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St. Bruno. A Miracle in the Church: investigation of the painting technique

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A detailed investigation of the painting *St. Bruno. A Miracle in the Church* (1674) from the St. Francis of Assisi (Bernardine) Church in Vilnius was carried out. The ground, pigments and restoration materials were identified using combined analytical methods. FTIR and preliminary microchemical spot test results showed that the restoration materials were adhesives of several kinds. The structure of painting, the order of the main layers of painting, the distribution and colours of pigments have been described according to the results of a stratigraphic analysis of samples with an optical microscope. Analysis by the SEM / EDX and micro-XRD methods revealed the ground to contain chalk, ochre, lead white, minium and black carbon pigments. Smalt, azurite, lead tin yellow (type I) pigments as well as the lead white pigment, which is a mixture of hydrocerussite and cerussite, have been identified.

Key words: painting, pigment, FTIR, optical microscopy, SEM / EDX, micro-XRD

INTRODUCTION

Paintings from the St. Francis of Assisi (Bernardine) Church in Vilnius have been preserved in the collection of the Lithuanian Art Museum. This set of twenty non-altar paintings includes images of saints and depictions of their lives, miracles and episodes from the lives of Bernardine monks. These paintings are the only ones that have survived, at least partially, and hence are unique and of a great historical, iconographic and artistic value. They have been discussed in art historical texts several times [1, 2]. The paintings have not been investigated yet in terms of their technology and restoration because their large-format canvases have decayed significantly and are hardly accessible to scholars. Starting from 2004, the first painting of a large format (283 × 281.5 cm) from the St. Francis of Assisi (Bernardine) Church in Vilnius has been restored at the Pranas Gudynas Restoration Centre of the Lithuanian Art Museum (*St. Bruno. A Miracle in the Church* painted by Johann Gotthard Berchhoff [3] in 1674 (Ap. 9152, T 10117)). Successful restoration of cultural heritage largely depends on the accuracy and reliability of research into its technologies, which helps the restorers to characterize correctly the composition and structure of a work of art [4].

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The aim of this study was to identify materials that had been used during earlier restorations and their effect on the original structure of the painting. Another objective was to identify the painting's pigments and describe their structure using combined analytical methods (microchemical analysis, optical microscopy, spectroscopic analysis, and X-ray microdiffraction). The information obtained is crucial in answering questions concerning the technological particularities of this work of art, its identity and authorship, the time of its creation and authenticity.

EXPERIMENTAL

Firstly, the preliminary microchemical qualitative analysis of the lining materials, ground and paints was carried out. In this case, it was not very important to identify the binding material of the ground and the paint because the painting had been restored several times. The restoration materials from different areas of the back side of the painting were investigated by Fourier transform infrared spectroscopy (FTIR). Paint samples of various colours were analysed as microfragments and their cross-sections by optical microscopy and scanning electron microscopy coupled with an energy-dispersive X-ray spectrometer (SEM / EDX). In one case, powder X-ray microdiffraction (micro-XRD) was

additionally used for the phase (mineral) analysis in the yellow paint sample. The microchemical qualitative analysis was conducted by observing samples and reactions performed in reflected light using the Nikon SMZ–1 / SMZ–1ESD microscope (magnification 7 to 30×). Infrared spectra of the restoration material samples were recorded using a FT-IR–8400S spectrophotometer (Shimadzu) connected to an IR AIM–8 800 microscope and an MCT detector. The spectra were registered under the following conditions: the sample was mixed with KBr and pressed into a pellet using a manual MHP-1 minipress; the spectrum interval ranged from 4 000 to 400 cm^{-1}, 100 scans in total, 4 cm^{-1} resolution. Cross-sections of colour layers were studied after embedding small samples of paints in polyester resin and polished across the paint layers. Optical microscopy (Olympus BX-60 in reflected visible light and UV light in the wavelength range 330–380 nm), and scanning electron microscopy (Philips XL-30 CP) with an RBS detector of back-scattered electrons and an EDX analyser were used to describe the layer stratigraphy and elemental composition of various colour paint samples. A micro-X-ray X'PertPro (PANalytical) diffractometer with a 0.15 mm diameter of the primary beam was used for the phase analysis of yellow colour layer cross-sections. For phase identification, a HighScore (PANalytical) with the 2005 release of PDF-2 database was used.

RESULTS AND DISCUSSION

Paint samples for chemical analysis were taken from areas of authentic painting. A scheme of paint samples taken for chemical analysis is given in Fig. 1. The marked numbers correspond to paint samples described further.

FTIR spectroscopy

Two dates of previous restorations can be identified from the available art historical and historical data: 1765 and 1860 [1].

Fig. 1. Scheme of taking paint samples. Johann Berchhoff, *St. Bruno. A Miracle in the Church*, 1674, oil on canvas, 283 × 281.5 cm, Lithuanian Art Museum, Ap. 9152, T 10117

Ten samples of restoration materials from different areas of the back side of the painting were taken for analysis. Summarized results of FTIR and microchemical qualitative analysis revealed that during previous restorations adhesives of several kinds had been used for gluing the lining, its folds and patches:

a) a paste made of flour glue, natural resin and chalk. The use of pastes of uneven thickness and different fractions for gluing the linen of folds and patches formed a rather thick layer of the lining material: up to four different patches were counted in some places. A biologist from the P. Gudynas Restoration Centre performed a comparative analysis of grains found when a patch of the lining canvas had been lifted. This process confirmed that wheat flour had been used for preparing the lining adhesive.

The IR spectra of the lining paste, standard wheat flour adhesive and chalk are shown in Fig. 2. The IR spectrum of the lining paste shows a broad absorption band between 3 000 and 3 750 cm^{-1}, characteristic of O–H vibrations, as well as absorption bands at 2 922 cm^{-1} and at 2 854 cm^{-1}, characteristic of $–CH_3$ stretching vibrations. Also, peaks of middle intensity at 1 650 cm^{-1} (–CO–NH–) and 1 550 cm^{-1} (N–H) are attributable to the vibrations of the protein functional group. The rather intensive absorption band with the maximum at 1 425 cm^{-1} and a sharp peak at 873 cm^{-1} correspond to C–O vibrations of chalk [5]. The spectrum does not reveal either the vibrations of the carboxyl group characteristic of natural resin at 1 715 cm^{-1} or the characteristic absorption bands in the middle area of the IR spectrum, because the content of resin in the lining material is too small compared to other components. The presence of resin in the lining material was established by extracting the analysed sample with ethanol and then recording the IR spectrum;

b) a red ground whose composition includes chalk, red ochre and oil as a binding material. The ground used for gluing patches is of hard consistence. It had deeply penetrated the original canvas and was difficult to remove;

c) synthetic glue based on vinyl acetate copolymer was used to glue a patch. The IR spectra of the synthetic glue and vinyl acetate ethylene copolymer (VAE) are shown in Fig. 3. The absorption bands in both spectra at 2 933 cm^{-1} (C–H), 1737 cm^{-1} (C = O), 1 436 cm^{-1}, 1 369 cm^{-1} (C–H), 1 246 cm^{-1}, 1 121 cm^{-1}, 1 028 cm^{-1} (C–O) are clearly present and coincide well enough. The absorption bands and peaks found in the IR spectrum of the synthetic glue are attributable to the vinyl acetate copolymer [6].

Optical microscopy and SEM / EDX analysis

Ten paint samples from areas of the original painting were taken for analysis based on the details of UV and X-ray photographs. Optical photographs of paint cross-sections in the visible and UV light provided information on the order of the main layers of painting, the size of pigment particles, their distribution within a paint as well as colour, as well as information on the layer(s) of varnish [7].

Description of three paint samples: light grey (No. 1), blue-brownish (No. 5), yellowish (No. 7)

The photograph of the stratigraphic image of the light grey (No. 1) paint sample is presented in Fig. 4. It is quite conspicuous that the paint sample consists of three layers of painting: a layer of a brown-red ground of uneven thickness; a layer of

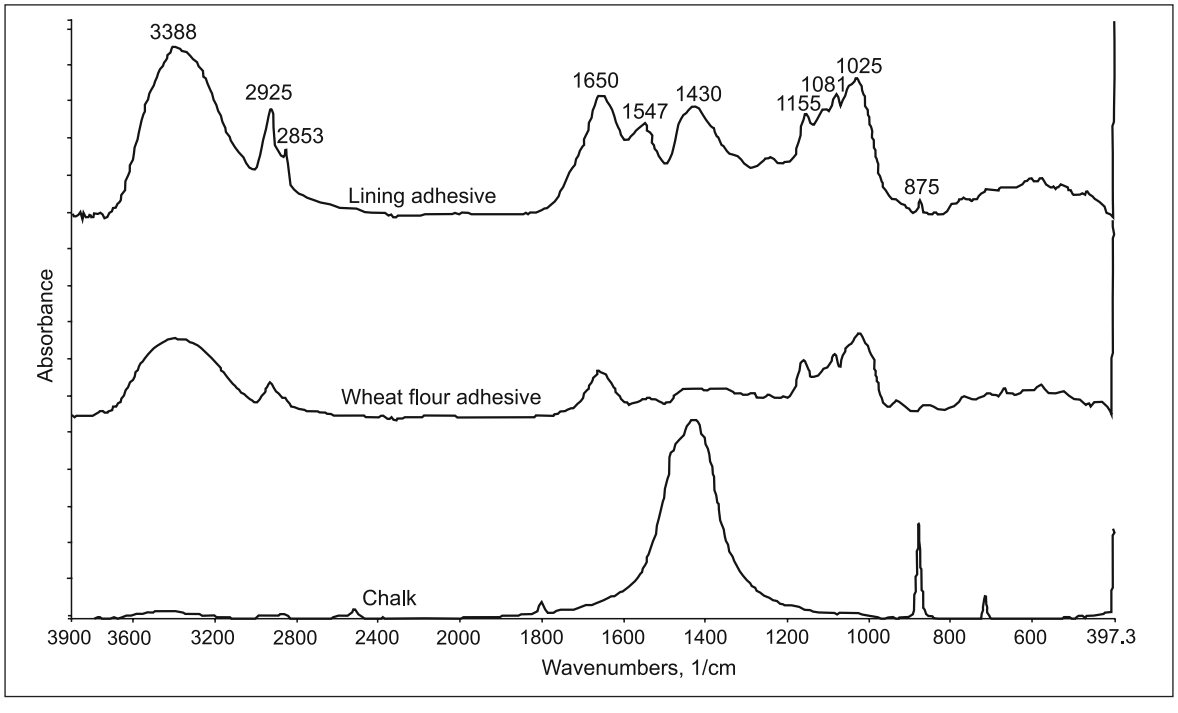

Fig. 2. FTIR spectra of lining adhesive, wheat flour adhesive and chalk

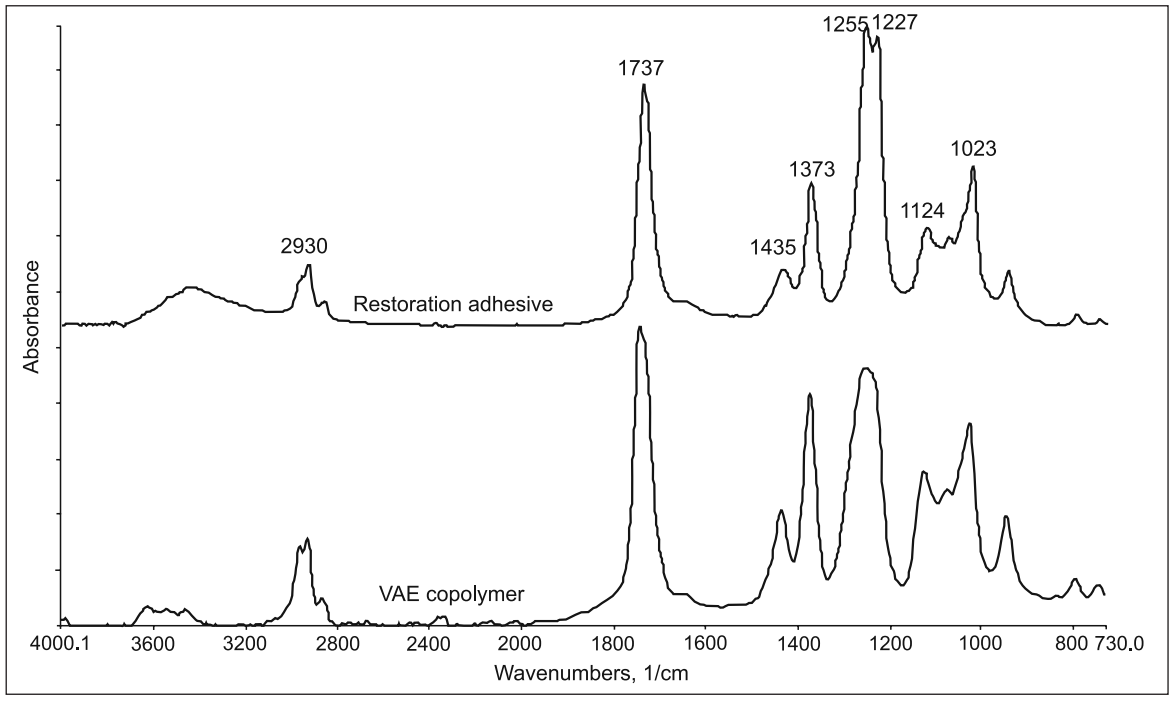

Fig. 3. FTIR spectra of restoration adhesive and vinyl acetate etilene copolymer (VAE)

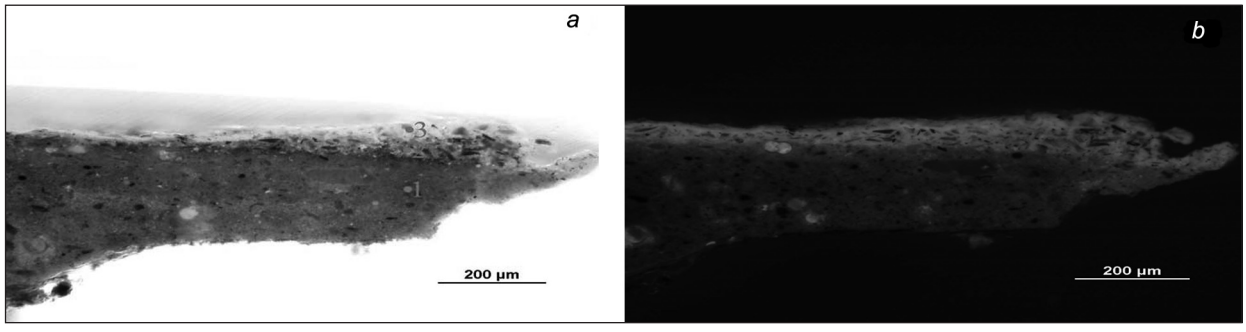

Fig. 4. Stratigraphic view of light grey paint (No. 1) sample, magnification 320×: a) visible light, b) UV light

a light grey paint, consisting of two layers of different blue colours: light greyish and dark blue vitreous smalt particles mixed with a white pigment.

The results of SEM / EDX analysis of the light grey paint (No. 1) at different cross-section points are listed in Table 1. The stratigraphic description of the light grey paint sample after the microchemical qualitative and EDX analysis has been summarized as follows:

I. The first layer is a brown-red ground that contains natural chalk, ochre, lead white, minium and black carbon pigments.

II. The second layer is an original layer of a dark blue paint, which consists of smalt and lead white pigments as well as chalk as small impurities.

III. The third layer is an original layer of a light greyish paint which contains smalt and lead white pigments. It also contains small amounts of chalk impurities.

Table 1. **SEM / EDX elemental composition of the light grey paint (No. 1) sample at different cross-section points (wt%)**

		Mg	Al	Si	Cl	K	Ca	Fe	Pb	Co	Ni	As
	Ground 1a	1.38	1.8	4.09	0.00	0.95	79.63	4.15	7.91	–	–	–
	Ground 1b	–	1.50	13.50	0.36	0.88	72.84	4.20	6.73	–	–	–
	Ground 1c	–	–	0.83	–	–	4.26	0.83	94.09	–	–	–
Paint layers	Paint layer 2a	–	1.18	24.75	–	5.09	4.87	1.75	59.07	1.80	1.13	0.35
	Paint layer 2b	–	1.67	65.00	–	14.53	2.76	2.08	10.18	3.29	–	0.51
	Paint layer 3a	–	1.47	59.41	–	24.97	2.06	1.56	7.34	2.28	–	0.92
	Paint layer 3b	–	1.15	20.56	–	1.81	9.20	0.77	65.95	0.57	–	0.00
	Paint layer 3c	–	1.57	54.52	–	25.37	2.45	2.08	9.86	3.30	–	0.85

The identified smalts of different colours (the 2nd and 3rd layers) contain a different amount of potassium, indicating that the processes of smalt production was different [8]. Moreover, the stability of smalt decreases as the content of K_2O increases. This may explain the different resistance of smalt to atmospheric conditions when its paling and greying are observed [9]. In our case, it is possible to explain the greying (clearing) of the third layer of paint because in this layer the smalt contained more potassium. Both layers of paint are original and have no streak of varnish. Smalt is potassium glass painted with cobalt oxide containing various impurities: SiO_2 66–72%, K_2O 10–21%, CoO 2–18%, As_2O_3 0–8%, as well as small amounts of calcium, manganese, iron, nickel and other oxides. This pigment was produced since the 15th century in Venice, Czechia and The Netherlands and was widely used in distemper, oil and wall paintings [10].

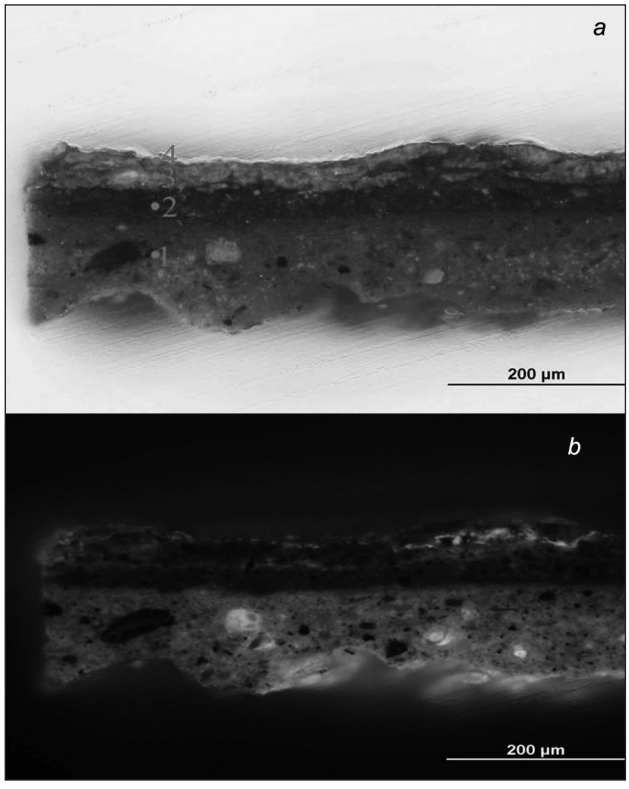

Fig. 5. Stratigraphic view of blue-brownish paint (No. 5) sample, magnification 225×: a) visible light, b) UV light

A photograph of the stratigraphic image of the blue-brownish (No. 5) paint sample is given in Fig. 5. It is possible to conclude that the paint sample consists of four layers of painting: the layer of a brown-red ground of uneven thickness, two layers of different blue-brownish colours of uneven thickness, and a layer of varnish.

The results of SEM / EDX analysis of the blue-brownish paint sample at different cross-section points are listed in Table 2. The stratigraphic description of the blue-brownish paint sample after summarizing the results of microchemical qualitative and EDX analysis is as follows:

I. The first layer is a brown-red ground that includes natural chalk, ochre, lead white, minium and black carbon pigments.

II. The second layer is an original layer of a brown-blue paint which includes smalt ($CoO \cdot K_2SiO_3$) in lead white pigment with azurite and chalk as small impurities.

III. The third layer is an original layer of a bluish-brownish paint, which contains azurite ($2CuCO_3 \cdot Cu(OH)_2$) in lead white pigment and chalk as small impurities.

IV. The fourth layer is varnish.

The layer of the blue-brownish paint consists of two layers of paint of a different chemical composition. The bottom layer contains cleared greyish smalt which is quite easily recognisable from elongated, sharp particles with visible broken edges [11], mixed with a pigment of bright blue azurite and lead white pigment, and the top layer is dominated by bright blue, roughly ground particles of the azurite pigment mixed with lead white pigment. IR spectroscopic analysis confirmed the presence of azurite pigment in the blue paint. The visible browning of the blue paint layer was caused by the binding materials of the paint and the fact that the layer of varnish covering the paint had yellowed.

Such a combination of two layers of a blue paint in paintings has been known from the 15th century written sources and the peculiarities of painting techniques of certain periods, which were partially determined also by the economic conditions of the time: due to wars in Turkey it was difficult to import natural ultramarine and azurite to Europe; thus, smalt was used more widely [8, 12]. The inexpensive smalt pigment, the ground melt of quartz sand, potash and cobalt,

Table 2. **SEM / EDX elemental composition of the blue-brownish (No. 5) paint sample at different cross-section points (wt%)**

		Mg	Al	Si	Cl	K	Ca	Fe	Cu	Pb	P
Paint layers	Ground 1a	–	1.42	5.14	–	1.27	74.88	6.15	1.18	9.96	–
	Ground 1b	–	–	–	–	–	3.85	0.66	0.80	94.69	–
	Ground 1c	2.45	1.51	2.60	–	–	32.30	6.45	2.66	52.03	–
	Ground 1d	1.20	2.50	4.85	6.41	0.72	76.87	3.91	1.51	7.15	1.29
	Paint layer 2a	1.63	2.12	8.87	–	2.68	4.85	1.23	32.29	39.93	–
	Paint layer 2b	–	1.17	2.56	3.19	0.69	5.34	0.57	73.74	12.74	–
	Paint layer 2c	1.01	1.49	17.75	4.62	2.52	8.55	1.80	31.12	31.13	–
	Paint layer 3a	–	–	1.73	7.50	0.19	1.64	0.72	80.68	7.55	–
	Paint layer 3b	–	0.49	1.52	9.18	–	2.05	0.69	65.93	20.13	–

had a tendency to turn pale and grey, especially if ground too finely, or when its production processes were not technologically sound and too much potash had been added into the melted mixture. Thus, smalt used to be mixed with bright blue but much more expensive pigments: ultramarine and azurite [13].

A photograph of the stratigraphic image of a yellowish paint (No. 7) sample is shown in Fig. 6. It is possible to assume that the sample consists of four layers of paint. The SEM / EDX results of the yellowish paint at different cross-section points are listed in Table 3.

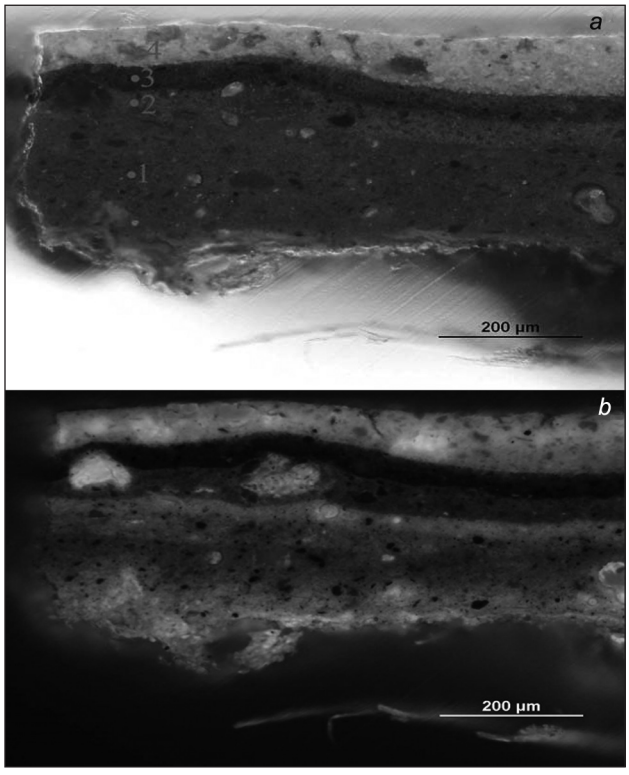

Fig. 6. Stratigraphic view of yellowish paint (No. 7) sample, magnification 225 ×: a) visible light, b) UV light

The stratigraphic description of the yellowish paint sample after summarizing the results of microchemical qualitative and EDX analysis are as follows:

I. The first layer is a layer of brown-red ground, which contains natural chalk, ochre, lead white, minium and carbon pigments.

II. The second layer is a brown layer that contains natural chalk, ochre (including Mn), lead white, minium and auripigment (As_2S_3) pigments.

III. The third layer is an original brown layer of paint, which contains natural chalk, ochre (including Mn) and lead white pigments.

IV. The fourth layer is a yellowish layer of paint that contains lead tin yellow (Pb_2SnO_4) and lead white pigments.

Micro-XRD analysis

The micro-XRD analysis of yellowish paint (No. 7, the fourth layer) has allowed us to establish that the yellow pigment is lead tin yellow (Pb_2SnO_4) type I. Its X-ray diffraction pattern is shown in Fig. 7. Three phases have been identified in the X-ray diffraction pattern of the yellowish paint and attributed to lead tin oxide (Pb_2SnO_4) (JCPDS No. 24-0589), lead white pigment consisting of hydrocerussite ($(2PbCO_3 \cdot Pb(OH)_2)$) (JCPDS No. 13-0131) and cerussite ($PbCO_3$) ((JCPDS No. 47-1734). After the XRD analysis of several painting samples from the Renaissance period, researchers [14] have discovered that the ratio of two lead carbonate phases (hydrocerussite and cerussite) found in the composition of the paint may be very different depending on a sample and could be characteristic of a certain period, technical knowledge of how to produce this pigment, and its geographical origin. Moreover, these data may be related to the conditions of chemical synthesis and preparation of lead carbonates.

The lead tin yellow pigment can be of two types: lead tin yellow type I (Pb_2SnO_4) and lead tin yellow type II ($PbSn_{1-x}Si_x0_3$) The lead tin yellow type I pigment had been widely used in painting since 1300, but it had been also used in

Table 3. **SEM / EDX elemental composition of yellowish paint (No. 7) sample at different cross-section points (wt%)**

		Mg	Al	Si	K	Ca	Fe	As	Pb	P	Ti	S	Mn	Sn
Paint layers	Ground 1a	2.09	2.53	8.08	1.01	69.12	6.32	–	10.85	–	–	–	–	–
	Ground 2a	0.78	6.40	11.55	0.89	50.45	9.22	–	18.88	1.25	0.58	–	–	–
	Ground 2b	–	–	–	–	4.73	0.42	–	93.85	–	–	–	–	–
	Ground 2c	–	–	1.07	–	2.83	0.91	45.61	–	–	–	49.58	–	–
	Ground 2d	–	5.31	6.70	1.51	17.65	5.47	–	63.36	–	–	–	–	–
	Ground 2e	1.65	4.31	13.51	1.07	35.47	16.73	–	20.38	4.21	0.75	–	1.91	–
	Ground 2f	–	2.27	4.39	–	11.48	4.20	–	77.67	–	–	–	–	–
	Paint layer 3a	–	–	92.02	–	2.09	0.91	–	4.98	–	–	–	–	–
	Paint layer 3b	1.40	3.74	8.93	0.93	40.29	16.08	–	24.08	2.27	0.90	–	1.38	–
	Paint layer 4a	–	5.20	8.56	–	3.28	3.87	–	72.36	–	–	–	–	6.74
	Paint layer 4b	–	2.03	4.56	–	2.48	1.58	–	69.16	–	–	–	–	20.20
	Paint layer 4c	–	–	0.84	–	2.51	0.86	–	54.26	–	–	–	–	41.53
	Paint layer 4d	–	–	0.87	–	1.77	1.13	–	96.23	–	–	–	–	–
	Paint layer 4e	–	–	2.61	–	5.92	2.73	–	88.74	–	–	–	–	–

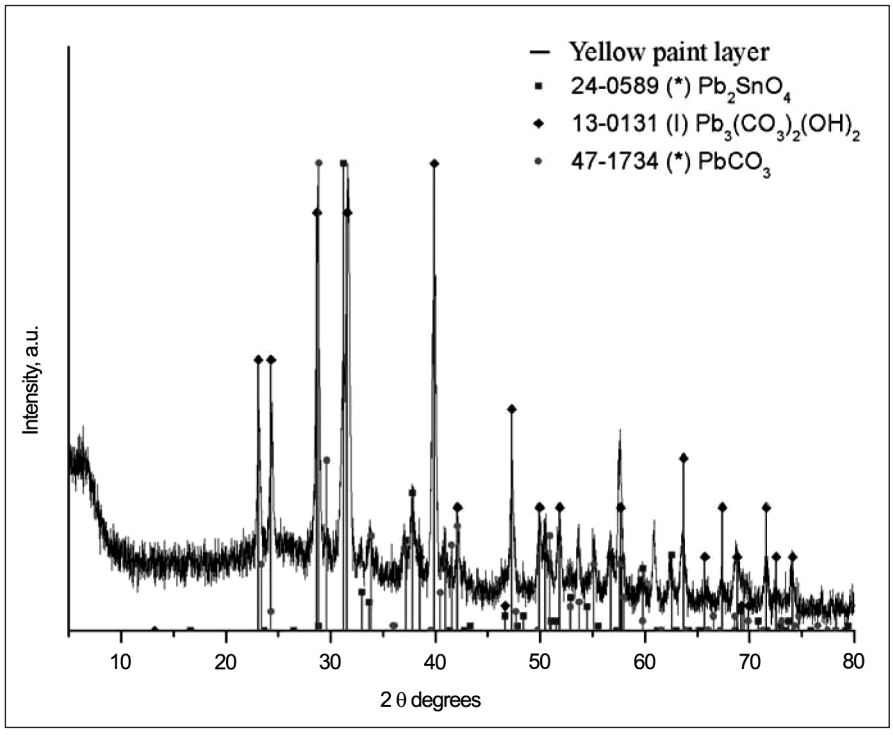

Fig. 7. X-ray diffraction pattern of yellow layer (4th layer, Fig. 6a) of yellowish paint sample No. 7

glass making since ancient times as a means to cloud the glass and a yellow pigment to paint the glass, and also when producing the lead tin yellow type II pigment [15–18].

CONCLUSIONS

A combination of microchemical qualitative analysis, optical microscopy, spectroscopic and micro-XRD analytical methods has been used to identify pigments and materials used during previous restorations. IR spectroscopic and microchemical qualitative analysis data showed that adhesives of several kinds were used for lining, folding and gluing the patches which had been used during previous restorations.

Based on the results of stratigraphic analysis of the samples with an optical microscope, the structure of painting, the order of the main layers of painting, the distribution of pigments and colours have been described. The SEM / EDX and micro-XRD analysis confirmed that the painting was painted on a ground that contains natural chalk, ochre, lead white, minium and black carbon pigments. Smalt, azurite, lead tin yellow type I pigments as well as a lead white pigment, which is a mixture of hydrocerussite and cerussite, have been identified.

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PAVEIKSLO *ŠV. BRUNONAS. STEBUKLAS BAŽNYČIOJE* TAPYBOS TECHNIKOS TYRIMAS

S a n t r a u k a

Atliktas išsamus 1674 m. Johanno Berchhoffo tapyto paveikslo *Šv. Brunonas. Stebuklas bažnyčioje* (Vilniaus Šv. Pranciškaus Asyžiečio (Bernardinų) bažnyčia, Ap. 9152, T 10117, 283 × 281,5 cm) tyrimas. Derinant kelis analizinius metodus nustatytos ankstesnių restauravimų metu naudotos medžiagos ir jų poveikis autorinei paveikslo struktūrai, identifikuotas paveikslo gruntas ir pigmentai, aprašyta tapybos struktūra. Atlikus IR spektrinę bei mikrocheminę kokybinę analizę nustatyta, kad paveikslo ankstesnių restauravimų metu dubliavimui, užlankoms ir lopams klijuoti buvo naudoti kelių rūšių klijai: a) kleisteris, kurio sudėtyje yra miltų klijai, natūrali derva ir kreida; b) raudonas gruntas; c) sintetiniai klijai polivinilacetatinės dervos pagrindu. Remiantis stratigrafinės mėginių analizės, optinės mikroskopijos rezultatais aprašyta tapybos struktūra, pagrindinių tapybos sluoksnių eiliškumas ir pigmentų pasiskirstymas bei spalva. Atlikus SEM / EDX bei XRD analizę nustatyta, kad paveikslas tapytas naudojant gruntą, kurio sudėtyje yra natūrali kreida, ochra, švino baltasis, surikas bei juodas anglies pigmentai. Identifikuoti smaltos, azurito, švino–alavo geltonojo tipo I pigmentai, taip pat švino baltojo pigmentas, kuris yra hidroceruzito ir ceruzito mišinys.