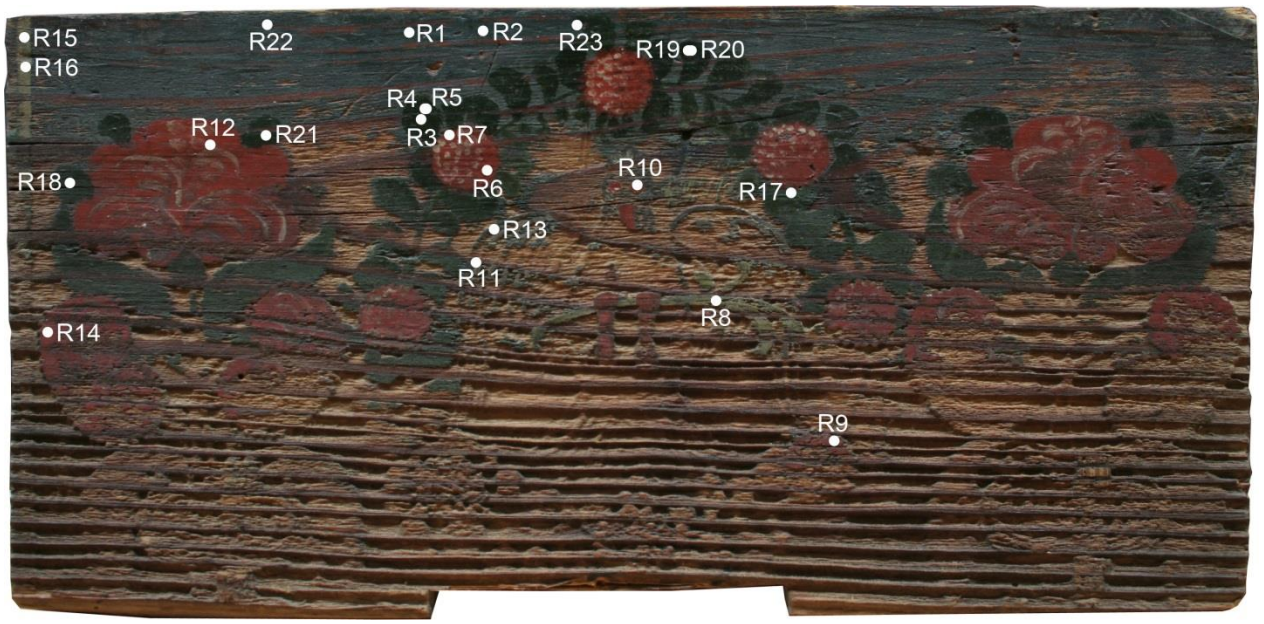


Figure 22: Marked locations of Raman analysis.

Figure 23: Marked locations of reflection FTIR analysis.

Figure 24: Marked locations of sample removal. The location of the removed sample is marked as PK3-1.

Table 23: Description of the removed samples

LABEL	TYPE	MICROLOCATION	PURPOSE
PK3-1	sample of paint layers on wooden support; sample consists of all stratigrafically present picture layers at the microlocation	middle part of the left edge of the panel; lower, uttermost left red flower; upper left edge of the flower	RAMAN, FTIR

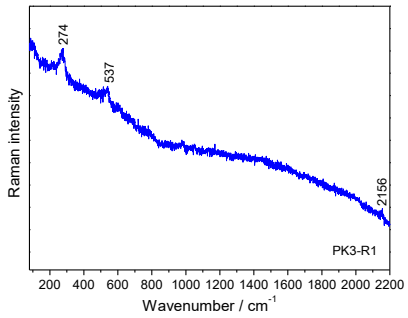
4.3.2 Raman spectroscopy

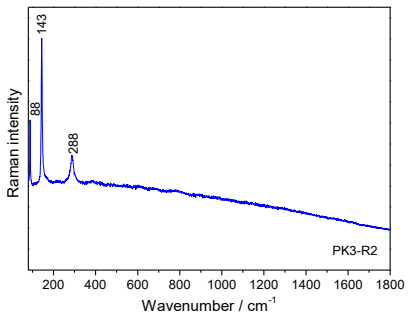
4.3.2.1 Non-invasive analysis

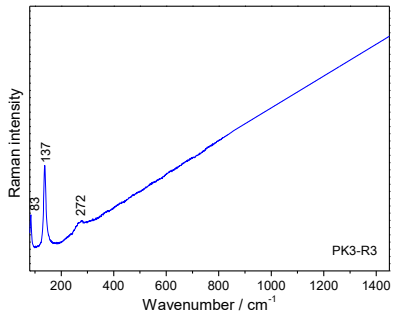
Raman spectra obtained at different locations on painted beehive panel marked as PK3 are presented on Table 24. Additionally, material identification based on the obtained spectra is gathered in.

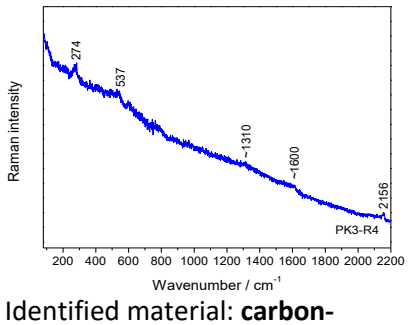
The locations of the obtained spectra from which no material could be identified are given in Figure 27 at the end of the report–said spectra are omitted from this report.

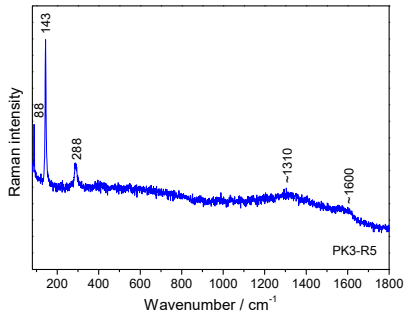
Table 24: Raman spectra obtained on different locations of beehive panel marked as PK3 with identification.

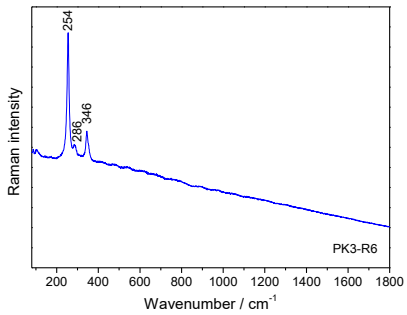
<table>
<tr><td>a) PK3-R1</td><td>b) PK3-R2</td><td>c) PK3-R3</td></tr>
<tr><td> 

Identified material: prussian blue (274, 537, 2156 cm^{-1}).</td><td> 

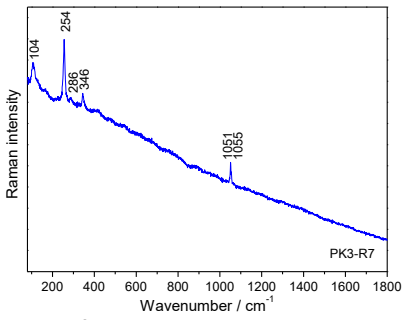
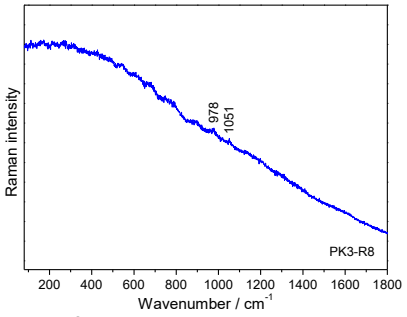
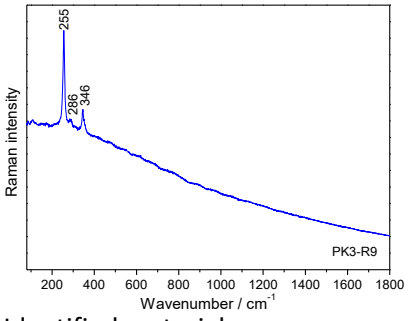
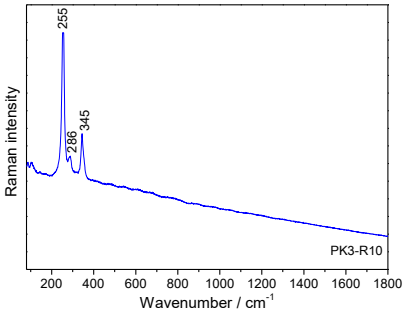
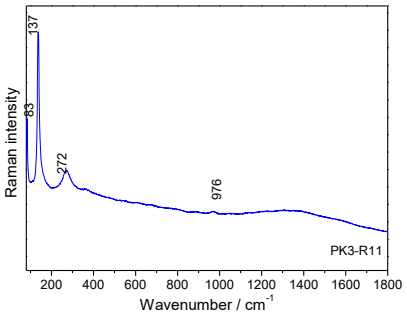
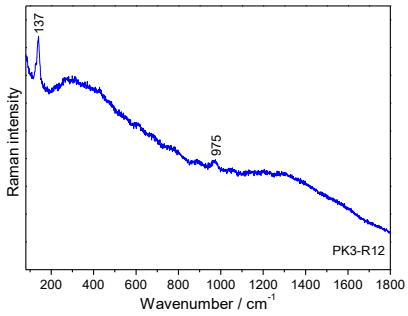
Identified material: lead oxide (likely massicot type – bands at 88, 143, 288 cm^{-1}).</td><td> 

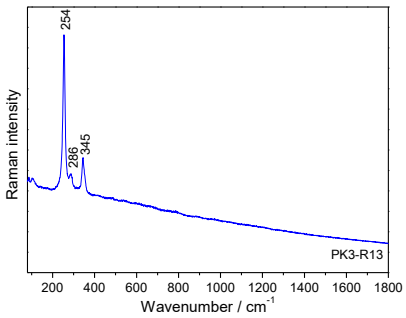
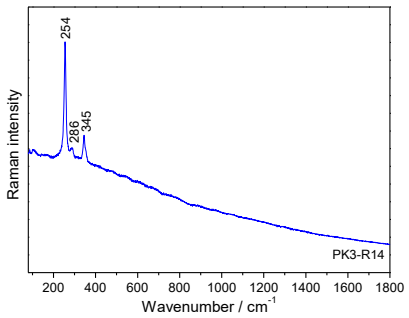
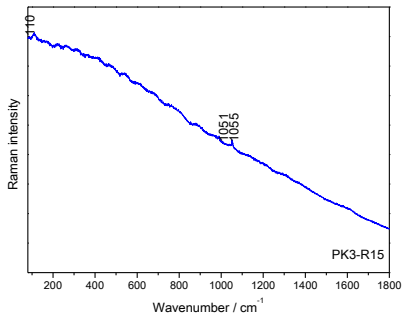
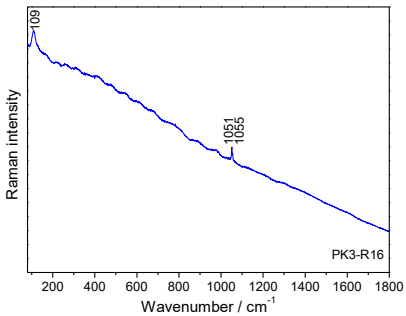
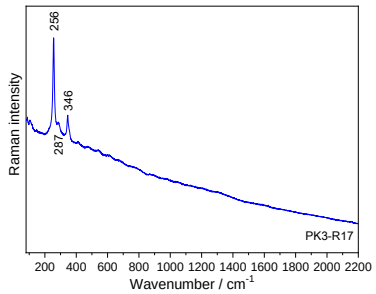
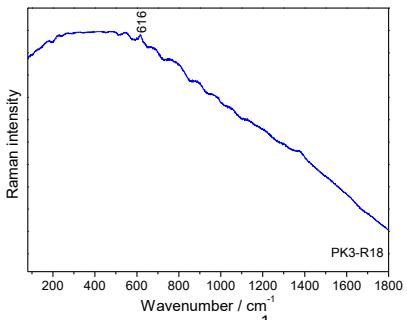
Identified material: lead oxide (likely massicot type – bands at 83, 137, 272 cm^{-1}).</td></tr>
<tr><td>d) PK3-R4</td><td>e) PK3-R5</td><td>f) PK3-R6</td></tr>
<tr><td> 

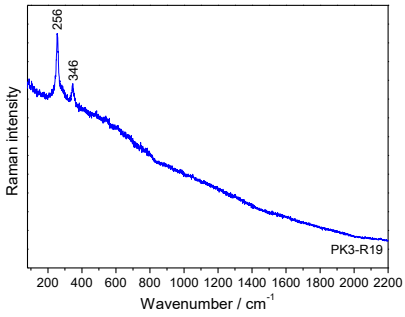
Identified material: carbon-based black (~1310, ~1600 cm^{-1}), prussian blue (274, 537, 2156 cm^{-1}).</td><td> 

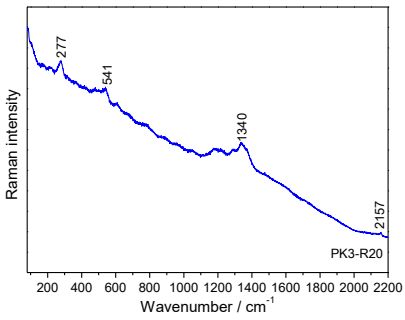
Identified material: lead oxide (likely massicot type – bands at 88, 143, 288 cm^{-1}), carbon-based black (~1310, 1600 cm^{-1}).</td><td> 

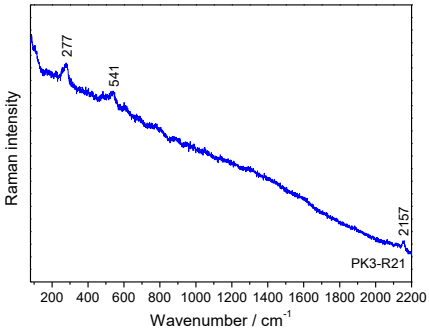
Identified material: cinnabar/vermilion (254, 286, 345 cm^{-1}).</td></tr>
</table>

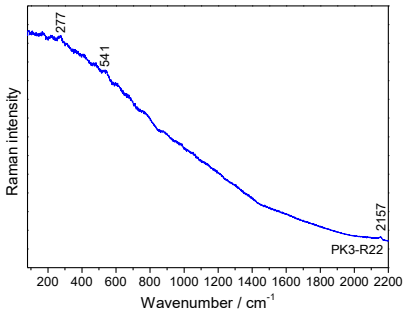
g) PK3-R7	h) PK3-R8	i) PK3-R9
 Identified material: **lead white** (104, 1051, 1055 cm^{-1}), **cinnabar/vermilion** (254, 285, 344 cm^{-1}).	 Identified material: **lead white** (1051 cm^{-1}), possibly lead sulphate (978 cm^{-1}).	 Identified material: **cinnabar/vermilion** (255, 286, 346 cm^{-1}).
j) PK3-R10	k) PK3-R11	l) PK3-R12
 Identified material: **cinnabar/vermilion** (255, 286, 345 cm^{-1}).	 Identified material: **lead oxide** (likely massicot type – bands at 83, 137, 272), possibly lead sulphate (976 cm^{-1}).	 Identified material: possibly lead sulphate (975 cm^{-1}), possibly lead oxide (likely massicot type – band at 137 cm^{-1}).

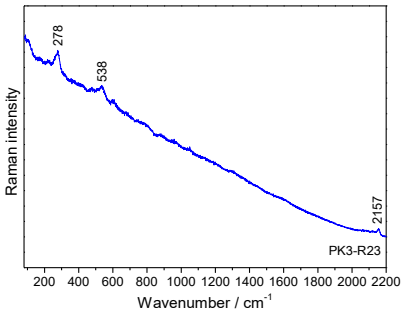
m) PK3-R13	n) PK3-R14	o) PK3-R15
 Identified material: **cinnabar/vermilion** (254, 286, 345 cm^{-1}).	 Identified material: **cinnabar/vermilion** (254, 286, 345 cm^{-1}).	 Identified material: **lead white** (110, 1051, 1055 cm^{-1}),
p) PK3-R16	q) PK3-R17	r) PK3-R18
 Identified material: **lead white** (109, 1051, 1055 cm^{-1}).	 Identified material: **cinnabar/vermilion** (256, 287, 346 cm^{-1}).	 Unidentified (616 cm^{-1}).

<table>
<tr><td>s) PK3-R19</td><td>t) PK3-R20</td><td>u) PK3-R21</td></tr>
<tr><td> 

Identified material: **cinnabar/vermilion** (256, 346 cm^{-1}) – impurity?.</td><td> 

Identified material: **prussian blue** (277, 541, 2157 cm^{-1}), unidentified (1340 cm^{-1}).</td><td> 

Identified material: **prussian blue** (277, 541, 2157 cm^{-1}).</td></tr>
<tr><td>v) PK3-R22</td><td>w) PK3-R23</td><td></td></tr>
<tr><td> 

Identified material: **prussian blue** (277, 541, 2157 cm^{-1}).</td><td> 

Identified material: **prussian blue** (278, 538, 2157 cm^{-1}).</td><td></td></tr>
</table>

4.3.2.2 Investigation of cross-sections of the removed samples

a) Sample PK3-1

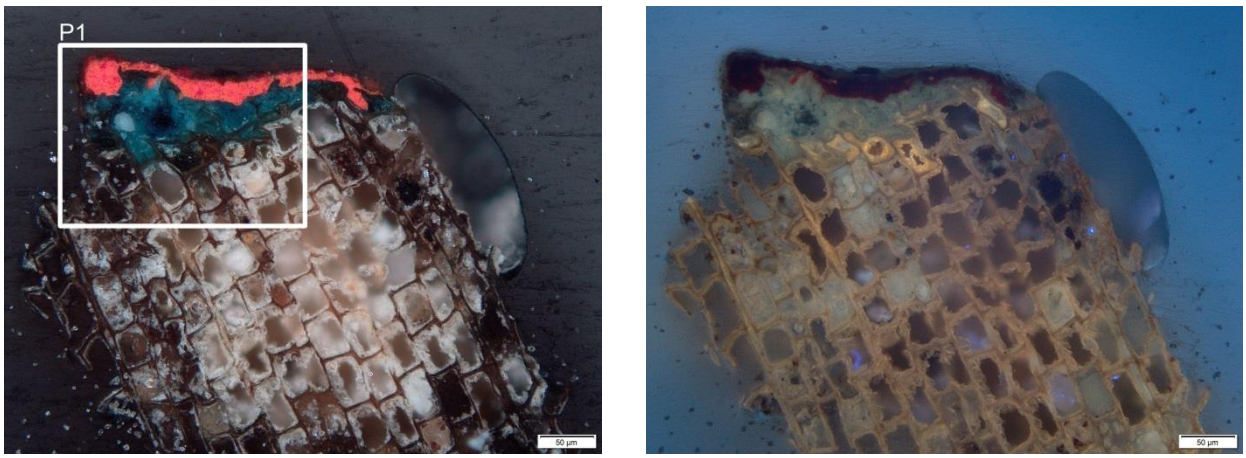


Figure 25: Optical images of cross-section of the sample PK3-1 in visible (left image) with marked general region of Raman analysis and UV-light (right image).

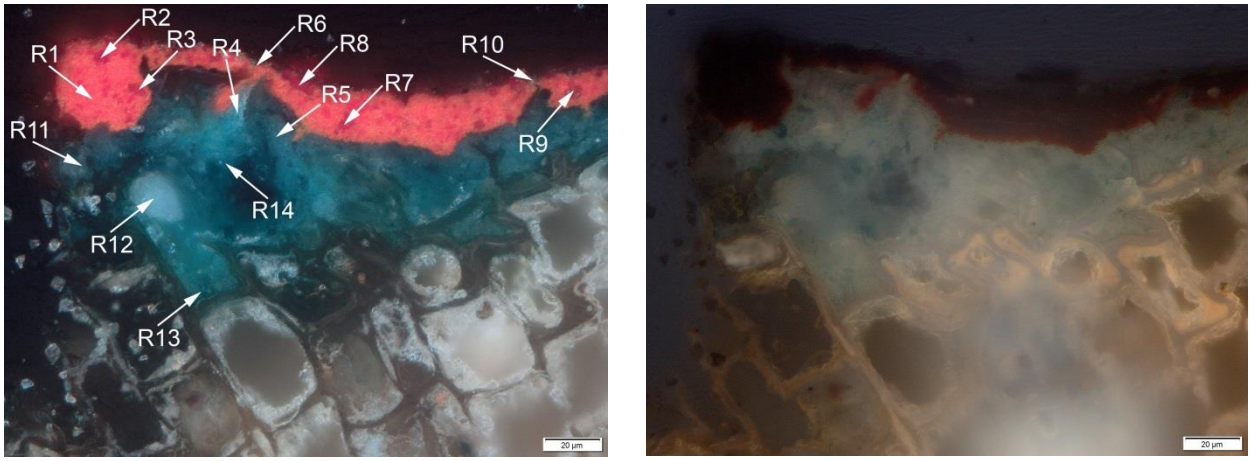
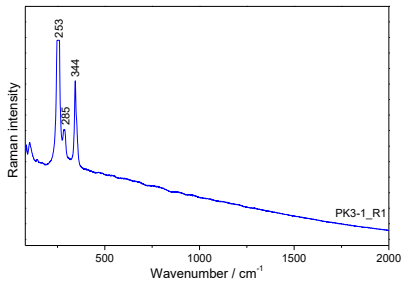
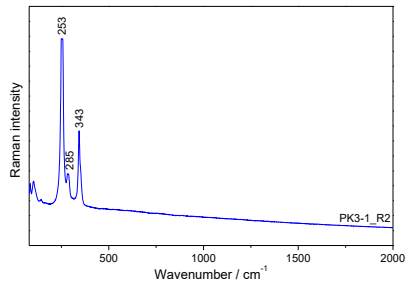
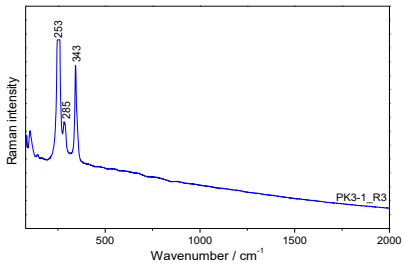
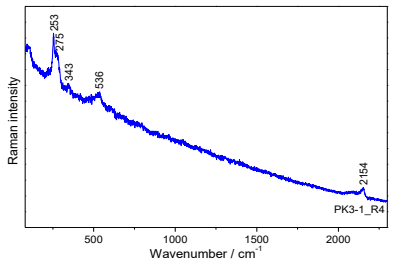
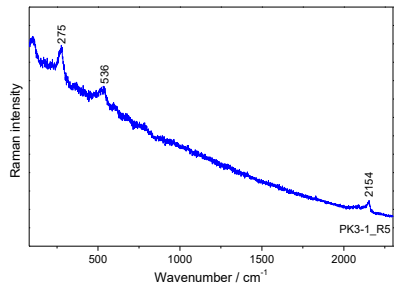
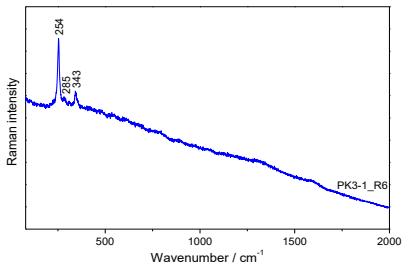
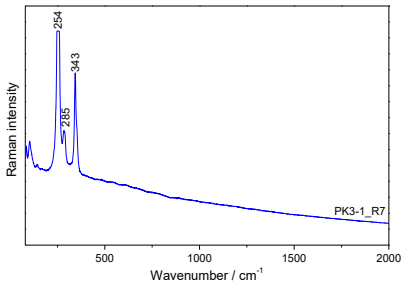
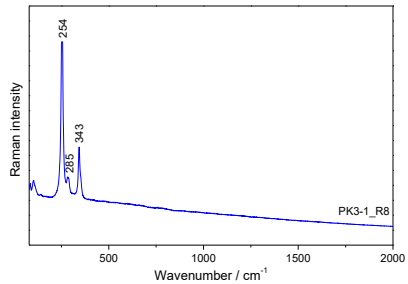
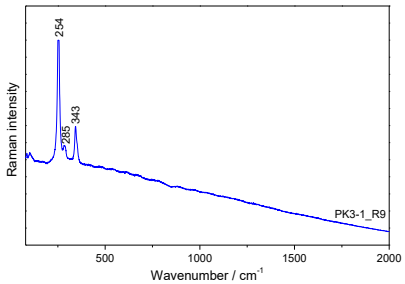
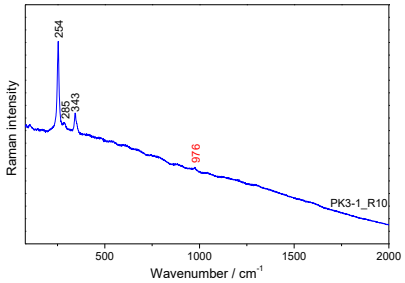
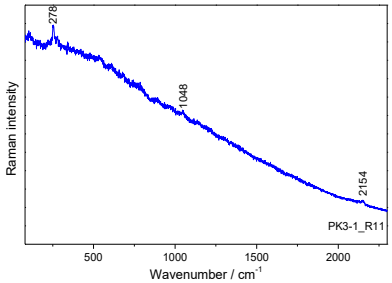


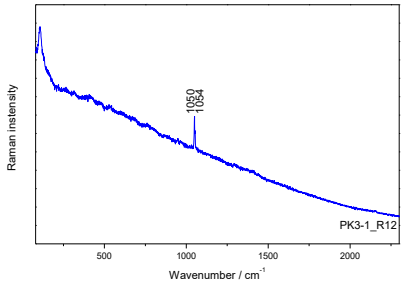
Figure 26: Optical images of region P1 of cross-section of the sample PK3-1 in visible (left image) with marked locations of Raman analysis (R1 - R14) and UV-light (right image).

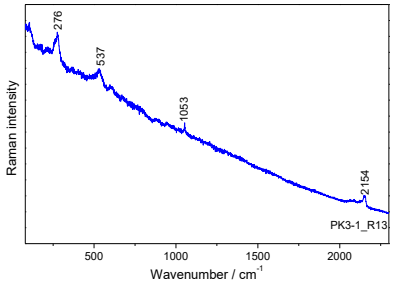
Table 25: Raman spectra obtained on different locations of cross section of the sample PK3-1 with identification.

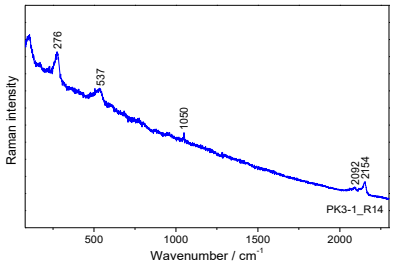
a) PK3-1-R1	b) PK3-1-R2	c) PK3-1-R3
 Identified material: **cinnabar** (253, 285, 344 cm^{-1}).	 Identified material: **cinnabar** (253, 285, 343 cm^{-1}).	 Identified material: **cinnabar** (253, 285, 343 cm^{-1}).
d) PK3-1-R4	e) PK3-1-R5	f) PK3-1-R6
 Identified material: **prussian blue** (275, 536, 2154), cinnabar due to proximity of red layer (253, 343 cm^{-1}).	 Identified material: **prussian blue** (275, 536, 2154 cm^{-1}).	 Identified material: **cinnabar** (254, 285, 343 cm^{-1}).
g) PK3-1-R7	h) PK3-1-R8	i) PK3-1-R9
 Identified material: **cinnabar**	 Identified material: **cinnabar**	 Identified material: **cinnabar**

<table>
<tr><td>(254, 285, 343 cm^{-1}).</td><td>(254, 285, 343 cm^{-1}).</td><td>(254, 285, 343 cm^{-1}).</td></tr>
<tr><td>j) PK3-1-R10</td><td>k) PK3-1-R11</td><td>l) PK3-1-R12</td></tr>
<tr><td> 

Identified material: cinnabar (254, 285, 343 cm^{-1}), potentially lead sulphate (976 cm^{-1}).</td><td> 

Identified material: prussian blue (278, 2154 cm^{-1}), lead white (1048 cm^{-1}).</td><td> 

Identified material: lead white (1050, 1054 cm^{-1}).</td></tr>
<tr><td>m) PK3-1-R13</td><td>n) PK3-1-R14</td><td></td></tr>
<tr><td> 

Identified material: prussian blue (276, 537, 2154 cm^{-1}), lead white (1053 cm^{-1}).</td><td> 

Identified material: prussian blue (276, 537, 2092, 2154 cm^{-1}), lead white (1050 cm^{-1}).</td><td></td></tr>
</table>

4.3.2.3 Other locations

In this chapter, the additional location of Raman measurments are marked, but the signal was obscured by the fluorescence.

Figure 27: Locations of noninvasive Raman measurments of beehive panel marked as PK3, where material identification was not possible due to fluorescence

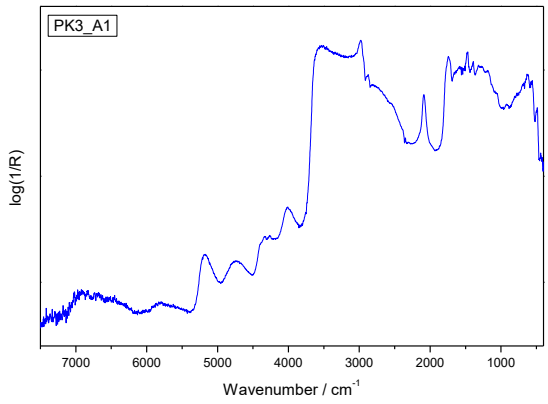
Table 26: Description of Raman spectroscopy measurment locations on beehive panel marked as PK3, where no material identification was possible

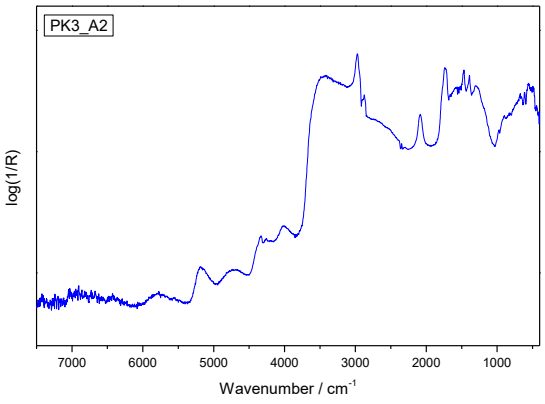
Label of analysis	Colour	Description	Laser wavelength [nm]
fl1	bluish-grey	background colour, upper left side of the panel	514
fl2	green	central garland; green leaf between topmost and left positioned red flowers	514
fl3	green	flower on the left-hand panel side; green leaf on the right side, below the upper central red flower	514
fl4	light green	olive branch in the claws of the dove/Holy Spirit; right side of the branch	514
fl5	red	central garland; bottom right flower (remains of red paint)	785

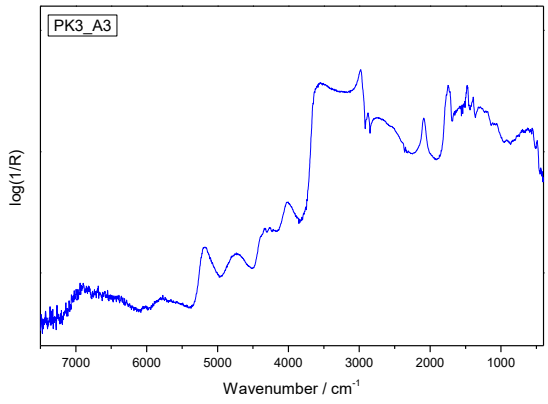
fl6	wood	flower on the right-hand panel side; bottom of the flower (bottom right side of the panel) –bottom of a flower vase; no visible paint present	785
fl7	yellow	flower on the right-hand panel side; bottom of the flower (bottom right side of the panel) – top of a flower vase; remains of yellow paint with brown stripes	785
fl8	yellow; green	flower on the left-hand panel side; bottom of the flower (bottom left side of the panel) – top of a flower vase; minute remains of yellow paint of the vase and green paint (presumably of the green leaf)	785
fl9	whitish-ochre	left edge of the panel; whitish-ochre painted border; bluish-grey background colour is present in the lower paint layer	785
fl10	yellow	flower on the right-hand panel side; bottom of the flower (bottom right side of the panel) – top of a flower vase; remains of yellow paint with brown stripes	785
fl11	yellow	flower on the right-hand panel side; bottom of the flower (bottom right side of the panel) – top of a flower vase; remains of yellow paint with brown stripes	785
fl12	yellow	flower on the right-hand panel side; bottom of the flower (bottom right side of the panel) – top of a flower vase; remains of yellow paint with brown stripes	785
fl13	wood; glossy surface	wood (tree ring); right of the upper right flower of the central garland	785

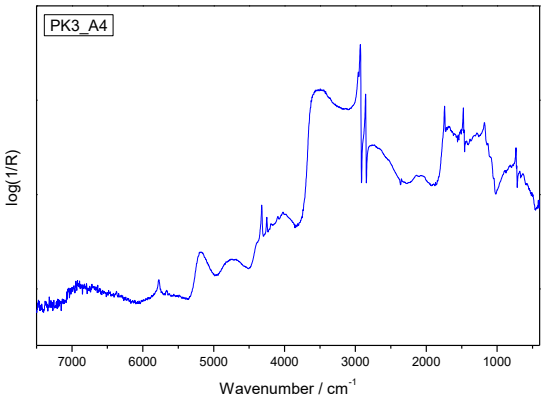
4.3.3 Reflection FTIR spectroscopy

Table 27: Reflection infrared spectra obtained on different locations of beehive panel marked as PK3 with identification.

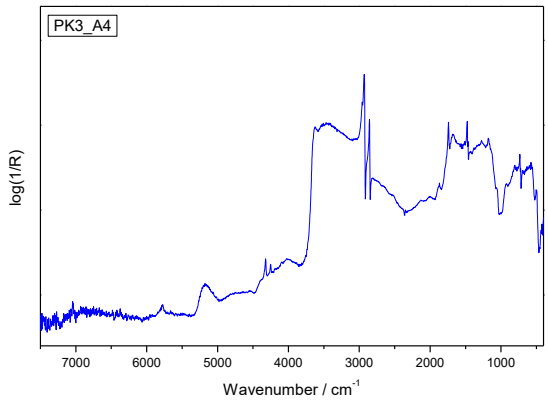
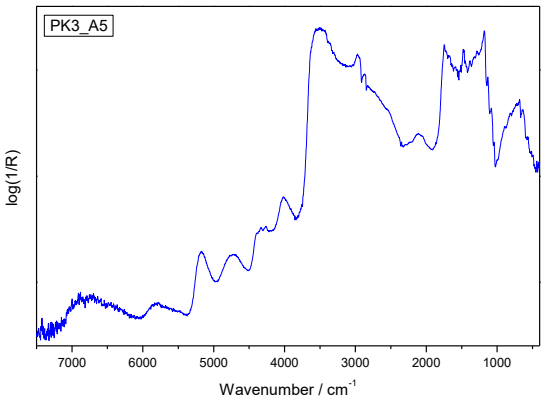
<table>
<tr><td>a) PK3-A1</td><td>b) PK3-A2</td></tr>
<tr><td> 

Identified material: lipids, Prussian blue, triterpenoid resin</td><td> 

Identified material: lipids, Prussian blue, triterpenoid resin (dammar)</td></tr>
<tr><td>c) PK3-A3</td><td>d) PK3-A4</td></tr>
<tr><td> 

Identified material: lipids, Prussian blue, triterpenoid resin</td><td> 

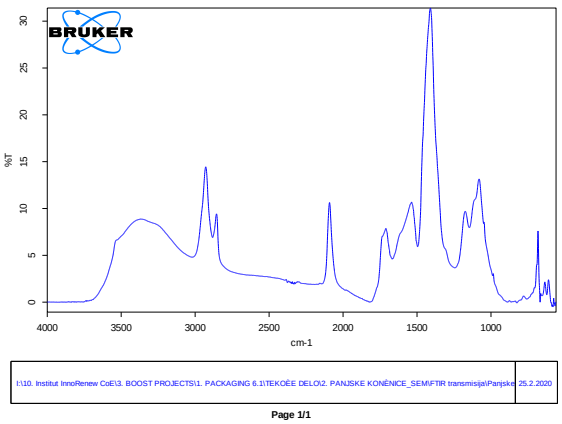
Identified material: wood, beeswax</td></tr>
</table>

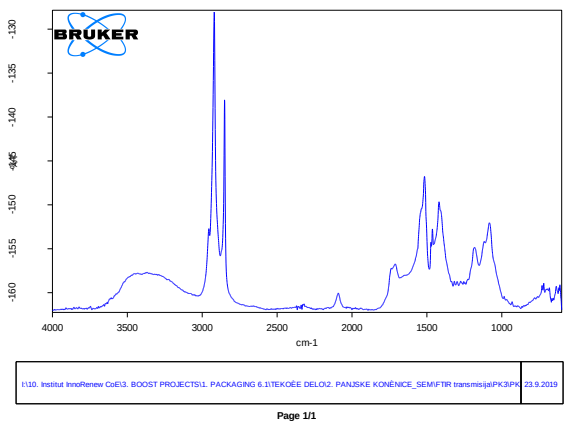
e) PK3-A4 (another spectrum)	f) PK3-A5
	
Identified material: **wood, beeswax**	Identified material:**lipids**, **wood, triterpenic resin**

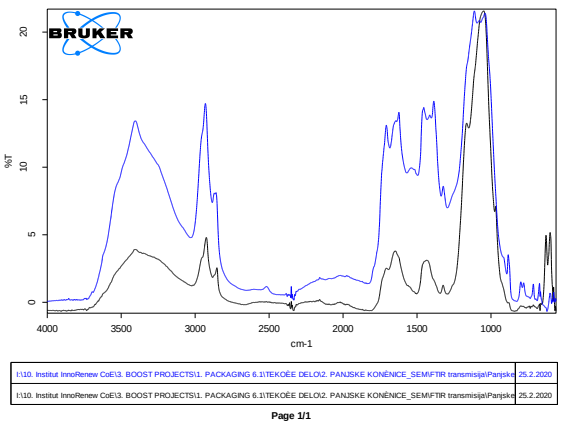
4.3.4 Transmission FTIR spectroscopy

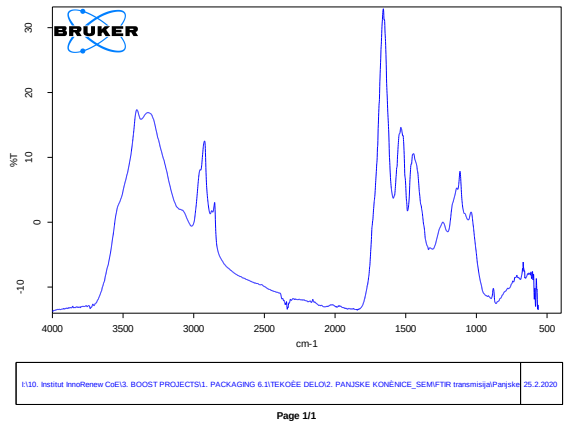
a) Sample PK3-1

Table 28: Transmission spectra obtained on different layers of sample marked as PK3-1 with identification.

<table>
<tr><td>a) PK3-1_layer 1_blue</td><td>b) PK3-1_layer 1_blue</td></tr>
<tr><td> 

Identified material: prussian blue, barium sulphate, lead white, lead carboxylate, lipid</td><td> 

Identified material: prussian blue, barium sulphate, beeswax, lipid, wood components</td></tr>
<tr><td>c) PK3-1_layer 2_red</td><td>d) PK3-1_layer 2_transparent</td></tr>
<tr><td> 

Identified material: lead sulphate, oxalate, triterpenoid resin, calcite, proteins, unidentified bands</td><td> 

Identified material: proteins, unidentified bands</td></tr>
</table>

4.3.5 Gathered results

Label of analysis	Surface paint colour/material	Location description	Identified material
R1	bluish-grey	background colour, upper left side of the panel	prussian blue
R2	bluish-grey	background colour, upper left side of the panel	lead oxide (likely massicot)
R3	green	central garland; upper left green leaf near the upper left flower; bluish-grey background colour might be present in the lower paint layer	lead oxide (likely massicot)
A3		flower on the right-hand panel side; upper left green leaf; bluish-grey background colour might be present in the lower paint layer	lipids, Prussian blue, triterpenoid resin
R4	green	central garland; upper left green leaf near the upper left flower; bluish-grey background colour might be present in the lower paint layer	carbon-based black, prussian blue
A4	wood	wood at the back of the panel	wood, beeswax
R5	green	central garland; upper left green leaf near the upper left flower; bluish-grey background colour might be present in the lower paint layer	lead oxide (likely massicot), carbon-based black
A5	wood	wood; bottom left side of the pannel	lipids, wood, triterpenic resin
R6	red	central garland; right side of the upper left flower; bluish-grey background colour and/or green colour of the leaves might be present in the lower paint layer	cinnabar/vermilion
A2			lipids, Prussian blue, triterpenoid resin
PK3-1		middle part of the left edge of the panel; lower, uttermost left red flower; upper left edge of the flower	Cinnabar, Prussian blue, lead white, lead sulphate, barium sulphate, lead carboxylate, lipids, beeswax, triterpenic resin, oxalate, wood components, unidentified bands
R7	white	central garland; left side of the upper left flower; white spot on a petal; red colour of the flower is present in the lower paint layer	lead white, cinnabar/vermilion
R8	light green	olive branch in the claws of the dove/Holy Spirit; right side of the branch	lead white, lead sulphate (?)

R9	red	central garland; right side of the bottom right flower (remains of red paint)	cinnabar/vermilion
R10	red	the dove/Holy Spirit; dove's left eye; red paint	cinnabar/vermilion
R11	brownish-white; brown; green	the dove/Holy Spirit; dove's right wing near the edge of the wing and green leaves on the left-hand central side of the garland; oter contour of the wing	lead oxide (likely massicot), lead sulphate (?)
R12	whitish	flower on the left-hand panel side; upper central flower; whitish line in the middle right side of the flower; red paint is present in the lower paint layer	lead oxide (likely massicot) (?), lead sulphate (?)
R13	brown; green	the dove/Holy Spirit; dove's right wing near the edge of the wing and green leaves on the left-hand upper central side of the garland; outer contour of the wing; green paint of the leaves might be present in lower paint layer	cinnabar/vermilion
R14	red	flower on the left-hand panel side; lower left flower; left edge of the flower	cinnabar/vermilion
R15	whitish-ochre	left edge of the panel; whitish-ochre painted border; bluish-grey background colour is present in the lower paint layer	lead white
R16	whitish-ochre	left edge of the panel; whitish-ochre painted border; bluish-grey background colour is present in the lower paint layer	lead white
R17	green; red	central garland; green leaves below the upper right flower; possible presence of red paint of the flower; bluish-grey background colour might be present in the lower paint layer	cinnabar/vermilion
R18	green	flower on the left-hand panel side; middle left green leaf of the upper central flower	*unidentified*
R19	green	central garland; green leaf on the right side of the top most flower; bluish-grey background colour might be present in the lower paint layer	cinnabar/vermilion (impurity?)
R20	green	central garland; green leaf on the right side of the top most flower; bluish-grey background colour might be present in the lower paint layer	prussian blue
R21	green	flower on the left-hand panel side; upper right green leaf of the upper central flower	prussian blue

R22	bluish-grey	background colour; upper left side of the panel	prussian blue
A1			lipids, Prussian blue, triterpenoid resin
R23	bluish-grey	background colour; top middle of the panel; left side of the topmost left green leaf	prussian blue

4.4 PK4

4.4.1 Marked locations of performed analysis

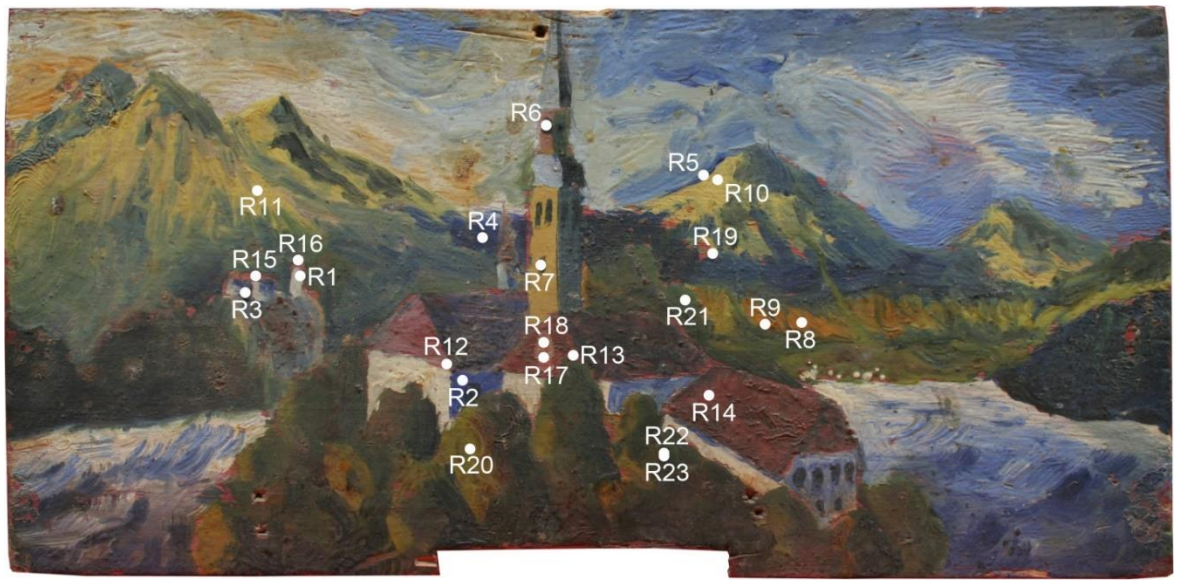


Figure 28:Marked locations of Raman analysis.

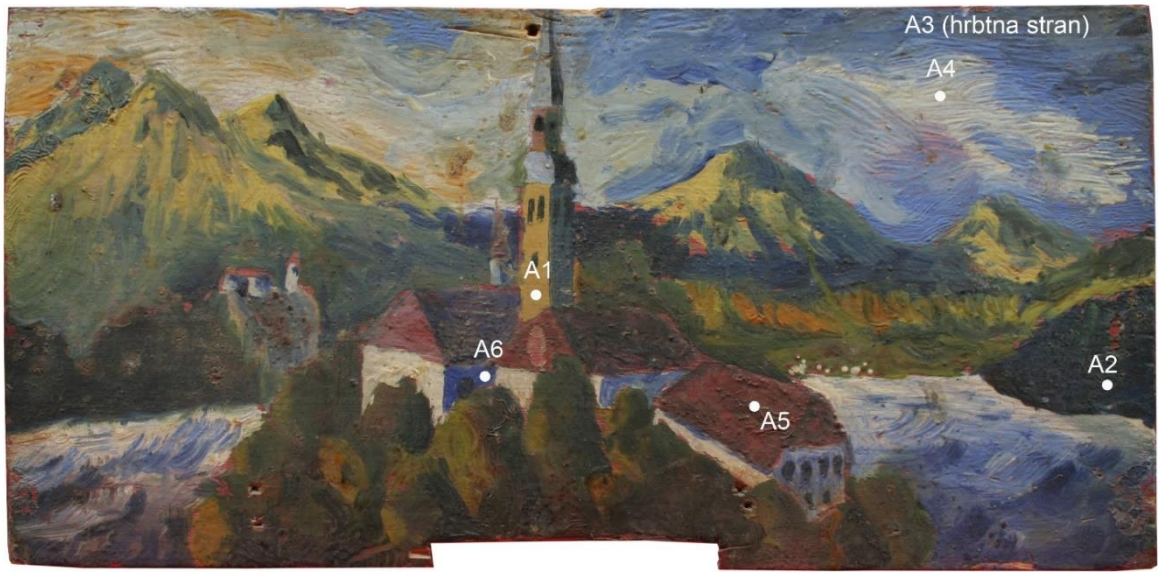


Figure 29: Marked locations of reflection FTIR analysis.

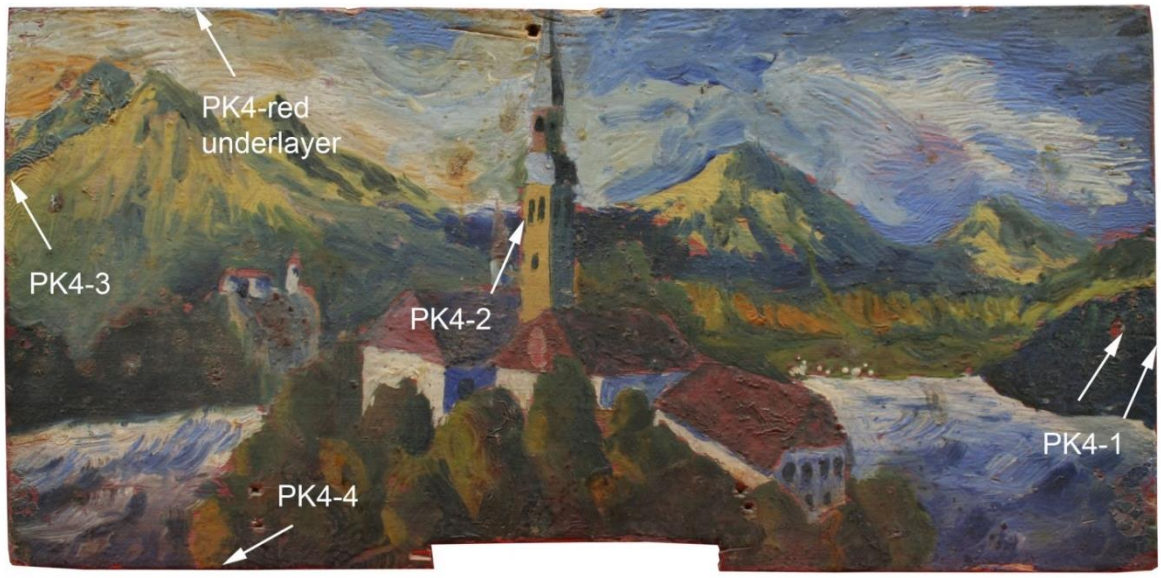


Figure 30: Marked locations of sample removal. Samples are marked as PK4-1, PK4-2, PK4-3, PK4-4, PK4-red underlayer.

Table 29: Description of the samples.

LABEL	TYPE	MICROLOCATION	PURPOSE
PK4-1	sample of paint layers on wooden support; sample consists of all stratigrafically present picture layers at the microlocation	right edge of the panel; dark greenish-blue hill near the river; paint sample taken from the outermost edge and from a damaged area at the top-middle of the hill	RAMAN, FTIR
PK4-2	sample of paint layers on wooden support; sample consists of stratigrafically present paint layers at the microlocation, without the layer of wooden support	main steeple in the middle of the panel; left edge of the ochre painted steeple wall, near the mullioned window	for additional research (i.e. GC)
PK4-3	sample of paint layers on wooden support; sample consists of all stratigrafically present	left edge of the panel; mountanins in the background; yellow and green painted mountain in the front left plane of the	RAMAN, FTIR

LABEL	TYPE	MICROLOCATION	PURPOSE
	picture layers at the microlocation	painting; yellowish-green painted area	
PK4-4	sample of paint layers on wooden support; sample consists of all stratigrafically present picture layers at the microlocation	bottom edge of the panel; left bottom side of island's greenery; ochre and green paint	RAMAN, FTIR

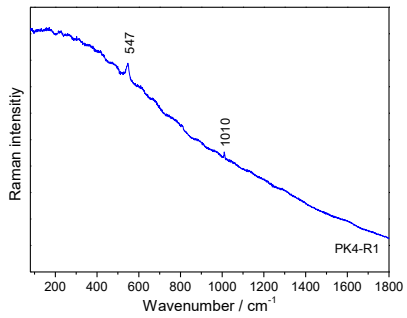
4.4.2 Raman spectroscopy

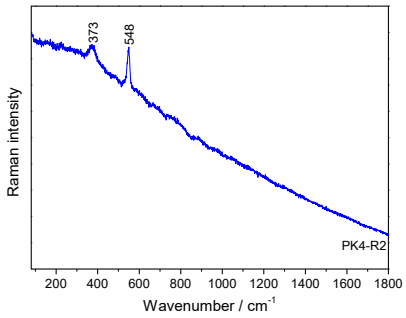
4.4.2.1 Non-invasive analysis

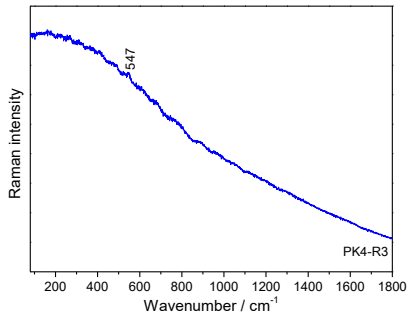
Raman spectra obtained at different locations on painted beehive panel marked as PK4 are presented in Table 30. Additionally, material identification based on the obtained spectra is gathered in.

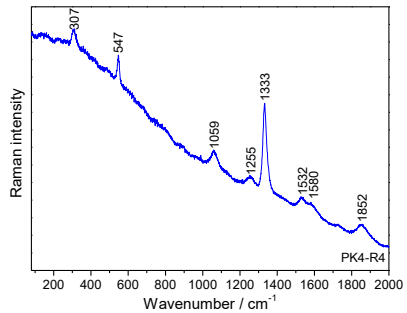
The locations of the obtained spectra from which no material could be identified are given in Figure 34 at the end of the report–said spectra are omitted from this report.

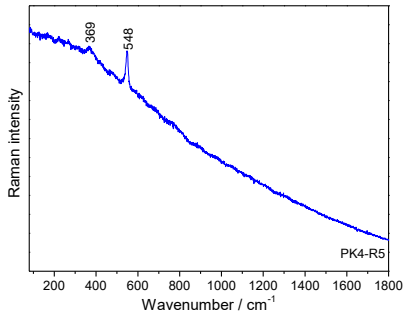
Table 30: Raman spectra obtained on different locations of beehive panel marked as PK4 with identification.

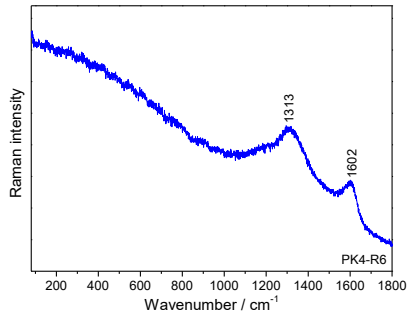
<table>
<tr><td>a) PK4-R1</td><td>b) PK4-R2</td><td>c) PK4-R3</td></tr>
<tr><td> 

Identified material: ultramarine (547 cm^{-1}), calcium sulphate (likely gypsum type – band at 1010 cm^{-1})??</td><td> 

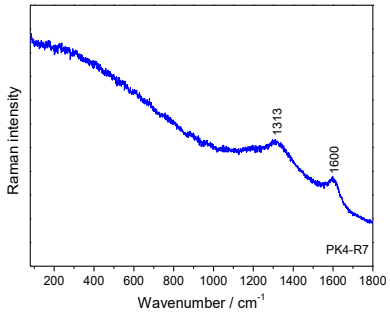
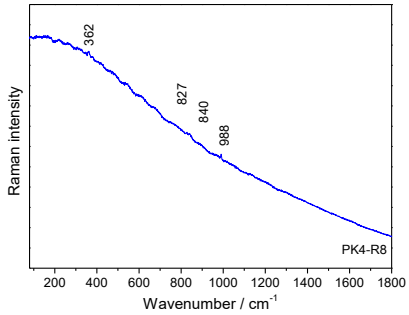
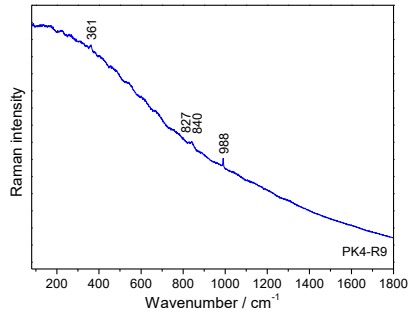
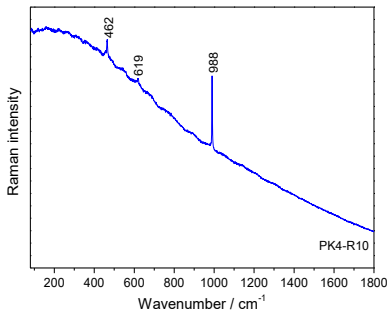
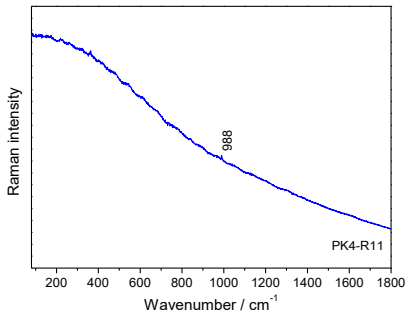
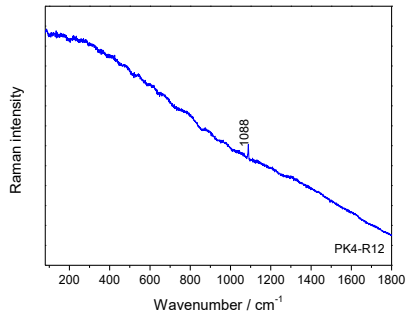
Identified material: ultramarine (373, 548 cm^{-1}).</td><td> 

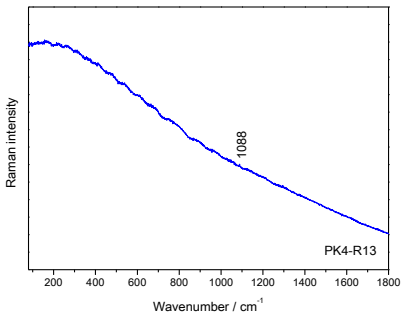
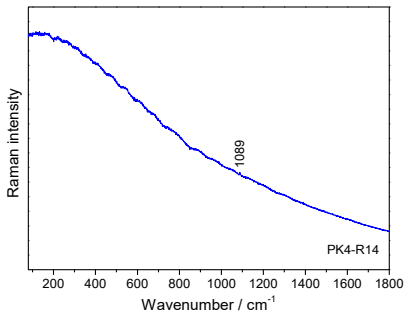
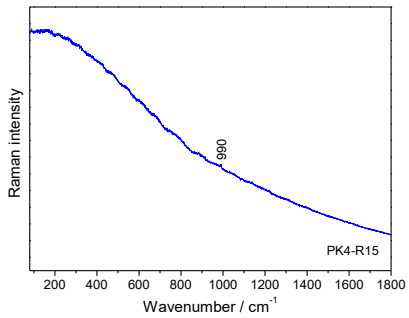
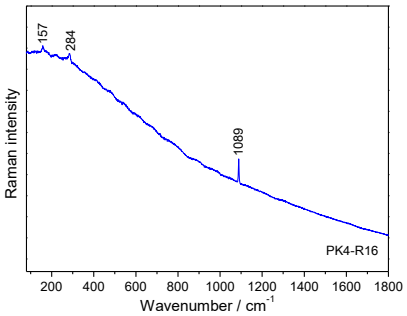
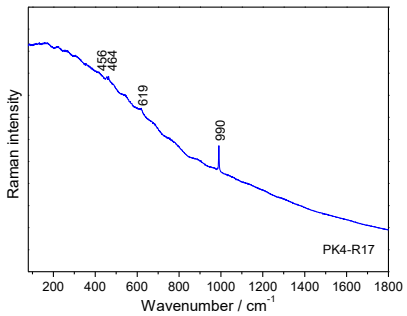
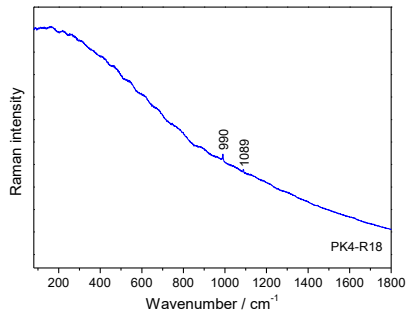
Identified material: ultramarine (547 cm^{-1}).</td></tr>
<tr><td>d) PK4-R4</td><td>e) PK4-R5</td><td>f) PK4-R6</td></tr>
<tr><td> 

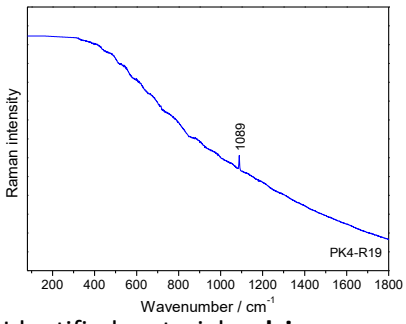
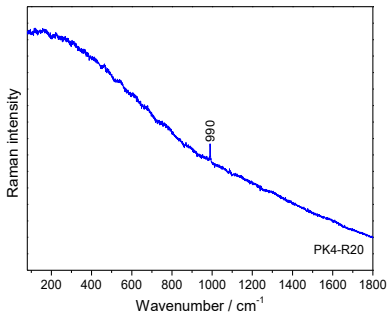
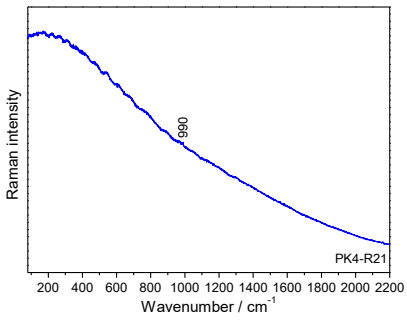
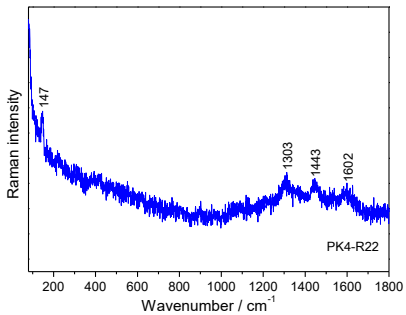
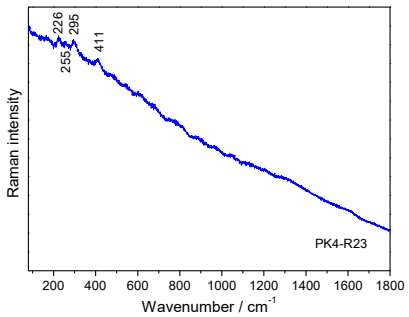
Identified material: ultramarine (547 cm^{-1}), unidentified (likely organic matter – bands at 307, 1059, 1255, 1333, 1532, 1580,</td><td> 

Identified material: ultramarine (369, 548 cm^{-1}).</td><td> 

Identified material: carbon-based black (~1313, 1602 cm^{-1}).</td></tr>
</table>

1852 cm^{-1}).		
g) PK4-R7	h) PK4-R8	i) PK4-R9
 Identified material: **carbon-based black** (~1313, 1600 cm^{-1}).	 Identified material: **barium sulphate** (988 cm^{-1}), possibly lead (II) chromate (362, 827, 840 cm^{-1}).	 Identified material: **barium sulphate** (988 cm^{-1}), possibly lead (II) chromate (361, 827, 840 cm^{-1}).
j) PK4-R10	k) PK4-R11	l) PK4-R12
 Identified material: **barium sulphate** (462, 619, 988 cm^{-1}).	 Identified material: **barium sulphate** (988 cm^{-1}	 Identified material: **calcium carbonate** (1088 cm^{-1}).

m) PK3-R13	n) PK4-R14	o) PK4-R15
 Identified material: **calcium carbonate** (1089 cm^{-1}).	 Identified material: **calcium carbonate** (1089 cm^{-1})**.**	 Identified material: possibly barium sulphate (990 cm^{-1}).
p) PK4-R16	**q) PK4-R17**	**r) PK4-R18**
 Identified material: **calcium carbonate** (likely of the calcite structure; 157, 284, 1089 cm^{-1}).	 Identified material: **barium sulphate** (456, 464, 619, 988 cm^{-1}).	 Identified material: **barium sulphate** (988 cm^{-1}), **calcium carbonate** (likely of the calcite structure; 1089 cm^{-1}).

s) PK4-R19	t) PK4-R20	u) PK4-R21
 Identified material: **calcium carbonate** (likely of the calcite structure; 1089 cm^{-1}).	 Identified material: **barium sulphate** (988 cm^{-1}).	 Identified material: **barium sulphate** (990 cm^{-1}).
v) PK4-R22	**a) PK4-R23**	
 Identified material: likely organic matter (147, 1303, 1443, 1602 cm^{-1}).	 Identified material: **iron oxide** (likely haematite type – bands at 226, 295, 411 cm^{-1}), possibly cinnabar/vermilion (255 cm^{-1}).	

4.4.2.2 Investigation of cross-sections of the removed samples

a) Sample PK4-1

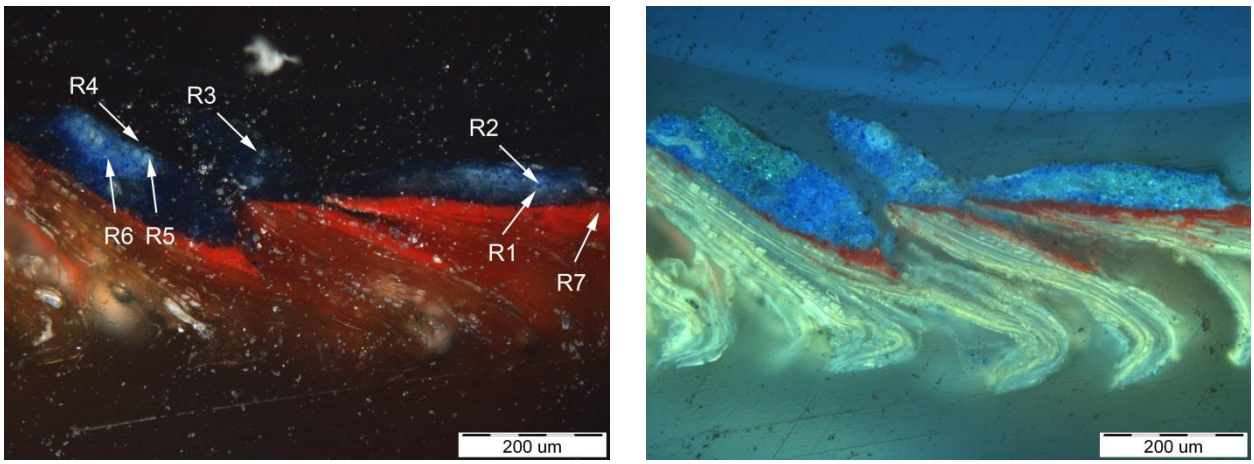
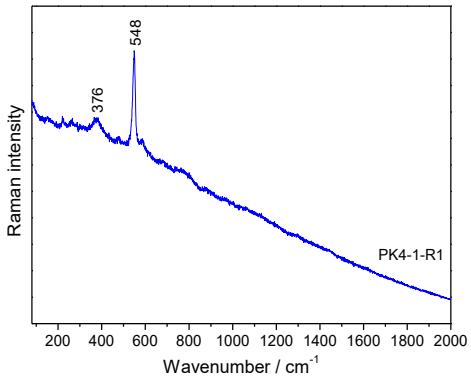
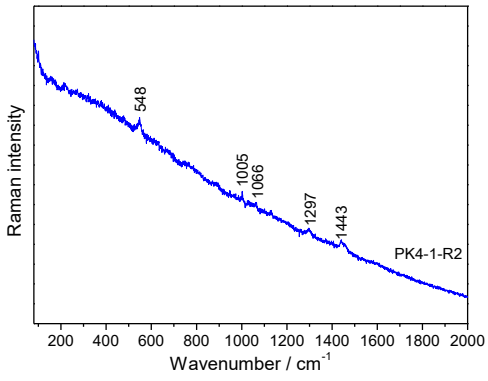
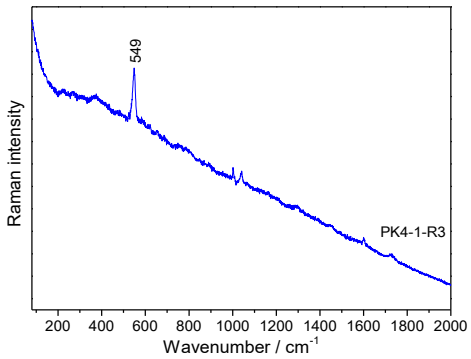
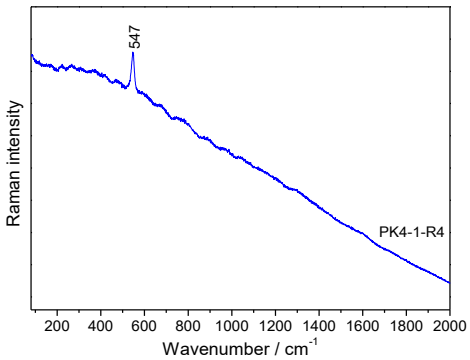
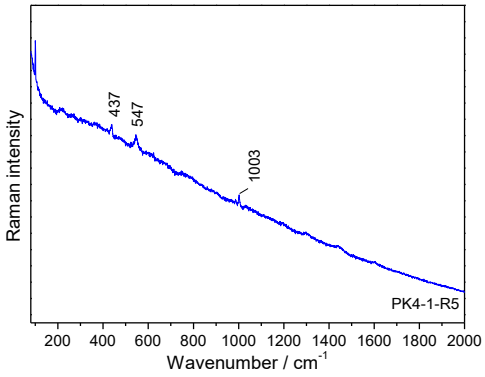
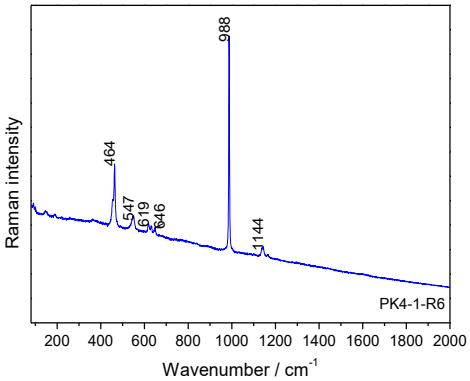
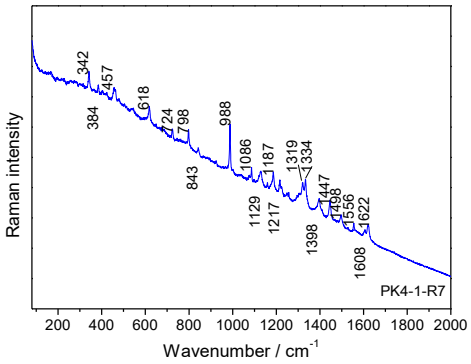


Figure 31: Optical images of the sample PK4-1 in visible light (left image) with marked locations of Raman analysis and in UV-light (right image).

Table 31: Raman spectra obtained on different locations of cross section of the sample PK4-1 with identification.

a) PK4-1-R1	b) PK4-1-R2
	
Identified material: **ultramarine** (548 cm^{-1}), unidentified peak: 376 cm^{-1}.	Identified material: **ultramarine** (548 cm^{-1}), likely organic matter (1005, 1066, 1297, 1443 cm^{-1}).

c) PK4-1-R3	d) PK4-1-R4
	
Identified material: **ultramarine** (cm^{-1}).	Identified material: **Ultramarine** (547 cm^{-1}).
e) PK4-1-R5	**f) PK4-1-R6**
	
Identified material: **ultramarine** (547 cm^{-1}),**zinc oxide** (437 cm^{-1}) unidentified: 1003 cm^{-1} – resin?).	Identified material: **barium sulphate** (464, 619, 646, 988, 1144 cm^{-1}), **ultramarine** (547 cm^{-1}).

g) PK4-1-R7	
 Identified material: **PR 3** (342, 384, 457, 618, 724, 798, 843, 988, 1086, 1129, 1187, 1217, 1319, 1334, 1398, 1447, 1498, 1556, 1608, 1622 cm^{-1}).	

b) Sample PK4-3

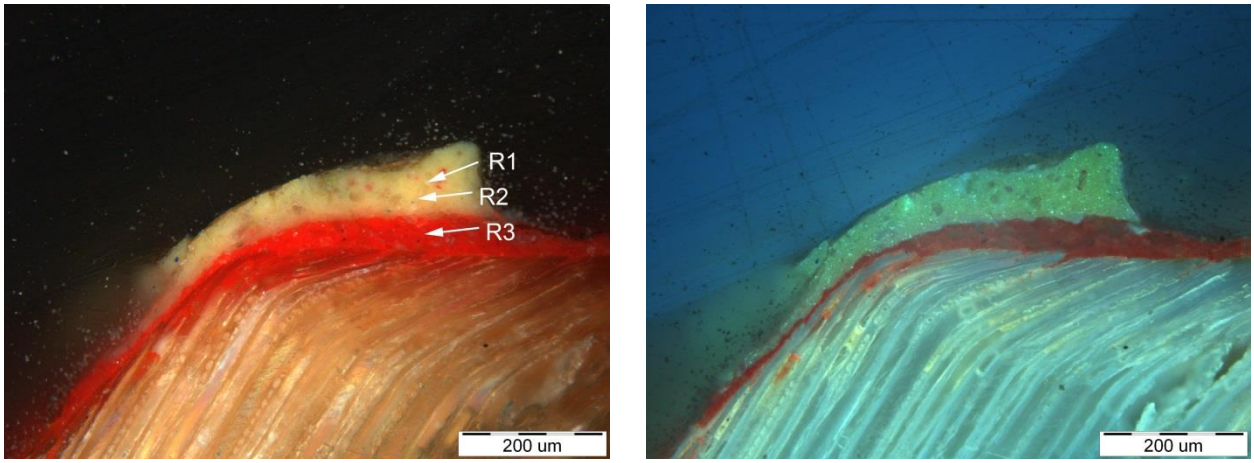
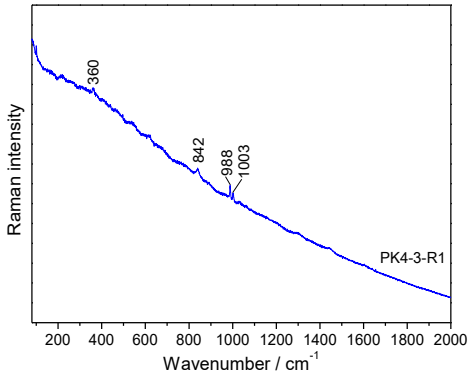
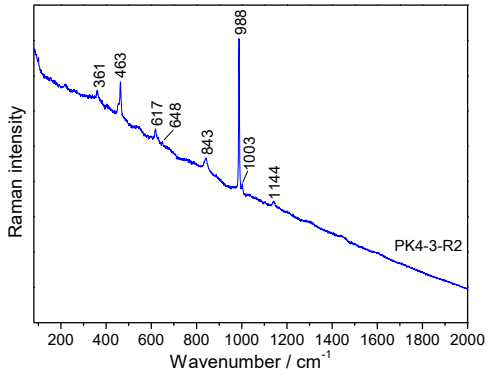
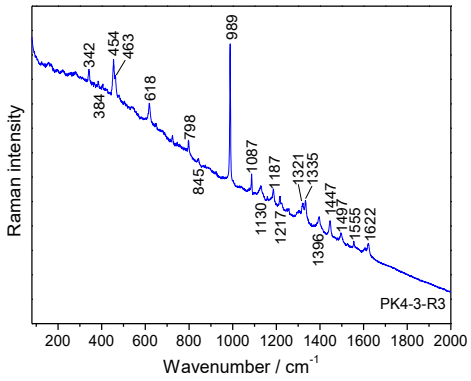


Figure 32: Optical images of cross-section of the sample PK4-3 in visible (left image) with marked locations of Raman analysis (R1, R2, R3).and UV-light (right image).

Table 32: Raman spectra obtained on different locations of cross section of the sample PK4-3 with identification.

a) PK4-3-R1	b) PK4-3-R2
	
Identified material: barium sulphate (988 cm^{-1}), lead(II) chromate (**chrome yellow,** 360, 842 cm^{-1}), unidentified: 1003 cm^{-1}.	Identified material: **barium sulphate** (464, 617, 648, 988, 1144cm^{-1}), lead(II) chromate (**chrome yellow,** 361, 842 cm^{-1}), unidentified: 1003 cm^{-1}.

c) PK4-3-R3	
 Identified material: **PR 3** (342, 384, 454, 618, 798, 845, 989, 1087, 1130, 1187, 1217, 1321, 1335, 1396, 1447, 1497, 1555, 1622 cm^{-1}), **barium sulphate** (463, 989 cm^{-1}).	

c) Sample PK4-4

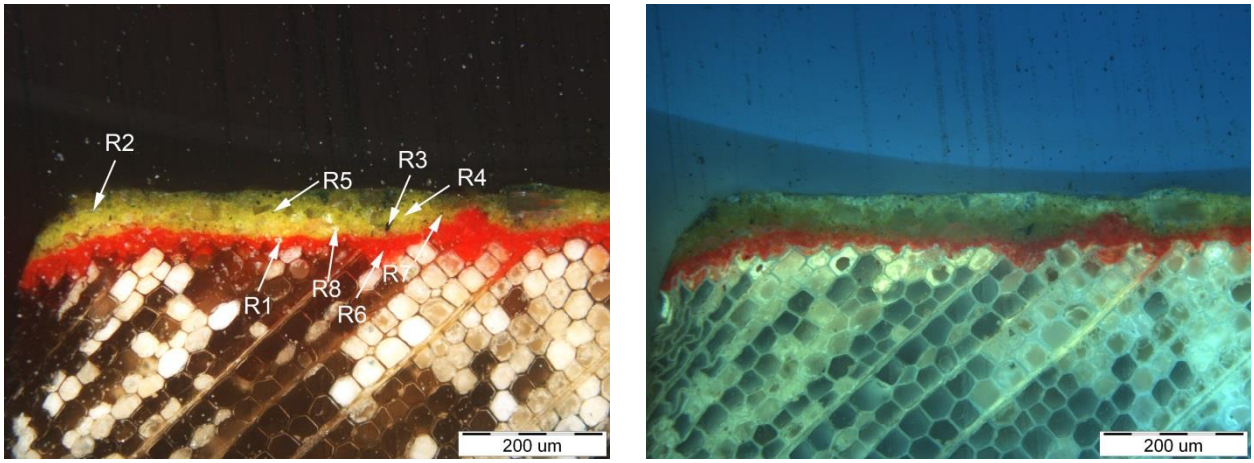
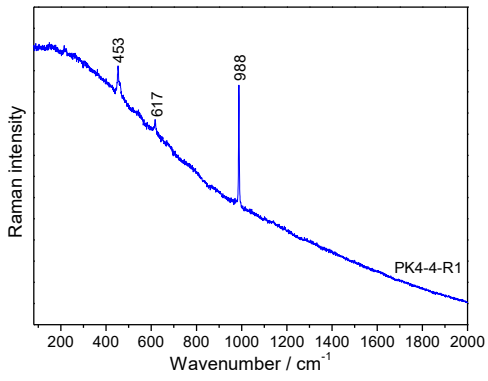
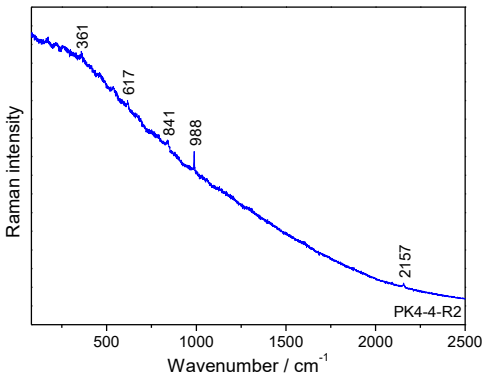
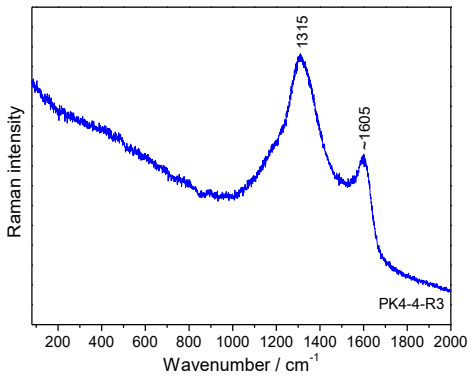


Figure 33: Optical images of cross-section of the sample PK4-4 in visible (left image) with marked locations of Raman analysis (R1 – R8).and UV-light (right image).

Table 33: Raman spectra obtained on different locations of cross section of the sample PK4-4 with identification.

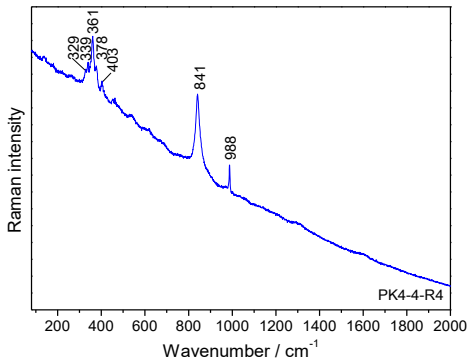
a) PK4-4-R1	b) PK4-4-R2
 Identified material: **barium sulphate** (453, 617, 988 cm^{-1}).	 Identified material: **barium sulphate** (617, 988 cm^{-1}), **prussian blue** (2157 cm^{-1}), lead(II) chromate (**chrome yellow,** 361, 842 cm^{-1}).

c) PK4-4-R3



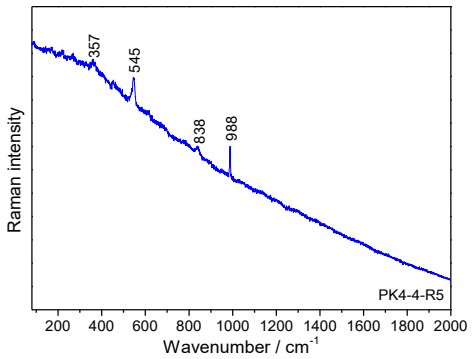
Identified material: **carbon-based black** (1315, ~1605 cm^{-1}).

d) PK4-4-R4



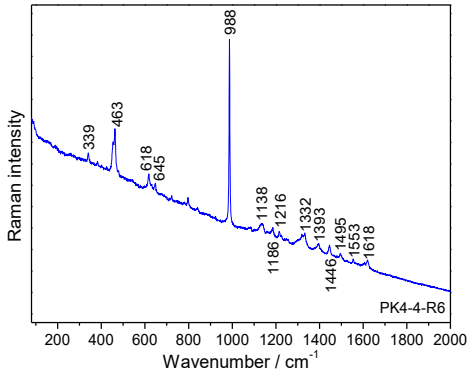
Identified material: lead(II) chromate (**chrome yellow,** 329, 339, 361, 378, 403, 841 cm^{-1}), **barium sulphate** (988 cm^{-1}).

e) PK4-4-R5

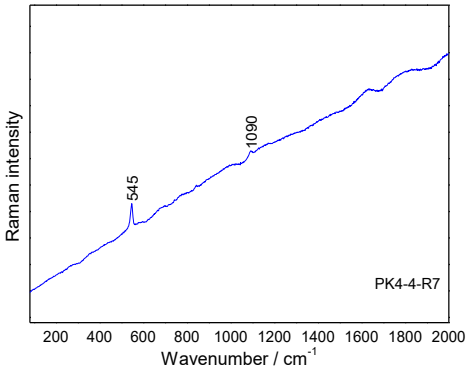
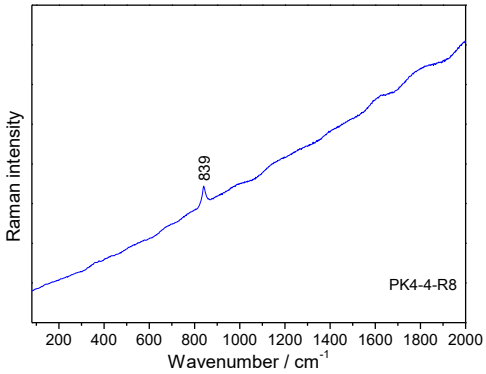


Identified material: **ultramarine** (545 cm^{-1}), lead(II) chromate (**chrome yellow,** 357, 838 cm^{-1}), **barium sulphate** (988 cm^{-1}).

f) PK4-4-R6



Identified material: **barium sulphate** (463, 618, 645, 988, 1138 cm^{-1}), **PR 3** (339, 1186, 1216, 1332, 1393, 1446, 1495, 1553, 1618 cm^{-1}).

g) PK4-4-R7	h) PK-4-R8
	
Identified material: **ultramarine** (545 cm^{-1}), **calcium carbonate** (1090 cm^{-1}).	Identified material: lead(II) chromate (**chrome yellow,** 839 cm^{-1}).

4.4.2.3 Other locations

In this chapter, the additional location of Raman measurments are marked, but the signal was obscured by the fluorescence.

Figure 34: Locations of noninvasive Raman measurments of beehive panel marked as PK4, where material identification was not possible due to fluorescence

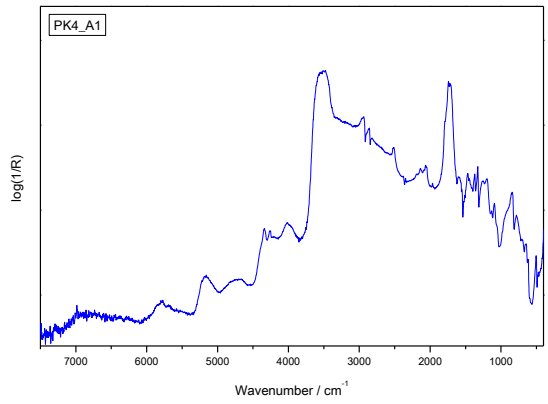
Table 34: Description of Raman spectroscopy measurment locations on beehive panel marked as PK1, where no material identification was possible

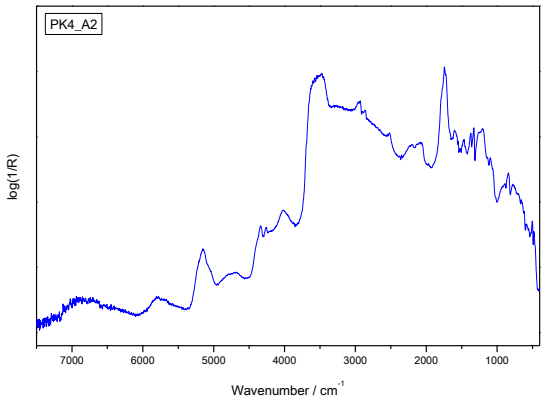
Label of analysis	Colour	Description	Laser wavelength [nm]
fl1	green	island in the middle of the panel; greenery in the first plane of the painting; upper row of trees; fourth tree from the left	514
fl2	light green	island in the middle of the panel; greenery in the first plane of the painting; upper row of trees; fourth tree from the left	514
fl3	light green	right side of the panel; foot of the mountain; above the dark greenish-blue hill	514

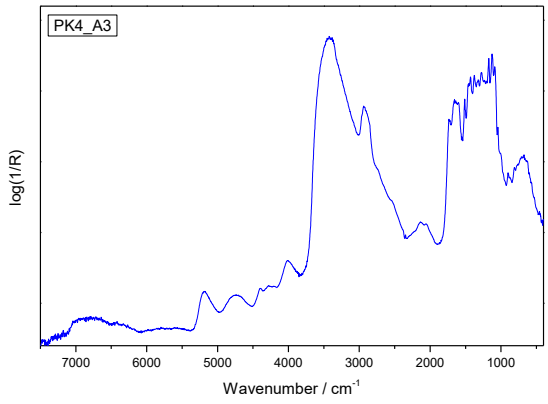
fl4	green	right side of the panel; mountains in the background; second mountain to the right of the main steeple; ridge on the right side of the mountain	514
fl5	pinkish-red	island in the middle of the panel; left-hand side building; middle part of the left side of the roof	785
fl6	ochre	left side of the panel; sky; ochre paint near the left edge of the panel	785
fl7	yellow	mountains in the background; third mountain from the left; left side of the mountain; yellow painted mountain slope	785
fl8	dark blue or black paint on red	island in the middle of the panel; middle building; bottom middle part of the right, shady side of the roof	785
fl9	white	right side of the panel; sky; white cloud	785
fl10	white	right side of the panel; river; white paint at the top left side	785
fl11	white	left side of the panel; river; white paint at the top middle part	785
fl12	white	island in the middle of the panel; middle building; left side of the white façade	785
fl13	brown	island in the middle of the panel; greenery in the first plane of the painting; upper row of trees; third tree from the left	785

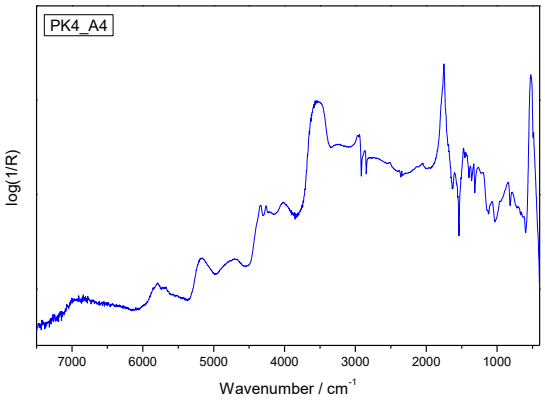
4.4.3 Reflection FTIR spectroscopy

Table 35: Reflection infrared spectra obtained on different locations of beehive panel marked as PK4 with identification.

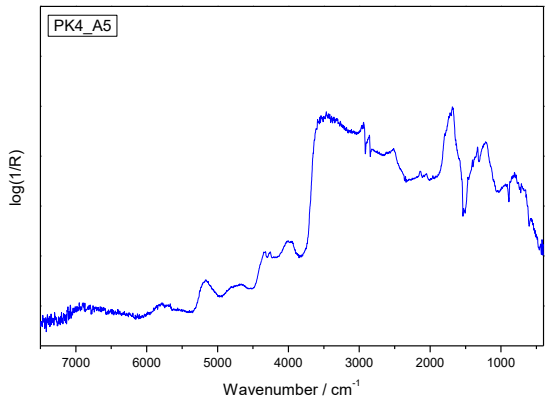
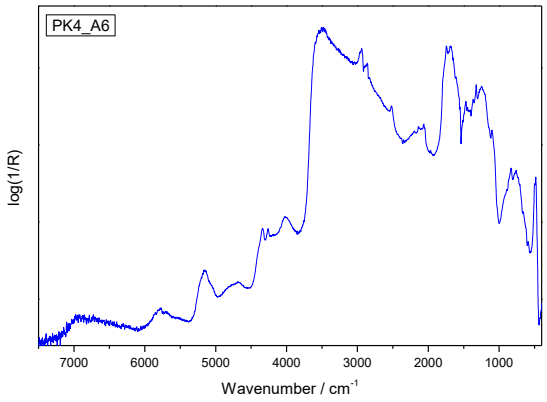
<table>
<tr><td>a) PK4-A1</td><td>b) PK4-A2</td></tr>
<tr><td> 

Identified material: lipids, calcium carbonate, barium sulphate, zinc carboxylate, zinc oxalate</td><td> 

Identified material: barium sulphate, lipids, calcium carbonate, zinc oxalate</td></tr>
<tr><td>c) PK4-A3</td><td>d) PK4-A4</td></tr>
<tr><td> 

Identified material: wood</td><td> 

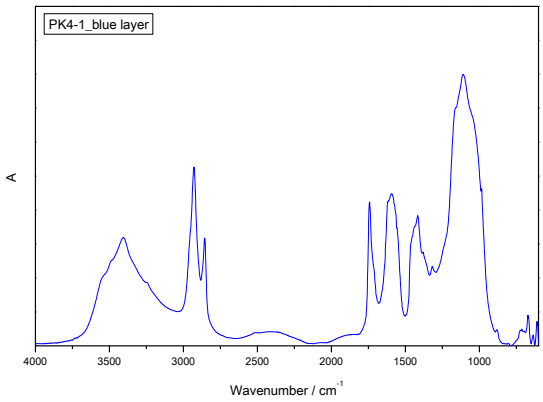
Identified material: zinc carboxylate, zinc oxalate, lipids,</td></tr>
</table>

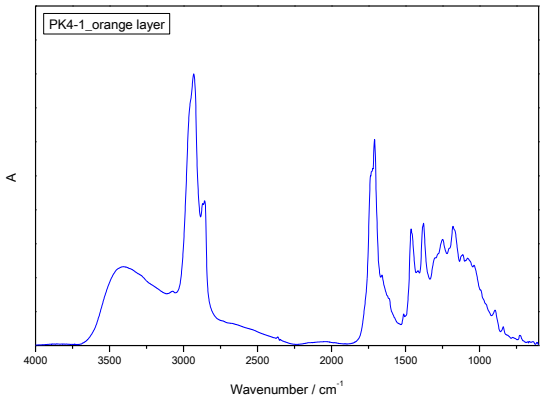
e) PK4-A5	f) PK4-A6
 Identified material: zinc carboxylate, **lipids, barium sulphate, calcium carbonate,** unidentified material	 Identified material: zinc carboxylate, **lipids**, **barium sulphate, calcium carbonate**

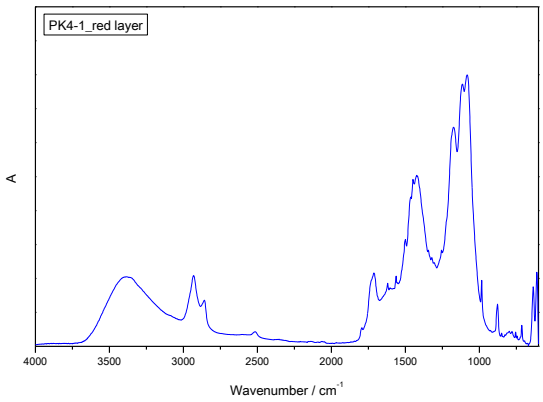
4.4.4 Transmission FTIR spectroscopy

a) Sample PK4-1

Table 36:Transmission spectra obtained on different layers of sample marked as PK4-1 with identification.

<table>
<tr>
<td>a) PK4-1-blue layer
 

Identified material: lipids, oxalate, barium sulphate, calcium carbonate</td>
<td>b) PK4-1-orange layer
 

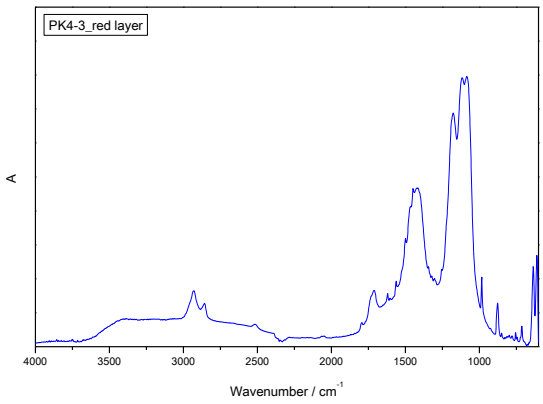
Identified material: Triterpenoid resin (dammar), lipids</td>
</tr>
<tr>
<td>c) PK4-1-red layer
 

Identified material: Barium sulphate, calcium carbonate, pigment red 3, lipids</td>
<td></td>
</tr>
</table>

b) Sample PK4-3

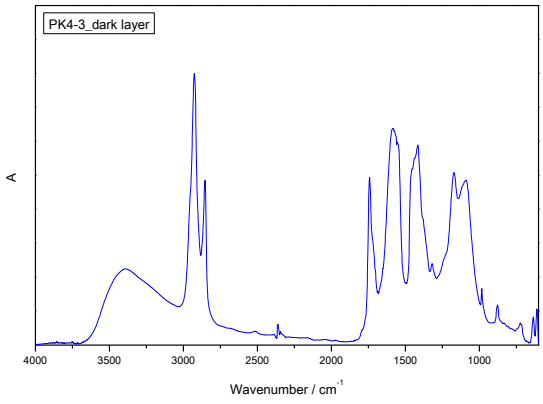
Table 37: Transmission spectra obtained on different layers of sample marked as PK4-3 with identification.

<table>
<tr>
<td>a) PK4-3-red layer

Identified material: Barium sulphate, calcium carbonate, pigment red 3, lipids</td>
<td>b) PK4-3-yellow layer

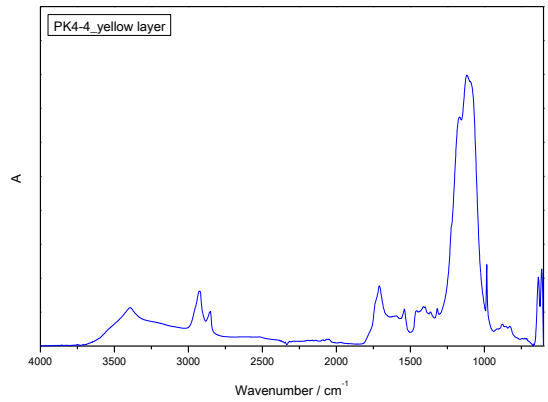
Identified material: Zinc carboxylate, Barium sulphate, lipids, oxalate, calcium carbonate, lead (II) chromate (chrome yellow)</td>
</tr>
<tr>
<td>c) PK4-3-dark layer

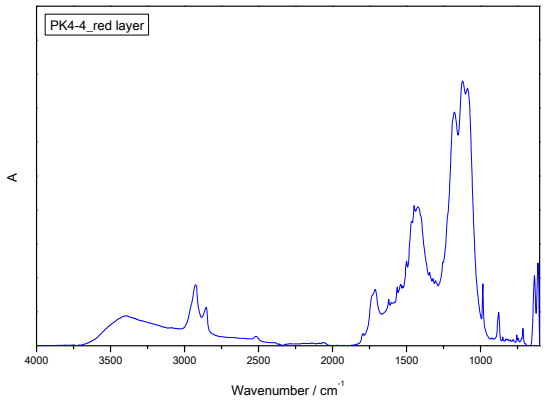
 

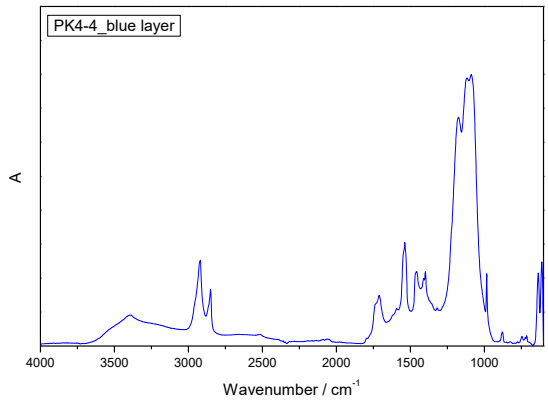
d) Identified material: Barium sulphate, lipids, oxalate, calcium carbonate, Zinc carboxylate</td>
<td></td>
</tr>
</table>

c) Sample PK4-4

Table 38: Transmission spectra obtained on different layers of sample marked as PK4-4 with identification.

<table>
<tr><td>a) PK4-4-yellow layer</td><td>b) PK4-4-red layer</td></tr>
<tr><td> 

Identified material: oxalate, barium sulphate, zinc carboxylate, lipids, lead(II) chromate (chrome yellow)</td><td> 

Identified material: barium sulphate, calcium carbonate, pigment red 3, lipids</td></tr>
<tr><td colspan="2">PK4-4-blue layer</td></tr>
<tr><td colspan="2"> 

Identified material: oxalate, barium sulphate, calcium carbonate, zinc carboxylate, lipids</td></tr>
</table>

4.4.5 Gathered results

Label of analysis	Surface paint colour/material	Location description	Identified material
R1	blue	left side of the panel; castle on the cliff; tower; window on the tower's façade	ultramarine
R2	blue	island in the middle of the panel; left-hand side building; shadow on the right façade painted blue	ultramarine
A6			lipids, barium sulphate, calcium carbonate, zinc carboxylate
A2	dark greenish-blue	right side of the panel; dark greenish-blue hill near the river at the right edge of the panel; lower middle part of the hill	barium sulphate, lipids, calcium carbonate, zinc oxalate
PK4-1			ultramarine, zinc oxide, barium sulphate, PR 3, lipids, oxalate, calcium carbonate, triterpenoid resin
R3	blue	left side of the panel; castle on the cliff; utmost left building; blue shadow on the façade	ultramarine
A3	wood	wood at the back of the panel	wood
R4	blue	middle of the panel; blue shadow of the hills in the backround; to the left of the steeples on the island	ultramarine, unidentified
A4	white	right side of the panel; sky; white cloud	lipids, zinc carboxylate, zinc oxalate
R5	blue	mountains in the background; yellow and green mountain to the right of the main steeple; darker blue paint above the yellow mountain ridge	ultramarine
R6	dark blue or black	island in the middle of the panel; main steeple; belfry; dark blue or black window on the left (pink) belfry façade	carbon-based black
R7	dark blue or black	island in the middle of the panel; main steeple; lowest dark blue or black window the left (ochre) steeple façade	carbon-based black
A1	ochre	island in the middle of the panel; main steeple; bottom of the left (ochre) steeple façade	lipids, calcium carbonate, barium sulphate, zinc carboxylate, zinc oxalate
R8	ochre	right side of the panel; hills in the background; ochre painted foot of a mountain	barium sulphate, lead(II) chromate (?)

R9	ochre	right side of the panel; hills in the background; ochre painted foot of a mountain	barium sulphate, lead(II) chromate (?)
R10	yellow	mountains in the background; yellow and green mountain to the right of the main steeple; yellow painted mountain slope	barium sulphate
R11	yellow	mountains in the background; yellow and green painted mountain in the front left plane of the painting; right side of the mountain; yellow painted mountain slope	barium sulphate
R12	pinkish-red	island in the middle of the panel; left-hand side building; left side of the roof; bottom right corner	calcium carbonate
R13	red	island in the middle of the panel; middle building; left side of the roof; right corner above the tree	calcium carbonate
R14	red	island in the middle of the panel; right-hand side building; left side of the roof near the edge on the left	calcium carbonate (?)
A5			lipids, barium sulphate, calcium carbonate, unidentified material
R15	red	left side of the panel; castle on the cliff; middle building; roof of the building; the paint of the roof is a red underpaint (or an isolation or preparatory layer), covering entire panel surface under the paint layers of the motif	barium sulphate (?)
R16	red	left side of the panel; castle on the cliff; tower; roof of the tower; the paint of the roof is a red underpaint (or an isolation or preparatory layer), covering entire panel surface under the paint layers of the motif	calcium carbonate (likely calcite)
R17	red	island in the middle of the panel; middle building; middle area of the left side of the roof; area of missing topmost paint layer – exposed red paint is presumably a red underpaint (or an isolation or preparatory layer), covering entire panel surface under the paint layers of the motif	barium sulphate
R18	red	island in the middle of the panel; middle building; middle area of the left side of the roof; area of missing topmost paint layer – exposed red paint is presumably a red underpaint (or an isolation or preparatory layer), covering entire panel surface under the paint layers of the	barium sulphate, calcium carbonate (likely calcite)

		motif	
R19	red	mountains in the background; yellow and green mountain to the right of the main steeple; visible red underpaint (or an isolation or preparatory layer), covering entire panel surface under the paint layers of the motif	calcium carbonate (likely calcite)
R20	light green	island in the middle of the panel; greenery in the first plane of the painting; upper row of trees; third tree from the left	barium sulphate
R21	green	middle part of the panel; trees to the right of the main steeple, above and right to the the middle building of the island	barium sulphate
R22	green	island in the middle of the panel; greenery in the first plane of the painting; upper row of trees; sixth tree from the left	likely organic matter
R23	green	island in the middle of the panel; greenery in the first plane of the painting; upper row of trees; sixth tree from the left	iron oxide (Fe_2O_3)
PK4-3	yellowish-green	left edge of the panel; mountains in the background; yellow and green painted mountain in the front left plane of the painting; yellowish-green painted area	barium sulphate, lead(II) chromate (chrome yellow), calcium carbonate, PR 3, lipids, zinc carboxylate, lipids, oxalate
PK4-4	ochre and green	bottom edge of the panel; left bottom side of island's greenery; ochre and green paint	Prussian blue, ultramarine, carbon-based black, barium sulphate, PR 3, calcium carbonate, lead(II) chromate (chrome yellow), oxalate, lipids, zinc carboxylate

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