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

David Hradil a,b,*, Tomáš Grygar a,b, Janka Hradilová b, Petr Bezdička a,b, Veronika Grünwaldová a,b, Igor Fogas ğ c, Costanza Miliani d

a Institute of Inorganic Chemistry ASCR, ALMA laboratory, 250 68 Řez, Czech Republic
b Academy of Fine Arts in Prague, ALMA laboratory, U Akademie 4, 170 22 Prague 7, Czech Republic
c Moravian Gallery in Brno, Husova 18, 662 26 Brno, Czech Republic
d CNR-ISTM and SMAArt, c/o Department of Chemistry, University of Perugia, via Elce di sotto 8, I-06123 Perugia, Italy

Received 15 December 2006; accepted 10 July 2007

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.

© 2007 Elsevier Masson SAS. All rights reserved.

Keywords: Naples yellow; Lead tin yellow; Lead antimony tin yellow; X-ray microdiffraction; European paintings; Colour layers

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
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 \((\text{Pb}_2\text{SnO}_4)\) and its modification called lead tin yellow type II written as \(\text{PbSnO}_3\) by Rooksby [3] or \(\text{PbSn}_x\text{Si}_{1-x}\text{O}_3\) by Clark et al. [4], Naples yellow \((\text{Pb}_2\text{Sb}_2\text{O}_7)\) 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 \((\text{Pb}_2\text{Sb}_2\text{O}_7)\) 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 \(\text{TiO}_2\), \(\text{SnO}_2\), and/or \(\text{ZnO}\) [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 Kühn [6], both lead tin yellows type I and II were introduced between 14th and 17th centuries. During 17th century lead tin yellows gradually evolved to lead antimonate (Naples) yellows and a joint occurrence of Pb, Sn and Sn in yellow colour layers could be temporally and regionally very specific [6].

The ternary pyrochlore type oxide \(\text{Pb}_2\text{Sn}_{2-x}\text{S}_{x}\text{O}_{7-x/2}\) could be a possible reason of a common occurrence of Pb, Sn, 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 \(\text{Pb}_2\text{SnS}_{0.5}\text{O}_{6.5}\) 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 \(\text{Pb}_2\text{Sn}_{2-x}\text{S}_{x}\text{O}_{7-x/2}\) 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 \(\text{SnO}_2\) was used as ground on the ceramics.

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula (PDF-2 card number)</th>
<th>Symmetry, cell size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead tin yellow type I (lead tin oxide)</td>
<td>(\text{PbSnO}_4) (e.g. 1-75-1846)</td>
<td>Orthorhombic, (a = 1.069-1.072)</td>
</tr>
<tr>
<td>Lead tin yellow type II (lead tin silicon oxide)</td>
<td>(\text{PbSnO}<em>3) (17-0607) (\text{PbSn}</em>{0.76}\text{Si}_{0.24}\text{O}_3) (49-1886) (\text{PbSnO}_3) (1-72-0002)</td>
<td>Cubic pyrochlore, (a = 1.096-1.072)</td>
</tr>
<tr>
<td>Naples yellow (lead antimony oxide)</td>
<td>(\text{Pb}_3\text{Sb}_2\text{O}_7) (42-1355, 1-73-1377, 1-074-1354)</td>
<td>Cubic pyrochlore, (a = 1.040-1.044)</td>
</tr>
<tr>
<td>Pb-Sb-Sn yellow (lead antimony tin oxide)</td>
<td>(\text{Pb}<em>2\text{SnS}</em>{0.5}\text{O}_{6.5}) (39-0928)</td>
<td>Cubic pyrochlore, (a = 1.056)</td>
</tr>
</tbody>
</table>
3. Experimental part

3.1. Laboratory synthesis and characterization of Pb-based yellows

The pigments were synthesized using Pb\textsubscript{2}O\textsubscript{4}, Sb\textsubscript{2}O\textsubscript{3}, Sb\textsubscript{2}S\textsubscript{3}, SnO\textsubscript{2}, NaCl, and K\textsubscript{2}CO\textsubscript{3} of analytical purity and SiO\textsubscript{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 Pb-based yellows, some syntheses were facilitated by an addition of flux agents according to the literature recipes, where rock salt NaCl and potash K\textsubscript{2}CO\textsubscript{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\textsubscript{2} by Darduni (17th century) according to translations and interpretations by Sandalinas and 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 usage 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.

3.2. 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 \( \sim 130 \) 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 díffractometry 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, HighScore (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\textsubscript{2}SnO\textsubscript{4} is easily obtained by calcination of a mixture of oxide components between 650 and 900 °C. In agreement with the spectra published by Kühn [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\textsubscript{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

\[ 6\text{PbO} + 3\text{SnO}_2 + 2\text{SiO}_2 = [3\text{PbO} - 2\text{SiO}_2] + 3[\text{PbSn}_1\text{Si}_1\text{O}_3] \]

where square brackets denote approximate composition, 
\[ [3\text{PbO} - 2\text{SiO}_2] \] is a colourless glassy phase giving one broad X-ray diffraction line centred at \( d \sim 3.1 \) Å, and 
\[ [\text{PbSn}_{1-x}\text{Si}_x\text{O}_3] \] 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\(_2\)SnO\(_4\) is formed. To form [PbSn\(_{1-x}\)Si\(_x\)O\(_3\)] 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\(_2\)SnO\(_4\) and [PbSn\(_3\)O\(_7\)] 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\(_2\)O\(_3\) and Sb\(_2\)O\(_3\) 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\(_2\)Sb\(_2\)O\(_7\)), but also orthorhombic Pb\(_2\)Sb\(_2\)O\(_7\) (card 39–834), Pb\(_3\)Sb\(_2\)O\(_8\) (card 34–1196), and PbSb\(_2\)O\(_6\) (rosaite, card 34–912). All the specimens containing orthorhombic Pb\(_2\)Sb\(_2\)O\(_7\) and Pb\(_3\)Sb\(_2\)O\(_8\) 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\(_2\)CO\(_3\) flux, recommended by the traditional recipes [5]; NaCl is a plain salt, and K\(_2\)CO\(_3\) 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\(_2\)CO\(_3\) 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\(_2\)CO\(_3\), 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\(_2\)CO\(_3\) produced pyrochlore with \( a = 10.56 \) Å, maybe with some K present in the pyrochlore.
lattice. When 5 or 10% of fine SiO2 (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 SnO2 (Table 2). Calcination of Pb2O4, Sb2O3 and SnO2 with 10% NaCl at 700, 800, or 900 °C produced Pb2Sb2−xSnO7−2x with the pyrochlore structure, usually as a mixture of two pyrochlore structures with different cell sizes and commonly with a trace of non-consumed SnO2 (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:Sn: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 K2CO3 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 Sb2S3 as a Sb source. There were two principal reasons for that: the term “antimony” in historical recipes did theoretically mean Sb, Sb2O3 or Sb2S3 [5,15]. Addition of potassium in the yellow pigment 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 Sb2S3 as a Sb source. There were two principal reasons for that: the term “antimony” in historical recipes did theoretically mean Sb, Sb2O3 or Sb2S3 [5,15]. Additionally, we found an admixture of Pb sulphates anglesite (PbSO4) and lanarkite (Pb2(O)SO4) in colour layers of the paintings containing Pb-Sb-Sn yellow (specimens J0516, J0527, and M0526, Table 3, Fig. 1) and we expect that Sb2S3 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 Sb2S3 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 SnO2 remained unconsumed and in some batches rosiaite (PbSb2O6) was formed from correspondingly unconsumed Sb. The following schemes describe the reactions producing pigments of good colour properties:

\[
\begin{align*}
5\text{PbO} + \text{Sb}_2\text{S}_3 + 2\text{SnO}_2 + 6\text{O}_2 & = \text{Pb}_5\text{S}_3\text{O}_{14} + 2\text{Pb}_2\text{SnO}_6 \\
& + 2\text{SO}_2
\end{align*}
\]

producing mainly anglesite (PbSO4) at temperatures 850 °C and lanarkite (Pb2(O)SO4) at 900 °C

\[
\begin{align*}
6\text{PbO} + \text{Sb}_2\text{S}_3 + 2\text{SnO}_2 + 6\text{O}_2 & = \text{Pb}_2\text{(O)SO}_4 + 2\text{Pb}_2\text{SnO}_6 \\
& + 2\text{SO}_2
\end{align*}
\]

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 Sb2S3 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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cell size [nm]</th>
<th>(222) diffraction [nm]</th>
<th>(222) diffraction [°] 2θ in CoKα</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb2SbO7, Naples yellow</td>
<td>1.0394−1.0424</td>
<td>0.2998−0.3007</td>
<td>34.71−34.61</td>
</tr>
<tr>
<td>Pb2SbO7, bindheimite, PDF 42−1355</td>
<td>1.0407</td>
<td>0.3004</td>
<td>34.65</td>
</tr>
<tr>
<td>M0421 (Pb-Sb yellow)</td>
<td>1.048</td>
<td>0.3023</td>
<td>34.42</td>
</tr>
<tr>
<td>Pb2SnO5, PDF 39−928</td>
<td>1.0564</td>
<td>0.3050</td>
<td>34.11</td>
</tr>
<tr>
<td>Pb-Sb-Sn yellow 2:1:1</td>
<td>1.055; 1.051</td>
<td>0.3044; 0.3032</td>
<td>34.18; 34.32</td>
</tr>
<tr>
<td>Pb-Sb-Sn yellow 2:1:1.33:0.67</td>
<td>1.056; 1.050</td>
<td>0.3047; 0.3036</td>
<td>34.15; 34.27</td>
</tr>
<tr>
<td>Pb-Sb-Sn yellow 2:1:5:0.5</td>
<td>1.055; 1.056</td>
<td>0.3044; 0.3017</td>
<td>34.18; 34.39</td>
</tr>
<tr>
<td>J0516, fragment 1 (Pb-Sb-Sn yellow)</td>
<td>1.057; 1.050</td>
<td>0.3050; 0.3029</td>
<td>34.11; 34.35</td>
</tr>
<tr>
<td>J0516, fragment 2 (Pb-Sb-Sn yellow)</td>
<td>1.056; 1.046</td>
<td>0.3049; 0.3020</td>
<td>34.12; 34.46</td>
</tr>
<tr>
<td>J0526, fragment 1 (Pb-Sb-Sn yellow)</td>
<td>1.056; 1.046</td>
<td>0.3048; 0.3018</td>
<td>34.13; 34.49</td>
</tr>
<tr>
<td>J0526, fragment 2 (Pb-Sb-Sn yellow)</td>
<td>1.056; 1.046</td>
<td>0.3048; 0.3017</td>
<td>34.13; 34.49</td>
</tr>
<tr>
<td>Lead-tint yellow type II [PbSnO4]</td>
<td>1.071</td>
<td>0.3090</td>
<td>33.66</td>
</tr>
</tbody>
</table>

Cell size of the cubic pyrochlores (Fe3Sn, space group 227) with composition ranging from Pb5S3O14 via Pb2Sb2−xSnO7−2x to [PbSnO2]. 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:Sn ratio.
b Also contains white lead (hydrocerussite and cerussite).
c Synthesis from Sb2O3, traces of non-reacted SnO2 remained in the product.
d Synthesis from Sb2S3 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.
Beside anglesite and/or lanarkite, another admixture typical for Pb-Sb-Sn yellows from Sb\(_2\)S\(_3\) and for real pigments is rosisaite (PbSb\(_2\)O\(_6\)), found, e.g., in specimen J0527 (Fig. 1). Rosisaite hence also supports our hypothesis that Sb\(_2\)S\(_3\) 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\(_2\)S\(_3\), SnO\(_2\), and Pb\(_3\)O\(_4\) 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
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 — Na₆Ca₃(Al₆-O₄)₄S₂, 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 (Pb₂SnO₄), 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 (PbSnO₃), 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 SiO₂, 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 Pb₂SnO₄ 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 (SiO₂) and cassiterite (SnO₂).

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

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.
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 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 ($\alpha$-FeOOH) yellow

![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 Fogasš.](image)

![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$_3$, white lead PbCO$_3$·Pb(OH)$_2$, quartz SiO$_2$ and K-feldspar KAlSi$_3$O$_8$, +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 lazulite with ivory black grains, +7 and +8 varnishes. Photo: Janka Hradilová.](image)
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 SiO₂ admixture was present in some cases.

X-ray diffraction coupled to X-ray fluorescence or electron microanalysis was proved suitable to distinguish Naples yellow (Pb₂Sb₂O₇) 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 Sb₂S₃, a Pb oxide, and SnO₂, while traditional Naples yellow was obtained from a Pb oxide and Sb₂O₃.

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.

Acknowledgement

The analysis by non-invasive XRF was carried out through the MOLAB Transnational Access with support of the EC within the 6th Framework Programme (Contract Eu-AR-TECH, RI3-CT-2004-506171). The laboratory syntheses and microanalyses were funded by the Ministry of Education of Czech Republic (research intention MSM 6046144603) and Grant Agency of Czech Republic (project 203/04/2091). Special thank should be given to Moravian Gallery in Brno for a close collaboration in the research and to all other owners of paintings for facilitation the sampling. The artworks were kindly sampled by restorers Karel Stretti, Markéta Pavlíková, David Frank, Blanka Valchárová, Theodora Popova, Mario Král, Renáta Zemanová and Miroslav Besta, samples of J0534 were supplied by Irma Pakutinsiene, Lithuania. The authors acknowledge a help by Petr Vorm with syntheses of pigments, Hana Kurková with preparation of painting layers with synthetic pigments, and Kamil Lang for providing access to Vis-spectroscopy and colour analysis.

References