Raman spectroscopy as a means for the identification of plattnerite (PbO$_2$), of lead pigments and of their degradation products

Lucia Burgio,† Robin J. H. Clark* and Steven Firth

Christopher Ingold Laboratories, University College London, 20 Gordon Street, London, UK WC1H 0AJ. E-mail: l.burgio@ucl.ac.uk; r.j.h.clark@ucl.ac.uk; s.firth@ucl.ac.uk

The Raman spectra of plattnerite [lead(IV) oxide, PbO$_2$] and of the lead pigments red lead (Pb$_3$O$_4$), lead monoxide [PbO, litharge (tetragonal) and massicot (orthorhombic)], lead white [basic lead carbonate, 2PbCO$_3$·Pb(OH)$_2$] and of their laser-induced degradation products were recorded using a range of different excitation lines, spectrometer systems and experimental conditions. The degradation of PbO$_2$ is more extensive along the pathway PbO$_2$ → Pb$_3$O$_4$ → PbO (litharge) → PbO (massicot) the shorter the wavelength of the excitation line and the higher its power. The Raman spectrum of PbO$_2$, which is black and of the rutile structure, is particularly difficult to obtain but three bands, at 653, 515 and 424 cm^{-1}, were identified as arising from the b$_{2g}$, a$_{1g}$ and e$_g$ modes respectively, by analogy with the corresponding modes of isostructural SnO$_2$ (776, 634 and 475 cm^{-1}). A further oxide was identified, PbO$_{1.55}$, the Raman spectrum of which does not correspond to that of any of the laser-induced degradation products of PbO$_2$ at any of the wavelengths used. The Raman results are critical to the future use of Raman microscopy for the identification of lead pigments on artworks.

Introduction

Lead(IV) oxide has been reported[1,2] to be formed from the degradation of lead-containing pigments in air. This reaction has a very conspicuous visual effect because the lead compounds traditionally used as pigments are brightly coloured whites, reds and yellows, whereas PbO$_2$ is dark brown to black. Superficially, PbO$_2$ appears very similar to lead sulfide (PbS), which is also black and a potential product of the reaction of lead pigments with sulfur-containing pigments, sulfur-containing species in the atmosphere or certain bacteria. It is known that PbO$_2$ is not very stable and easily loses oxygen to give red lead, Pb$_3$O$_4$.[3] However, it has also been shown that the combination of an alkaline environment (such as that present when painting a fresco) and high humidity conditions can easily trigger the reverse process, *viz.*, the oxidation of low valent lead pigments to PbO$_2$.[1]

The purposes of this study were (1) to record and establish the Raman spectrum of plattnerite [tetragonal lead(IV) dioxide, PbO$_2$[4]] and of its laser-induced degradation products, which are important matters in pigment identification studies of artwork, (2) to record the Raman spectra of the laser-induced degradation products of the pigments lead white [basic lead carbonate, 2PbCO$_3$·Pb(OH)$_2$], red lead (trilead tetroxide, Pb$_3$O$_4$), litharge and massicot (the tetragonal and orthorhombic forms of lead monoxide, respectively), in order to validate spectra obtained previously on a less sensitive instrument[5,6] and to define the reduction path for PbO$_2$ and (3) to investigate the formation of other lead oxides with stoichiometries intermediate between those of PbO$_2$ and Pb$_3$O$_4$, and to characterise them as appropriate.[7]

---

† Present address: Victoria and Albert Museum, Conservation Department, Science Section, Cromwell Road, South Kensington, London, UK SW7 2RL.

Experimental

Raman microscopy studies of lead(IV) oxide (plattnerite 99.9%, Aldrich) and of red lead (Aldrich) were carried out using excitation lines with the following wavelengths: 488.0 and 514.5 nm (Coherent I70 argon ion laser), 647.1 nm (Coherent I301 krypton ion laser) 781.8 nm (Renishaw diode laser) and 1064 nm (Nd:YAG laser). Massicot was analysed using the 647.1, 514.5 and 1064 nm lines, whereas litharge was analysed using the 488.0, 514.5, 632.8 and 1064 nm lines. The experiments using lines at 488.0 and 647.1 nm and some of those at 514.5 nm were carried out using a Dilor XY spectrometer. Other experiments using lines at 514.5, 632.8 and 781.8 nm were carried out with a Renishaw Raman System 1000 spectrometer. The experiments using 1064 nm excitation were carried out using a Bruker RFS 100/S FT-Raman spectrometer. For each set of experiments the power at the sample was varied from the minimum to the maximum setting with the aid of a set of neutral density filters (1, 10, 33, 50, 80 and 90% transmittance) in order to collect the spectra of the non-degraded compounds and then of the eventual laser-induced degradation products. Under typical operating conditions, a power at the sample of 1 mW corresponds to an irradiance of 5 kW cm^{-2}.

X-ray diffractograms between 20 and 70° (2θ) were collected in steps of 0.02° (2θ) with an integration time of 2 s, using Cu-Kα$_1$ radiation at λ = 0.154 06 nm, monochromatised using a curved graphite crystal on a Philips PW1710 diffractometer. The crystal structure of each sample was identified using the PC-APD program, version 3.6.

Results

The analysis of each pigment is discussed separately and in some detail, since the spectra obtained are dependent on both

the wavelength and power of the excitation line. It is shown that it is critically important to define the correct conditions for obtaining the Raman spectra of any particular lead compound.

Plattnerite [tetragonal lead(IV) oxide, PbO₂]

Lead(IV) oxide is a very weak Raman scatterer, principally because it is black and therefore absorbs most of both the incident and scattered radiation and will therefore degrade unless the laser power is kept suitably low. Early studies[8] had indicated that it is not possible to obtain a Raman spectrum from a bulk sample of reagent grade PbO₂. Later it was suggested[9] that any Raman bands reported previously for PbO₂ might arise from lower oxides of lead formed by laser-induced decomposition of PbO₂. In 1995 a spectrum of PbO₂ was reported[10] to contain a single weak band of unspecified wavenumber. These remarks were kept in mind during the present Raman analysis of lead(IV) oxide.

1064 nm. The power at the sample ranged from 3 to 100 mW. The sample degrades in the laser beam and, when a power higher than 30 mW is used, a microscopic indentation forms (yellow in the centre and orange around the edge) where the beam hits the sample. No spectra can be acquired under these conditions because the laser beam erodes the sample, whose superficial morphology changes continuously; this means that the sample cannot be kept in focus. Once the indentation has formed, however, its surface can be analysed using a laser beam set at a suitably low power, for example 25 mW, which is insufficient to induce any further degradation of the orange and yellow materials. Raman analysis of the yellow area at the centre of any such indentation yields the spectrum of massicot, while that of the orange borders yields the spectrum of red lead in admixture with massicot and litharge.

781.8 nm. The power at the sample ranged from 0.05 to 5 mW. At < 1.25 mW, the sample gave a Raman spectrum with no degradation. However, it turned orange if the power was 2.5 mW or higher; new Raman bands appeared, the strongest being at 122 and 147 cm⁻¹, corresponding to the strongest bands of red lead and litharge, respectively.

647.1 nm. The power at the sample was set to between 0.22 and 2 mW. No bands appeared between 30 and 450 cm⁻¹ when the power was kept at < 0.55 mW. However when the power was increased to 0.76 mW two bands appeared, at ~ 117 and ~ 138 cm⁻¹ (weaker). Longer exposures of PbO₂ to the laser beam caused the interchange of the relative intensities of these two bands and the appearance of other bands.

632.8 nm. The power at the sample was kept between 0.25 and 1.25 mW, yielding the spectrum shown in Fig. 1. At these laser powers, degradation of PbO₂ is unlikely to occur; the spectrum shown is similar to that reported in literature[10] and is considered to be that of non-degraded lead(IV) oxide (plattnerite). The spectra of powdered and pressed discs of PbO₂ are identical.

Three separate samples were then irradiated with higher laser powers of 2.7, 3.25 and 5.2 mW. Each sample changed colour from black to orange–red, and gave the spectra shown in Fig. 2 (upper trace in each case). The degraded areas were then analysed at much lower power, 0.06 mW, and yielded the spectra shown in the lower traces in each case. It is noteworthy that the spectra obtained while the samples were degrading in the laser beam at higher power are different from those obtained by analysing the degraded areas with an excitation line of lower power. The bands present in the spectra of the latter are due to

massicot, litharge and red lead: the higher the initial power used to degrade the sample, the higher was the relative intensity of the massicot bands. However, when the sample of PbO₂ was degraded at the lowest power used here, 2.7 mW, no massicot was found to be present, only litharge and red lead.

514.5 nm. The power at the sample was kept between 0.2 and 10 mW. PbO₂ is very sensitive to irradiation at this wavelength and degraded immediately, even at the lowest power used. When degrading in the laser beam, the sample became light orange for a fraction of a second, then pale yellow, yielding the spectrum shown in Fig. 3(b). If the yellow phase was then analysed at a suitably low power, 1 mW, the spectrum obtained corresponded to that of massicot (orthorhombic PbO).

A sample of PbO₂ was also irradiated at a laser power of ~ 50 mW at the sample. The products of this laser-induced degradation were then analysed with the Bruker spectrometer using 1064 nm excitation in order to avoid any further degradation of the sample. When the sample was degraded under these extreme conditions, a yellow phase appeared immediately, and at its edges were traces of an orange phase. The yellow phase gave the spectrum of massicot, whereas the orange phase gave bands corresponding to those of red lead. Bands of massicot were also seen in the spectrum of the orange phase, these being due to the poor spatial resolution associated with 1064 nm excitation.

488.0 nm. The power at the sample was kept between 0.6 and 6.7 mW. PbO₂ did not give any spectrum if the power was set at 0.6 mW, but it degraded to orange when the power was 2.3 mW or higher. The spectrum obtained by irradiation with a beam of 2.3 mW is shown in Fig. 3(a).

Red lead (Pb₃O₄)

Red lead (or minium, as both the mineral and the synthetic pigment are called in an artistic context[11,12]) is a bright orange–red pigment, used as such since antiquity.[12,13] It is stable when analysed with red, far-red or infrared wavelengths, but degrades when it is analysed with green or blue excitation lines of any power, as detailed below.

1064, 647.1 nm. Spectra were collected with the power at the sample of up to 270 mW with 1064 nm excitation and at up to 2.3 mW with 647.1 nm excitation. The spectra obtained were due to red lead alone, with no changes at higher laser powers;
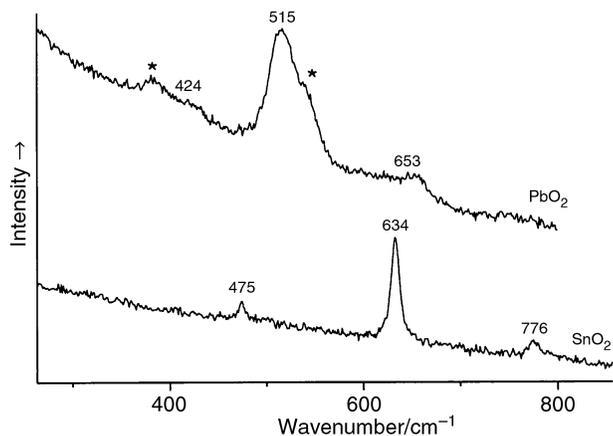
Fig. 1 Raman spectrum of a pressed disc of plattnerite, tetragonal PbO₂, obtained using 0.27 mW of 632.8 nm excitation. The weak features at ~ 390 and ~ 546 cm⁻¹ are considered to arise from trace amounts of Pb₃O₄, which is a very strong Raman scatterer. The spectrum of the isostructural SnO₂ is also shown.

that obtained at 50 mW of 1064 nm excitation is shown in Fig. 4 (top spectrum).

514.5 nm. The power at the sample ranged from 0.2 to 29 mW. The sample degraded very easily even under very low power. Above 0.2 mW the sample yielded a spectrum [Fig. 3(c)] that did not correspond to that of red lead, but was similar to that obtained on degrading Pb_3O_4 with the 488.0 nm excitation line [Fig. 3(d)], or degrading PbO_2 or litharge under the same experimental conditions. After being exposed to the laser beam, the sample glittered slightly yellow under the microscope. Upon irradiation at a power of 29 mW the sample became yellow, and yielded a spectrum corresponding to that of massicot.

One sample was first degraded at a power of 8 mW and then analysed in order with powers of 4, 2 and 0.8 mW (Fig. 5). The spectrum obtained using the highest power was characterised by very broad bands, whilst that obtained by analysing the same spot with a beam of lower power shows narrower bands which are shifted towards higher wavenumbers.

488.0 nm. The power at the sample ranged from 0.6 to 15 mW. The sample degraded very easily even under a very low power, changing colour from red–orange to yellow. Fig. 3(d) shows the spectrum obtained when the power at the sample was set at 7.6 mW. If the power at the sample was sufficiently high (15 mW), the complete transformation of red lead into massicot was induced.

Litharge (tetragonal PbO)

Litharge has been used as a pigment since antiquity, its colour ranging from yellow to red. It is a strong Raman scatterer.

1064 nm. The power at the sample was kept between 16 and 270 mW. No sign of degradation of the sample was seen, either in the spectra recorded (Fig. 4) or by eye under the microscope.

632.8 nm. The power at the sample ranged from 0.9 to 9 mW. The sample partially degraded to massicot at the maximum power used.

514.5, 488.0 nm. The power at the sample was kept between 0.2 and 35 mW of 514.5 nm radiation and between 0.6 and 15 mW of 488.0 nm radiation. The sample did not degrade if the power was kept at ≤ 0.4 mW [514.5 nm, Fig. 3(e)] or ≤ 0.6 mW (488.0 nm), but with powers progressively higher than these, the spectra obtained showed increasing amounts of degradation. At 10 mW of 514.5 nm excitation, degradation to an orange product was seen under the microscope. The spectrum obtained under these conditions is shown in Fig. 3(f). Upon irradiation at 35 mW of 514.5 nm radiation, the sample became yellow: when this yellow phase was analysed at 0.4 mW the spectrum was recognised to be that of massicot [Fig. 3(g)]. The spectra obtained whilst degrading the sample with 488.0 nm radiation are identical with those described above.

Massicot (orthorhombic PbO)

Massicot has been used as a yellow pigment since antiquity.[12,13] It is a very good Raman scatterer and appears to be stable under the experimental conditions used here. Only when irradiated with 514.5 nm radiation at very high laser power did it show some partial degradation.
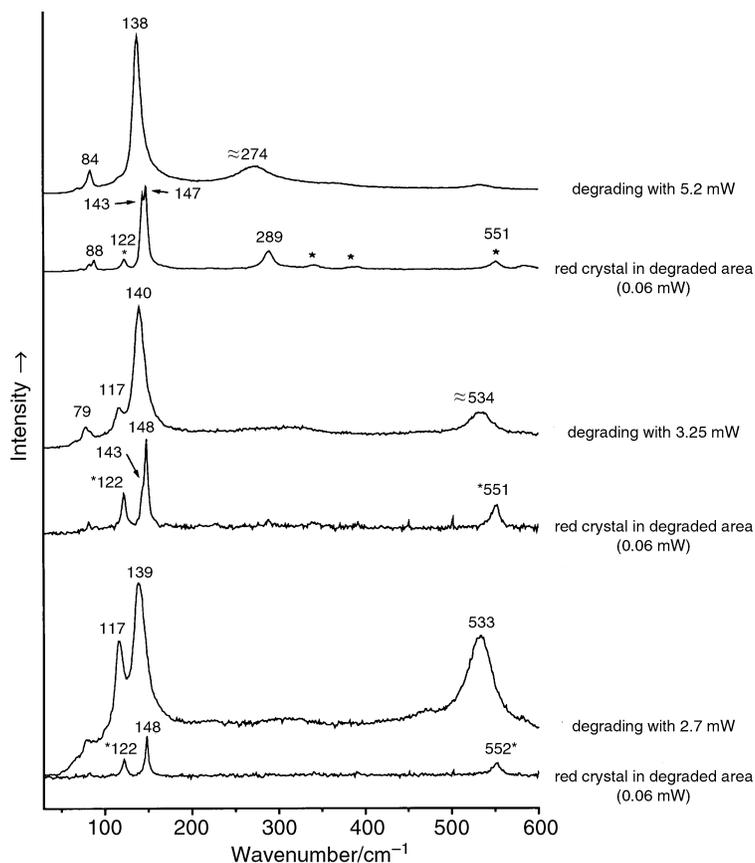
Fig. 2 Raman spectra showing the degradation of PbO_2 at 632.8 nm. With 2.7 mW the Raman bands of litharge (tetragonal PbO) and red lead (Pb_3O_4, peaks marked with an asterisk) are seen. At 3.25 mW red lead (Pb_3O_4, peaks marked with an asterisk), litharge (tetragonal PbO) and traces of massicot (orthorhombic PbO, main band at 143 cm^{-1}) are formed. At 5.2 mW litharge (tetragonal PbO), massicot (orthorhombic PbO) and traces of red lead (Pb_3O_4, peaks marked with an asterisk) are formed.

1064, 647.1 nm. The power at the sample was kept at 16 mW (1064 nm excitation) and 0.55 mW (647.1 nm excitation). No degradation was seen to occur; the spectrum recorded with 1064 nm excitation is shown in Fig. 4.

514.5 nm. The power at the sample ranged from 0.2 to 10 mW. The spectra obtained are in agreement with those of massicot in the literature[6] and with other spectra taken in this laboratory.[7] When using the laser at full power (10 mW) there was some visible degradation of the sample, which became slightly ochre-like. However, the Raman spectrum, albeit of diminished intensity, remained that of massicot. This decrease in intensity was presumably due to the decrease in the concentration of massicot in the sample as it degraded. The degradation product (possibly metallic lead) is a poor Raman scatterer and did not give a Raman spectrum.

Lead white, $2PbCO_3 \cdot Pb(OH)_2$

Lead white is one of the earliest synthetic pigments, having been used since antiquity.[12,14] It is a moderately strong Raman scatterer.

1064, 632.8, 514.5 nm. The power at the sample ranged from 180 to 300 mW at 1064 nm, 6 mW at 632.8 nm and 25 mW at 514.5 nm. No degradation of lead white could be detected, either from the spectra obtained or by visual examination down the microscope, under any of these experimental conditions. The spectrum collected with 160 mW of 1064 nm radiation is shown in Fig. 4.

Discussion

One of the purposes of this study was to determine under which conditions of laser wavelength, power and irradiation time the various lead oxides degrade, and through which pathways. PbO_2 was found to degrade following the pathway PbO_2 (plattnerite) $\rightarrow Pb_3O_4$ (red lead) $\rightarrow PbO$ (litharge) $\rightarrow PbO$ (massicot); Pb_3O_4 tends to degrade to litharge, and ultimately to massicot; and a fresh sample of litharge converts to massicot. This is to be expected as massicot is the most stable form of PbO at temperatures higher than 491 °C.[15–18] These results are summarised in Table 1.

The extent of laser-induced degradation of any lead oxide is determined by the choice of the laser wavelength; for example, red lead has an absorption maximum between 400 and 600 nm. If analysed with 647.1 nm radiation within the range of powers that are used in experiments on art objects (0.05–5 mW), it does not degrade. A near-infrared laser beam, such as that at 1064 nm, does not degrade the sample even when the power is set at 270 mW. However, red lead degrades immediately if irradiated with 514.5 or the 488.0 nm radiation, giving a spectrum which is similar to that of massicot [Fig. 3(c) and (d)]. Setting the 514.5 and 488.0 nm lines at a power higher than that normally used for Raman microscopy experiments on pigments, for example 15 mW, the whole sample turns yellow. When the yellow material is analysed with a very low power in order not to degrade it any further, the Raman spectrum of massicot is obtained.
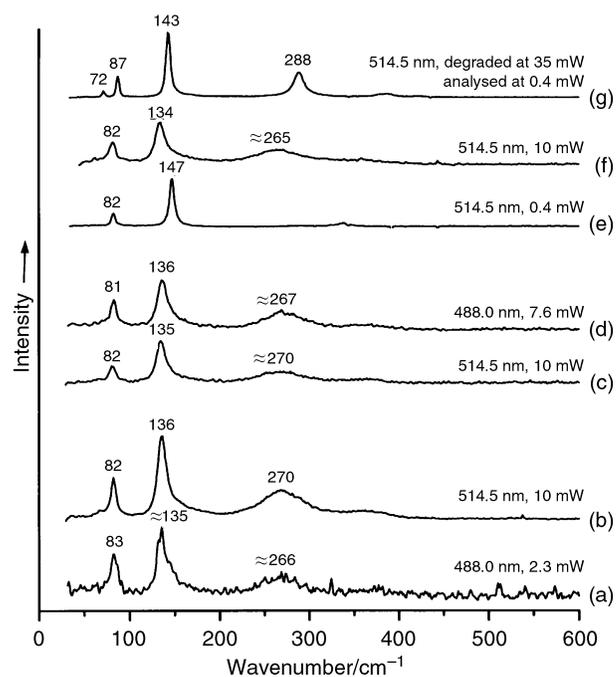
Fig. 3 Raman spectra showing the degradation of plattnerite, PbO_2 (a and b) and red lead, Pb_3O_4 (c and d) with 514.5 and 488.0 nm excitation. Raman spectra of undegraded litharge, PbO, with 0.4 mW of 514.5 nm excitation (e), and degrading with 10 mW (f), and the spectrum analysed at 0.4 mW after being degraded at 35 mW (g).
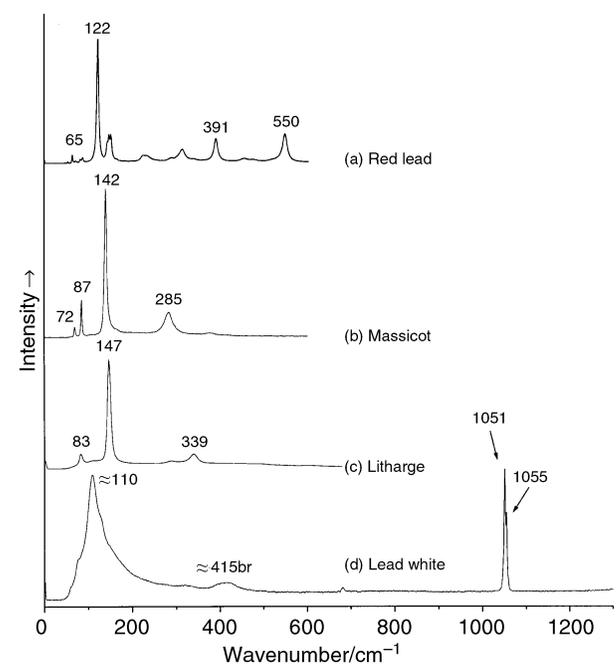
Fig. 4 FT-Raman spectra ($\lambda_0 = 1064$ nm) of non-degraded (a) red lead (50 mW); (b) massicot and (c) litharge (both at 16 mW); (d) lead white (160 mW).
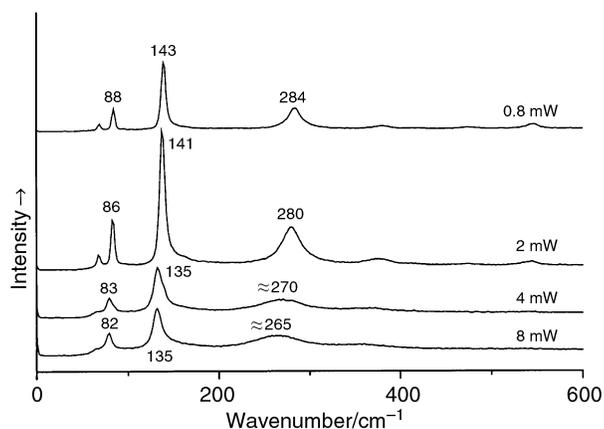
Fig. 5 Raman spectra obtained during the degradation of a sample of red lead with 514.5 nm radiation. The relative intensities of the lower two spectra have been scaled for easier comparison.

As a general trend, whenever the degradation of any sample takes place under a laser beam, the spectrum obtained *while* degrading the sample is different from that obtained by analysing the sample with a laser beam of very low power *after* it has been degraded. The analysis of the degraded sample with low power always reveals the presence of one or more of the known lead oxides, whereas the spectrum of the degrading sample does not correspond to the Raman spectrum of any established lead oxide (see Figs. 3 and 5, for example). However, there is a correlation between the two sets of spectra: when compared with the spectra of the degraded samples (obtained at low power), the spectra of the degrading samples have broader bands and are shifted to lower wavenumbers. Fig. 2 is a good example of this: it shows spectra of samples of lead(IV) oxide being degraded at 632.8 nm (upper spectra), then analysed at a suitably low power so as not to degrade further (lower spectra). The degraded areas consist of massicot, litharge and red lead, the relative amounts of which depend on the power at the sample of the beam which caused the degradation. The higher the laser power, the higher the proportion of massicot generated. Lower powers produce variable amounts of red lead and litharge.

It could be argued that the spectra obtained whilst degrading the samples of PbO_2 should be attributed to high temperature species present only when the laser power (and hence the temperature at the sample) is high. This would explain why the use of low laser power only leads to the detection of species that are found at room temperature. However, examination of the spectra reveals that there is a close correlation between the wavenumbers of the peaks seen at high power and the identities of the species detected at low power. For example, it is significant that the bands at 117 and ~ 534 cm^{-1} in the spectra of the degrading PbO_2 are only seen when red lead is found in the degradation products. Red lead is characterised by bands at 122 and ~ 550 cm^{-1}, wavenumbers which are slightly higher than those of bands from the degrading material. When red lead is present only in trace amounts in the spectrum of the degraded material (Fig. 2, bottom spectrum), the band at 117 cm^{-1} in the spectrum of the degrading material (upper spectrum) is very weak. Similarly, the broad bands at ~ 138–140 cm^{-1} in the upper spectrum are related to the main bands of litharge and/or massicot in the bottom spectrum.

Attempts have been made by thermogravimetry to define the nature of the thermal decomposition process of PbO_2 and to characterise any compounds of stoichiometry intermediate between those of PbO_2 and Pb_3O_4. Old literature indicates that the steps leading to the formation of Pb_3O_4 are as follows:[19]

$$PbO_2 \rightarrow \alpha\text{-}PbO_x \quad (x \approx 1.66, \approx 280\ ^{\circ}C)$$

$$\alpha\text{-}PbO_x \rightarrow \beta\text{-}PbO_y \quad (y \approx 1.5, \approx 375\ ^{\circ}C)$$

$$\beta\text{-}PbO_y \rightarrow Pb_3O_4 \quad (> 375\ ^{\circ}C)$$
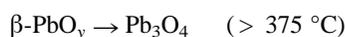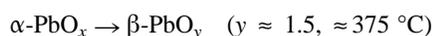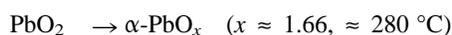
However, the results were unsatisfactory owing to difficulties in controlling the decomposition process, which was found to be determined by the atmosphere (air, O_2 or N_2), the rate of heating

of the sample and the quenching procedure adopted at any particular temperature to obtain an intermediate at room temperature for Raman study. Curiously, one such intermediate phase, $PbO_{1.55}$, was identified by XRD; however, the FT Raman spectrum of this phase (Fig. 6) did not correspond to that of any species generated by laser-induced degradation. Possibly this is because thermal equilibrium cannot be obtained under laser irradiation.

The Raman spectrum of PbO_2 (Fig. 1) is very weak, and it contains two weak bands which probably derive from trace amounts of the very strongly scattering Pb_3O_4. Pure PbO_2 is known to lose oxygen rapidly, with 5% loss being reported 15 h after preparation.[20] The remaining three bands, at 653 (m), 515 (s), and 424 (m) cm^{-1} appear to be the analogues of the 776 (w/m) (b_{2g}), 634 (s) (a_{1g}) and 475 (w/m) (e_g) cm^{-1} modes of SnO_2,[21] with which PbO_2 is isostructural (each has the rutile structure, space group $D_{4h}{}^{14}$, $P4/mnm$). Both the intensity and wavenumber patterns of the Raman spectrum of each dioxide match each other closely. The assignments given for PbO_2 are much more appropriate than those adopted for force field calculations on rutile structures[22] from the results of inelastic neutron scattering experiments.[23]

Conclusion

The Raman spectrum of PbO_2 can be recorded without causing any degradation to the sample provided that a laser beam of sufficiently long wavelength and very low power is used. The Raman spectrum thus obtained is distinguishable from that of any other lead-containing pigments (such as massicot, red lead and litharge) and can therefore be used for identification purposes. The detection of PbO_2 by Raman microscopy is nonetheless difficult since this material is only a very weak Raman scatterer (and very strong absorber) and so any other
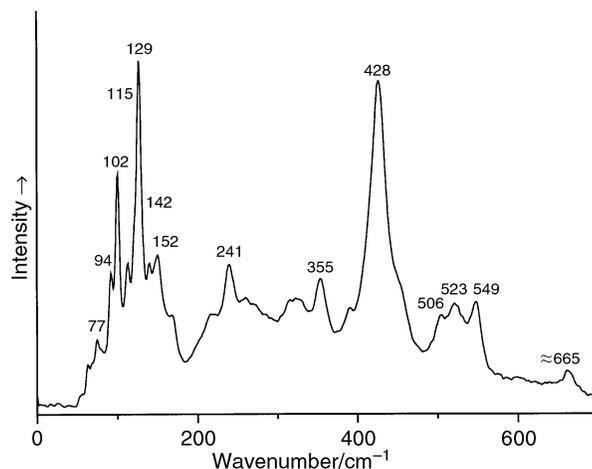
Fig. 6 FT-Raman spectrum of a sample obtained by heating PbO_2 to 425 °C. $\lambda_0 = 1064$ nm, power 3 mW, 18 000 scans, resolution 2 cm^{-1}.

Table 1 Stabilities of the lead oxides in laser beams of different wavelength

	PbO_2 power/mW		Pb_3O_4 power/mW		PbO (litharge) power/mW	
λ_o/nm	Raman spectrum obtainable	Sample decomposes	Raman spectrum obtainable	Sample decomposes	Raman spectrum obtainable	Sample decomposes
1064	No	> 30	< 270[a]	No	< 270[a]	No
781.8	0.05–1.25	≥ 2.5				
647.1	No	≥ 0.76	< 2.3[a]	No		
632.8	0.25–1.25	> 1.25			< 0.9	≥ 9
514.5	No	≥ 0.2	No	> 0.2	≤ 0.4	> 0.4
488.0	No	≥ 2.3	No	> 0.6	≤ 0.6	> 0.6

[a] Highest power used.

pigment present in admixture therewith might yield a Raman spectrum sufficiently intense to swamp the signal from PbO_2.

Acknowledgements

References

1 S. Giovannoni, M. Matteini and A. Moles, *Stud. Conserv.*, 1990, **35**, 21.
2 H. C. Howard, in *Proceedings of Historical Painting Techniques, Materials, and Studio Practice, Leiden, June 1995*, Getty Conservation Institute, 1996, p. 91.
3 N. V. Sidgwick, *The Chemical Elements and their Compounds*, Clarendon Press, Oxford, 1950.
4 A. M. Clark, *Hey's Mineral Index*, Natural History Museum: Chapman and Hall, London, 1993.
5 R. J. H. Clark and P. J. Gibbs, *Anal. Chem.*, 1998, **70**, 99.
6 I. M. Bell, R. J. H. Clark and P. J. Gibbs, *Spectrochim. Acta, Part A*, 1997, **53**, 2159.
7 L. Burgio, PhD Thesis, University of London, 2000.
8 R. J. Thibeau, C. W. Brown, A. Z. Goldfarb and R. H. Heidersbach, *J. Electrochem. Soc.*, 1980, **127**, 37.
9 K. R. Bullock, *J. Electroanal. Chem.*, 1987, **222**, 347.
10 L. Black, G. C. Allen and P. C. Frost, *Appl. Spectrosc.*, 1995, **49**, 1299.
11 C. Cennini, *The Craftsman's Handbook: the Italian 'Il Libro dell'Arte'*, transl. D. V. Thompson, Dover Publications, New York, 1954.
12 E. West-Fitzhugh, in *Artists' Pigments: a Handbook of Their History and Characteristics*, ed. R. L. Feller, National Gallery of Art, Washington, DC, 1986. vol. 1.
13 K. Wehlte, *The Materials and Techniques of Painting*, Van Nostrand Reinhold, London, 1975.
14 R. J. Gettens, H. Kuhn and W. T. Chase, in *Artists' Pigments: a Handbook of Their History and Characteristics*, ed. R. L. Feller, National Gallery of Art, Washington, DC, 1986, vol. 1.
15 J. D. Donaldson, M. T. Donoghue and S. D. Ross, *Spectrochim. Acta, Part A*, 1974, **30**, 1967.
16 R. Soderquist and B. Dickens, *J. Phys. Chem. Solids*, 1967, **28**, 823.
17 D. M. Adams and D. C. Stevens, *J. Chem. Soc., Dalton Trans.*, 1977, 1096.
18 L. D. Madsen and L. Weaver, *J. Am. Ceram. Soc.*, 1998, **81**, 988.
19 G. L. Clark, N. C. Schieltz and T. T. Quirke, *J. Am. Chem. Soc.*, 1937, **59**, 2305.
20 R. Wagner in *Handbook of Preparative Inorganic Chemistry*, ed. G. Brauer, Academic Press, New York, 1965, p. 1669.
21 P. S. Peercy and B. Morosin, *Phys. Rev. B*, 1973, **7**, 2779.
22 V. A. Maroni, *J. Phys. Chem. Solids*, 1988, **49**, 307.
23 R. Varma, J. Eckert, V. A. Maroni, J. A. Goldstone, C. Giordano, T. Cehelnik, R. Kumar, S. Siegel and B. Tani, in *Extended Abstracts of the 35th Meeting of the International Society for Electrochemistry*, Berkeley, CA, 5–10 August 1984, 1984, pp. 90–92; R. Varma, J. Eckert, J. A. Goldstone, A. D. Taylor and J. D. Jorgensen, *Electrochemical Soc. Extended Abstr.*, 1983, **83**, 188.