

## ARTIFICIAL YELLOW PIGMENTS: PRODUCTION AND CHARACTERIZATION THROUGH SPECTROSCOPIC METHODS OF ANALYSIS

FULL PAPER

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**Artificial yellow pigments (lead-tin yellow type I and type II, lead antimonate yellow and lead-tin-antimony yellow) have been produced, starting from various recipes and from pure chemicals, in different experimental conditions. The products were analysed using micro-Raman spectroscopy. Differences in stoichiometric ratios, in melting temperatures and in crucible typologies were examined. Other analytical techniques were required to characterize the stoichiometric ratios of the obtained products (X-ray diffraction, scanning electron microscopy with energy dispersive spectroscopy and differential thermal analysis). The results are analysed and discussed in terms of correlations among chemical composition, melting conditions and colour hue.**

### 1 Introduction

Through centuries, yellows of different compositions, based on lead, tin and antimony, have been used either as opacifiers in glasses, glazes and majolicas or as paint pigments. The long period of use of lead-tin and antimony based yellow pigments led to many documents in different languages employing various names describing the same compound, for instance *giallolino* in the southern sources and *massicot* in the northern ones that according to Kühn refer to the same compound (lead-tin yellow).<sup>1</sup> In southern Europe artists and writers regularly used the term *giallolino* to indicate a pale yellow material of varied composition (see Table 1).

Author	Mention of <i>giallolino</i>
Cennini	"... che questo color sia propria prieta, nata in luogo di grande arsura di montagne ...." <sup>2</sup>
Lorenzo Lotto	<i>Zalolin, Zallolin da vasari</i> <sup>3</sup>
Borghini	<i>di vetro, di Fiandra, di Venezia</i> <sup>4</sup>
Lomazzo	<i>di fornace, di Fiandra, di Alemagna</i> <sup>5</sup>
Vasari	<i>giallolino e giallo di vetro</i> <sup>6</sup>
Bernardo Strozzi	<i>di vetro</i> <sup>6</sup>
Richard Symonds	<i>specie in sfumature dal giallo al rosso</i> <sup>6</sup>

Table 1: Some artists and writers who mentioned *giallolino* in their books.

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The main manuscripts containing recipes for the production of lead, tin and

antimony based yellow pigments are reported in Table 2. These manuscripts can be considered as the first examples of written recipes based on oral sources and on workshop notes that the master glassmakers kept with great care. The problem arises from the transcription of these notes. In fact this operation was made by copyists and not by expert glassmakers. So during the transcription many mistakes were made that were handed down to us creating problems in identifying and differentiating these yellow pigments.

Pigment	Manuscript	Recipe
Lead-tin yellow type I and type II	Bolognese manuscript (first half of the 15 <sup>th</sup> century) <sup>7</sup>	Recipe 272
		Recipe 273
Lead antimonate	Piccolpasso <sup>8</sup> (1559)-Passeri (1758) <sup>9</sup>	different recipes for the production of <i>Zalulino</i> and <i>Giallolino</i>
		Recipe 137 (c. 32v.)
	Brunoro manuscript (1645) <sup>10</sup>	<i>Giallo dei vasari</i>
	Valerio Mariani from Pesaro treatise (1620) <sup>11</sup>	
Lead, tin and antimony yellow	Darduin book of recipes (about 1644) <sup>12</sup>	Recipe D 60
		Recipe D 187 (verso)
		Recipe D 187 (recto)

Table 2: Manuscripts and treatises dealing with the production of lead-tin-antimony based pigments.

A full account of literary sources and manuscript recipes is beyond the aim of this paper and it can be found elsewhere.<sup>13</sup>

The aim of this work was the production and characterization of artificial yellow pigments by micro-Raman spectroscopy and other techniques starting from the results obtained in previous papers.<sup>14-15</sup> By analyzing the various recipes concerning lead-tin-antimony yellows, it was possible to reconstruct the original production methods of these pigments though the experimental conditions were not clear (temperatures are not indicated, time is often unspecified and materials are not clearly reported).

We produced lead-tin yellow type I ( $\text{Pb}_2\text{SnO}_4$ ) and lead-tin yellow type II ( $\text{PbSnO}_3$  or  $\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$ ) following the indication of recipes 272 and 273 of the fifteenth century Bolognese Manuscript, lead antimonate yellow ( $\text{Pb}_2\text{Sb}_2\text{O}_7$ ), called Naples yellow, according to the treatises written by Piccolpasso, Passeri and Valerio Mariani from Pesaro, and lead-tin-antimony yellow ( $\text{Pb}_2\text{SnSbO}_{6,5}$ ) from the Darduin, Valerio Mariani from Pesaro and other authors' recipes.<sup>15</sup> More recent works, dealing with the production and analysis of artificial yellow pigments, were taken into account.<sup>1,16-21</sup> The obtained products were

characterized using micro Raman spectroscopy, X-ray diffraction (XRD) analysis, scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) and differential thermal analysis (DTA).<sup>15</sup> Raman spectroscopy is a very useful and powerful technique for the characterization of cultural heritage materials owing to the facts that it may be used in situ, is non-destructive, has high spatial resolution and is highly specific. Moreover Raman spectroscopy can analyse one crystal at a time, like SEM-EDS, and so evaluate the presence of compounds with different stoichiometric ratios, like XRD, but SEM-EDS does not provide a molecular fingerprint for the particle under observation and XRD analysis cannot analyse every single crystal. The produced pigments have been also characterized by other techniques like XRD and SEM-EDS because at present reference Raman spectra of standard pigments are not always available. Moreover Raman spectra found in spectral databases are sometimes referred to commercial products that are not pure. Thus, another aim of this work was to discuss the Raman spectra obtained in our work in comparison with literature references and to investigate the influence of the experimental conditions on the chemical and physical characteristics of the produced materials.

A case study is also reported as comparison with the synthesized products.

## 2 Materials and Methods

Pure oxides ( $\text{PbO}$ ,  $\text{Pb}_3\text{O}_4$ ,  $\text{SnO}_2$ ,  $\text{Sb}_2\text{O}_3$  and  $\text{SiO}_2$ ) supplied by Acros (Acros Organics, New York, USA) were used for the production of lead-tin-antimony yellow pigments. The oxides were mixed in agate mortars and then introduced into the furnace at room temperature. They were heated up to the required temperatures. According to literature data<sup>1,16-21</sup> temperature was different depending on the typology of the pigment to be produced (670, 800 and 900 °C for lead-tin yellow type I and type II; 900 and 950 °C for lead antimonate; 925 °C for lead-tin-antimony yellow). The temperature was maintained constant for 5 h. Only for the production of lead-tin yellow type I was a time of 3 h also tested. Then the samples were allowed to cool slowly inside the furnace (see Table 3). In order to evaluate the influence of cooling condition, lead-tin-antimony yellow was also cooled in cold water at 10 °C following Cascales's instructions.<sup>16</sup> For the production of lead-tin yellows porcelain crucibles were used; for lead antimonate and lead-tin-antimony yellow porcelain crucibles and terracotta tiles covered by filter paper were used. Each sample was identified by an alphanumeric system with capital letters and numbers. The abbreviation PSA

indicates lead-tin yellow type I, PSB lead-tin yellow type II, APA lead antimonate, APSA lead-tin-antimony yellow. The abbreviations are followed by a number that specifies the experimental conditions.

The obtained products were analysed by SEM-EDS, XRD, DTA and micro-Raman spectroscopy. The SEM-EDS analysis was carried out using a JSM 5400 system (Jeol, Tokyo, Japan) with EDS2000 electron probe micro analysis supplied by Oxford Instruments - Microanalysis System (Oxford Instruments, Abingdon, Oxfordshire UK, www.oxford-instruments.com) ; the crystal area was 10 mm<sup>2</sup> and the work distance 22 mm. The probe operated at 25 kV and 60 mA.

The X-ray analytical equipment was a Philips PW1830 diffractometer (Philips, Eindhoven, The Netherlands) with Cu tube, using the 1.5418 Å Cu-K $\alpha$  radiation; operating at 40 kV accelerating voltage and 30 mA beam current. The differential thermal analysis (DTA) was performed by means of a simultaneous TGA/DSC/DTA instrument model Q600 from TA Instruments (TA Instruments, New Castle, Delaware, USA). The powders were heated up to 1500 °C with a temperature ramp from 0.1 to 100 °C/min.

The micro-Raman spectrometer was a Labram Model of the Dilor JobinYvon (Jobin Yvon, Horiba Group, New Jersey USA) with a spatial resolution of 2  $\mu$ m and the possibility of fast detecting owing to the use of a CCD detector cooled to -50 °C. The exciting wavelength was the 632.8 nm red line of a He-Ne laser. Integration times varied between 10 and 20 s with 5 accumulations. The laser power was 3.2 mW.

### 3 Results and Discussion

Table 3 summarizes the production processes and the main characteristics of the obtained yellow pigments. Each artificial yellow pigment will be dealt with separately.

#### 3.1 Lead-tin yellow type I

Lead-tin yellow type I was produced at a temperature of 800 °C for 5 h. PSA2 is in fact the most homogeneous pigment as regards composition and colour hue (Figure 1). At a lower temperature the compound Pb<sub>2</sub>SnO<sub>4</sub> was not completely formed, colour is warm yellow probably due to the presence of unreacted orange red lead. DTA analysis showed that lead-tin yellow type I begins

Chemicals	Amount	%mol	Experimental Conditions	Sample	Visual Observation of the Produced Pigments
Pb <sub>3</sub> O <sub>4</sub> , SnO <sub>2</sub>	3.0g; 1.0g	Pb:Sn=2:1	t=670 °C for 5h porcelain crucible	PSA1	Warm yellow homogeneous powder
Pb <sub>3</sub> O <sub>4</sub> , SnO <sub>2</sub>	3.0g; 1.0g	Pb:Sn=2:1	t=800 °C for 5h porcelain crucible	PSA2	Light yellow homogeneous powder
Pb <sub>3</sub> O <sub>4</sub> , SnO <sub>2</sub>	3:1 in volume	Pb:Sn=2.6:1	t=670 °C for 5h porcelain crucible	PSA3	Orange powder
Pb <sub>3</sub> O <sub>4</sub> , SnO <sub>2</sub>	3:1 in volume	Pb:Sn=2.6:1	t=800 °C for 5h porcelain crucible	PSA4	Deep orange powder
PbO, SnO <sub>2</sub>	3.0g; 1.0g	Pb:Sn=2:1	t=900 °C for 3h porcelain crucible	PSA5	Very light yellow homogeneous powder
PbO, SnO <sub>2</sub>	3.0g; 1.0g	Pb:Sn=2:1	t=800 °C for 5h porcelain crucible	PSA6	Light yellow homogeneous powder
PbO, SnO <sub>2</sub>	3.0g; 1.0g	Pb:Sn=2:1	t=670 °C for 5h porcelain crucible	PSA7	Light yellow homogeneous powder
PSA1, SiO <sub>2</sub>	1.0g; 1.0g	SiO <sub>2</sub> 50% (w/w)	t=800 °C for 5h porcelain crucible	PSB1	White-yellow homogeneous powder
PSA3, SiO <sub>2</sub>	3.0g; 0.3g	SiO <sub>2</sub> 10% (w/w)	t=900 °C for 5h porcelain crucible	PSB2	Unhomogeneous powder with lemon yellow and orange grains
PSA2, SiO <sub>2</sub>	2.0g; 0.2g	SiO <sub>2</sub> 10% (w/w)	t=800 °C for 5h porcelain crucible	PSB3	Yellow fine powder
PSA2, SiO <sub>2</sub>	2.0; 0.2g	SiO <sub>2</sub> 10% (w/w)	t=670 °C for 5h porcelain crucible	PSB4	Light yellow fine powder
PSA2, SiO <sub>2</sub>	0.5g; 0.05g	SiO <sub>2</sub> 10% (w/w)	t=900 °C for 5h porcelain crucible	PSB5	Yellow homogeneous powder
Pb <sub>3</sub> O <sub>4</sub> , Sb <sub>2</sub> O <sub>3</sub>	5.94g; 3.79g	Pb:Sb=1:1	t=900 °C for 5h porcelain crucible	APA1	Yellow glaze attached to the porcelain crucible
Pb <sub>3</sub> O <sub>4</sub> , Sb <sub>2</sub> O <sub>3</sub>	5.94g; 3.79g	Pb:Sb=1:1	t=950 °C for 5h porcelain crucible	APA2	Large brown grains
Pb <sub>3</sub> O <sub>4</sub> , Sb <sub>2</sub> O <sub>3</sub>	5.94g; 3.79g	Pb:Sb=1:1	t=900 °C for 5h terracotta with filter paper	APA3	Warm yellow powder
PbO, SnO <sub>2</sub> , Sb <sub>2</sub> O <sub>3</sub>	1.78g; 0.60g; 0.58g	Pb:Sn:Sb=2:1:1	t=925 °C for 5h terracotta, cooled in water 10°C	APSA1	Warm yellow powder
PbO, SnO <sub>2</sub> , Sb <sub>2</sub> O <sub>3</sub>	1.78g; 0.60g; 0.58g	Pb:Sn:Sb=2:1:1	t=925 °C for 5h terracotta	APSA2	Warm yellow powder

Table 3: Experimental conditions and characteristics of the produced yellow pigments.

to form between 519 and 548 °C (Figure 2). Over 1200 °C only  $\text{PbSnO}_3$  is present.



Figure 1: Photographs of the produced powders with the corresponding marks.

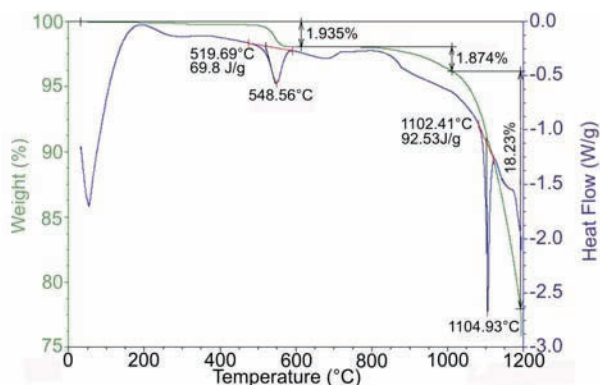


Figure 2: DTA experiment obtained during the heating of a mixture of  $\text{Pb}_3\text{O}_4$  and  $\text{SnO}_2$ . Blue line represents the heat flow, the green one is the weight variation (%).

The correct stoichiometric ratio was  $\text{Pb}:\text{Sn} = 2:1$ ; the volume ratio was incorrect and orange samples were obtained (different reflectance spectra of PSA3 and PSA4 obtained with a volume ratio  $\text{Pb}_3\text{O}_4:\text{SnO}_2 = 3:1$  i.e. a stoichiometric ratio  $\text{Pb}:\text{Sn} = 2.6:1$ ).<sup>15</sup> The orange colour of PSA3 and PSA4 is due to the presence of exceeding red lead.

Using  $\text{Pb}_3\text{O}_4$  or  $\text{PbO}$  does not change the final product. Raman spectrum of sample PSA2 is shown in Figure 3. Characteristic Raman bands at  $129\text{ cm}^{-1}$  (vs),  $195\text{ cm}^{-1}$  (m),  $274\text{ cm}^{-1}$  (wm),  $291\text{ cm}^{-1}$  (w) and  $455\text{ cm}^{-1}$  (wm) are visible and correspond to those found by other authors.<sup>17,22-23</sup>

Samples PSA5 and PSA6 give the same Raman spectra. The very strong peak at  $129\text{ cm}^{-1}$  is due to a lattice Pb-O stretching mode and its wavenum-

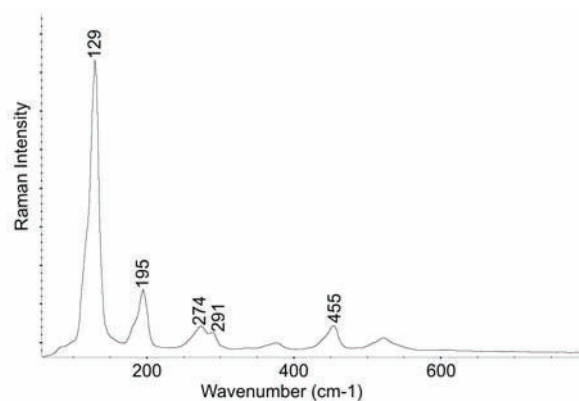


Figure 3: Micro-Raman spectrum of sample PSA2.

ber seems to be dependent on firing temperatures.<sup>22</sup> The other Raman peak wavenumbers seem to be not influenced by firing temperature. The other obtained materials (PSA1, 3, 4 and 7) also give Raman spectra of lead oxides depending on the analysed area. In fact Raman spectrum of red lead ( $\text{Pb}_3\text{O}_4$ ) is obtained in several areas of these samples.

XRD analysis of samples PSA1, PSA2 and PSA5 gives the pattern of  $\text{Pb}_2\text{SnO}_4$  corresponding to the JCPDS file 24-0589 (tetragonal crystal structure). The main  $d(\text{Å})$  values are: 3.30, 2.80, 2.75 and 1.72. Red lead,  $\text{Pb}_3\text{O}_4$ , has also been found by this technique (JCPDS 41-1494) in samples PSA1, PSA3, PSA4 and PSA7.

### 3.2 Lead-tin yellow type II

Lead-tin yellow type II was produced at a temperature of 800 °C or higher using the compound  $\text{Pb}_2\text{SnO}_4$  (PSA2) and  $\text{SiO}_2$  (10% w/w). The use of PSA3, which contains also red lead, as discussed above, led to the production of an unhomogeneous powder with an orange hue (see Figure 1). At lower temperatures (670 °C) a mixture of  $\text{Pb}_2\text{SnO}_4$  and  $\text{PbSnO}_3$  was formed. Colour of sample PSB1 is almost white due to the presence of an excess of  $\text{SiO}_2$ .

Raman spectrum of sample PSB3 is shown in Figure 4. The main Raman bands at  $136\text{ cm}^{-1}$  (vs),  $322\text{ cm}^{-1}$  m(br) and  $449\text{ cm}^{-1}$  w(br) are visible. These bands are in clear agreement with literature reports.<sup>17,22-23</sup> As for lead-tin yellow type I, the very strong band at  $136\text{ cm}^{-1}$  is due to a Pb-O lattice mode. Some authors have reported that its wavenumber depends on the firing temperature.<sup>22</sup>

XRD analysis gives the pattern of  $\text{PbSnO}_3$  corresponding to the JCPDS file 17-0607 (cubic pyrochlore crystal structure). The main  $d(\text{Å})$  values are: 3.10, 2.69, 1.90 and 1.62. Other compounds

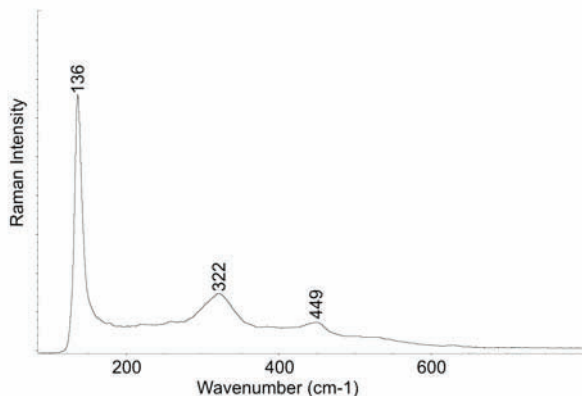


Figure 4: Micro-Raman spectrum of sample PSB3.

like  $\text{Pb}_2\text{SnO}_4$  and  $\text{SiO}_2$  have been also found by this technique.

### 3.3 Naples yellow

Lead antimonate or Naples yellow was synthesized according to different recipes but in all cases a mixture of compounds was obtained. The most homogeneous pigment was APA3 produced at  $t=900\text{ }^\circ\text{C}$  for 5h with a stoichiometric ratio

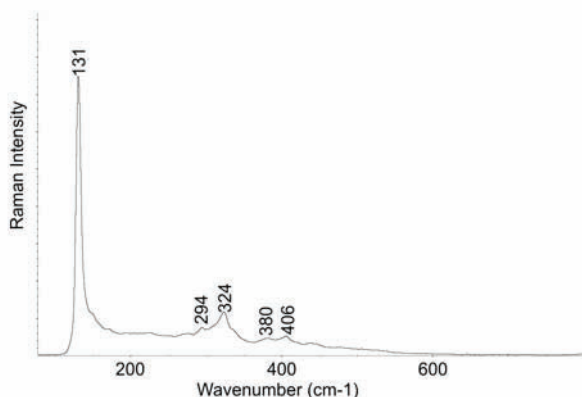


Figure 5: Micro-Raman spectrum obtained for samples APA1, APA2 and APA3

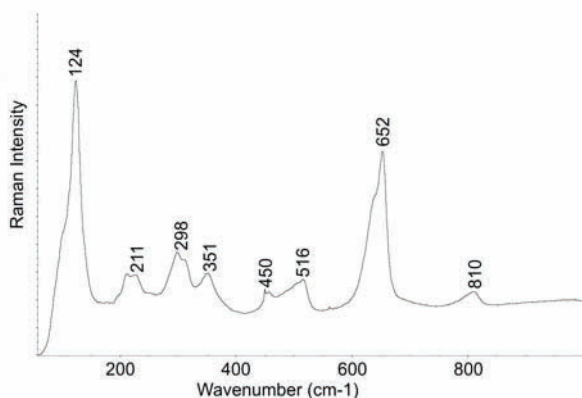


Figure 6: Micro-Raman spectrum obtained for samples APA1, APA2 and APA3.

$\text{Pb}:\text{Sb}=1:1$  over terracotta tile. APA3 exhibits a homogeneous warm yellow-orange colour, whereas APA1 and APA2 show grains of different colours (Figure 1). Sample APA3 contains  $\text{Pb}_2\text{Sb}_2\text{O}_7$ , identified by XRD (JCPDS 18-687, pyrochlore crystal structure) and SEM-EDS ( $\text{Sb}:\text{Pb} = 0.5$  weight ratio) analyses,<sup>15</sup> but also other types of lead antimonate with different stoichiometry. In particular XRD analysis revealed the presence of the following compounds:  $\text{Pb}_{2.5}\text{Sb}_{1.5}\text{O}_{6.75}$  (JCPDS 43-0883),  $\text{Pb}_{3+x}\text{Sb}_2\text{O}_{8+x}$  (JCPDS 34-1196) and  $\text{PbSb}_2\text{O}_6$  (JCPDS 34-0912) found out also by other authors.<sup>18</sup> Raman analysis put in evidence the presence of different compounds in all the examined products demonstrating the difficulty to obtain exclusively the compound  $\text{Pb}_2\text{Sb}_2\text{O}_7$ . In confirmation of this statement two Raman spectra obtained in several areas of samples APA1, APA2 and APA3 are shown in Figures 5 and 6.

Moreover, only for sample APA1 the spectrum in Figure 7 has been also obtained.

Many bands observed in the spectrum of Figure 6 have been described in literature<sup>24</sup> and they may be likely related to a disorder-induced symmetry lowering due to distortion of the  $\text{SbO}_6$  octahedra or displacements of the Pb cations.

The presence of two strong bands at 131 and 146  $\text{cm}^{-1}$  in the spectrum of Figure 7 demonstrates that different compounds have been obtained, as discussed by other authors.<sup>26</sup> They can be due to different arrangements of Pb-O bond in the crystal structure and to different stoichiometric ratios of Pb and Sb.

Raman spectra of the obtained products have been compared with literature data<sup>17, 23-28</sup> but direct comparison is difficult. The only standard literature Raman spectrum is that of a commercial pigment (Kremer) whose production mode is unknown.<sup>17</sup> Moreover there is no matching

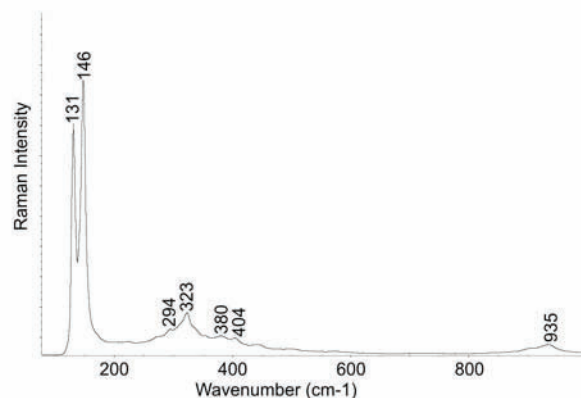


Figure 7: Micro-Raman spectrum obtained for some grains of sample APA1.

between different literature Raman spectra for Naples yellow. In particular the very strong peak of the lattice Pb-O stretching of lead antimonate has been found at different wavenumbers, from 125 to 147  $\text{cm}^{-1}$  according to the firing temperatures,<sup>22,27</sup> and the other bands are often difficult to be detected in the Raman spectrum of micro samples taken from works of art due to the presence of binders and others pigments (see case study in 4). Moreover the peak at 144-147  $\text{cm}^{-1}$  could be associated also to PbO (orthorhombic Massicot which exhibit also a strong peak at 289  $\text{cm}^{-1}$  or tetragonal Litharge) often found in the painted layers. We think that more prudence should be used to assess the presence of Naples yellow using only Raman analysis. In fact few authors report the Raman spectrum of a laboratory produced pigment or indicate the production modes. Only one literature reference<sup>27</sup> has been found, which relates the Naples yellow band at 125-134  $\text{cm}^{-1}$ . According to this work the strong, characteristic lattice Pb-O stretching band wavenumber in the Raman spectrum depends on the firing temperature. The authors discuss the Raman shift of the strong band from 134  $\text{cm}^{-1}$  for Naples yellow obtained at 800 °C to 124  $\text{cm}^{-1}$  for the product obtained at 1100 °C. The lead antimonate obtained at 950 °C exhibits the strong band at 130  $\text{cm}^{-1}$ .

Raman spectra of our lead antimonates exhibit the bands referred by Clark et al.<sup>17</sup> and Daniilia et al.<sup>25</sup> but the wavenumbers are different and other bands are present. So it has been necessary to analyze the produced pigments by other techniques like XRD and SEM-EDS. XRD diffractograms showed the presence of  $\text{Pb}_2\text{Sb}_2\text{O}_7$  (JCPDS 18-687) but also of other compounds as mentioned above. The spectrum in Figure 5 exhibits peaks at 131  $\text{cm}^{-1}$  (vs), 324  $\text{cm}^{-1}$  (m) and 406  $\text{cm}^{-1}$  (w) that according to Sakellariou et al.<sup>27</sup> should correspond to Naples yellow obtained at 950 °C.

The spectrum in Figure 6 is completely different. The main bands were assigned to rosielite ( $\text{PbSb}_2\text{O}_6$ ) a compound easily obtained during the production of Naples yellow.<sup>18,26</sup> The main characteristic bands of rosielite are those at 211  $\text{cm}^{-1}$  (m), 516  $\text{cm}^{-1}$  (m) and 652  $\text{cm}^{-1}$  (s)<sup>26</sup>. This compound has been characterized also by XRD analysis, JCPDS 34-0912 with the main  $d(\text{Å})$  values at: 3.48, 2.65 and 2.11. SEM-EDS also confirmed the presence of this compound in many of the examined areas (Sb:Pb = 1.2 weight ratio) of the produced samples. The other Raman bands are probably to be referred to the other obtained compounds. At last in the spectrum of Figure 7 two more bands are

present at 146  $\text{cm}^{-1}$  and 935  $\text{cm}^{-1}$ . Probably they may be referred to other phases of lead antimonate that at present cannot be associated to a specific compound.

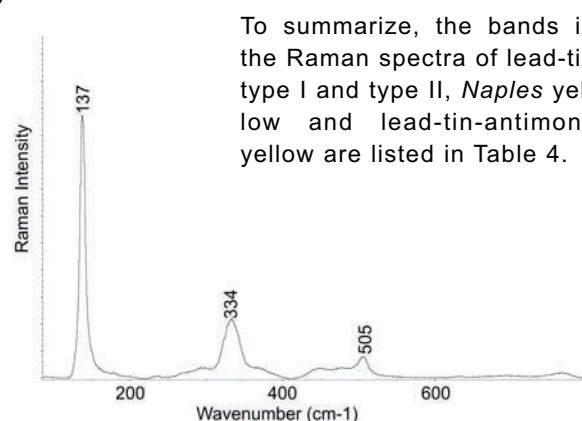
These results demonstrate the difficulty in obtaining a single compound in the production of Naples yellow and the fact that the temperature with regards to the synthesized yellow materials is critical.

### 3.4 Lead-tin-antimony yellow

Lead-tin-antimony yellow was produced at 925 °C for 5 h. In one case after the firing time the powder has been cooled in water at 10 °C. In both experiments the obtained compounds correspond to the formula  $\text{Pb}_2\text{SnSbO}_{6,5}$  (JCPDS 39-0928), main  $d(\text{Å})$  values 3.07, 2.66, 1.87, 1.60 and 1.21. The colours of the two produced pigments are similar and appear warm yellow.

Raman spectrum of the compound APSA1 is shown in Figure 8. The main bands of this yellow pigment are visible at 137  $\text{cm}^{-1}$  (vs), 334  $\text{cm}^{-1}$  (m), 505  $\text{cm}^{-1}$  (w) and 771  $\text{cm}^{-1}$  (vw). They are in clear accordance with literature data.<sup>24,26,29-30</sup>

The addition of tin oxide to lead and antimony oxides seemed to facilitate the production of the yellow pigment in comparison with that of Naples yellow.



To summarize, the bands in the Raman spectra of lead-tin type I and type II, Naples yellow and lead-tin-antimony yellow are listed in Table 4.

Figure 8: Micro-Raman spectrum of sample APSA1.

Pigment	Chemical formula	Wavenumber (cm-1)
Lead-tin yellow type I	$\text{Pb}_2\text{SnO}_4$	129(vs), 195(m), 274(w), 291(w), 455(w)
Lead-tin yellow type II	$\text{PbSnO}_3$ or $\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$	136(vs), 322br(wm), 449br(vw)
Naples yellow	$\text{Pb}_2\text{Sb}_2\text{O}_7$ , $\text{Pb}_{2.5}\text{Sb}_{1.5}\text{O}_{6.75}$ , $\text{Pb}_{3+x}\text{Sb}_2\text{O}_{8+x}$ , $\text{PbSb}_2\text{O}_6$	124-146(vs), 211(w), 294-298(m), 324(w), 351(w) 380(vw), 406(vw), 450(w), 516(m), 652(s), 810(w)
Lead-tin-antimony yellow	$\text{Pb}_2\text{SnSbO}_{6,5}$	137(vs), 334(m), 505(w)

Table 4: Raman bands of the manufactured compounds.

#### 4 Case Study

As an example of the difficulty to characterize Naples yellow on works of art, Raman analysis on a painting is reported. The oil painting has been attributed to a Roman artist of the end of 18<sup>th</sup> century. The paint represents *The Virgin Coronation*



Figure 9: Image of the painting *The Virgin Coronation* with the Holy Trinity, Saint John the Baptist and Saint Carlo Borromeo, after the restoration. Photographic archive of Restoration Laboratory of Viterbo Province (Italy).

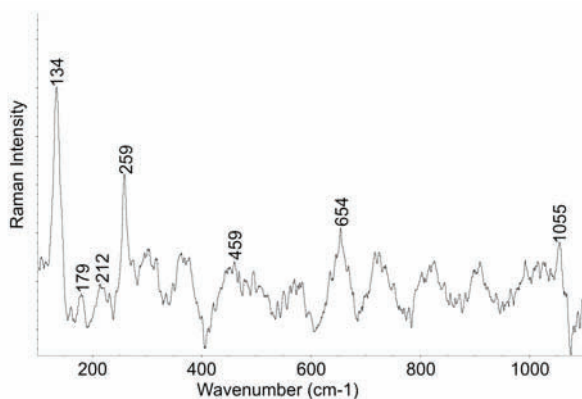


Figure 10: Micro-Raman spectrum of a sample from the painting *The Virgin Coronation* with the Holy Trinity, Saint John the Baptist and Saint Carlo Borromeo.

with the Holy Trinity, Saint John the Baptist and Saint Carlo Borromeo (Figure 9) and it is housed at the church of Saint John the Apostle and the Evangelist in Valentano (Central Italy).<sup>31</sup>

SEM-EDS analysis revealed the presence of Pb and Sb allowing the use of Naples yellow to be assessed in the area surrounding the dove. Mercury was also found in this area of the painting. Raman analysis carried out in many areas of the samples revealed the presence of vermilion, lead white, rosiaite and another phases of lead antimonate (Figure 10). The presence of rosiaite is crucial to assess the presence of Naples yellow more than the single peak at 134 cm<sup>-1</sup>.

In this case SEM-EDS analysis has not been useful to determine the stoichiometry of the compounds because the presence of lead white affects the Pb:Sb ratio.

#### 5 Conclusions

Raman, XRD and SEM-EDS analyses showed that lead-tin yellow type I (Pb<sub>2</sub>SnO<sub>4</sub>), lead-tin yellow type II (PbSnO<sub>3</sub> or PbSn<sub>1-x</sub>Si<sub>x</sub>O<sub>3</sub>) and lead-tin-antimony yellow (Pb<sub>2</sub>SnSbO<sub>6.5</sub>) may be produced as pure materials whereas lead antimonate yellow is very difficult to be obtained. Very often mixtures of compounds with different stoichiometric ratios result.

Experimental tests showed that temperature played an important role in the composition and colour of the produced pigments. The stoichiometric ratio of the metal elements in the chemical oxides was also an important parameter. In fact the use of a volume ratio led to the production of the expected pigments but some reagents remained in the final product. In this preliminary phase of the research we chose to make a simplification of the recipes, in particular to eliminate some ingredients whose role was not completely clear. Further experimental tests will be tried out for a better understanding of the role of these ingredients (*tuccia*, *tartaro emetico* and NaCl) indicated in the recipes.

The study of lead, tin and antimony based yellow pigments, produced in laboratory with the ancient procedure, is also useful for investigations on similar materials used in works of art.<sup>32</sup> Indeed, it is very probable that artists chose their painting materials by selecting the colour hue, which depended on the production method. The choice of the painting materials was probably subjected also to economic reasons. Therefore, it is important to state a correlation between chemical composi-

tions, ancient production methods, and the final colour hue of the produced yellow pigments.

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