

Synthesis, Structural Characterisation and Raman Spectroscopy of the Inorganic Pigments Lead Tin Yellow Types I and II and Lead Antimonate Yellow: Their Identification on Medieval Paintings and Manuscripts

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Lead tin yellow type I (Pb_2SnO_4) and type II ($\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$) have each been prepared in a high-temperature furnace, and the preparative conditions defined. The crystal structure of type II has been refined from powder X-ray diffraction data and indicates that the Sn and Si atoms are randomly distributed over the same type of site with Sn/Si ratio $\approx 3/1$ (i.e., $x \approx \frac{1}{4}$). The Raman spectra of each form and also that of lead antimonate yellow ($\text{Pb}_2\text{Sb}_2\text{O}_7$) have been obtained. Raman microscopy is shown to be an effective technique whereby these inorganic yellow pigments as minute ($\approx 1 \mu\text{m}$) grains may be identified on medieval manuscripts and paintings.

Raman microscopy¹ is becoming an important technique for the identification of pigments on medieval manuscripts owing to the facts that it may be used *in situ*, is non-destructive, has high spatial resolution ($< 1 \mu\text{m}$), is highly specific, and is usually free from interference from problems such as fluorescence of the binder, etc.²⁻⁴ Thus the components of pigment mixtures can readily be identified by focusing the microscope onto each individual grain in turn, and then comparing the resulting spectrum with that in an appropriate data base.

There are several reasons for wishing to identify the pigments used on a manuscript or painting, the most important being to do with art restoration. Restorers obviously should use the original pigments or combination of pigments in the conservation of damaged or faded/degraded pictures in order to reproduce the intended effects. But the type of pigment used is also important in art history, since the availability of particular pigments is linked to the existence or otherwise of particular trading routes, to pigment costs, to contemporary tastes, and sometimes to the perceived importance of the figures illustrated. Moreover the identification of a pigment may aid in the authentication of a painting since some pigments were preferred to others at particular periods in time, and synthetic ones were obviously only available from the dates of their first manufacture.

The usage of lead tin yellow as a pigment has a complicated history, owing to the (not originally appreciated) existence of two forms, type I which is Pb_2SnO_4 ⁵⁻⁸ and the less studied type II which is $\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$ ^{9,10} (with a previously unspecified silicon content), and also to the possibility of confusion of type II with the structurally related compound lead antimonate yellow, which is $\text{Pb}_2\text{Sb}_2\text{O}_7$ (commonly known as Naples yellow).¹¹⁻¹³ All three pigments are brilliant yellows (Munsell hue 5Y) with high refractive indices (all > 2) and thus have good covering power. They are alkali fast, insoluble in water and in organic solvents, and (by contrast to PbO) light fast. Both types of lead tin yellow are compatible with all other pigments and so is lead antimonate yellow, except when used in fresco with barium yellow (BaCrO_4). Lead tin yellow of either type is essentially unaffected by inorganic acids and is thermally stable

to ca. 900 °C; lead antimonate yellow is soluble in inorganic acids and in 4 mol dm⁻³ NaOH. Lead tin yellow is blackened by hydrogen sulfide or soluble sulfides owing to the formation of lead sulfide. All three pigments are toxic to prolonged ingestion or inhalation or on contact with the skin.

Following a brief survey of the history of the usage of these pigments, this paper presents the Raman spectra of both laboratory-synthesised samples and samples on original paintings and manuscripts and so defines an effective method based upon Raman microscopy for the identification of these pigments of similar hues (note, however, that lead tin yellow type I is much paler than either lead tin yellow type II or lead antimonate yellow). In addition, the crystal structure refinement of lead tin yellow type II, to assess the extent of incorporation of Si in this structure, is reported.

Historical Background and Nomenclature

The long period of usage of lead-based yellow pigments dating back to 1600 B.C. has led to many different documents in different languages using particular words to mean the same pigment.⁶ European sources have regularly used (among others) a term 'giallino' or 'giallorino', which is derived from the word 'giallo' meaning pale yellow; it is, however, not specific, since it has referred to three different pigments at different periods of time, viz. massicot [lead(II) oxide], lead tin yellow or lead antimonate yellow.^{10,11} Kühn^{5,6} has concluded that, on the evidence below, the terms 'giallino' mentioned in Italian literary sources and 'massicot' (or 'masticot' of northern manuscripts) referred to lead tin yellow. Thus:

(1) Yellow lead oxide (PbO , i.e. genuine massicot) has only very rarely been found in any painting made between the 13th and 20th centuries.

(2) Lead tin yellow has been identified in Munich on over 150 paintings of known date, provenance and authorship; similar results have been found elsewhere.

(3) In his investigations of Italian paintings, no other pigment could be found which could be convincingly identified with the 'giallino' frequently mentioned in the Italian manuscripts.

(4) After analysing several old samples of lead oxide, the ones labelled 'massicot' were found to be lead tin oxides mixed in with lead oxide (PbO).

Kühn first demonstrated that there are in fact two types of

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lead tin yellow, types I and II, and that they could be prepared by essentially 15th century Bolognese procedures; however, the latter are not well defined, particularly with respect to optimum temperatures and reaction times for their preparation.

Lead tin yellow was the substance used to opacify ancient (Roman or immediate post-Roman) yellow glass and has been used as an artists' pigment since around 1300 A.D.; it is not, however, the only lead-based yellow pigment to have been used by artists. The main yellow pigments which have been used are listed below, together with very approximate dates of their usage.

Pre 1300:	orpiment (As ₂ S ₃), massicot (PbO)
1300–1650:	lead tin yellow type II (PbSn _{1-x} Si _x O ₃)
1450–1750:	lead tin yellow type I (Pb ₂ SnO ₄)
1700–1850:	Naples yellow (Pb ₂ Sb ₂ O ₇)
1800–:	lead chromate (PbCrO ₄)
1850–:	cadmium sulfide (CdS), cobalt yellow (K ₃ [Co(NO ₂) ₆])

There are, however, exceptions to this somewhat oversimplified chronology of the pigments' usage. Moreover, since there is considerable overlap between the starting and terminal dates of usage of each pigment, it is difficult to make an identification on this basis. Type II has been identified in a late-Roman shard of glass (4th–5th century A.D.) by X-ray fluorescence and diffraction.¹¹

The rise and fall in the usage of lead tin yellow type II has been linked to the economic success of particular geographic regions. This pigment is thought to have been first used as a glaze (opacifier) in the glass industry before becoming a genuine artists' pigment and it is significant that, at the time of the two main periods of its usage (14th century in Florence and 16th century in Venice and Bohemia), there were successful local glass industries in existence.

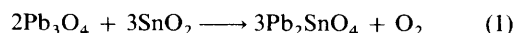
Although lead tin yellow had been used in European art since around 1300 none of the studies on its occurrence has revealed any example which dated after 1750. There is no reference to it in any of the art literature sources on colours from the 19th and 20th centuries up to 1941, when it was rediscovered by Jacobi.^{11,14} de Wild identified yellow lead oxide in 39 paintings dating from 1400 to 1700 and found that the term 'massicot' in the corresponding literature had probably related to lead tin yellow instead.¹¹ Naples yellow has been identified in some paintings from the Renaissance but only tested for the presence of lead and not for antimony; these too, were probably lead tin yellow. Since their rediscovery in 1941, lead tin yellow types I and II have been identified at the Doerner Institute (Munich) in over 154 paintings and four polychrome statues using emission spectrometric studies and by Martin and Duval⁷ in 114 paintings using energy dispersive X-ray analysis of samples in a scanning electron microscope. Both the studies concluded that lead tin yellow type I was the more commonly used, despite the fact that it first came into usage later than type II; this is doubtless a consequence of the higher price for type II, owing to its more involved synthesis.

Both types of lead tin yellow were replaced by lead antimonate yellow around 1750. This pigment, commonly known as Naples yellow, had been manufactured as early as 1600–1400 B.C. at which time it was the only yellow colourant and opacifier available to Egyptian glass makers. Thus it had been found in glass fragments from a site in Thebes (1450–1422 B.C.). It then fell into disuse until it came back into favour in ca. 1750. However, it too was replaced towards the end of the 19th century by other synthetic pigments, notably lead chromate and cadmium sulfide.

Experimental

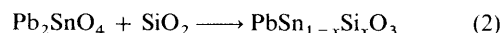
Preparation of Compounds.—Reactions were carried out in a platinum crucible using a Eurotherm furnace programmable at

different ramp-up and ramp-down rates. Lead tin yellow type I was prepared by heating a finely ground intimate mixture of Pb₃O₄ and SnO₂ in air at 900 °C for 3 h, [equation (1)].



Heating above 900 °C leads to decomposition of the product (and loss, by volatilization, of PbO), but heating below 800 °C leads to incomplete reaction, contrary to the recommendations of Jacobi (650–800 °C for 5 h);¹⁴ medieval recipes do not refer either to the temperature or to the length of the heating period. A stoichiometric excess of Pb₃O₄ leads to the presence of PbO (massicot, a thermal decomposition product of Pb₃O₄) in the sample.

Lead tin yellow type II was a by-product of the glass industry, but enjoyed less usage than its precursor and has been identified in significantly fewer paintings. It cannot, apparently, be prepared directly from its binary oxide components, but was prepared optimally by heating a 1 : 1 mixture of type I and silica at 900 °C for 5 h [equation (2)]. Continued heating above



950 °C causes the product to decompose to its original constituents, tin(IV) oxide, lead(II) oxide and silica, which form a glassy mass. The exact extent to which silicon replaces tin is investigated in this paper. The structure is not known to undergo a phase transition on change of temperature.

Lead antimonate yellow was supplied by Kremer Pigments; it can be prepared by heating Pb₃O₄ with Sb₂O₃ at 900–1000 °C for 5 h. A product deficient in antimony can also be prepared; this may be Pb^{II}_ySb^V_{2-x}O₇, where 0 ≤ x ≤ 1 and 2 ≤ y ≤ 3.¹⁵

Instrumentation.—Raman spectra were recorded on a DILOR XY spectrometer or on a Ramalog 14018 (R6) Spex spectrometer, in conjunction with Coherent argon-ion or krypton-ion lasers operating at powers at the sample of 2–5 mW. Spectra were recorded both at room temperature using the Raman microscope and at liquid-nitrogen temperature using conventional macro sampling modes; the latter equipment gave the better spectrum in each case.

The Fourier-transform (FT) Raman spectra were taken on samples at room temperature with a Nicolet 910 FT Raman spectrometer, in conjunction with a Nd:YAG laser operating at 1064 nm.

The UV/VIS spectra were recorded with an Oriel Instaspec III 0.25 m polychromator equipped with a photodiode array detector and 200 groove mm⁻¹ grating. The electronic spectra of the pigments are similar (Fig. 1), type II absorbing more strongly at longer wavelengths than type I.

Spectra of lead tin yellow types I⁸ and II, lead antimonate yellow,¹³ Pb₃O₄,⁸ PbO,¹⁶ SiO₂¹⁷ and SnO₂¹⁸ are highly characteristic and were all recorded for analytical purposes and in order to determine the optimum preparative conditions for the pigments.

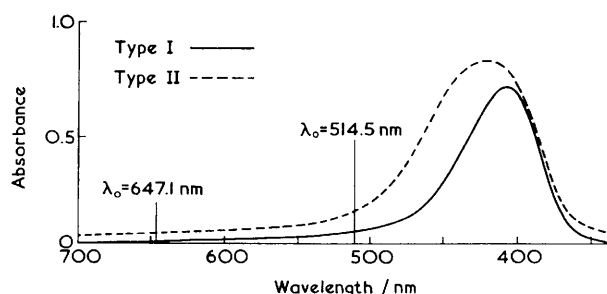


Fig. 1 Electronic spectra of lead tin yellow types I and II

Powder X-ray diffraction was used for phase identification of the materials prepared in this work, as well as for an assessment of the Sn/Si ratio in the lead tin yellow type II. For these experiments, powder X-ray diffraction data were recorded at room temperature in transmission mode on a Siemens D5000 diffractometer using Ge-monochromatised Cu-K α 1 radiation. The diffraction data were collected in the 2θ range 13–66° in steps of $\Delta(2\theta) = 0.02^\circ$, with a total data measurement time of ca. 6 h. In each experiment, the polycrystalline sample was ground, and the powder X-ray diffractogram recorded for a fine layer of the ground material mounted between two layers of transparent tape.

Results and Discussion

Structural Characterization.—Lead tin yellow type I: Pb_2SnO_4 . The crystal structure¹⁹ (Fig. 2) of lead tin yellow type I is reported to be orthorhombic, with space group $Pbam$. This structure is very closely related to that of Pb_3O_4 , which is tetragonal (space group $P4_2/mbc$) at ambient temperature (but undergoes a tetragonal \rightarrow orthorhombic transition at 170 K on being cooled). The Pb_3O_4 structure consists of chains of $\text{Pb}^{\text{IV}}\text{O}_6$ octahedra joined by pyramidally co-ordinated Pb^{II} atoms; when treated with SnO_2 , the Sn^{IV} substitutes for the Pb^{IV} in the $\text{Pb}^{\text{IV}}\text{O}_6$ octahedral chains. Both Pb_3O_4 and Pb_2SnO_4 may be regarded as mixed-valence materials^{20,21} of general formula $\text{M}_2^{\text{II}}\text{M}^{\text{IV}}\text{O}_4$. Powder X-ray diffraction confirmed that the structural identity of the lead tin yellow type I sample synthesised in this work was the same as the reported crystal structure¹⁹ of Pb_2SnO_4 .

Lead tin yellow type II: $\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$. The crystal structure²² of PbSnO_3 (space group $Fd\bar{3}m$, $a = 10.719$ Å) can be described as a defect pyrochlore ($\text{A}_2\text{B}_2\text{X}_6\text{X}'$) structure in which $\text{A} = \text{Pb}$, $\text{B} = \text{Sn}$, $\text{X} = \text{O}$ and $\text{X}' = \text{vacant O site}$. It has been reported⁹ that the colour becomes deeper yellow on incorporation of Si into this structure.

For lead tin yellow type II, $\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$, we have carried out a crystal structure refinement (in space group $Fd\bar{3}m$) from its powder X-ray diffractogram, using the Rietveld refinement procedure embodied within the GSAS program package.²³ For these Rietveld refinement calculations, the reported crystal structure of PbSnO_3 was used as the initial structural model. After convergence of the refinement assuming the initial stoichiometry PbSnO_3 , a variable amount of Si was allowed to occupy the Sn sites in this structure, such that the sum of the Sn

and Si occupancies on these sites was unity (with the isotropic thermal parameters constrained to be equal for these Sn and Si atoms). This corresponds to refinement of the parameter x in the formula $\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$. Isotropic thermal parameters were assumed for the Pb and O atoms. In the fully refined crystal structure (corresponding to $R_{\text{wp}} = 0.0673$ and $R_p = 0.0532$, where R_{wp} and R_p are the weighted-profile and profile R-factors, respectively), the stoichiometry is $\text{PbSn}_{0.76}\text{Si}_{0.24}\text{O}_3$ (i.e., $x = 0.24$); other structural parameters relating to the fully refined structure are given in Table 1. [Note that a significant improvement in fit was obtained on adding Si to the Sn sites; structure refinement using the same diffraction data but assuming the stoichiometry PbSnO_3 (i.e., $x = 0$) corresponded to $R_{\text{wp}} = 0.0794$ and $R_p = 0.0574$.] The crystal structure is shown in Fig. 3, and the powder X-ray diffractogram calculated for this structure is compared with the experimental powder X-ray diffractogram in Fig. 4. The comparatively low estimated standard deviation [$\sigma(x) \approx 0.012$] in the value of x is noteworthy, and gives considerable confidence to our assignment of the stoichiometry of this material, and clarifies the uncertainty concerning whether Si is indeed incorporated into the structure of lead tin yellow type II.

It is relevant to note that the powder X-ray diffractogram of the lead tin yellow type II sample used for this Rietveld refinement calculation also contained a subset of peaks due to contamination by a minor phase, which was identified as SnO_2 (one of the original reagents). The presence of this second phase was included in the Rietveld refinement calculation.

Lead antimonate yellow: $\text{Pb}_2\text{Sb}_2\text{O}_7$. Lead antimonate yellow also has the pyrochlore structure^{24,25} (space group $Fd\bar{3}m$, $a = 10.47$ Å) but, unlike lead tin yellow type II, it is not defective. In this case $\text{A} = \text{Pb}$, $\text{B} = \text{Sb}$ and $\text{X} = \text{X}' = \text{O}$. It is the isostructural anhydrous analogue of the mineral Bindheimite.

Table 1 Structural parameters relating to the fully refined crystal structure of $\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$ [space group $Fd\bar{3}m$, $a = 10.715$ (4) Å]

Atom	X/a	Y/b	Z/c	Occupancy	$U_{\text{iso}}/\text{\AA}^2$
Pb	0	0	0	1	0.039 (4)
Sn	0.5	0.5	0.5	0.758 (12)	0.038
Si	0.5	0.5	0.5	0.242 (12)	0.038
O	0.4240 (22)	0.125	0.125	1	0.082 (9)

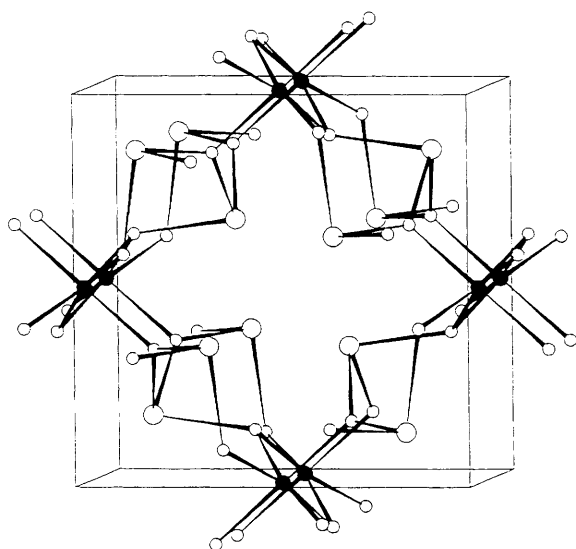


Fig. 2 Crystal structure of lead tin yellow type I (Pb_2SnO_4) viewed approximately along $[001]$; structural parameters are taken from ref. 19 [Sn, filled circles; Pb, large open circles; O, small open circles]

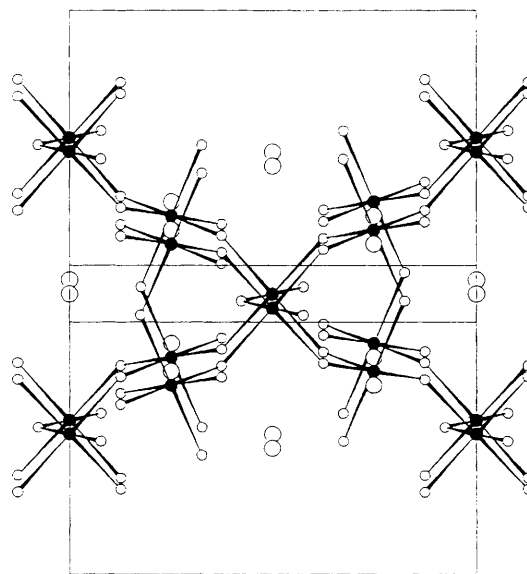


Fig. 3 Crystal structure of lead tin yellow type II ($\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$) viewed approximately along $[101]$; structural parameters are specified in Table 1 [Sn/Si, filled circles; Pb, large open circles; O, small open circles]

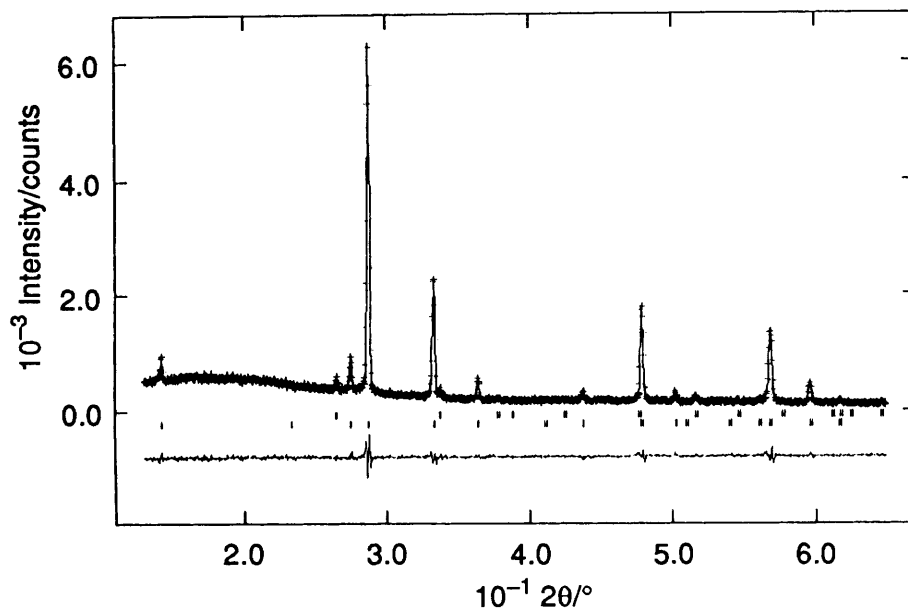


Fig. 4 Experimental (+), calculated (solid line) and difference (bottom trace) powder X-ray diffraction profiles for the Rietveld refinement of lead tin yellow type II ($\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$) containing an impurity amount of SnO_2 . Marks represent positions of reflections (upper marks, SnO_2 ; lower marks, $\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$). The calculated powder X-ray diffraction profile is for the final refined crystal structure; details of the refined structure of $\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$ are specified in Table 1. Agreement factors for this structure refinement are $R_{\text{wp}} = 0.0673$ and $R_p = 0.0532$.

Table 2 Characteristic Raman bands of the pigments and related metal oxides

Compound	λ_0/nm	Wavenumber/ cm^{-1}
Pb_2SnO_4	514.5	35w, 58w, 80m, 129vs, 196m, 274w, 291wm, 379w, 454wm, 524w, 613w
Pb_3O_4	647.1	121vs, 152m, 223w, 232w, 313w, 391w, 477w, 549s
$\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$	514.5	40m, 66m, 85 (sh), 138vs, 324wm (br), 444w (br)
$\text{Pb}_2\text{Sb}_2\text{O}_7$	514.5	76s, 147vs, 343s, 464m, 513wm
PbO massicot (orthorhombic, yellow)	647.1	87s, 144vvs, 171 (sh), 217vw, 289vs, 385m, 424w
PbO litharge (tetragonal, reddish)	647.1	81s, 147vvs, 322vw, 338s

Powder X-ray diffraction confirmed that the crystal structure of the sample of $\text{Pb}_2\text{Sb}_2\text{O}_7$ used in this work was the same as that reported previously.^{24,25} More than one phase can be produced, depending on the ratio of reactants, reaction time and temperatures used.

A second modification¹² of $\text{Pb}_2\text{Sb}_2\text{O}_7$ (not known to have been used as a pigment) has a slightly distorted non-centrosymmetric structure related to that of Weberite (space group $I2cm$, $a = 7.484$, $b = 7.857$, $c = 10.426$ Å). The coordination numbers of Pb(1) (distorted prism +2) and Pb(2) (distorted hexagonal bipyramid) are both eight, with these polyhedra linked by SbO_6 octahedra. It is not known whether this modification can be induced to undergo a structural phase transition to the pyrochlore modification.¹²

Raman Spectroscopy.—The principal bands in the Raman spectra of lead tin yellow types I and II (Figs. 5 and 6), Pb_3O_4 , $\text{Pb}_2\text{Sb}_2\text{O}_7$ and PbO are listed in Table 2, together with the intensity designators relevant to 514.5 or 647.1 nm excitation. Comparison of Figs. 5 and 6 indicates that there is no evidence for resonance effects on changing from 1064 to 514.5 nm excitation for lead tin yellow types I and II, nor is there for the other compounds mentioned. However, Pb_3O_4 must be handled with low power excitation only, otherwise it decom-

poses into PbO . The FT Raman spectra of these pigments are of high quality, with very good signal-to-noise ratios.

The Raman spectrum of Pb_2SnO_4 is similar to that recorded by Vigouroux *et al.*⁸ except that the band they reported at 540 cm^{-1} is observed in this work at 524 cm^{-1} both by conventional (514.5 nm excitation) as well as by FT (1064 nm excitation) Raman spectroscopy. The similarity of the Raman spectra of lead tin yellow type II and lead antimonate yellow reflects both the close similarity of the structures of these two pigments and the similarity of the atomic masses of tin and antimony.

The very strong bands in the Raman spectra of Pb_3O_4 , Pb_2SnO_4 , $\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$ and $\text{Pb}_2\text{Sb}_2\text{O}_7$ at 121, 129, 138 and 147 cm^{-1} , respectively, are assigned to a lattice Pb–O stretching mode.

Applications.—Raman spectra taken of a painting *in situ* or of a pigment section removed therefrom for analysis are unlikely to relate to the pigment alone, but may also include bands due to the binding medium (traditionally egg tempera or an oil such as poppy oil) as well as bands due to any varnish which may have been applied to the painting. For this reason, samples of lead tin yellow types I and II were prepared in a poppy oil medium and painted onto pieces of card and canvas; the canvas had already been covered in a brilliant white paint which was identified as containing rutile (TiO_2) by the intense Raman bands at 448 and 612 cm^{-1} (Fig. 7).^{26,27} The yellow pigments could easily be identified in this test, whether they were painted out on canvas or card.

The yellow pigments were then identified on the following items:

(1) Painting by Titian, 'Death of Actaeon' (National Gallery: accession no. 6420): sample taken from the yellow-leaved bush in the foreground [see Plate 1(a)] was shown to be lead tin yellow type I (the principal identifying features are the strong/very strong bands at 80, 129 and 196 cm^{-1}). The identification of this pigment on the painting is consistent with the date of its execution, which is known to have been towards the end of Titian's life.

(2) Painting by Paulo Veronese, 'Allegory of Love,' IV (National Gallery: accession no. 1326): sample taken from bright yellow of man's cloak [see Plate 1(b)] was shown to be lead tin yellow type II (the principal identifying features are those at 138 and 324 cm^{-1}). This painting originates from the last quarter of the 16th century.

(a)



(b)



Plate 1 (a) Identification of lead tin yellow type I on 'The Death of Actaeon', by Titian at the National Gallery. Highlight on foreground foliage. Reproduced by Courtesy of the Trustees, the National Gallery, London. (b) Identification of lead tin yellow type II on 'Allegory of Love', IV, by Paolo Veronese at the National Gallery. Bright yellow of man's cloak. Reproduced by Courtesy of the Trustees, the National Gallery, London

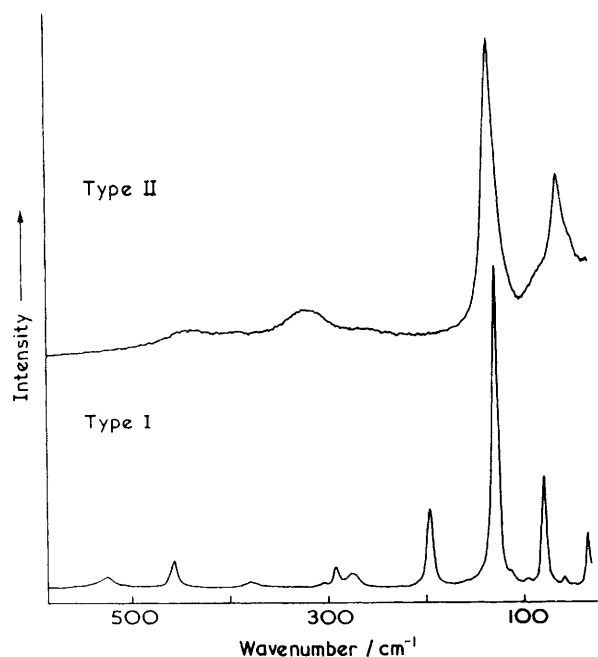


Fig. 5 Raman spectra of lead tin yellow types I and II with 514.5 nm excitation

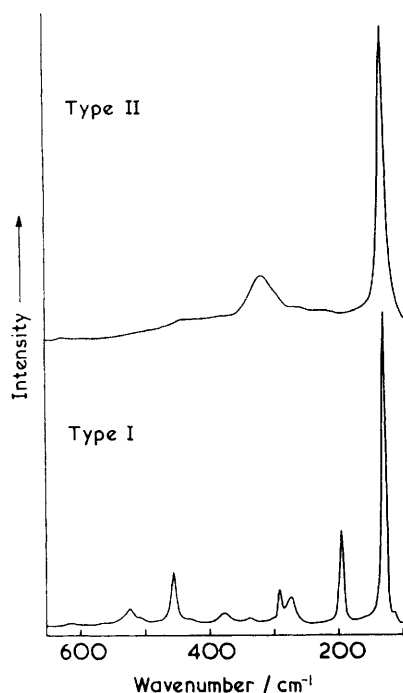


Fig. 6 FT Raman spectra of lead tin yellow types I and II with 1064 nm excitation

(3) Unattributed oil painting on panel, 'The Lamentation with Saints Peter, John, Mary Magdalene and Jerome' (Sotheby's Old Master Paintings auction, 21st April 1993): sample taken from bright yellow of man's cloak in the foreground on the left was shown to be lead tin yellow type I. The identification of this pigment is consistent with the date of ca. 1500 which is given in Sotheby's catalogue.²⁸

(4) Portrait of Lady Spenser, by John Betts (1590). * A sample

* This sample was supplied by courtesy of Lane Fine Art. The painting is now in private ownership.

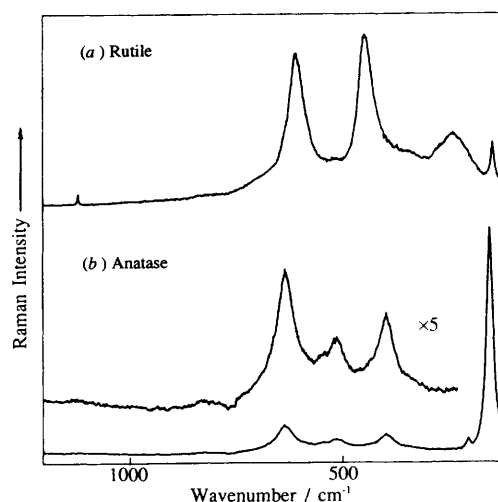


Fig. 7 The Raman spectra of the rutile (a) and anatase (b) forms of titanium(IV) oxide

was taken from the fringe border at the top of the painting; the Raman spectrum of this sample is thought to provide the first identification of lead tin yellow on a piece of English art; both types I and II were identified as being present on this painting.

(5) Historiated initial 'R' from a 16th century German choir book, illustrated in ref. 3. The top of the grey column in this illustration consists of a mixture of seven different pigments, one of which is lead tin yellow type I.

Conclusion

Lead tin yellow type II was successfully synthesised by fusion of an intimate mixture of lead tin yellow type I and silica at a 1:1 mole ratio. A higher value for this ratio gave a product with Raman bands attributable to both types I and II, whereas a lower value gave a product with Raman bands attributable to type II and unreacted silica. The extent of incorporation of Si in the structure of lead tin yellow type II has been determined by crystal structure refinement from powder X-ray diffraction data.

Raman microscopy is at the forefront of methods available for the *in situ* analysis of pigments. The technique is easy to apply, and readily permits a distinction to be drawn between lead tin yellow types I and II; the former has a very strong band at 129 cm⁻¹ and a medium strength band at 196 cm⁻¹, whereas the latter has a very strong band at 138 cm⁻¹ and a weaker, broad band at 324 cm⁻¹. Both may readily be distinguished from lead antimonate yellow since this has a Raman spectrum dominated by a very strong band at 147 cm⁻¹ and a strong band at 343 cm⁻¹.

Acknowledgements

The authors thank the SERC, the Leverhulme Trust, the ULIRS and the Royal Commission for the Exhibition of 1851 for financial support, and Dr. A. Roy, Sam Fogg, Sotheby's and Lane Fine Art for samples of the pigments and access to works of art.

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Received 30th March 1995; Paper 5/02002F