DIFFERENCES IN COMPOSITION OF NAPLES YELLOW AND SYNTHESIS OF ITS MAIN PHASES

Dohnalová Ž.[1], Luxová J.[1], Šulcová P.[1], Šefců R.[2], Antušková V.[2]

[1]*University of Pardubice, Studentská 95, 532 10 Pardubice, Czech Republic*
[2]*National Gallery Prague, Staroměstské náměstí 12, 110 15 Prague 1, Czech Republic*
Zaneta.dohnalova@upce.cz

Abstract

The main objective of the submitted work is to study the effect of reaction conditions on phase composition and colour parameters of $Pb_2Sb_2O_7$ and $PbSb_2O_6$. These substances are the most often identified in composition of a historical pigment known as Naples yellow. The conditions of the calcination process as well as a molar Pb:Sb ratio were found to significantly influence the quality of multiphase $Pb_2Sb_2O_7$ product. Colour parameters of the products were compared with three commercial samples of the Naples yellow. The white powder of $PbSb_2O_6$ was synthetised in high purity in an opened tube furnace by calcination in two steps. The recommended calcining temperature of the first step is 600 °C with duration time of 12 hours and the temperature of the second step should be 850 °C for 72 hours.

Introduction

Naples yellow, is one of the oldest known synthetic pigments, which the small-scale production has been mentioned 3 500 years ago. In this time, it was widely used especially in Egypt, Mesopotamia and Babylon and mainly served as a colouring agent for colouring of glass and glaze. In the Middle Ages, it began to appear in a variety of European enamel pigments and from the end of the 14th century it became the main yellow pigment for colouring of ceramics and majolica. Its use in painting was discovered as early as the end of the 15th century, however, the presence of the Naples yellow in the painter colours is more frequented for the 17th century [1-4].

The Naples yellow with theoretical chemical formula $Pb_2Sb_2O_7$ belongs to the group of pyrochlore compounds. It is an isostructural anhydrous analogue to the natural mineral bindheimite $Pb_2Sb_2O_6(O,OH)$, which crystallizes in the cubic system. However, it is not clear whether this natural mineral has been used as a colouring agent in the past. In the description of the Naples yellow also other compositions with different Pb:Sb ratio including $Pb_3(SbO_4)_2$, $Pb(SbO_3)_2$, $Pb_8(SbO_4)_2$, $PbSb_2O_4$, $Pb_2Sb_2O_6$ and other unidentified components have been given as well[5,6].

Many works studying the preparation of $Pb_2Sb_2O_7$ can be found in the current literature. These works can be divided into works that relating to the old-new synthesis of yellows according to the preserved recipes of individual workshops and modern synthesis, where preparation conditions of lead-yellows are studied. The work of the author Dik et al. can be included in the first group of old-new preparations[3]. They were engaged in the reconstruction of the preparation of the Naples yellow according to Marian's and Darduin's manuscripts (both 17th century). Although both ancient manuscripts contain "instructions" for the preparation of the Naples yellow, old producers did not specify exactly some of raw materials, firing temperatures or firing times. Therefore, the authors of this work dealt with the identification of suitable initial materials and subsequently the preparation conditions. As starting materials were used PbO, Sb_2O_3, Sb_2S_3, Sb; mineralizers NaCl and potassium tartrate. They also studied different weight ratios of raw materials. The starting materials were calcined in the temperature range 650–1100 °C for 24 h. The calcination was performed in high temperature unglazed crucibles. The result of the work is their specific recommendation, when they obtained the highest purity product of $Pb_2Sb_2O_7$ (>95 %), i.e., for synthesis to use PbO, Sb_2O_3 and NaCl as mineralizer in a weight ratio of 5: 3: 1; calcination temperature 750–1000 °C/24 h. The XRD records of the samples are not presented. Higher temperatures, up to 1100 °C, led to yellow colour of the pigments, while at lower temperatures the pigments had a more reddish tone. The research does not include spectrophotometric measurement of the pigment reflectivity. Pigment colour was only assessed based on a subjective colour rating.

Into the second group of "modern" works can include the works of the main authors Rosi and Hradil et al[1,2,4]. In their work[4], the Naples yellow was prepared from Pb_3O_4, Sb_2O_3 or Sb_2S_3 in a Pb: Sb weight ratio of 1:1. NaCl and K_2CO_3 (10–20 wt. %) were used as flux agents. The calcination process was performed at temperatures of 700–1000 °C for 4-10 h. Since the authors evaluate the products primarily in comparison to another type of the Naples yellow, containing Pb-Sb-Sn, the work does not include the effect of the calcination mode on the phase composition and colour parameters of the products. In their next collective work[1], they continued in further research, where they synthesized $Pb_2Sb_2O_7$ under the previous best synthesis conditions (materials Pb_3O_4, Sb_2O_3,

mineralizer NaCl 10 wt.%, T = 900 °C) and investigated the effect of changing the molar ratio Pb:Sb (from 0.8:1 to 1.2:1) on the Naples yellow structure. The formation of major pyrochlore structures was detected, whose lattice parameters increase with the increasing Pb:Sb ratio. This ratio also modifies the Raman spectrum in its low-wavelength part. The next step in the research of the Naples yellow was the investigation of compounds which were prepared by repeated calcination[2]. The first one was prepared from Pb_3O_4 and Sb_2O_3 (molar ratio Pb:Sb 1:1) and K_2CO_3 as mineralizer (10 wt.%) and the calcination process was carried out at 900 °C/12 h and 900 °C/12 h (double heating). The XRD measurement indicated the presence of $Pb_{3+x}Sb_2O_{8+x}$ as the major phase in the orange sample. The second sample was synthesized from Pb_3O_4 and Sb_2O_3 (molar ration Pb:Sb 3:2) without the mineralizer. The calcination was performed at 800 °C/12 h and 800 °C/12 h (double heating). The XRD pattern of this sample also indicates the presence of the $Pb_{3+x}Sb_2O_{8+x}$ phase, but most of the diffraction lines were not identified. Colour of the samples was orange brown. Authors also prepared rosiaite $PbSb_2O_6$, by firing a homogenized mixture containing Pb_3O_4 and Sb_2O_3 in the Pb:Sb molar ratio of 1:2, to which no flux was added. The mixture was fired twice at 900 °C for 10 h. The presence of bindheimite as an impurity next to the main rosiaite phase was detected in the yellow final product.

Other work dealing with the search for conditions of the synthesis of the Naples yellow is a work from the collective Pelosi, Agresti et al. In their first work[7], $Pb_2Sb_2O_7$ was synthesized from Pb_3O_4 and Sb_2O_3 in a Pb:Sb ratio of 1:1 and at temperatures of 900 and 950 °C with maintained time of 5 hours at maximum temperature. The authors of this work studied an effect of used ceramic crucibles (terracotta and porcelain) and an effect of cooling after calcination. Colour of the samples varies between yellow to brown. An analysis of the phase composition revealed a formation of multiphase products composed from $Pb_2Sb_2O_7$ as the main phase, but also other types of lead antimonate with different stoichiometry were detected, $Pb_{2.5}Sb_{1.5}O_{6.75}$, $Pb_{3+x}Sb_2O_{8+x}$ and $PbSb_2O_6$. Next research of the Naples yellow uses various combinations of PbO and Pb_3O_4 with Sb_2O_3 and mineralizers NaCl and potassium tartrate[8]. In the terms of calcination conditions, it was a repeated firing - two-stage. Both firings were performed at temperature of 800 °C for 5 hours. Colour of the pigments was pale yellow, and their colour parameters varied in values L* = 61.1–71.1; a* = 11.1–19.6 and b* = 43.9–52.2. Raman spectra were quite difficult to interpret, but the authors identified some common bands that can be attributed to the compound $Pb_2Sb_2O_7$ and to the rosiaite.

None of the above publications contains clear information concerning the links between the conditions of the Naples yellow synthesis, the phase composition obtained and the colour parameters. Knowledge of these parameters can help to identification of historic pigments used in arts. Therefore, the main objective of the submitted work is to study the effect of reaction conditions on phase composition and colour parameters of $Pb_2Sb_2O_7$ and $PbSb_2O_6$. The quality of the synthetised pigments is compared with the commercial pigments of the Naples yellow.

Experiment

Both pigments, $Pb_2Sb_2O_7$ and $PbSb_2O_6$, were prepared by solid state reaction at high temperature. The samples of $Pb_2Sb_2O_7$ were prepared by calcination of a homogenised mixture of PbO and Sb_2O_3 in a different molar ratio of Pb:Sb (2:2; 1.9:2; 1.8:2) and NaCl mineralizer in amount of 10 % wt (all Lachema n.p., CZE). The reaction mixtures were calcined in a muffle furnace in two steps and in three calcination modes, in total 9 samples were prepared. The first step represents temperature of 800, 850 or 900 °C for 10 hours with rate 5 °C.min^{-1}. After the first step, the mineralizer NaCl was removed from the samples by decantation in hot water and the dry samples were calcined in the second step under the same conditions as the first step. Three commercial Naples yellow pigments (Kremer Pigmente GmbH & Co. KG, DEU) were used as the comparative materials. The pigments are sold under names Naples yellow from Paris (order no. 10130), Naples yellow, dark (order no. 43125) and Naples yellow, reddish (order no. 43130).

Initial reagents Pb_3O_4 (Lachema n.p., CZE) and 99.5 % Sb_2O_3 (Bochemie s.r.o. CZE) in molar ratio Pb:Sb 1:2 were used for synthesis of $PbSb_2O_6$. Homogenised reaction mixtures were placed into the alumina crucibles and heated at temperature of 600 and 850 °C in an electric muffle furnace or in a tube furnace opened to air atmosphere[9,10]. Calcination rate of both steps was 10 °C.min^{-1}. The details of the synthesis conditions are summarised in Table I.

Table I

Synthesis conditions of the pigments $PbSb_2O_6$

Sample	1st calcination	2nd calcination	Furnace
1.1	T=600 °C / 60 h	T=850 °C / 24 h	muffle
1.2	T=600 °C / 60 h	T=850 °C / 48 h	muffle
1.3	T=600 °C / 60 h	T=850 °C / 72 h	muffle
2.1	T=600 °C / 60 h	T=850 °C / 24 h	tube

Sample	1st calcination	2nd calcination	Furnace
2.2	T=600 °C / 60 h	T=850 °C / 48 h	tube
2.3	T=600 °C / 60 h	T=850 °C / 72 h	tube
3.1	T=600 °C / 12 h	T=850 °C / 24 h	tube
3.2	T=600 °C / 12 h	T=850 °C / 48 h	tube
3.3	T=600 °C / 12 h	T=850 °C / 72 h	tube

The elemental analysis was performed using a JEOL 6460 LA scanning electron microscope with an energy-dispersive X-ray detector in low-vacuum mode with a voltage of 20 kV and BSE detector. The particles of pigments were placed on a carbon tape on an aluminium stub and subsequently documented on a secondary electron (SE), under a high vacuum, at an accelerating voltage of 15 keV.

The phase composition of the samples was studied by X-ray diffraction analysis. The diffractograms of the samples were obtained by using a MiniFlex 600 (Rigaku, Japan) diffractometer working in Bragg-Brentano ($\theta/2\theta$) geometry with 1D d/teX Ultra silicon strip detector and Kβ filter. The data were collected within 2θ angle from 10-80 ° at a step size of 0.02 °and a speed of 10 °C.min^{-1} by using CuK_α line. Cu$K_{\alpha1}$ (λ=0.15418 nm) radiation was used for the angular range of 2θ < 35°, and Cu$K_{\alpha2}$ (λ=0.15405 nm) was used for the range of 2θ > 35°. The identification of individual phases was based on the matching of the obtained diffraction patterns with the data contained in the JCPDS database.

Colour of the synthesized pigments was evaluated after their application to the organic matrix (dispersive acrylic paint Luxol, AkzoNobel). The slurry containing 1 g of the pigment and 0.5 g of the organic matrix was homogenized in an agate mortar. Coloured films were prepared by deposition of the slurries on the white non-absorbing paper. The thickness of the wet film was 100 μm. The colour properties of the films were objectively evaluated by measuring the spectral reflectance by using a spectrophotometer Ultra Scan VIS (HunterLab, USA). The measurement conditions were as follows: an Illuminant D65 and measuring geometry d/8°. For description of colour, the CIE L*a*b* colour space (also referred as CIELAB) was used[11]. Parameter of chroma was calculated according to formula $C = (a^{*2}+b^{*2})^{1/2}$.

Discussion and results analysis

Characterization of the commercially available samples of the Naples yellow is given in Table II. Although, the chemical composition announced by the manufacturer is $Pb(SbSn)O_3$, $Pb_2Sb_2O_7$ and $Pb_3(SbO_4)_2$, also other elements were detected by EDS analysis. The results of X-ray diffraction analysis confirmed multiple phase compositions of all samples, including the presence of unidentified phases. This demonstrates a complicated situation when it comes to comparing the phase composition and colour parameters of the commercial pigments of Naples yellow with pigments used in art or with the synthesized pigments of $Pb_2Sb_2O_7$.

Table II
Chemical characterization of the commercially available Naples yellow pigments

Order no.	Chemical composition	EDS analysis [wt. %]							
		Al_2O	SiO_2	ZnO	SnO_2	Sb_2O_3	CeO_2	PbO	Total
10130	$Pb(SbSn)O_3$	3.36	0	17.62	0.72	35.26	0	43.04	100
43125	$Pb_2Sb_2O_7$	9.07	0	0	0	28.52	0	62.41	100
43130	$Pb_3(SbO_4)_2$	3.48	32.4	0	0	14.51	3.47	46.13	100

The synthesis of $Pb_2Sb_2O_7$ pigments did not produce a single-phase composition at any calcining temperature. In almost all cases, the cubic structure of $Pb_2Sb_2O_7$ was detected as the main phase, producing mainly the bindheimite, but also oxyplumboromeite phase. The increase of the calcining temperature supports the formation of the bindheimite phase, which is reflected in the increasing intensities of the diffraction lines. The sample (1.8:2) prepared by calcination at 800 °C did not contain the bindheimite phase, but next to oxyplumboromeite, also $Pb_2Sb_2O_7$ in its orthorhombic structure was detected by XRD analysis (Table III). Flux agent NaCl caused formation of sodium antimony oxides in several stoichiometric ratios. A lower molar ration of Pb:Sb than 2:2 is associated with the formation of the next phase, which is rosiaite ($PbSb_2O_6$). The intensities of the diffraction lines of rosiaite decrease with the increasing temperature. In addition, the diffraction lines with very low intensities that can be associated to the presence of lead oxide and antimony oxide were detected in all samples.

Table III
Main phases detected in the samples $Pb_2Sb_2O_7$

Molar ratio	Temperature [°C]		
Pb:Sb	800	850	900
2:2	$Pb_2Sb_2O_7$ (B+Oxy); $Na_2Sb_4O_7$; $NaSb_5O_8$;	$Pb_2Sb_2O_7$ (B+Oxy); $Na_2Sb_4O_7$;	$Pb_2Sb_2O_7$ (B+Oxy); $Na_2Sb_4O_7$;
1.9:2	$Pb_2Sb_2O_7$ (Oxy); $PbSb_2O_6$; $Na_4Sb_4O_7$;	$Pb_2Sb_2O_7$ (B+Oxy); $PbSb_2O_6$; $Na_2Sb_4O_7$; $NaSbO_3$;	$Pb_2Sb_2O_7$ (B+Oxy); $PbSb_2O_6$; $Na_2Sb_4O_7$;
1.8:2	$Pb_2Sb_2O_7$ (Oxy+ Orth); $Na_2Sb_4O_7$;	$Pb_2Sb_2O_7$ (B+Oxy); $PbSb_2O_6$; $NaSb_5O_{13}$;	$Pb_2Sb_2O_7$ (B+Oxy); $PbSb_2O_6$; $Na_2Sb_4O_7$;

* B = bindheimite; Oxy = oxyplumboromeite; Orth =orthorthorombic structure

Although the elemental composition of the commercial samples of the Naples yellow is not in an agreement with the synthetised ones, their colour parameters were compared (Table IV, Figure 1). Elemental composition of the commercial samples of the Naples yellow does not affect values of chroma C, that varies between 62.5 to 62.8. Though the values of chroma are comparable, the bigger differences between parameters describing colour hues of the samples are visible in Figure 1. The Naples yellow no. 43130 contains the highest amount of red hue, its colour can be defined as reddish orange. This sample also has the lowest value of the b* coordinate, expressing amount of yellow hue and the lowest value of lightness. The Naples yellows no. 43125 and no. 10130 have nearly the same lightness, chroma and the amount of yellow hue, the difference being the amount of red hue. Yellow pigments $Pb_2Sb_2O_7$ with similar colour parameters to the Naples yellow no. 43125 were synthetised at temperatures of 850 °C and 900 °C, mainly in the molar ratio of Pb:Sb 2:2. The lower molar ratios of Pb:Sb led to the formation of the powders with less red hue and higher lightness. This means that the samples are lighter, which may be due to phase composition, in particular the presence of the rosiaite phase $PbSb_2O_6$.

Table IV
Colour parameters of the commercial samples of the Naples yellow and synthetised $Pb_2Sb_2O_7$

Sample	800 [°C]		850 [°C]		900 [°C]	
	L*	C	L*	C	L*	C
2:2	75.9	58.0	76.0	63.2	74.7	64.2
1.9:2	78.9	59.3	79.2	63.6	79.1	72.1
1.8:2	85.9	60.2	88.0	63.5	89.2	64.5
Sample	L*a*	C				
10130	75.1	62.62				
43125	75.4	62.54				
43130	65.9	62.82				

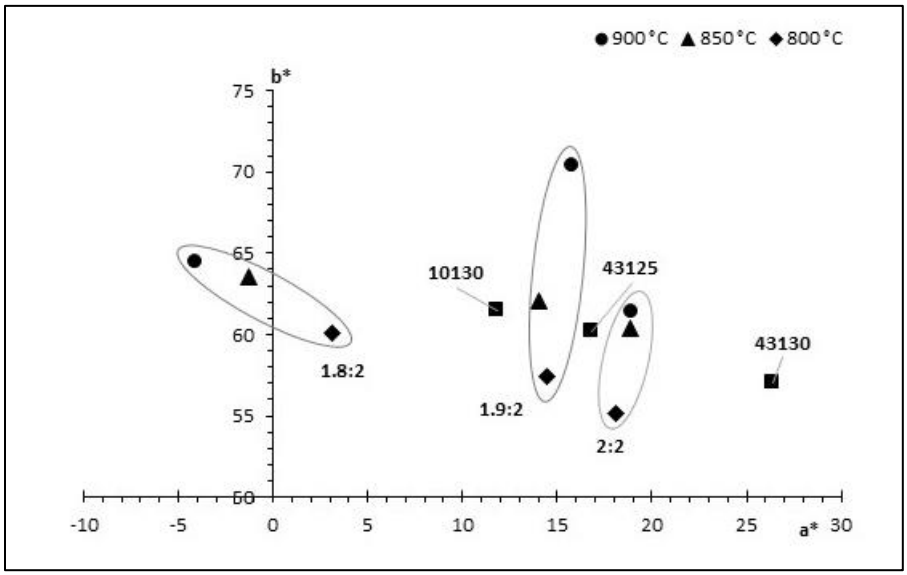

Figure 1. a*b* diagram of the samples $Pb_2Sb_2O_7$ and the commercial samples of Naples yellow.

Synthesis of the second type of mixed lead antimony oxide $PbSb_2O_6$ led to the formation of multi-phase products at all reaction conditions. The differences in phase composition of the prepared samples were already evident in their subjective observations, as the samples differed significantly from one another not only in colour, but also in the fineness of the powdered grains. Colour of the powders varied between light yellow to white. The samples with the finest particle size distribution were obtained by synthesis in the tube furnace in the case of samples no. 2.1-2.3. Only these samples contain one of the minority phases consisting of cubic $Pb_2Sb_2O_7$ in oxyplumboromeite modification, next to the main $PbSb_2O_6$ rosiaite phase (Table V). Colour of the samples of no. 2.1-2.3 is the light yellow, which is also caused by the presence of cubic $Pb_2Sb_2O_7$. The darkest sample no. 2.1 (L* = 87.1) was obtained by calcination in the tube furnace at 600 °C for 60 hours and consequently at 850 °C for 24 hours. Extending the calcining time at temperature of 850 °C from 24 hours to 48 and then up to 72 hours promotes the formation of rosiaite and reduces the amount of produced $Pb_2Sb_2O_7$. This fact is visible also in Table V in the decreasing character of the values of colour parameter b*, which expresses amount of yellow hue in final colouration. On the other hand, an increasing amount of rosiaite phase raises of lightness of the samples. The same calcination conditions, but implemented in the muffle furnace, led to the formation of the desired rosiaite phase, as the main phase, and in addition lead and antimony oxides were detected alongside it in the samples no. 1.1-1.3. Light yellow resultant colour is composed from yellow and green colour hues. The colour parameter a* in negative values expresses amount of green colour hue and its value increases with calcination time at temperature of 850 °C. Amount of yellow colour hue can be considered as constant as well as chroma of the colour.

The best results were obtained by calcination of the reaction mixture containing Pb_3O_4 and Sb_2O_3 in the tube furnace for 12 hours at temperature of 600 °C and consequently at temperature of 850 °C. The pale yellow powder was obtained after a second calcination at 850°C and a duration time of 24 hours only. The major diffraction lines of $PbSb_2O_6$ and minor phases of PbO_2 and SbO_2 were detected in the sample 3.1. Longer calcination at 850 °C supported the reaction between lead and antimony oxides. Intensities of the diffraction lines of rosiaite were higher and intensities of lead oxide and antimony oxide were very weak after calcination longer than 24 hours at temperature of 850 °C. The intensity of the PbO diffraction lines in sample 3.3 is at the noise limit. The change in the relative ratio of the individual phases detected in the samples 3.2 and 3.3 was also reflected by the change in their colour parameters. The amount of yellow hue and thus the values of the parameter b* have decreased, as well as the value of chroma C. Resultant colour of the samples 3.2 and 3.3 is white with the high value of lightness L* (Table V).

Table V
Main phases detected in the samples $PbSb_2O_6$ and their colour parameters.

Sample	Detected phases	L*	a*	b*	C
1.1	$PbSb_2O_6$ (R); Sb_2O_4, Pb_3O_4	90.23	-0.5	26.0	26.0
1.2	$PbSb_2O_6$ (R); PbO; Sb_2O_4,	91.22	-2.5	26.5	26.6
1.3	$PbSb_2O_6$ (R); Sb_2O_4,	91.95	-3.3	25.4	25.6
2.1	$PbSb_2O_6$ (R); Sb_2O_5; $Pb_2Sb_2O_7$ (Oxy); Pb_3O_4	87.1	0.6	39.7	39.7
2.2	$PbSb_2O_6$ (R); $P_2Sb_2O_7$ (Oxy); PbO_2; Sb_2O_4	91.4	-3.3	26.4	26.6
2.3	$PbSb_2O_6$ (R); $P_2Sb_2O_7$ (Oxy); PbO_2; Sb_2O_4	92.2	-3.4	22.2	22.4
3.1	$PbSb_2O_6$ (R); PbO_2; SbO_2	87.1	-0.1	30.8	30.8
3.2	$PbSb_2O_6$ (R); Sb_6O_{13}; PbO_2	92.1	-1.0	9.0	9.0
3.3	$PbSb_2O_6$ (R), PbO	92.6	-1.0	8.5	8.6

* R = rosiaite; Oxy = oxyplumboromeite

Conclusion

The submitted work deals with the synthesis and characterization of the historical pigment known as the Naples yellow, whose composition is described by the formula $Pb_2Sb_2O_7$. The composition of the Naples yellow is highly complicated and heavily dependent on reaction conditions, which also affect its colour properties. In addition, commercially available samples of the Naples yellow contain other metal than the expected lead and antimony and therefore their use to identify the pigments used in fine art is very problematic.

Pb_2SbO_7 in the modification of bindheimite and $PbSb_2O_6$ in the modification of rosiaite are compounds which are the most often identified in phase composition of Naples yellow. Intensive yellow colour of $Pb_2Sb_2O_7$ is strongly affected by molar ration of Pb:Sb and by calcining conditions. The yellow pigment with the highest value of coordinate b* is possible to prepare by calcination in two steps at temperature of 900 °C from the reaction mixture containing PbO and Sb_2O_3 in the molar ratio of Pb:Sb = 1.9:2 and 10 wt % of NaCl. The best result from

the point of phase composition is synthesis of the three-phase sample which contains $Pb_2Sb_2O_7$ in bindheimite and oxyplumboromeite modification and $Na_2Sb_4O_7$. This sample was prepared in molar ration of Pb:Sb 2:2 and two calcination at 850 or 900 °C. Single phase powder of $Pb_2Sb_2O_7$ was not prepared at all.
White pigment $PbSb_2O_6$ were successfully synthesized by solid state reaction with calcination in the tube furnace in two steps. The first step of calcination was at temperature of 600 °C for 12 hours and the second calcination at the temperature of 850 °C for 72 hours. This calcination conditions lead to the formation of the rosiaite modification of $PbSb_6O_6$ with the presence of the PbO minor phase whose diffraction lines are at the noise limit of the equipment. The colour parameters of this sample are L*/a*/b* = 92.6/-1.0/8.5.

Acknowledgement

This research has been supported by the programme of the Ministry of the Interior of the Czech Republic: Strategic Support for the Development of Security Research of the Czech Republic ČR 2021–2025 (IMPAKT 1), grant project: The Development of a Strategic Cluster for Effective Instrumental Technological Methods of Forensic Authentication of Modern Artworks, identification code VJ01010004.

References

1 Rosi F., Manuali V., Miliani C., Brunetti B. G., Sgamellotti A., Grygar T., Hradil D.: J. Raman Spectrosc., *40,* 107 (2009).
2 Rosi F., Manuali V., Grygar T., Bezdicka P., Brunetti B.G., Sgamellotti A., Burgio L., Seccaroni C., Miliani C.: J. Raman. Spectrosc., *42*, 407 (2011).
3 Dik J., Hermens E.: Archaeometry *47,* 593 (2005).
4 Hradil D., Grygar T., Hradilová J., Bezdička P., Grűnwaldová V., Fogaš I., Miliani C.: J. Cult. Herit., *8*, 377 (2007).
5 Feller R. L.: *Artists' Pigments: A Handbook of their History and Characteristics*, National Gallery of Art, Washington, 1986.
6 Eastaugh N., Walsh V., Chaplin T., Siddall R.: *Pigment Compendium: A Dictionary and Optical Microscopy of Historical Pigments*, Routledge, New York, 2013.
7 Pelosi C., Agresti G., Santamaria U., Mattei E.: e-PS., *7*, 108 (2010).
8 Agresti G., Baraldi P., Pelosi C., Santamaria U., Color Res. Appl., *41,* 226 (2016).
9. Zhang K.L., Lin X.P., Huang F.Q., Wang W.D.: J. Mol. Catal. A Chem. *258,* (2006) 185
10. Roper A. J., Leverett P., Murphy T. D., Williams P. A.: Mineral. Mag., *79*, (2015) 537.
11. *Commission Internationale de l'Eclairage, "Recommendations on uniform colour spaces, colour difference equations, psychometric colour terms*", Supplement No.2 of CIE publication No. 15 (E1-1,31) 1971, Paris Bureau Central de la CIE, 1978.