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An investigation of the lead tin yellows type I and II and their use in Bohemian panel paintings from the Gothic period

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Abstract

Background: Presented article summarizes the results of a broad-based survey on painting techniques used during the High and Late Gothic period in the Bohemian panel paintings located in the collections of the National Gallery in Prague. The work is focused on the specific use of yellow pigments – lead tin yellow type I and type II in the panel painting from the period around 1340–1550. In the scientific investigation supplementary microscopic and spectral analyses were made. A representative range of 57 micro-samples collected from the 36 panel paintings of the 21 Masters and their workshops was investigated by the methods of optical microscopy on polarizing microscope (OM). Molecular analysis of both types of yellow was performed using Raman micro-spectroscopy (RMS). The use of this technique was crucial for the nondestructive differentiation between each type of lead-tin yellow.

Results: Thanks to the Raman spectroscopy it was possible for the first time to map the usage of lead tin yellow type I and II in such a broad range. Combination of the analytical techniques brought the knowledge about the morphology of the grains and variability of the use of the lead tin yellows in the Bohemian panel paintings.

Conclusions: The contribution offers a systematic view on the outcomes and in a synoptic way consults the results of respective scientific methods. It clearly confirms both the temporally and locally specific use of both types of lead tin yellows. The presented facts are the results of interdisciplinary collaboration among the scientists and the art historian.

Keywords: Lead tin yellow type I, Lead tin yellow type II, Pigment, Bohemian panel paintings, Medieval period, Raman micro-spectroscopy

Introduction

In the presented article we would like to introduce the results of our survey focused on the painting techniques used during the High and Late Gothic period in the Bohemian panel paintings located in the collections of the National Gallery in Prague, in particular on the specific use of yellow pigments – lead tin yellow type I and lead-tin yellow type II. These types of pigments were identified on the panel paintings from the period around 1340–1550. A number of important Bohemian artworks was studied, among others the paintings of the Master of the Vyšší Brod Cycle (Höhenfurth, around 1340–1350), Magister Theodoricus and assistants (around 1360–1370) [1], the Master of the Třeboň Altarpiece (Wittingau, around 1370–1390) [2], the Master of the Rajhrad Altarpiece (around 1430), the Master of the St George Altarpiece (around 1470–1480), the oeuvre of the Master of the Litoměřice Altarpiece (around 1500-1520/1525) [3] and the Monogrammist IW (around 1520–1550) [4-9].

The oldest references that mention the usage and preparation of lead tin yellow pigments can be found in medieval manuscripts [10-12], but the situation is complicated by the ambiguous denominations of the yellows in various sources. According to Marrifield [13] three types of lead yellows existed, one of them called in Italian literature giallolino or giallorino with attribution fino or di Fiandra [14,15], in Western European literature it was called massicot [16,17]. The second type was denoted as giallo di vetro and was probably of Italian origin, the third one was Naples yellow, which contained also antimony [18]. The first two types are supposed to be lead-tin yellows and the literature sources illustrate that

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the preparation was connected with glass production [19,20]. From these literature sources we should mention the Bolognese Manuscript or more illustrative books of recipes of ancient glassmakers and the examples from the scientific literature that are preserved in transcriptions from the 16th and 17th century. These documents evidence the usage of lead and tin in preparation of yellow glass, enamels or ceramics and their connection with painting [21].

Lead tin yellow type I and type II can be distinguished by the chemical composition. Lead tin yellow type I has the chemical formula Pb_2SnO_4 with orthorhombic crystal structure and space group Pbam. Chemical formula of lead tin yellow type II was determined to be $PbSn_{1-x}Si_xO_3$ and should have the structure of pyrochlore with space group Fd3m.

Some historical manuscripts contain the recipes with more detailed instructions for the preparation of the pigments, describing the amount of main substances [10], or the ratio of the components. Nevertheless, the precise directions for the preparation, which would include also the experimental conditions, are not known. For this reason some of the previous research works were focused on the preparation of the lead tin yellow type I and II and registered the conditions in which these pigments can be manufactured [22-24].

Lead tin yellow type I was prepared mixing the lead (II, IV) oxide Pb_3O_4 (lead (II) oxide PbO or both components are also possible) with tin oxide SnO_2, and calcining them at elevated temperature.

$$2Pb_3O_4 + 3SnO_2 \rightarrow 3Pb_2SnO_4 + O_2$$

The firing temperature was found to be higher than expected at the beginning by Jacobi, rather around 800–900°C. At lower temperatures the presence of minium Pb_3O_4 was detected in the final product (the reaction was incomplete). At higher temperatures the decomposition of final product can occur and the presence of PbO and SnO_2 can be expected in the mixture. However the presence of PbO as massicot can arise also from the improper ratio of primary substances even if the process is done at suitable temperatures [22,25].

Lead tin yellow type II was prepared by the calcination of lead tin yellow type I and silicon oxide at temperatures between 800–900°C.

$$Pb_2SnO_4 + SiO_2 \rightarrow PbSn_{1-x}Si_xO_3$$

Also here the primary substances can be found in final mixture if the temperature is lower than necessary. At higher temperatures the pigment can decompose to the lead oxide PbO, silicon oxide SiO_2 and tin oxide SnO_2.

The first identification of lead tin yellows by means of advanced instrumental techniques was carried out in 1940 in the Doener Institut in Munich by the emission spectroscopy [23]. Since then thanks to the development of the instrumental analytical techniques it was possible to confirm the presence of lead tin yellows in many other artworks. X-ray diffraction (XRD) or Raman spectroscopy can be used for this purpose [26-28]. Elemental analysis (such as scanning electron microscopy with energy dispersive analysis or X-ray fluorescence) could be used as a complementary technique [29], but the differentiation of each type by the presence of silica could be misleading because of the frequent combination with earth pigments that contain quartz [30].

A summary of the historical usage of both types of yellow pigments in paintings was published by Kühn [31]. The work reports that the lead tin yellow type I was commonly used from the half of the 15th to the 18th century in the whole European region [19]. On the other hand an extended use of the lead tin yellow type II was documented in the period from the beginning of the 14th century to the first half of the 15th century especially in the Italian paintings where the connection to the glass production is pointed out [20]. Presence of this pigment in Italian paintings was relatively widely investigated and it was identified in paintings from the region of Tuscany (Florence, Pisa, Siena), Veneto (Venice) and Lazio (Viterbo) [32]. There are some rare examples in the literature where the Bohemian paintings are mentioned, usually in connection to the Bohemian glass production [20]. No broader investigation that would report on the presence of these pigments in Bohemian paintings has been carried out so far. From the beginning of the 15th century till the end of the 16th century there are some rather unique findings in the paintings of the Italian High Renaissance masters (Tintoretto) and the Dutch painter Hendrick ter Brugghen [33].

The use of both types of lead-tin yellows detected in a single painting is rare, for example in the painting by Veronese or El Greco. [34,35] In these cases the lead tin yellows type I and II were used always in the different parts of the painting, probably with the intention to obtain the different colour tone. On the other hand on the painting Gonfalone della Giustizia by Perugino (1496, Galleria Nazionale dell'Umbria, Perugia) and on the portrait of Lady Spenser by the British artist John Bettes (1590, private collection) the presence of both types of yellow in one layer was detected [36]. Thanks to the scientific examinations carried out in the National Gallery in Prague it was possible to extend the knowledge about the use of lead tin yellows and confirm the presence of lead tin yellow type I and II in many precious artworks of Bohemian provenance.

Experimental

For the identification of lead tin yellows in the 36 artworks of Bohemian provenance 57 micro-samples from archive of the chemical-technological laboratory of the National Gallery in Prague were used. These samples were collected and archived in the period from 70‘ of the 20th century till now, usually in context of the interventions of restoration and the connected scientific examinations. The samples are conserved in the form of cross-sections embedded in resins based on methyl methacrylate (Spofacryl, Clarocit), as microscopical preparations or also as individual pieces that remained after the microchemical analysis. Permanent microscopical preparations were prepared by fixing a small amount of pigment to the Canada balsam or acrylate binding media (Veropal KP 709) dissolved in organic solvents. Through the years standard analyses were performed in chemical-technological laboratory including especially analysis by means of optical microscopy, microchemical analyses or X-ray fluorescence [37]. Standard analyses of the elemental composition were carried out on the cross-sections using a scanning electron microscope with energy-dispersive X-ray analysis (SEM/EDX) [38]. The element identification was done in points directly on the pigment particles or on small areas in the layers. Analyses using the SEM/EDX method were carried out on a JEOL JSM 6460 LA in the chemical-technological laboratory of the National Gallery in Prague or on a JEOL JXA 50A/EDAX electron micro-analyzer in the Geological Institute of the Academy of Sciences of the Czech Republic.

Raman spectroscopy was used during the investigations of all samples as the fundamental technique which allows to distinguish between the molecular structures of both types of yellow [39]. Standard pigments were analyzed before the real samples investigation by means of Raman spectroscopy and by optical microscopy. These pigments were acquired from Kremer Pigmente or Böke & Fritz company and were indicated with the trademarks Lead Tin Yellow deep type I (Kremer No. 10110), Lead Tin Yellow I (Böke & Fritz Art. No. 101-7) and Lead Tin Yellow type II (Kremer No. 10120). Other standard pigments were investigated during the study because their presence was expected to be found in the real samples (Table 1). These pigments were also provided by Kremer Pigmente or Böke & Fritz company.

Optical microscopy (OM)

Observation of the cross sections was carried out on a polarizing microscope Eclipse 600 Nikon in reflected and transmitted light, in a dark field and after excitation by UV light using the UV filter of 330–380 nm and 450–490 nm. Morphological characteristics of individual pigment grains in microscopical preparations were examined in transmitted polarized light in parallel (PPL) and crossed (XPL) nicols. The magnification used was usually 200-1000×. Micrographs of the preparations and also of the cross sections of real samples were made with a digital camera Nikon Coolpix 4500 and DS-Fi2.

Raman micro-spectroscopy (RMS)

Molecular analysis by means of Raman micro-spectroscopy (RMS) was performed on the individual pigment grains or on the cross-sections using the mapping mode for better observation of individual components present in colour

Table 1 Raman band wavenumbers of lead-tin yellow I and II and inorganic pigments that were usually observed in the painting layers

Pigment	Chemical formula	Manufactured	Wavenumbers (cm^{-1}), laser 780 nm
Azurite	$2\ CuCO_3 \cdot Cu(OH)_2$	Böke & Fritz	83 s, 112w, 153 s, 178w, 234 m, 237w, 263vw, 278vw, 328w, 398vs, 538vw, 762w, 837w, 934w, 1094s, 1416 m, 1426bm, 1455vw, 1574 m, 1650vw
Chalk (Calcit)	$CaCO_3$	Böke & Fritz	155w, 282 m, 712vw,1086vs,
Lead tin yellow, type I.	Pb_2SnO_4	Kremer 10100	80 m, 130vs, 196 m, 275sh, 292w, 379w, 457w, 525vw
Lead tin yellow, type I.	Pb_2SnO_4	Böke & Fritz	80 m, 130vs, 196 m, 272sh, 290w, 379w, 454w, 525vw
Lead tin yellow, type I. (red particles)	Pb_2SnO_4	Böke & Fritz	80 m, 130vs, 196 m, 272sh, 290w, 379w, 454w, 525vw, 547vw
Lead tin yellow, type II.	$Pb(Sn,Si)O_3/PbSn_{1-x}SixO_3$	Kremer 10120	67 s, 138vs, 263 vw (sh), 325vw (sh), 450 sh, 635vw (sh)
Lead white	$2\ PbCO_3 \cdot Pb(OH)_2$	Kremer 46000	74 s, 104 s, 129 s, 142br, 414vw, 680vw, 966w, 1051s, 1364vw, 1476vw(br)
Malachite	$2\ CuCO_3.Cu(OH)_2$	Kremer 44400	78 m, 151 s, 178 s, 218 m, 269 m, 353 m, 432 s, 533w, 719w, 753w, 795vw, 1093w, 1367w, 1491s
Minium	Pb_3O_7	Kremer 42500	63 m, 86vw, 121vs, 143 m, 151 m, 220w, 289sh, 314w, 319 m, 417vw, 455vw, 549 s
Massicot	PbO	Kremer 43101	71 m, 87 s, 143vs, 288 s, 384vw
Vermilion	HgS	Kremer 10610	101w, 252vs, 282w(sh), 341 m
Yellow ochre	FeO(OH)	Böke & Fritz	92 m, 144 m, 247w(sh), 263w, 301 m, 399vs, 480w(sh), 558w, 705vw

All standard pigments were manufactured by the companies Kremer or Böke & Fritz; s - strong, m - medium, w - weak, v - very, sh - shoulder, br - broad.

layers. Raman spectra were collected by the Raman microscope Nicolet DXR (Thermo Scientific, USA), equipped with a CCD camera for signal detection. Two diode lasers with wavelength of 532 nm and 780 nm and maximum power of 10 mW and 24 mW, respectively, were used as the excitation source. The laser was focused on the sample through a 50× and 100× objective lens.

First of all the investigation of standard pigments was performed to identify the suitable measuring conditions for the pigments in order to keep the analytical technique nondestructive. Both types of laser were used for the analysis of standard pigments and the maximum power (MP) of each excitation source was determined. For the analysis of real samples the laser of 780 nm was preferred because of the lower energy of the excitation source and thus the higher resistance of the samples. The power of the laser depended on the composition of the pigment mixture and the sensitivity of individual components. Usually the power of 2–10 mW was used with acquisition time from 5 to 15 minutes. Mapping was performed on the selected samples using lower power of the laser and acquisition time from 1 to 3 minutes. The step of the acquisition was chosen to be 2–3 μm investigating different areas of the samples. Raman spectra were processed in the program Omnic 9.

Results and discussion

The results that were obtained from the standard pigments pointed out some diversities and specifics in the identification of both yellows. From the real samples the use of the lead tin yellow type I and II in the artworks of Bohemian provenance was widely evidenced (Table 2).

Standard pigments

The particles of lead-tin yellow type I are made of very fine grains accumulated in the aggregates with angular, irregular, crumb-like morphology. The colour of the particles is very light yellow to white in reflected light. The particles are anisotropic, birefringent, under crossed polars white or light yellowish. On the other hand the particles of lead-tin yellow type II are bigger than the particles of type I and form medium-sized grains. The particles are translucent and have light yellow to orange yellow colour, very high relief and their surface has a rough, glassy appearance. The particles are isotropic under crossed polars and with lemon yellow internal reflections [40].

During the measurements of standard pigments (Kremer No. 10110, 10120, Böke & Fritz Art.No.101-7) by means of Raman micro-spectroscopy a higher sensitivity of both yellows on the excitation laser of 532 nm was observed. The MP for laser of 532 nm was 1 mW for lead tin yellow type I and 4 mW for lead tin yellow type II. Laser of 780 nm was used for the investigation of the samples from the artworks because of the resistance of both pigments to the excitation source in full range of power. The disadvantage of this laser lies in the worse detection of some green pigments present in the pigment mixtures because of the very low Raman signal. These pigments (verdigris or malachite) were detected already during the previous investigations and were identified by means of optical microscopy, micro-chemical tests and SEM/EDS.

In Figures 1 and 2 Raman spectra collected from both types of standard pigments are presented. Composition of presented pigments lead tin yellow type I from Böke & Fritz Art.No.101-7 as well as type II from Kremer No. 10120 shows certain non-uniformity from the chemical point of view. Spectrum of the type I shows the typical Raman bands (Table 1), with the main band at 130 cm^{-1}, assigned to the lattice vibration of Pb-O [23]. Variations in the spectral curve were observed in the region between 500-550 cm^{-1}, where the double peak at 525 cm^{-1} and 547 cm^{-1} was observed in some cases (see Figure 1a, b). Variations in this region observed also by Clark, who was comparing the spectra of this pigment with the spectra collected by Vigouroux [41]. Both authors found in this region a single peak in their spectra and these peaks differ in maxima corresponding to the maxima of this doublet (Vigouroux - 540 cm^{-1}, Clark - 524 cm^{-1}). Raman band with the maximum around 549 cm^{-1} could be found also in the Raman spectrum of minium (Pb_3O_4, spectrum in Figure 1c and the details below), which could be one of the components involved in the manufacture of the pigment, according to the literature sources [10]. The presence of minium in the composition of lead tin yellow type I can be caused by improper firing conditions, for example by the lower temperature during the calcination. Pigment lead tin yellow deep type I from Kremer No. 10110 demonstrated uniform composition within the measurements.

Lead tin yellow type II gave the typical bands in Raman spectra, with the main maximum corresponding to the vibration of Pb-O at 138 cm^{-1} [23]. This type of yellow showed also non-uniform composition as showed in Figure 2a and b. The Raman band at about 635 cm^{-1} is probably caused by the presence of tin oxide (SnO_2 - cassiterite - in Figure 2c and the detail below), that could be also formed by improper firing conditions, for example by a higher calcination temperature.

Paintings

The wide investigation of the paintings of the Bohemian provenance clearly demonstrated the utilization of the lead tin yellow type II as an individual pigment earlier than was documented till now (see Table 2). This pigment was confirmed in the artworks assigned to the period from 1345(50) to 1420. The oldest examples of its use were detected in the panel paintings of the Master of the Vyšší

Table 2 Description of the analysed panel paintings and samples

Artist	Title of panel painting	Gallery/ Inv. No.	Dating	Sample no.	Colour and description of sampling area	Type of lead-tin yellow	In mixture of pigments
Master of the Vyšší Brod Cycle	Vyšší Brod Cycle - Adoration of the Magi	CA, O 6788	1345-1350	98-42-3	green reverse side of the cloak of Virgin Mary	II	lead white, cooper green pigment, probably earth pigments
Master of the Vyšší Brod Cycle	Vyšší Brod Cycle - Christ on the Mount of Olives	CA, O 6789	1345-1350	98-88-5	green cloak of St John	II	lead white, cooper green pigment
Master of the Vyšší Brod Cycle	Vyšší Brod Cycle - Resurrection	CA, O 6792	1345-1350	03-54-4	yellow reverse side of the cloak	II	-
Master of the Vyšší Brod Cycle	Vyšší Brod Cycle - Descent of the Holy Ghost	CA, O 6794	1345-1350	07-48-3	green reverse side of the red cloak	II	yellow ochre, lead white, copper green pigment
				07-48-10	yellow cloak on the left side	II	-
Magister Theodoricus	Chapel of the Holy Cross at castle Karlštejn – John Baptist	NPU, KA 3671	1360-1364	KA 3671-1B	green in cross in the halo of the lamb	II	copper green pigment
Magister Theodoricus	Chapel of the Holy Cross at castle Karlštejn – Angel	NPU, KA 3710	1360-1364	KA 3710-1	green wing of angel	II	copper green pigment, yellow ochre
Magister Theodoricus	Chapel of the Holy Cross at castle Karlštejn – Lamb of god	NPU, KA 3711	1360-1364	KA 3711-1	green in the halo of the lamb	II	copper green pigment, yellow ochre, traces of azurite
Anonym (Prague)	Votive Panel of John Očko from Vlašim	NG, O 84	before 1371	91-6-7	green reverse side of the cloak of Virgin Mary (highlight)	II	traces of vermilion, black
				91-6-8	green reverse side of the cloak of Virgin Mary (shadow)	II	copper green pigment, traces of black, vermilion
				91-6-14	yellow robe of the St Ludmila	II	yellow ochre, vermilion, traces of black
				91-6-16	yellow robe of the St Ludmila (shadow)	II	yellow ochre, traces of black
				91-6-20	yellow handle of the sword	II	lead white
Master of the Třeboň Altarpiece and his workshop	Crucifixion from the church of St Barbora	NG, O 577	late 1370s	08-43-3	decorated robe of soldier	II	cooper green pigment (probably verdigris) (degraded)
				H-6	soldier's robe	II	-
				H-12	reverse side, imitation of the marble	II	-
Master of the Třeboň Altarpiece	Deposition/SS Giles, Augustine, Jerome	NG, O 1266	after 1380	10-28-2B	decorated yellow robe of St Jerome	II	lead white
Anonym (Prague,?)	Madonna with SS Bartholomew and Margaret	NPU	ca. 1390	11-32-2	green cloak of St Margaret (highlight)	II	yellow ochre, lead white, cooper pigment (probably verdigris)
				11-32-3	green cloak of St Margaret (shadow)	II	yellow ochre, lead white, cooper pigment (probably verdigris)

Table 2 Description of the analysed panel paintings and samples *(Continued)*

Master of the Třeboň Altarpiece and his workshop	Our Lady Ara Coeli	NG, O 1457	1385-1390	08-35-1	yellow cloak of St Jerome	II	lead white
				08-35-2	green cloak of St Margaret	I and II	verdigris, lead white
				08-35-8	green robe of Prophet Ezekiel	II	verdigris, lead white
Anonym (Prague)	Votive Panel, called from Dubeček	NG, O 693	before ca. 1390	08-41-12	green drapery of St Vitus	I	verdigris, lead white
Anonym(Prague)	Triptych with Death of the Virgin called the Roudnice Altarpiece - inside of right wing, Man of Sorrows and eight kneeling devotes	NG, O 1466	ca. 1410-1420	10-56-6	yellow collar of the bishop	I and II	lead white, vermilion
Master of the Rajhrad Altarpiece	Last supper	MGB, A 624	ca. 1430-1440	11-16-2	green cloak	I	lead white, verdigris
Master of the Saint George Altarpiece	St Vitus/ Eagle - Symbol of the St John the Evangelista	NG, O 7035	ca. 1470	09-27-2	brown cloak of St Vitus	I	lead white, verdigris
Hans Maler Jr. (?)	Retable, called from Kadaň – Annunciation/Nativity	NG, O 7036	ca. 1480	12-57-7	yellow robe of angel	I	lead white
Master of the Vejprnice (Budňany) Altarpiece and workshops	Annunciation to the Virgin Mary, Circumcision/Crucifixion, Crowning of Christ with Crown of Thorns	NG, O 1334	after 1490	09-38-2	Veronica's veil	I	lead white, verdigris
				09-38-3A	green cloak of angel	I	lead white, verdigris
				09-38-5A	white robe of angel	I	lead white
Master of the Vejprnice (Budňany) Altarpiece and workshops	Nativity, Adoration of the Magi/Resurrection, Assumption	NG, O 1335	after 1490	09-39-1A	guard's turban and background	I	lead white, yellow ochre
				09-39-5A	king's robe	I	verdigris, lead white
Master of the Rakovnik Altarpiece	The scourging of Christ	TGM Rakovnik	1496	06-77-1	yellow, soldier's leg	I	lead white, quartz, red pigment
Master of the Rokycany Altarpiece	Adoration of the Magi	NM, VO 11260	before 1500	06-51-8	grey drapery	I	verdigris
Master of the Rokycany Altarpiece	Bearing of the Cross	NM, VO 11260	before 1500	06-57-3	yellow turban	I	lead white
				06-57-7	green ground	I	verdigris, lead white, traces of yellow ochre
Master of the Litoměřice Altarpiece	St Andrew (fragment)	MGB	around 1500	06-52-4	green cloak	I	azurite, cooper green pigment (verdigris), lead white
				06-52-5	green background	I	azurite, lead white, red ochre
Master of the Litoměřice Altarpiece	Litoměřice Altarpiece - Nativity	SGVU	1500-1505	06-84-3	grey background	I	lead white, ochres, vermilion

Table 2 Description of the analysed panel paintings and samples *(Continued)*

Master of the Litoměřice Altarpiece	Litoměřice Altarpiece - Bearing of the Cross	SGVU	1500-1505	06-89-1	yellow armour of soldier	I	lead white, red lake, fluorite
				06-89-7	green drapery	I	verdigris, lead white
Master of the Litoměřice Altarpiece	Strahov Altarpiece - Annunciation	KKPS	around 1505	12-32-1	yellow ray of light	I and II	lead white
Master of the Litoměřice Altarpiece and workshop	St Anne with the Virgin Mary and the Christ Child	NG, O 4102	around 1510	08-51-6	yellow belt of St Anna	I	lead white, yellow ochre
Master of the Litoměřice Altarpiece and workshop	Altarpiece panels, called from Theyn (Týn) – St Barbara	MHMP	after 1510	06-60-3	green robe	I	azurite, lead white
Master of the Litoměřice Altarpiece and workshop	Altarpiece panels, called from Theyn (Týn) – St Peter and St Andrew	MHMP	after 1510	99-33-2	green cloak of St Andrew (highlight)	I	verdigris, lead white
				99-33-3	green cloak of St Andrew (shadow)	I	verdigris, lead white
Master of the Litoměřice Altarpiece	St Catherine Altarpiece – St Catherine before the Emperor Maxentius	NG, O 17425	around 1515	98-79-4	yellow stocking	I	lead white, yellow ochre, vermilion
				98-79-5	green cloak of the Emperor	I and II	verdigris, lead white
				98-79-12	yellow robe of St Catherine	I	lead white, yellow ochre
Master of the Litoměřice Altarpiece and workshop	St Catherine Altarpiece – Entombment of St Catherine	NG, O 17426	around 1515	98-78-5A	green robe of angel	I	verdigris, lead white, yellow ochre
				98-78-10	green wing of angel	I	lead white, azurite, vermilion
Master of the Litoměřice Altarpiece and workshop	Martyrdom of St Catherine	NG, O 12306	around 1515	99-13-3	green cloak of the Emperor	I	verdigris, lead white
Master of the Litoměřice Altarpiece and workshop	St Catherine Reading	NG, O 12306	around 1515	99-17-8	green cloak of the Emperor	I	verdigris, lead white
Monogrammist IW	St Wenceslas/SS Catherina, Barbara	NG, O 1258	around 1520	09-49-3	yellow reverse side of the cloak of St Barbara	I	lead white
Monogrammist IW	Altarpiece with the Execution of St Barbara, called the St Barbara Altarpiece from Osek - St Sebastian/St Paul	NG, DO 5428	after 1546	02-18-S1	flesh (highlight), St Sebastian	I	lead white, black pigment, chalk, red pigment
				02-18-S2	flesh (shadow), St Sebastian	I	lead white, black pigment, chalk, red pigment
				02-18-Pa1	flesh, St Paul	I	lead white, red lake

CA - Cistercian Abbey at Vyšší Brod, NG – National Gallery in Prague, NPÚ - National Heritage Institute, NM - National Museum in Prague, TGM Rakovník – Museum of Tomáš Garrigue Masaryk, MGB – Moravian Gallery in Brno, SGVU – SGVU Art Gallery in Litoměřice, MHMP - Museum of Prague, KKPS - Royal Canonry of Premonstratensians at Strahov.

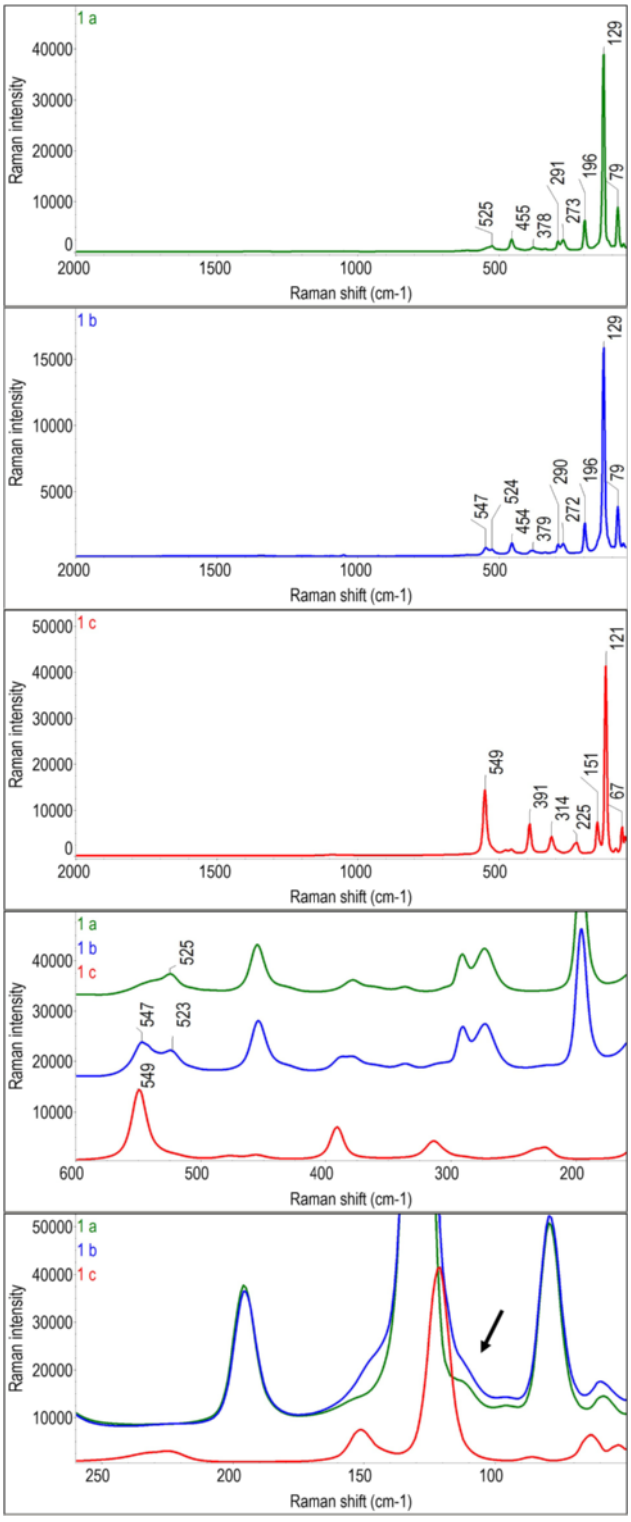

Figure 1 Raman spectra of standard pigment lead tin yellow type I. Raman spectra of lead tin yellow type I and minium in the range of 50–2000 cm^{-1} with two details of spectra variation observed in the region 50–600 cm^{-1}: 1a) and 1b) lead tin yellow type I (Böke & Fritz Art.No.101-7); 1c) minium (Kremer No. 42500). Fourth picture from above: Raman spectra of all pigments in the region of 160–600 cm^{-1}, in the spectrum 2b higher Raman band at 547 cm^{-1} is visible; last picture: Raman spectra of all pigments in the region of 40–260 cm^{-1}, in the spectrum 2b broadening of the Raman band around 131 cm-1 is showed with the arrow.

Brod Altarpiece (1345–1350), where the lead tin yellow type II was used in green and yellow draperies of the clothing (Figure 3a and b). Pigment was found usually in the green cloak of St. John the Baptist or in the yellow reverse cloaks of Virgin Mary and other saints and was most often mixed with lead white, yellow ochre, earth pigments and green copper pigments.

In the Luxembourg period, especially during the rule of the emperor Charles IV., the royal city of Prague was the cosmopolitan center of art and culture of Central Europe. Consequently, new stimuli were assumed in the field of art and handicrafts. Already in the 40' of the 14th century the Bohemian art reflected the trends of the art of Western Europe (esp. France, Rhineland, Italy) not only in iconography and style, but also in the production technology. The Bohemian panel paintings of the 50' and 60' of the 14th century are apparently linked to Italy (initially in particular to Tuscany); that is manifested by the specific formation of the flash and the choice of the decorative techniques. Apart from wandering artists the domestic masters came in contact with Italian art also through imported contemporary artworks.

For this reason the question about the provenance of the lead tin yellow type II in the workshop of the Master of the Vyšší Brod Cycle is very interesting. In Bohemia there is also very significant medieval tradition of glass-making. The most numerous group of findings from this period is the group of sodium-calcium glasses (Na_2O-CaO-SiO_2). However, a glass containing lead oxide PbO was found marginally [42]. The painting technique, dating of the artwork and also findings in the literature sources indicate rather the import of the pigment from Italy.

Analogical use of the lead tin yellow type II was discovered also in the workshop of Magister Theodoricus, even though the findings were limited to a small amount of samples, usually taken from green areas of the paintings. The major yellow pigments of this important workshop were yellow ochre and earth pigments [43].

More variable usage of the lead tin yellow type II was documented in the artwork Votive Panel of John Očko from Vlašim and in particular in the workshop of the Master of the Třeboň Altarpiece. The yellow pigment was found in the plain areas of green and yellow draperies as well as in the decorative painting brocade of the cloak of St. Jerome (Master of the Třeboň altarpiece, Deposition/SS Giles, Augustine, Jerome) and soldier's robe on the panel painting Crucifixion from the church of St. Barbora of the same author. In this ultimate panel painting the yellow was found not only on the important painting brocade but also on the robe of saints and assisting figures and on the fragments of the marbling on the reverse side.

Decorative painting brocade was in major part carried out using the pattern for the application of the lead tin yellow type II on a silver leaf with an admixture of gold (cvishgolde). The green shadows were applied using the copper green pigment on the dark organic glazing (Figure 4a and b).

Samples from the artworks of the Master of the Vyšší Brod altarpiece and the Master of the Třeboň Altarpiece that were analyzed by means of Raman spectroscopy contain lead tin yellow type II that shows uniform composition from the chemical point of view (Raman spectra presented in Figures 3b and 4b). In the cross-sections and microscopical preparations isotropic glassy like particles with lemon yellow internal reflections, translucent with light yellow colour and very high relief were observed by means of optical microscopy (see Figure 3a). Among the presence of other pigments the lead white was frequently found in the layer with the lead tin yellow type II. There were marginally identified also the admixtures of vermilion, black pigment and ochre. For example, both shadow and light areas of the yellow robe of St. Ludmila on the Votive Panel of John Očko from Vlašim were coloured with the yellow ochre.

The last example of individual employment of the lead tin yellow type II was found on the Triptych with the Death of the Virgin called the Roudnice Altarpiece - inside of right wing, painting of the Man of Sorrows and eight kneeling devotees assigned to the period 1410–1420. Lead tin yellow type II was identified in particular in the painting of the bishop's collar and was located in the lower layer applied on the white layer of lead white (imprimiture) on the ground made of chalk. This lower yellow layer is then covered by a second lighter yellow layer in which the presence of lead tin yellow type I alone was confirmed. This unusual combination of layers will be subjected to an additional investigation (to be published separately).

The earliest use of the lead tin yellow type I was identified on the artwork Votive panel, called from Dubeček which has been assigned already before c. 1390. This pigment was then confirmed on all the investigated artworks that were dated up to 1550 (Table 2). It was used frequently in yellow draperies, most often in mixture with lead white, as well as in green areas of the paintings where the combination with copper green pigments, usually verdigris with lead white, were mostly confirmed. In rare cases the admixtures of ochre or earth pigments, azurite or black pigment were identified. In the artwork Altarpiece with the Execution of St. Barbara, called the St. Barbara Altarpiece from Osek – St. Sebastian/St. Paul by the Monogrammist IW the lead tin yellow type I was found in the layers of flash, together with lead white, chalk, black pigment, vermilion and red lake.

A special group of artworks are the paintings where the presence of both types of yellows in one layer was

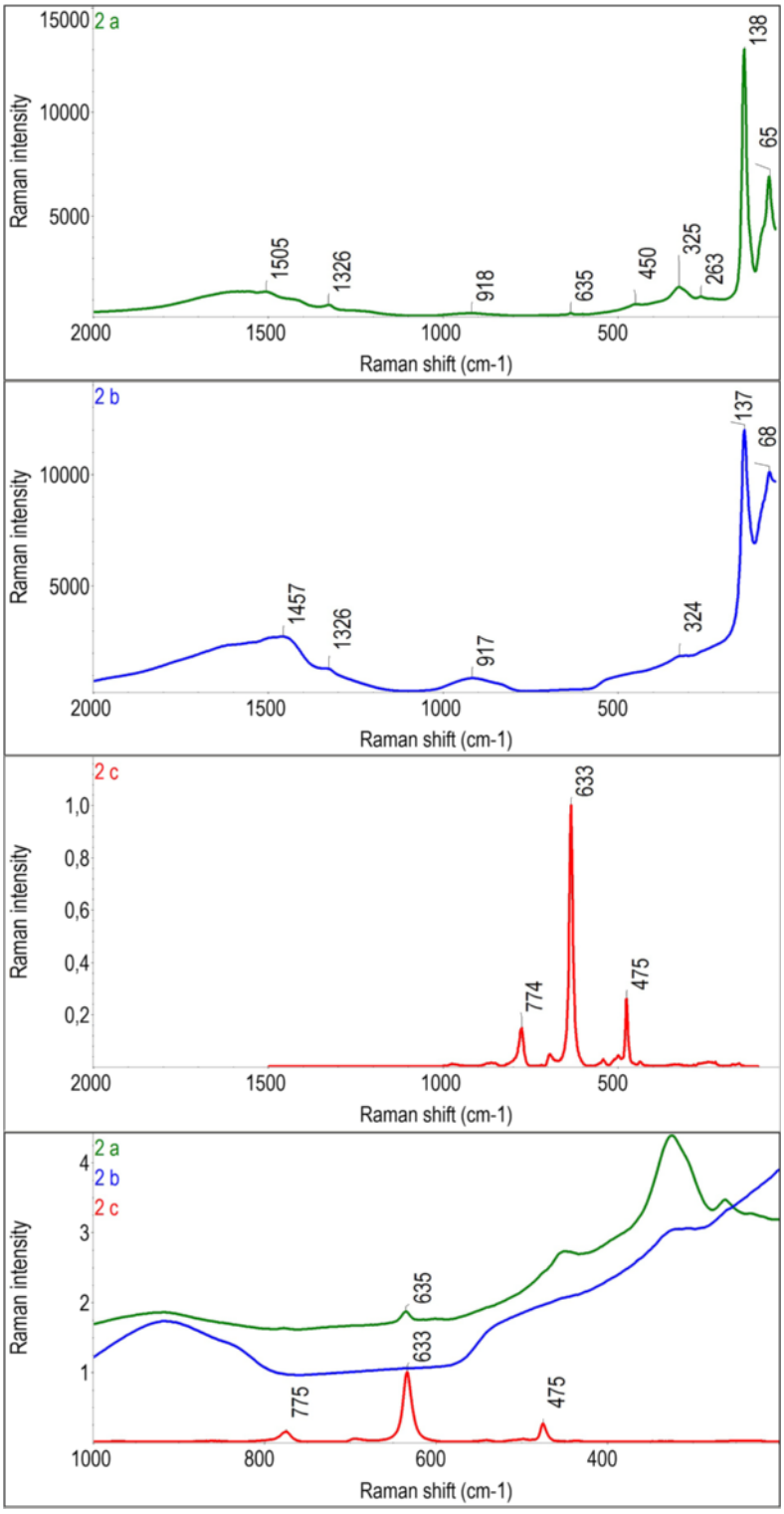

Figure 2 Raman spectra of standard pigment lead tin yellow type II. Raman spectra of lead tin yellow type II and cassiterite (SnO_2) in the range of 50–2000 cm^{-1} with one detail of spectra variation observed in the region around 633 cm^{-1}: 2a) and 2b) lead tin yellow type II (Kremer No. 10120); 2c) mineral cassiterite (SnO_2). Detail: Raman spectra of all pigments in the region of 200–1000 cm^{-1}, in the spectrum 2b Raman band at 635 cm^{-1} is visible that indicates the presence of mineral cassiterite (SnO_2).

confirmed by the Raman spectroscopy. This occurrence was documented on two different artworks and in both cases the pigments were detected by measurement of individual grains in diverse areas. The first artwork is the painting from the Master of the Litoměřice Altarpiece, St. Catherine Altarpiece – St. Catherine before the Emperor Maxentius (Figure 5a and b). The pigments were found in particular in the green cloak of the Emperor where the minor content of lead tin yellow type II was identified in predominant type I. This combination was found for example in the work of Perugino [36]. The contamination of the lead tin yellow type I by silica during the preparation can not be excluded because of the close connection between the preparations of both types of yellows. The second case is the painting from the Master of the Třeboň Altarpiece and his workshop, Our Lady Ara Coeli. Here the mixture was detected in the green cloak of St. Margaret and the dominant component was the lead-tin yellow type II with a minor content of type I. Considering that this sample contains also an individual grain of non-uniform composition where both types of yellow as well as minium were found, we presume that what is found are secondary products from an insufficient firing during the production of the pigment. These findings are now under other studies and will be published soon in a separate report.

Conclusions

Investigation and scientific analysis, especially the combination of optical microscopy and Raman microspectroscopy, showed the frequent use of lead tin yellow type I and II during the High and Late Gothic period in the Bohemian panel paintings. Lead tin yellow type II was confirmed in the artworks assigned to the period from c. 1345 to 1420. Lead tin yellow type I was confirmed on the paintings from 1390 on. On panel paintings both yellows were used like single pigments or in various pigment mixtures in the colour painting layers. In the yellow areas, the most common combinations were with lead white and earth pigments. Sometimes mixtures with vermilion and red lake were found. In the green areas lead tin yellows were mixed with copper green pigments and lead white. The lead tin yellow type II occurs in this country in the 14th century on better quality artworks where the close links to progressive trends can be assumed. The knowledge of the use of the lead tin yellow type II was a normal part of workshop practice. Various techniques using the lead tin yellow type II were

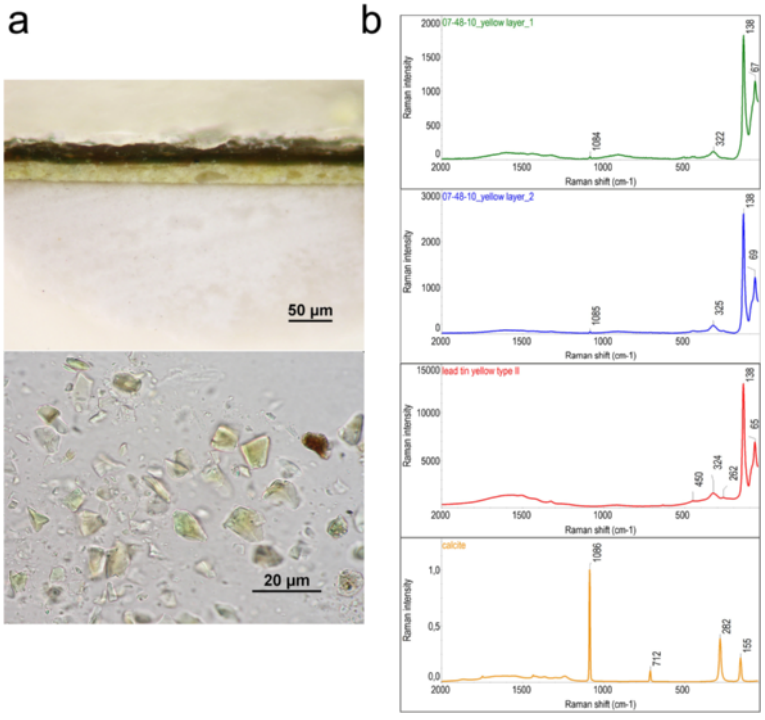

Figure 3 Master of the Vyšší Brod Cycle, Vyšší Brod Cycle - Descent of the Holy Ghost (O 6794). **a** Cross-section and microscopical preparation of sample taken from the yellow cloak on the left side. The yellow layer of lead tin yellow type II is located on the white ground layer of chalk. Microscopical preparation shows the isotropic glassy like particles with lemon yellow internal reflections, translucent with light yellow colour and very high relief. Photo©2014 National Gallery in Prague. **b** Raman spectra collected from the yellow layer of the sample. The spectra show the typical Raman bands of lead tin yellow type II: 1) Raman spectrum collected from the sample 07-48-10 no. 1, 2) Raman spectrum collected from the sample 07-48-10 no. 2, 3) Raman spectrum of the standard pigment lead tin yellow type II, 4) Raman spectrum of calcite (chalk).

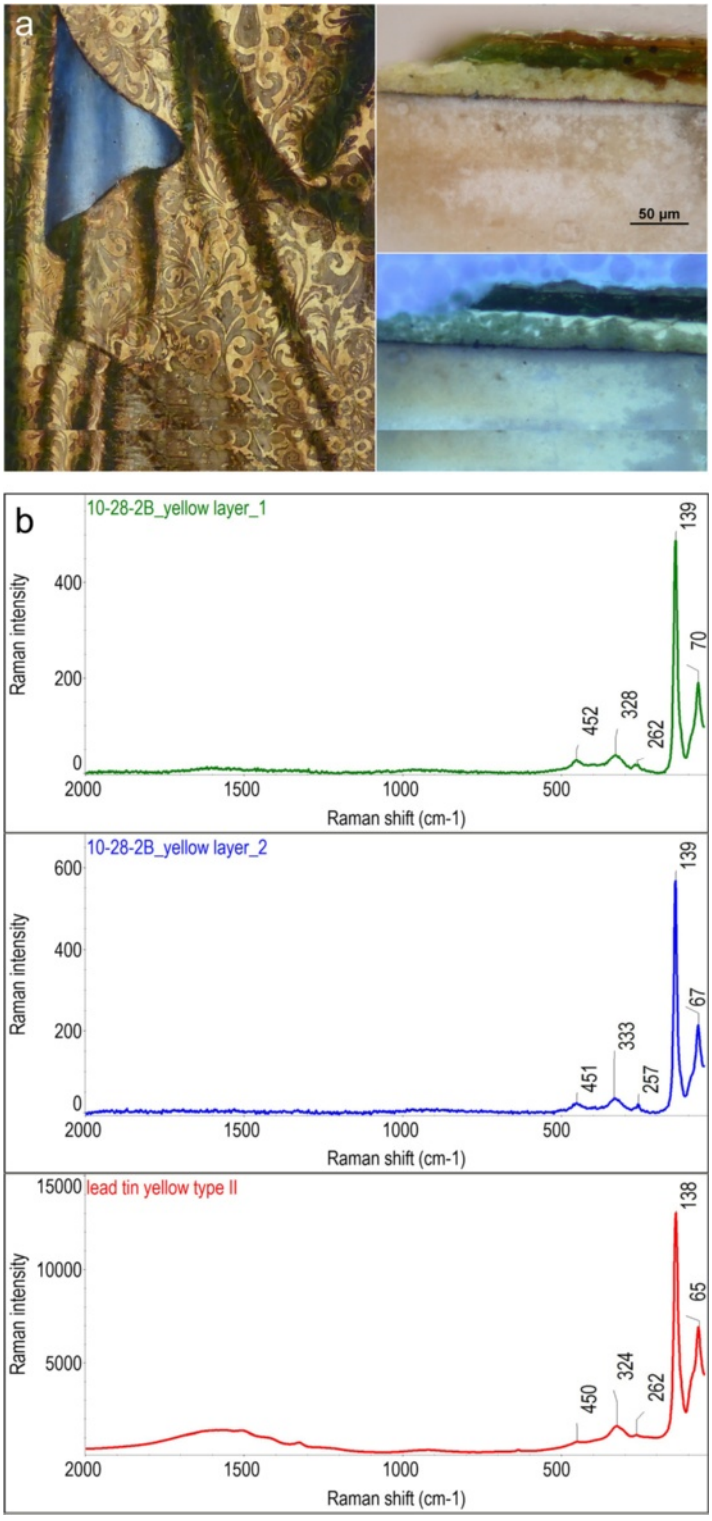

Figure 4 Master of the Třeboň Altarpiece, SS Giles, Augustine, Jerome (O 1266). **a** Detail and cross-section of the sample taken from decorated yellow robe of St Jerome observed in optical microscope in normal and ultraviolet light. Cross-section shows yellow layer of lead tin yellow type II mixed with lead white on a silver leaf with the admixture of gold (cvishgolde). The final green shadows were realized by applying the copper green pigment on the dark organic layer. Photo©2014 National Gallery in Prague. **b** Raman spectra collected from the sample of decorated yellow robe of St Jerome, detail in Figure 4a. By means of Raman spectroscopy uniform composition of the pigment lead tin yellow type II was observed: 1) Raman spectrum collected from the yellow layer of the sample 10-28-2B no. 1, 2) Raman spectrum collected from the yellow layer of the sample 10-28-2B no. 2, 3) Raman spectrum of the standard pigment lead tin yellow type II.

combined in a single workshop (Master of the Třeboň Altarpiece) with regard to the requirements of the final aesthetic quality (drapery, decorative painting). It is attractive to assume that the first use of this technique in Bohemia was linked with the arrival of foreign masters, especially those from the area of Italy, working on prestigious orders in connection with the flourishing of the royal court. It is also highly probable that some local masters were acquainted with the use of the lead tin yellow type II as a specific pigment during their travels.

This broader survey brings the first summary of the findings acquired within the framework of the historical art fund of Bohemia. It was initiated in particular with regard to present more general conclusions, in an effort to provide support for the identification of lead tin yellows within the framework of the analyses

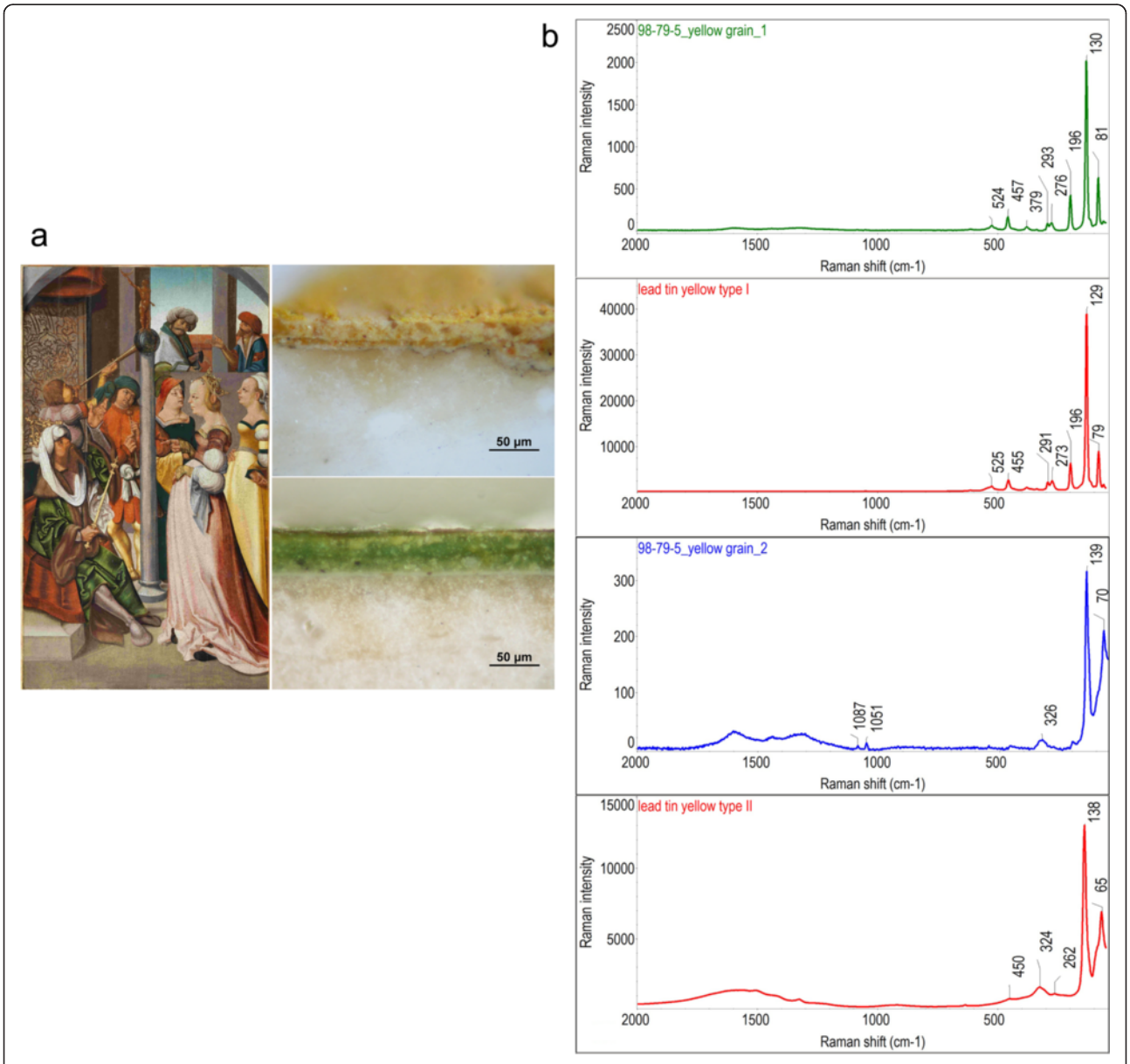

Figure 5 Master of the Litoměřice Altarpiece, St Catherine Altarpiece – St Catherine before the Emperor Maxentius (O 577). **a** The painting and cross-sections of the samples collected from the yellow stocking (lead-tin yellow type I, yellow ochre, lead white, vermilion) and green cloak of the Emperor (lead-tin yellow type I and II, verdigris, lead white). Photo©2014 National Gallery in Prague. **b** Raman spectra collected from the yellow grains in the green layer, sample collected from the green cloak of the Emperor, painting in Figure 5a. In the green layer both types of yellow were detected: 1) Raman spectrum collected from the yellow grain 1 which shows the characteristic Raman bands of lead tin yellow I; 2) Raman spectrum of the standard pigment lead tin yellow type I; 3) Raman spectrum collected from the yellow grain 2 corresponding to the pigment lead tin yellow type II; 4) Raman spectrum of the standard pigment lead tin yellow type II.

of material research. Raman micro-spectroscopy proved to be a crucial method for identification of both lead tin yellow pigments.

Competing interests
The authors declare that they have no competing interests.

Authors' contributions
RŠ as conservation scientist performed the analysis by means of Raman spectroscopy, carried out the laboratory work and significantly contributed to the scientific part of the article. ŠC as art historian contributed significantly to the historical aspects of the work, both during the project realization as well as by the contribution to the article. AH as conservation scientist performed the analysis by means of Raman spectroscopy, carried out the laboratory work and significantly contributed to the scientific part of the article. All authors read and approved the final manuscript.

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