Original article

Microanalytical identification of Pb-Sb-Sn yellow pigment in historical European paintings and its differentiation from lead tin and Naples yellows

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Abstract

The work is focused on identification of lead tin yellow types I and II, Naples yellow, and also on discrimination of a less common, distinct yellow pigment, the ternary Pb-Sb-Sn oxide.

The knowledge about all those Pb-based yellows was in fact forgotten after introduction of modern synthetic yellows in 19th century. As late as in the last decade of the 20th century, the existence of Pb-Sb-Sn yellow and its production have been rediscovered, and only then it has been identified in colour layer of artworks.

Pb-Sb-Sn yellow has recently been identified in colour layer of 17th century Italian paintings by Sandalinas and Ruiz-Moreno [C. Sandalinas, S. Ruiz-Moreno, Lead tin-antimony yellow, historical manufacture, molecular characterization and identification in seventeenth-century Italian paintings, Stud. Conserv. 49 (2003) 41—52], and here we report the finding of this pigment in Mid-European painting of the 18th and 19th centuries. Lead tin yellows, lead antimony yellow (Naples yellow), and lead antimony tin yellow were synthesized in laboratory following historical recipes, their colour was analyzed, and their structure was confirmed to provide a basis for their routine identification in microsamples of artworks by X-ray microdiffraction. Unequivocal identification of Pb-based yellows could help in authentication of traditional European paintings, because their use was temporally and also geographically specific. Combination of elemental microanalysis (X-ray fluorescence electron microanalysis) and X-ray powder microdiffraction were found very efficient in the microanalysis of colour layers of artworks with Pb-based yellows and their unequivocal identification.

1. Research aims

The aim of this work is to describe the synthesis, colour properties, and occurrence of Pb-Sb-Sn yellow in several oil paintings of 18th and 19th centuries, and to compare the use of all Pb-based yellows − lead tin, Naples and lead antimony tin yellows − in European paintings of 15th−19th century. A suitable approach to the unequivocal identification of these particular pigments on painting is non-invasive X-ray

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fluorescence analysis or SEM/EDX analysis on selected micro samples followed by X-ray powder microdiffraction. The mineralogical analysis, e.g., using X-ray diffraction, is necessary to interpret the elemental analysis of Pb-based yellows in terms of the actual pigments used.

2. Introduction

There are several yellow mixed oxides of Pb, originally used to colour glass and glazes and subsequently also as artist pigments in easel and wall painting, polychromy, and illumination [1,2]. There are lead tin yellow type I (Pb_2SnO_4) and its modification called lead tin yellow type II written as $PbSnO_3$ by Rooksby [3] or $PbSn_xSi_{1-x}O_3$ by Clark et al. [4], Naples yellow ($Pb_2Sb_2O_7$) and its variations with more complex structure containing tin, zinc or other suitable elements [5–7]. The names, formulae and structure of these pigments are summarized in Table 1. All Pb-based yellows used in European fine art were produced artificially by calcination or melting of their components and technological additives. Their use in painting was adopted from glass making and pottery where they were used since early historical times [3,9–11].

Lead tin yellows do not occur naturally. The historical use of natural yellow mineral bindheimite ($Pb_2Sb_2O_7$) as a pigment, isostructural with Naples yellow, is not satisfactorily proved. Very early studies, e.g. Watin in 1773 [12], placed the origin of Naples yellow to Naples, Italy, as a manufactured colour, or naturally formed mineral found near the sulphur mines on Mount Vesuvius. Already in 1437, Cennini [13] mentioned the term ''giallorino'', generally used in Italy for all Pb-based yellows, to describe a yellow mineral pigment, originating in the neighborhood of great volcanoes. By Cennini, this pigment is ''a colour produced artificially, though not by alchemy''. Regarding these speculations and terminological confusions the use of natural bindheimite as pigment in Europe before the 18th century cannot be fully excluded, but there is no clear evidence for it. In the history, Pb yellows were generally used simultaneously with natural ferric ochres [14], which were available in a range of hues from light to dark, reddish, or brownish yellow.

The historical recipes for making Pb-based yellows are, especially in the case of Naples yellow, rather uncertain for what is concerning the nature of reagents, usually denoted by their unclear historical names, and also vague information is given regarding temperature and time of calcination [5,7,15]. And to make the case even more complex, one should expect that not all recipes were recorded in writing. However historical recipes can be used as inspiration to laboratory testing [9,15,16]. The reagents were usually the individual oxides, and sodium chloride, potassium carbonate, or silica sand acting as flux agents [2,5]. Naples yellow as a painting pigment was probably also prepared with addition of other metal oxides, such as TiO_2, SnO_2, and/or ZnO [5,15], and actually the Ti- and Zn-containing oxides are currently provided, e.g., by Kremer Pigmente (Germany). It is known than the popularity of each of the Pb-containing yellows in European fine art changed with time. According to Wainwright et al. [5] and Kűhn [6], both lead tin yellows type I and II were preferred between 14th and 17th centuries. During 17th century lead tin yellows gradually evolved to lead antimonate (Naples) yellows and a joint occurrence of Pb, Sb and Sn appeared in some Italian paintings [2]. The term ''luteolum Napolitanum'' was used by Andrea Pozzo in his Latin treatise on fresco painting of 1693–1700. Naples yellow then prevailed among Pb-based yellows in the period from 1750 to 1850 [6]. With respect to these facts, Pb-containing yellows are considered suitable for dating, and a joint occurrence of Pb, Sb, and Sn in yellow colour layers could be temporally and regionally very specific [6].

The ternary pyrochlore type oxide $Pb_2Sb_{2-x}Sn_xO_{7-x/2}$ could be a possible reason of a common occurrence of Pb, Sb, and Sn in yellow colour layers, identified, e.g., by electron microanalysis or X-ray fluorescence analysis. The synthesis and structure of single-phase pyrochlore $Pb_2SbSnO_{6.5}$ was first described as late as in the 1980s [8], and only since the 1990s, this pigment has been unequivocally identified in artworks and distinguished from Naples yellow. Also this pigment was first used in glass making: for example, it was identified by scanning electron microscopy (SEM) with elemental analysis EDX and X-ray diffraction in yellow glass produced in 7th century [11]. According to Sandalinas and Ruiz-Moreno [1] and Ruiz-Moreno et al. [17] it was systematically used in Italian painting of 17th century. Probably due to only recent description of Pb-Sb-Sn yellow to current science, it has not been identified in so many cases as Naples [5] and lead tin [6] yellows because it has not been searched for, and it is possible that $Pb_2Sb_{2-x}Sn_xO_{7-x/2}$ yellow was more common than it has been expected. Its identification cannot be based only on the elemental analysis, as it was shown by Dik et al. [15] in an example of yellow majolica containing all three elements: it was found that SnO_2 was used as ground on the ceramics

Table 1
The overview of principle Pb-based yellows used in traditional painting and recognized as distinct well defined species in contemporary literature [5–7]. The last item, $Pb_2SbSnO_{6.5}$, a modern synthetic phase [8] is also given.

Name	Formula (PDF-2 card number)	Symmetry, cell size a
Lead tin yellow type I (lead tin oxide)	Pb_2SnO_4 (e.g. 1-75-1846)	Orthorhombic
Lead tin yellow type II (lead tin silicon oxide)	$PbSnO_3$ (17-0607)	Cubic pyrochlore, $a = 1.069–1.072$ nm
	$PbSn_{0.76}Si_{0.24}O_3$ (49-1886)	
	$Pb_2Sn_2O_6$ (1-72-0002)	
Naples yellow (lead antimony oxide)	$Pb_2Sb_2O_7$ (42-1355, 1-73-1737, 1-074-1354)	Cubic pyrochlore, $a = 1.040–1.044$ nm
Pb-Sb-Sn yellow (lead antimony tin oxide)	$Pb_2SbSnO_{6.5}$ (39-0928)	Cubic pyrochlore, $a = 1.056$ nm

and Naples yellow was applied on the superficial layer. For the direct and unequivocal identification of the actual composition of pyrochlore-like Pb-yellows and differentiation from other pigments, X-ray diffraction is very useful because the lattice parameter depends on actual oxide composition [3,11]. Raman spectroscopy was recently used to distinguish Naples yellow and its Si and Sn containing analogues [2]. However, a routine analysis of Pb-containing yellows in artworks is usually based only on elemental composition, which is obviously insufficient.

We have recently identified Pb-Sb-Sn yellows in five European paintings from the end of 18th and from 19th century. This dating and provenance are rather remote with respect to the well demonstrated usage of Pb-Sb-Sn-yellow in Italian painting of 17th century [1,17]. In any case, its relation to the other yellows is currently unknown, i.e., it is not clear what caused simultaneous usage of Naples and Pb-Sb-Sn yellows. To try to understand the using of this particular pigment, we synthesized the Pb-base yellows and compared their preparation and colour. It is possible, that the actual composition of the traditional Pb-based yellows depended on the actual accessibility of the raw materials, but maybe the Pb-Sb-Sn yellow had some technological peculiarity. There is a question whether its usage could be useful in evaluation of provenance and dating of artworks. For the identification of the Pb-based yellows we used laboratory powder X-ray microdiffraction [18] that is very suitable to routine analysis of microsamples of artworks.

3. Experimental part

3.1. Laboratory synthesis and characterization of Pb-based yellows

The pigments were synthesized using Pb_3O_4, Sb_2O_3, Sb_2S_3, SnO_2, NaCl, and K_2CO_3 of analytical purity and SiO_2 in the form of silica gel for chromatography. The basic synthesis procedures were adopted from the literature [2,5,7,15]. In the case of Sb-based yellows, some syntheses were facilitated by an addition of flux agents according to the literature recipes, where rock salt NaCl and potash K_2CO_3 were mentioned by Piccolpasso (16th century), Mariani (17th century), and Passeri (18th century) according to translations and interpretations by Wainwright et al. [5], Eastaugh et al. [7], and Dik et al. [15], and SiO_2 by Darduni (17th century) according to Sandalinas and Ruiz-Moreno [1]. For X-ray diffraction analysis of synthetic pigments, conventional powder diffractometer D5005 (Bruker) was used. Colour properties were evaluated using spectrometer Lambda 35 (Perkin Elmer) equipped with an integrating sphere (Labsphere) for diffuse reflectance measurement. The spectra were obtained with integration sphere set to exclude the specular reflection and then they were recalculated to CIE 1964 colour system (10 degree field of view) using software COLOR 3.00 (Perkin Elmer). For the visual evaluation of the pigments, they were mixed with oil binder (linseed oil, Kremer Pigmente, Germany) and painted on a white ground layer on wooden plates.

3.2. The artworks and their analyses

A complex materials research of 37 easel paintings, 3 wall paintings and 4 polychrome artworks containing Pb-based yellows have been made. All the artworks were connected to Mid-European region either by their origin, location, or authorship. Five paintings were investigated by non-invasive X-ray fluorescence analysis prior to sampling and in two of them the sampling of Pb-based yellows was not allowed by the artwork owners. Samples were analysed as microfragments and their cross-sections by optical microscopy and electron microscopy with EDS elemental analysis. In 14 cases, powder X-ray microdiffraction was additionally used for the phase (mineral) analysis (Table 4). The dating of original paints and repaints with Pb yellows was based on interpretation of layer stratigraphy with regarding all other results of artistic and historical evaluation of paintings.

In situ non-invasive investigation of selected paintings was performed by portable X-ray fluorescence spectrometer provided by MOLAB (MObile LABoratory) through the European project Eu-ARTECH. It is equipped with a tungsten anode and a silicon drift detector having resolution of ∼130 eV at 5.9 KeV. Element mapping ($Z > 13$) with a spatial resolution of 4 mm was achievable.

Cross-sections of colour layers were studied after embedding in polyester resin and cross sectioning. Optical microscopy (Olympus BX-60 in reflected visible light and UVA light in the wavelength range of 330−380 nm), and electron microscopy (Philips XL-30 CP) with RBS detector of back-scattered electrons and EDS analyser was used to describe the layer stratigraphy and elemental composition of yellow pigment grains in cross-sections whenever the sampling of colour layer was allowed. Micro-X-ray diffractometer X'PertPro (PANalytical) with 0.15 mm diameter of the primary beam was used to the phase analysis of microfragments (<1 mm) and cross-sections of colour layers [18]. For the phase identification, High-Score (PANalytical) with the 2005 release of PDF-2 database was used. The lattice size of the pyrochlore structures were refined using code PowderCell 2.4, kindly provided by W. Kraus and G. Nolze, Federal Institute for Materials Research and Testing (BAM), Unter den Eichen 87, D-12205 Berlin.

4. Results and discussion

4.1. Preparation and characterization of Pb-based yellows

The synthesis of Pb-Sn yellow type I is a simple solid-state synthesis: the phase-pure, bright yellow orthorhombic phase Pb_2SnO_4 is easily obtained by calcination of a mixture of oxide components between 650 and 900 °C. In agreement with the spectra published by Kűhn [6], higher calcination temperature produces lighter pigment, i.e. pigments with a higher total reflectance and a lower yellow coordinate $b*$ in the CIE-$L*a*b*$ colour space. Pb-Sn yellow type II, traditionally obtained by calcination of the yellow type I with SiO_2 [3,6], can also be produced by a single-step synthesis, i.e.

calcination of Pb, Sn, and Si oxides in molar ratio such as 2:1:1 and 6:3:2, with optimal temperature about 850 °C. The approximate stoichiometry of the reaction between the components is

$$6PbO + 3SnO_2 + 2SiO_2 = [3PbO - 2SiO_2] + 3[PbSn_{1-x}Si_xO_3]$$

where square brackets denote approximate composition, $[3PbO - 2SiO_2]$ is a colourless glassy phase giving one broad X-ray diffraction line centred at $d \sim 3.1$ Å, and $[PbSn_{1-x}Si_xO_3]$ is a rich yellow phase with variable composition [4]. Its actual composition is not easy to estimate due to a simultaneous presence of lead-silica glass matrix as it has already been noticed by Rooksby [3]. Any inappropriate stoichiometry of reactants produces admixture of further crystalline phases. In even a slight excess of SiO_2 over the Pb:Sn:Si ratio of 2:1:1, PbO forms preferentially a glassy phase and SnO_2 remains unconsumed that both decreases the colour strength of the product. At larger excess of SiO_2, creamy or milky white, opalescent, highly sintered mass is obtained. In an excess of Pb, yellow Pb_2SnO_4 is formed. To form $[PbSn_{1-x}Si_xO_3]$ phase, the presence of SiO_2 is essential, and so calcination of 1:1 mixture of PbO and SnO_2 with insufficient amount of SiO_2 yields a mixture of Pb_2SnO_4 and $[PbSnO_3]$ beside a glassy phase. The sensitivity of the composition of the crystalline products in lead tin yellow type II to even small variation of the stoichiometry means that one could hardly expect to find a single-phase pigment in a colour layer of artworks. That could possibly be the case of mixture of lead tin yellows type I and II in yellow layer of Renaissance canvas painting reported by Borgia et al. [19].

The synthesis of Naples yellow is also a more complicated than synthesis of led-tin yellow type I, and depends not only on the kind of raw material, but also on a possible presence of flux agents. On heating Pb_3O_4 and Sb_2O_3 between 700 and 900 °C without flux, obviously heterogeneous, bicolour products were obtained, and temperatures as high as about 1000 °C were required to complete the reaction (in agreement with reports [5,9]). At 900 °C, such heterogeneous mixtures turned ochreous or dull yellow after grinding and the colour is not substantially improved by a repeated heating without a flux agent. We used 4–10 h periods of calcination, because we assumed that the traditional thermal treatment was performed in the pottery furnaces [15]. After 900 °C calcination without flux, reddish to brownish mixtures contained not only cubic bindheimite ($Pb_2Sb_2O_7$), but also orthorhombic $Pb_2Sb_2O_7$ (card 39–834), $Pb_{3+x}Sb_2O_{8+x}$ (card 34–1196), and $PbSb_2O_6$ (rosiaite, card 34–912). All the specimens containing orthorhombic $Pb_2Sb_2O_7$ and $Pb_{3+x}Sb_2O_{8+x}$ admixtures were dull ochreous. Similar phase admixtures were also found by other authors attempting to reproduce the historical recipes [16,17]. Although a repeated grinding and calcination were recommended in traditional recipes "*until a desired colour is obtained*", the solid state diffusion is so slow at 900 °C that the formation of intermediate phases departing from 1:1 stoichiometry would hardly lead to a single phase product in a reasonable time and with a reasonable effort. It seems vital for a sustainable successful synthesis to obtain the target compounds mostly in the first run.

The reaction course is substantially improved by addition of NaCl or K_2CO_3 flux, recommended by the traditional recipes [5]; NaCl is a plain salt, and K_2CO_3 was available as calcined wine lees, containing potassium hydrogen tartrate [16]. Single phase pyrochlore was most easily formed in the presence of 10 or 20% of NaCl flux on heating at 700 °C–900 °C and also the homogeneity and colour of the product was much improved. A salt flux is a common way to enhance the crystal growth in the modern solid state chemistry and technology, and obviously this knowledge is very old. NaCl was not found by X-ray diffraction in the product calcined at 800 or 850 °C at least 10 h and at above 850 °C for at least 5 h due to its volatility above its melting point. Dik et al. [15] found NaCl in their products calcined at 650 °C, and we found it in calcines obtained at or below 800 °C after shorter calcination times (4 h). The presence of soluble and hygroscopic salts in pigments is always highly detrimental, and obviously the calcination temperature must have been at least a bit higher to avoid the necessity of washing out the product by water. K_2CO_3 flux also produced yellow products, but the colour properties of the products were not as good as with NaCl flux, and at a larger excess of K_2CO_3, the product was sintered. K was either converted to potassium antimonate or remained unconsumed; such excess must have been washed out before its usage as a pigment. Interestingly, Pb-Sb oxide mixture calcined with 10% K_2CO_3 produced pyrochlore with a = 10.56 Å, maybe with some K present in the pyrochlore

Table 2
Synthesis way leading to products with the simplest phase composition, colour properties and phase composition of pigments synthesized

Pigment	Synthesis	Colour		
		L^*	a^*	b^*
Lead tin yellow I	Pb_3O_4, SnO_2, Pb:Sn 2:1, 650–800°C	92–96	(−2)–(−9)	37–49
Lead tin yellow II	Pb_3O_4, SnO_2, SiO_2, Pb:Sn:Si 6:3:(3-1), 800–900°C	83–88	2–6	57–66
Naples yellow	Pb_3O_4, Sb_2O_3, NaCl (10%), Pb:Sb 1:1, 850-900°C	83–85	6–11	60–63
Pb-Sb-Sn yellow	Pb_3O_4, Sb_2O_3, SnO_2, NaCl (10%), Pb:Sb:Sn 2:1.5:0.5, 800–900°C	85–89	2–9	55–64
Pb-Sb-Sn yellow with Pb sulphates	$PbCO_3$, Sb_2S_3, SnO_2, Pb:Sb:Sn 2.2:1:1, 850–900°C	82–88	1–10	49–59

Colour coordinates are L^*: lightness, a^* green (negative values) to red (positive values) colour coordinate, and b^* blue (negative) to yellow (positive) colour coordinate.

lattice. When 5 or 10% of fine SiO_2 (silica gel) was used, the product had a pinkish orange, salmon hue. The pure, single phase Naples yellow had a warm yellow hue, with a significant red coordinate in CIE-$L*a*$b colour space (Table 2).

Pure yellow without or almost without reddish or ochreous hue was obtained much easier than Naples yellow in the presence of SnO_2 (Table 2). Calcination of Pb_3O_4, Sb_2O_3 and SnO_2 with 10% NaCl at 700, 800, or 900 °C produced $Pb_2Sb_{2-x}Sn_xO_{7-x/2}$ with the pyrochlore structure, usually as a mixture of two pyrochlore structures with different cell sizes and commonly with a trace of non-consumed SnO_2 (Table 3). Both pyrochlores have always the lattice size larger than Naples yellow (Tables 1 and 3) hence it can be used for identification of the lattice substitution, i.e. the presence of Pb-Sb-Sn yellow. The bimodality of the lattice size was observed in both Pb:Sb:Sn compositions tested (2:1:1 and 2:1.5:0.5). It is not clear whether this phenomenon has a kinetic or a thermodynamic nature. Surprisingly, the same bimodality in the cell size of Pb-Sb-Sn yellows was also found in real artworks (Table 3, Fig. 1), proving that it was not a specific drawback of our synthesis route.

As it was found in Naples yellow specimen prepared in K_2CO_3 flux, also this element can increase the cell size of the pyrochlore almost to value typical for Pb-Sb-Sn yellow. The identification of the lattice size of the pyrochlore pigments should hence also include identification of possible content of potassium in the yellow pigment.

The syntheses of Naples and Pb-Sb-Sn yellows were also performed with Sb_2S_3 as a Sb source. There were two principal reasons for that: the term "antimony" in historical recipes did theoretically mean Sb, Sb_2O_3 or Sb_2S_3 [5,15]. Additionally, we found an admixture of Pb sulphates anglesite ($PbSO_4$) and lanarkite ($Pb_2(O)SO_4$) in colour layers of the paintings containing Pb-Sb-Sn yellow (specimens J0516, J0527, and M0526, Table 3, Fig. 1) and we expect that Sb_2S_3 raw material could have been responsible for that, because lead sulphate has only rarely been used as a white painting pigment [7]. EDS or X-ray fluorescence identification of S beside Pb is complicated by an overlap of L line of Pb and K line of S, and X-ray diffraction (or possibly Raman spectroscopy) is then indispensable to complete analysis of yellow colour layers.

The syntheses of Pb-Sb-Sn yellows from Sb_2S_3 had the following particularities: No NaCl flux was necessary, but a slight excess of Pb was required to compensate a side reaction of Pb oxide to Pb sulphates. Without the Pb excess, some SnO_2 remained unconsumed and in some batches rosiaite ($PbSb_2O_6$) was formed from correspondingly unconsumed Sb. The following schemes describe the reactions producing pigments of good colour properties:

$$5PbO + Sb_2S_3 + 2SnO_2 + 6O_2 = PbSO_4 + 2Pb_2SbSnO_{6.5} + 2SO_2$$
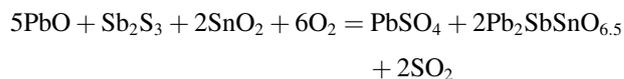
producing mainly anglesite ($PbSO_4$) at temperatures 850 °C and lanarkite ($Pb_2(O)SO_4$) at 900 °C

$$6PbO + Sb_2S_3 + 2SnO_2 + 6O_2 = Pb_2(O)SO_4 + 2Pb_2SbSnO_{6.5} + 2SO_2$$
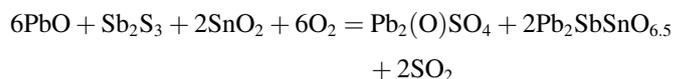
The actual reaction stoichiometries depend on the duration of calcination and raw Pb oxide and serve here as an example based on the actual composition of two of our particular synthesis products. When Sb_2S_3 was used as a Sb raw, the best results regarding the colour of the product were hence obtained at 10 or 20% excess of Pb oxide with respect to Sb + Sn.

Table 3
Summary of X-ray diffraction results

Sample	Cell size [nm]	(222) diffraction [nm]	(222) diffraction [° 2Θ in CoKα]
$Pb_2Sb_2O_7$, Naples yellow[a]	1.0394−1.0424	0.2998−0.3007	34.71−34.61
$Pb_2Sb_2O_7$, bindheimite, PDF 42−1355	1.0407	0.3004	34.65
M0421 (Pb-Sb yellow)[b]	1.048	0.3023	34.42
$Pb_2SbSnO_{6.5}$, PDF 39−928	1.0564	0.3050	34.11
Pb-Sb-Sn yellow 2:1:1[c]	1.055; 1.051	0.3044; 0.3032	34.18; 34.32
Pb-Sb-Sn yellow 2:1.33:0.67[d]	1.056; 1.050	0.3047; 0.3036	34.15; 34.27
Pb-Sb-Sn yellow 2:1.5:0.5[c]	1.055; 1.046	0.3044; 0.3017	34.18; 34.39
J0516, fragment 1 (Pb-Sb-Sn yellow)[e]	1.057; 1.050	0.3050; 0.3029	34.11; 34.35
J0516, fragment 2 (Pb-Sb-Sn yellow)[f]	1.056; 1.046	0.3049; 0.3020	34.12; 34.46
M0526, fragment 1 (Pb-Sb-Sn yellow)[g]	1.056; 1.046	0.3048; 0.3018	34.13; 34.49
M0526, fragment 2 (Pb-Sb-Sn yellow)[g]	1.056; 1.046	0.3048; 0.3017	34.13; 34.49
Lead-tin yellow type II, [$PbSnO_3$][h]	1.071	0.3090	33.66

Cell size of the cubic pyrochlores (Fd3m, space group 227) with composition ranging from $Pb_2Sb_2O_7$ via $Pb_2Sb_{2-x}Sn_xO_{7-x/2}$ to [$PbSnO_3$]. The position is given of the most intensive diffraction line (222) of synthetic pigments and corresponding characteristics of the pyrochlore-type pigments in the colour layer of artworks.

[a] The lattice size depended on the actual Pb:Sb ratio.
[b] Also contains white lead (hydrocerussite and cerussite).
[c] Synthesis from Sb_2O_3, traces of non-reacted SnO_2 remained in the product.
[d] Synthesis from Sb_2S_3 at 900 °C, the product contained 12% lanarkite.
[e] ∼30% anglesite, ∼10% lanarkite.
[f] ∼30% anglesite.
[g] ∼40% anglesite.
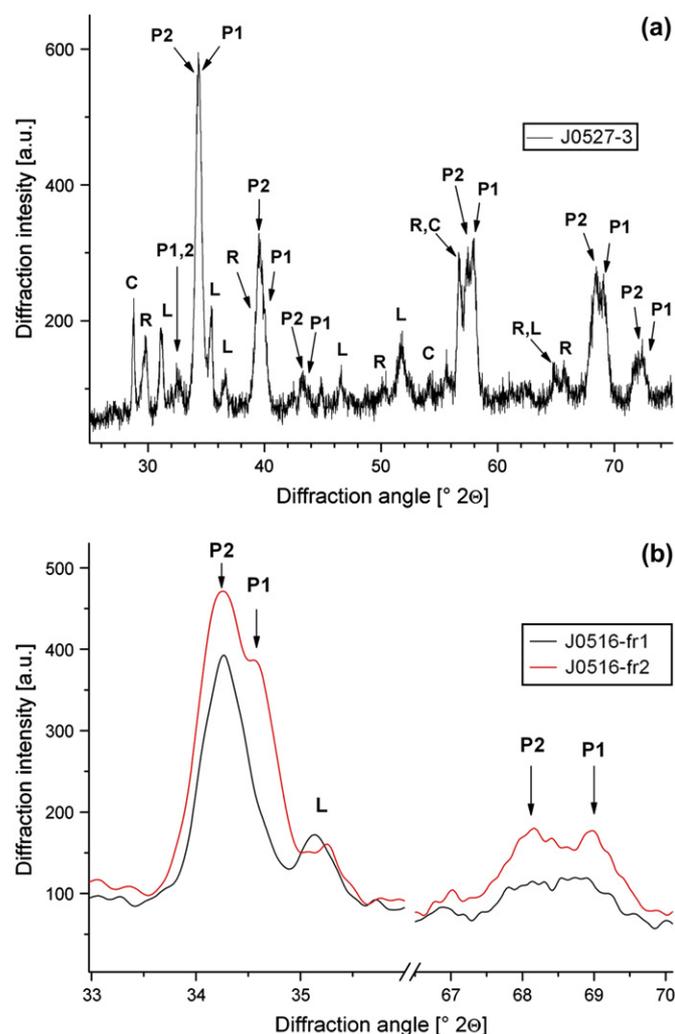[h] Synthesis at ratio Pb:Sn:Si 6:3:1 at 900 °C.

Fig. 1. X-ray diffraction pattern of yellow layer of J0527 sample 3 (a) and a detail of Pb-Sb-Sn pattern of two fragments of yellow layer in J0516 with diffractions (222) and (622) (b). The latter pattern was smoothed by 5-point FFT filter. Phase abbreviations: **C** cerussite ($PbCO_3$, white lead), **R** rosiaite ($PbSb_2O_6$), **L** lanarkite ($Pb_2(O)SO_4$), **P1** and **P2** two close pyrochlore structures of Pb-Sb-Sn yellows producing "splitting" of the most relevant diffractions as shown in detail in (b).

Beside anglesite and/or lanarkite, another admixture typical for Pb-Sb-Sn yellows from Sb_2S_3 and for real pigments is rosiaite ($PbSb_2O_6$), found, e.g., in specimen J0527 (Fig. 1). Rosiaite hence also supports our hypothesis that Sb_2S_3 could be used as the Sb source in Pb-Sb-Sn yellows. Interestingly, no original historical Italian recipes of Pb-based yellows listed in current literature mention a synthesis from Sb_2S_3, SnO_2, and Pb_3O_4 without a salt flux.

4.2. Evaluation of individual Pb-yellows

The production of different Pb-based yellows was likely controlled by several factors: technological requirements of their synthesis and technological properties of the individual yellows, their colour properties, actual knowledge of the producers and the raw materials available. The last two aspects

substantiate the hypothesis that the Pb-based yellows could be useful in evaluation of the provenance of materials used in paintings. The syntheses of the individual yellows and their colour coordinates are summarized in Table 2. Colour layers of some of the pigments in an oil medium are shown in Fig. 2.

Lead tin yellow type I does not require flux agents, its synthesis is successful in lower calcination temperatures (650–800 °C), as higher temperature produces lighter pigments, and its hue is greenish. The greenish hue surely made this pigment a valuable alternative to ferric ochres, of which shade is never greenish but rather reddish. Maybe that is why lead tin yellow type I was also mixed with blue and green pigments to obtain light green hues. The ease of its synthesis and a particular colour of lead tin yellow type I are in contrast to end of use of this pigment before the end of the Middle Ages. The only possible drawback of its synthesis could be its sensitivity to higher calcination temperature: at 900 °C, it is much lighter yellow, or perhaps a shortage of SnO_2 raw.

Lead tin yellow type II requires to carefully control the excess of SiO_2 because Pb forms preferentially a colourless glassy silicate phase, the colour is developed at a bit higher temperature (800–900 °C), and its hue is neutral yellow (Table 2, Fig. 2). The calcination temperature affects the resulting hue: lower temperature produces pigments with a reddish hue (Fig. 2). The limiting factor of the synthesis could have been the need of the most careful stoichiometry control and hence also a careful selection of raw materials, and a good knowledge and experience of the producers.

The synthesis of Naples yellow is successful only in the presence of fluxing agents, namely NaCl or less
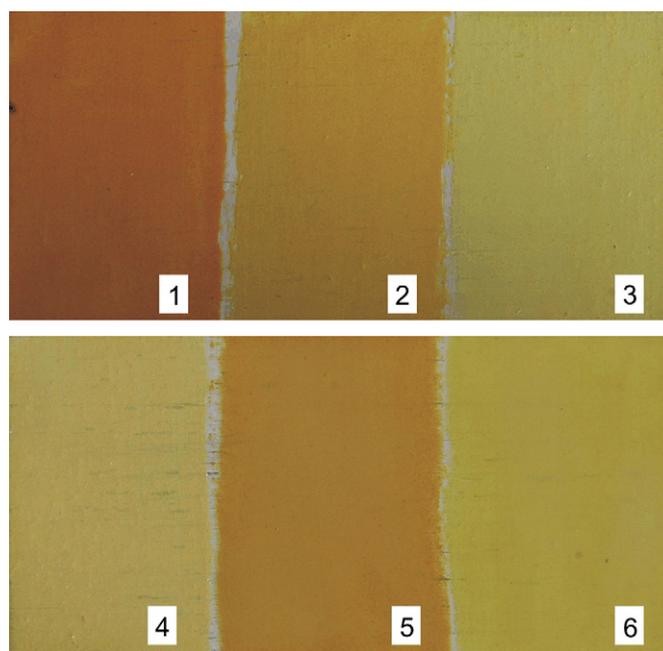

Fig. 2. Selected Pb-based yellows in an oil binding medium. Naples yellow (1), Naples yellow with 20% excess Sb (2), Pb-Sb-Sn yellow from oxides, Pb:Sb:Sn 2:1.5:0.5 (3), Pb-Sb-Sn yellow from Pb and Sn oxides and Sb_2S_3, Pb:Sb:Sn 2:1:1 (4), Pb-Sn yellow type II calcined at 850 °C (5) and 900 °C (6). Photo: Hana Kurková.

Table 4
List of X-ray powder microdiffraction results: distinguishing of type I and II of lead tin yellow and Pb-Sb-Sn yellow and Naples yellow, respectively, in real samples of paintings (ordered by their age)

Code	Name and description	Painting technique	Dating	Analytical methods	Type of Pb-based yellow
M0605	Master from Vyšší Brod: Lady Day, National Gallery − Prague	Tempera on wood	1st half of 15th century	SEM/EDS, micro-pXRD	Pb-Sn Type I
M0608	Unknown painter: Assumpta from White Mountain; National Gallery − Prague	Tempera on canvas	15th century	SEM/EDS, micro-pXRD	Pb-Sn Type I
M0405	Funeral crown of the Czech king Charles IV., Prague Castle	Tempera on wood	1471	SEM/EDS, micro-pXRD	Pb-Sn Type I
M0429 M0524	Lucas Cranach, Franciscan Monastery at Kadaň	Tempera wall painting	1472−1553	SEM/EDS, micro-pXRD	Pb-Sn Type I
M0356	Michiel Coxie: Altar piece; National Gallery - Prague	Oil tempera on wood	1498−1590	SEM/EDS, micro-pXRD	Pb-Sn Type I
J0517	Unknown author: Virgin Mary with Child	Polychromy on wood	Late Gothic	SEM/EDS, micro-pXRD	Pb-Sn Type I
J0534	Unknown painter: Miracle in Church (Lithuania)	Oil on canvas	1677 (?)	SEM/EDS, micro-pXRD	Pb-Sn Type I
M0366	Unknown painter: Decapitation of St. Catharina, Museum of Walachia in the Open Air in Rožnov pod Radhoštěm	Oil on canvas	18th century	SEM/EDS, micro-pXRD	Pb-Sn Type I
J0513	Unknown painter: Celebration; Velké Losiny Castle	Oil on canvas	18th century (?)	SEM/EDS, micro-pXRD	Pb-Sn Type I
M0526 M0601 M0602	Unknown painter: Calvary − III., V. and VII. Interception; Franciscan Monastery in Kadaň	Oil on canvas	After 1770	SEM/EDS, micro-pXRD	Pb-Sb (Naples), Pb-Sb-Sn
M0420	Franz Cauzig: Themistokles is Looking for Recourse chez Admét King; Velké Losiny Castle	Oil on canvas	1755−1828	SEM/EDS, micro-pXRD	Pb-Sb (Naples)
M0421	Franz Cauzig: Hyrnéthó is Dieing in Déiphoto's arms; Velké Losiny Castle	Oil on canvas	1755−1828	SEM/EDS, micro-pXRD	Pb-Sb (Naples)
J0527	J.B. Lampi young: Portrait of Young Women with Flowers; Moravian Gallery − Brno	Oil on canvas	1775−1837	XRF, SEM/EDS, micro-pXRD	Pb-Sb-Sn
J0516	Friedrich Amerling: Portrait of Young girl in Oriental Turban; Moravian Gallery − Brno	Oil on canvas	1825−1830	XRF, SEM/EDS, micro-pXRD	Pb-Sb-Sn

The artworks are placed in Czech Republic unless other country is given at the description. Abbreviations: micro-pXRD X-ray powder microdiffraction, XRF non-invasive X-ray fluorescence spectrometry, SEM/EDS electron microscopy with EDS analyser.

advantageously K_2CO_3 (added traditionally as calcined potassium hydrogen tartrate), the calcination temperature should be rather higher (best 850−900 °C with NaCl flux), and its colour is warm yellow, i.e. with reddish hue (Table 2, Fig. 2). The hue of Naples yellows could be tuned to some extent by the actual Pb:Sb ratio (Fig. 2). The Pb-Sb-Sn yellow is formed under similar conditions as Naples yellow, i.e. in NaCl flux between 750−900 °C, and its colour closely resembles lead tin yellow type II, i.e. it lacks the orange hue of Naples yellow. If Sb_2S_3 was used instead of Sb_2O_3, the salt flux was not necessary, and excess of Pb should compensate the formation of Pb sulphates by-products. Naples and Pb-Sb-Sn yellows hence required a good knowledge on their technology. The hue of Naples yellow is very similar to hue of some ferric ochres and there is a question why this pigment was produced. Maybe its usage in painting was only a secondary purpose beside glass and glaze making. On the other hand, the clear yellow colour of Pb-Sb-Sn yellow made it unique with respect to yellow ochres.

One more reason to produce different Pb-based yellows during the history of fine arts was an actual access to raw materials. The access to important stibnite (Sb_2S_3) deposits and Sb metallurgy in Caucasia probably allowed using $Pb_2Sb_2O_7$ as pigment in Egyptian glass of the second millennium BC [10]. Further large deposits of stibnite are in Turkey, and maybe this caused that the European knowledge of Naples yellow is searched for in the Near East production in the beginning of the second millennium AD [5]. Actually the low availability of Sb reportedly caused usage of Fe oxides as a substitute of Naples yellow in decoration on ceramics produced in Sicily during Renaissance [16]. Similarly, huge cassiterite (SnO_2) deposits in the north-east Bohemia used since the early Middle Ages might favour using lead tin yellows and also Pb-Sb-Sn yellows in Mid-European art. The access to raw materials probably also affected the choice of flux agents: vine lees and its calcine were surely easier available in Mediterranean countries with huge vine production than in northland.

4.3. Analysis of artworks

For a routine estimation of pigments in colour layers of artworks, elemental composition measured by SEM/EDS or X-ray fluorescence analysis are commonly used. According to results of elemental analyses of 44 artworks we concluded that none of the yellows in the paintings dated to the period from 15th to 17th century contained antimony; only lead tin yellow was used in a typical association with white lead (basic lead carbonate) in yellows and verdigris (copper acetates) or malachite (basic copper carbonate) in light greens. Type I is exclusively present as confirmed by X ray microdiffraction in 9 cases (Table 4).

Yellow ochres alternated lead tin yellow in warmer yellow colours but these two pigments were only rarely mixed together.

Ochres presence was inferred from EDS analysis revealing Si, Al, Fe and eventually K and Ca. When it was necessary, namely in the cases of lead tin and Pb-Sb-Sn yellows, X-ray diffraction was used to identify the pigments.

In the first half of the 18th century, the composition of yellows rapidly changed from lead tin yellows to pure Pb-Sb type found by EDS in more than 80% of cases; the rest is still represented by lead tin yellow. The mixing of Naples yellow and lead tin yellow together in one layer was not evidenced in any case. In the 2nd half of 18th century ternary Pb-Sb-Sn appears possibly soon after Naples yellow. In the 19th century Pb-Sb-Sn yellow dominated among Pb-containing yellows. Pb-based yellows of 18th century were usually mixed with yellow ochres (in warm yellows) and with ultramarine − $Na_6Ca_2(Al_6$-$Si_6O_{24})S_2$, Prussian blue − Iron(III)-hexacyanoferrate(II) or green earth pigments (in greens). Afterwards, in 19th century, they were gradually replaced by modern cadmium sulphates and chrome-containing yellows [20]. Such a rapid disappearance of Sn from the technology of yellow pigments at the end of 17th century and then its partial 'come-back' in ternary Pb-Sb-Sn yellows within one century could be connected with a lack of tin evoked by a temporary decay of tin mining in Europe [21].

Discrimination between the lead tin yellows type I and type II based on elemental analysis is not realistic. EDS analysis of yellow grains in artworks showed that only in 8 analysis from 63 the Pb/Sn ratio corresponded approximately to the stoichiometry of the lead tin yellow type I (Pb_2SnO_4), i.e. Pb/Sn = 1.8−2.2 while in five cases it was higher and in all other cases it was lower than 1.8. In 18 analyses it was very close to the stoichiometry of the lead tin yellow type II ($PbSnO_3$), i.e. between 0.8 and 1.2. In most cases the ratio Pb/Sn could apparently be increased by a very common admixture of white lead, and because of a common admixture of SiO_2, one could

not use the elemental ratio as a proof of the presence of lead tin yellow type II. Bohemia is mentioned as a traditional region where the type II was used [6,7], and we were hence surprised that no sample with lead tin yellow additionally analyzed by powder X-ray microdiffraction contained lead tin yellow type II, but only well-crystallized Pb_2SnO_4 was detected in all these cases.

The analysis of the gothic wooden funeral crown of the king Charles IV. (specimen M0405, Table 4) dated to the 15th century is a very illustrative example of how careful one must be in identification of the type of lead tin yellows. The yellow layer on fragment 4 of the crown did not contain white lead and Pb/Sn ratio was 0.77 in average. The content of Si was relatively high, about 13 at-%, and no Al or Fe was present, i.e. no admixture of yellow ochres was expected. Although the excess of Sn over Pb and Si presence could apparently point to lead tin yellow type II, X-ray microdiffraction analysis proved a presence of lead tin yellow type I, quartz (SiO_2) and cassiterite (SnO_2).

The utilization of X-ray diffraction is also substantiated in the case of lead antimony yellows. The first sign that a pigment in a colour layer of artworks could be Pb-Sb-Sn yellow and not Naples yellow can be the result of X-ray fluorescence or electron microanalysis (Tables 5 and 6). But mere simultaneous presence of the three elements is insufficient to identify Pb-Sb-Sn yellow unless a simultaneous presence of Naples and lead tin yellow is excluded, although such a combination in one colour layer might seem unexpected from the present-day art-historical point of view. In an original colour layer of two paintings of Vienna Academy by J.B. Lampi, the younger (1775−1837) (specimens J0527 and J0539, Table 4 and 5) and also in one painting by F. Amerling (1803−1887) (specimen J0516, Tables 4 and 5, Figs. 3 and 4), we first revealed a simultaneous presence of Pb, Sb, and Sn by non-invasive

Table 5

Elemental analyses of yellows in paintings of Vienna Academy (non-invasive analysis by XRF and/or EDS analysis of yellow grains in microsamples)

	Pb	Sb	Sn	Fe	Si	Al	Ca	Na	K	Other
J0539, J.B. Lampi, the elder (1751−1830) Portrait of Catharina II., yellow-green leafs										
Non-invasive XRF (2 points)[a]	x	x		x			x		?	Mn
J0528, J.B. Lampi, the elder (1751−1830): Portrait of Serény, hair (XRF) and sample 1 − brown at bottom margin (EDS)										
Non-invasive XRF (2 points)[a]	x	x		x			x		?	Ba
Average EDS of yellow grains (2 points)	20	23		3	27	12	9		6	
J0506, J.B. Lampi, the younger (1775−1837) Portrait of young man, waistcoat										
Non-invasive XRF (3 points)[a]	x	x	x	x			x		?	Ba
J0527, J.B. Lampi, the younger (1775−1837): Young Women with Flowers, sample 3, yellow flower										
Non-invasive XRF (3 points)[a]	x	x	x	x			x		?	Mn, Ti
Average EDS of yellow grains containing Sn (2 points)	43	25	15	0.5	7		8	3		
Average EDS of yellow grains not-containing Sn (7 points)	39	43		5	76		7			
J0516, F. Amerling (1803−1887): Young girl in oriental turban, sample 1 − yellow locket										
Non-invasive XRF (3 points)[a]	x	x	x	x			x			Ba, Cr
Average EDS of light yellow grains containing Sn (4 points)	45	31	12		6	6				
Average EDS of yellow grains not-containing Sn (2 points)	42	37		10	6	4				

Paintings can be divided into 2 groups − with no Sn in Naples yellow (painted by J.B. Lampi, the elder) and with Sn in Pb-Sb-Sn yellow (painted by J.B. Lampi, the younger and F. Amerling).

[a] Non-invasive measurements do not allow deciding whether Fe, Ca and "other" elements come from colour or ground layers.

Fig. 3. Friedrich Amerling: Portrait of Young Girl in Oriental Turban (J0516), Moravian Gallery in Brno 1825–1830(?). Pb-Sb-Sn yellow was used in the decoration of turban (detail of fringes – sample J0516-5) and the dress. Photo: Igor Fogaš.

analysis by X-ray fluorescence. Only Pb and Sb was detected in the Pb-based yellows in two paintings by J.B. Lampi, the elder (1751–1830), i.e. of an almost the same period. Not all the mentioned paintings were available for a further
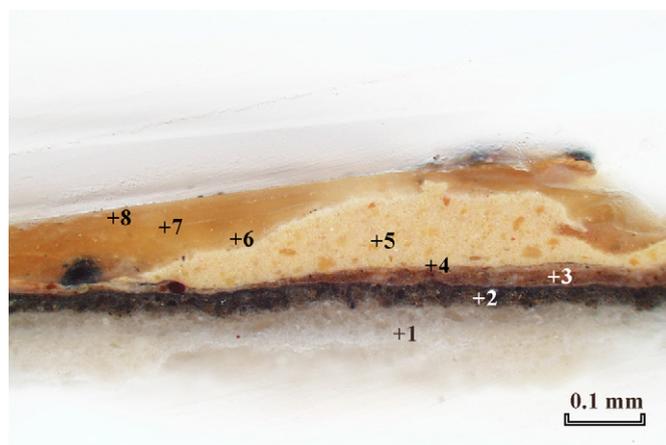

Fig. 4. Light yellow grains of Pb-Sb-Sn yellow in original layer (+5) of the sample J0516-5 observed in the cross-section of painting layers in reflected visible light. Layer contains also grains of pure Naples (Pb-Sb) yellow. Simplified description of the stratigraphy: +1 light ground with dolomitic chalk $CaMg(CO_3)_2$ + $CaCO_3$, barite $BaSO_4$, white lead $PbCO_3.Pb(OH)_2$, quartz SiO_2 and K-feldspar $KAlSi_3O_8$, +2 dark layer with ivory black (calcium phosphate) and Fe ochres, +3 pentimenti – iron pigments and white lead, +4 surface impurities, +5 Pb-Sb-Sn-yellow (yellow grains) and Fe ochres, +6 lazule with ivory black grains, +7 and +8 varnishes. Photo: Janka Hradilová.

laboratory microanalysis. More detailed SEM/EDS analysis of two samples from the paintings by J.B. Lampi, the younger and F. Amerling showed two types of the pigment grains: dark yellow containing Pb and Sb in atomic ratio 1:1 (within uncertainty of the analysis) and light yellow containing Pb, Sb, and Sn in atomic ratio about 2:1.5:0.5 (Table 5, Fig. 4). A similar pigment was found in one painting by J.M. Navrátil (1798–1865) with similar two types of yellow grains (M0402, Tables 4 and 6). Pb-Sb-Sn stoichiometry is here influenced by an important admixture of white lead (Table 6). Two other findings are from paintings of the Calvary cycle (interceptions V and VII, M0526 and M0602, Tables 4 and 6) from the second half of 18th century, but in these cases the distinguishing of two kinds of grains is unclear. In another painting from the same Calvary cycle (interception III, M0601, Tables 4 and 6), painted by the same unknown painter, only pure Naples yellow occurs. Contrarily to paintings of the Vienna Academy (J.B. Lampi, the younger and F. Amerling) where using of Naples and Pb-Sb-Sn yellows can be a sign of author's preference, the Calvary cycle is an example of synchronous use of both pigments by the same author.

It is worthy mentioning that ferric ochres were mixed with Naples and Pb-Sb-Sn yellows in the artworks studied. Fe ochres can contain only few % of Fe, but they are unequivocally identified by the simultaneous presence of quartz (SiO_2), clay minerals, and/or calcite $(CaCO_3)$, as it is revealed by Si, Al, K and Ca presence (Tables 5 and 6). The ratio of the mineral admixtures beside the goethite $(\alpha\text{-FeOOH})$ yellow

Table 6

EDS analyses of Pb-Sb-Sn yellows found in paintings not connected to the Vienna Academy – oil on canvas painting of J.M. Navrátil (1798–1865) "Scenery with ruin" and of interceptions V and VII of the Calvary painted by unknown painter in the 2nd half of 18th century (Kadaň, Czech Republic)

	Pb	Sb	Sn	Fe	Si	Al	Ca	Na	K
M0402, J.M. Navrátil (1798–1865): Scenery with ruin, sample 1 – yellowish background									
Average EDS of yellow grains not containing Sn (2 points)	61	33		2	5				
Average EDS of yellow grains containing Sn (3 points)	50	31	12		5	2			
M0526, Unknown painter (2nd half of 18th century): Calvary – interception V									
Sample 3 – cloak of Roman soldier									
Average EDS of yellow grains (8 points)[a]	30	25	4	5	18	9	9		
M0602, Unknown painter (2nd half of 18th century): Calvary – interception VII									
Sample 2 – red trouser-leg of soldier									
EDS of yellow grain (1 point)	41	19	15	6	9	3	8		
M0601, Unknown painter (2nd half of 18th century): Calvary – interception III									
Sample 1 – green terrain									
Average EDS of yellow grains (2 points)	14	22		3	39	12	6	2	1

[a] Distinguishing among grains with and without tin is not possible; the content of tin in Pb-Sb-Sn yellow is generally lower than in previous case.

pigment depends on the ochre provenance [14,22]. Both Naples yellow (e.g. J0528 in Table 5) and Pb-Sb-Sn yellow (e.g. M0526 in Table 6) were mixed with ferric ochres.

5. Conclusion

The discrimination between Pb based yellow pigments cannot be done only on the base of their elemental composition of the yellow colour layers. We found that Pb/Sn ratio is not specific to the actual type of the lead tin yellows, and the molecular structure of lead-oxide should best be identified by X-ray diffraction or possibly by other method of direct mineral identification such as Raman spectroscopy. We did not identify lead tin yellow type II by X-ray diffraction in any painting studied although the actual Pb/Sn ratio was commonly close to 1 and SiO_2 admixture was present in some cases.

X-ray diffraction coupled to X-ray fluorescence or electron microanalysis was proved suitable to distinguish Naples yellow ($Pb_2Sb_2O_7$) and Pb-Sb-Sn yellow. Both these pigments were used in Italian painting in 17th century [2,17]. The usage of Pb-Sb-Sn yellow in 18th–19th century paintings is described for the first time. We identified this pigment in five Mid-European paintings. The pigment was accompanied by Pb sulphates that points to its synthesis from Sb_2S_3, a Pb oxide, and SnO_2, while traditional Naples yellow was obtained from a Pb oxide and Sb_2O_3.

The specimens of Pb-Sb-Sn yellows synthesized in our laboratory had lower red coordinate in CIE-$L^*a^*b^*$ space, i.e. their hue was clearer yellow than that of Naples yellow. An actual availability of Sb and Sn raw materials could contribute to the specific spatial and/or temporal usage of Pb-Sb-Sn yellow practically simultaneous with common Naples yellow. The discrimination between these two pigments can hence provide a clue to the provenance of paintings.

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