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# Laser-induced degradation of lead pigments with reference to Botticelli's *Trionfo d'Amore*

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**Abstract**

The recent analysis of the palette used in Botticelli's *Trionfo d'Amore* by Raman microscopy has led to the erroneous identification of the spectrum of a degradation product, most likely that of massicot (orthorhombic PbO), as that of plattnerite ($PbO_2$) [Anal. Chim. Acta 429 (2001) 279]. The error is shown to arise from the laser-induced degradation of both the painting and a reference sample of pure $PbO_2$. The spectrum of undegraded $PbO_2$ is presented, and the common problem of laser-induced degradation of lead pigments in art conservation studies utilising Raman microscopy is discussed. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Raman microscopy; Laser-induced degradation; Lead pigments

## 1. Introduction and discussion

Raman microscopy has found widespread use in the analysis of pigmented artwork and artefacts due to its non-destructiveness, high spatial resolution, relative immunity to interference, ease of application, and specificity to both organic and inorganic compounds [2,3]. Most objects can be analysed in situ with little or no preparation, even when their size or shape would preclude the use of other spectroscopic techniques. Because of these qualities, Raman microscopy has been widely applied in the fields of archaeometry and art analysis, usually with much success in ascertaining the composition of an item or in identifying the palette used in its creation. However, in a few cases, great care is needed to avoid thermally degrading the pigment under study. When Raman microscopy is applied to priceless artwork and historical materials, such degradation must be avoided.

Red lead or minium ($Pb_3O_4$) and reddish-yellow litharge (tetragonal PbO) are examples of common lead-based pigments that require particular attention when being analysed by Raman microscopy [4]. Furthermore, plattnerite ($PbO_2$) and galena (PbS), which have not themselves been known to have been used as pigments, can appear in artwork as pigment degradation products. Black/brown $PbO_2$ is formed when the common pigment lead white ($2PbCO_3{\cdot}PbOH_2$) is oxidised by peroxides present in a display or storage environment. Black PbS can be generated either by the reaction of the same white pigment with sulfurous gases present in the surroundings [5] or generated in situ by bacteria [6], or by the reaction of lead white with sulfide pigments used in the illumination [7]. These two dark contaminants are extremely weak Raman scatterers and are highly

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susceptible to laser-induced degradation [4,8]. As a result, their Raman spectra have sometimes been misidentified in the literature, confused instead with those of their laser-induced degradation species, or have been characterised only by weak, ill-defined spectral features [9–13].

A recent report appearing in this journal [1] and briefly described elsewhere [14] details the Raman analysis of a coloured drawing, *Trionfo d'Amore*, attributed to Sandro Botticelli. Unfortunately, Andalò et al. have fallen victim in that analysis to the difficulties involved in recording the Raman spectra of lead-containing species commonly found on artwork. They mistakenly assert a positive identification of $PbO_2$ in admixture with ochre pigments based on the Raman analysis of the brown paint used in the illumination. The presence of $PbO_2$ has been attributed to the oxidation of lead white which they believe to have been used for the highlights in these areas.

A Raman spectrum collected from the brown areas using 5.0 mW of 632.8 nm excitation is presented in their report [1] and compared with that of a reference sample of pure $PbO_2$. However, *neither of the resulting spectra is that of plattnerite*, but rather each can be attributed to the same degradation product generated by the laser-induced transformation of both the reference and the painted sample during the course of the analysis. A careful study of the effects of laser excitation wavelength and power on the Raman spectrum of $PbO_2$ and other lead oxides has recently been carried out by one of the authors [15] and reported in the literature [4]. This study shows that, when excited with 632.8 nm radiation, the Raman spectrum of genuine plattnerite can only be recorded when the laser power is below 1.25 mW.

A spectrum of undegraded $PbO_2$ recorded using 0.27 mW of 632.8 nm radiation is shown in Fig. 1(a). The spectrum was recorded using a Renishaw System 1000 spectrometer with a Leica microscope and ×50 objective. The bands at 424, 515, and 653 $cm^{-1}$ are assigned to the $e_g$, $a_{1g}$, and $b_{2g}$ modes, respectively, based on a comparison with the analogous Raman bands of the isostructural compound $SnO_2$ [4]. Fig. 1(b) shows the Raman spectrum collected from $PbO_2$ using 5.2 mW of 632.8 nm radiation, these being essentially the same experimental parameters as used in the analysis of the Botticelli drawing [1]. At this excitation power, plattnerite degrades in the laser beam to form a compound whose Raman spectrum very closely resembles that of massicot, with bands observed at 84, 138, and 274 $cm^{-1}$, i.e. slightly red-shifted from those established for massicot [4,16,17]. Unfortunately, no

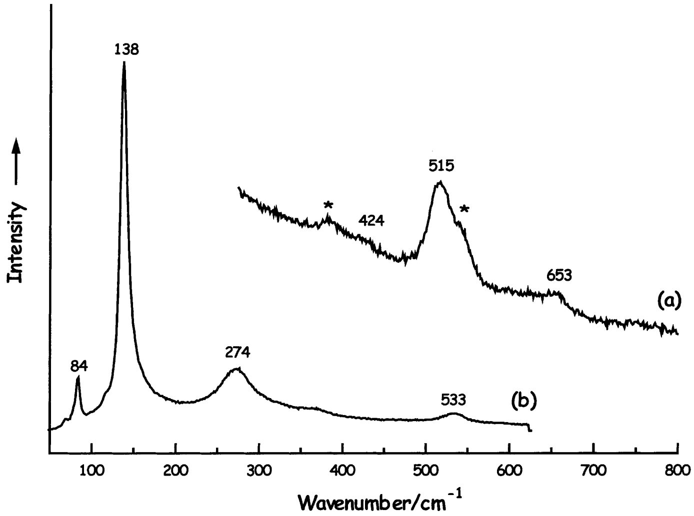

Fig. 1. Raman spectrum of plattnerite, $PbO_2$, using 632.8 nm excitation at (a) 0.27 mW which gives the genuine spectrum, and at (b) 5.2 mW which gives a spectrum of the degraded material, essentially massicot (orthorhombic PbO). Asterisks in (a) mark bands due to residual red lead.

band wave number are specified in the Raman spectra presented by Andalò et al. Nevertheless, their published spectra appear by eye to be in excellent agreement with that shown in Fig. 1(b).

It is now clear that the spectrum resulting from the Raman analysis of the brown paint is attributable to a laser-induced degradation species, not to $PbO_2$; some of the latter might, nevertheless, be present in the drawing. However, the presence of any of the other common lead oxides used as pigments in admixture with the ochre can be ruled out based on their known behaviour to 632.8 nm laser radiation [4]. At 5 mW excitation power, and even well above that, pure massicot is known to provide a spectrum nearly identical to that in Fig. 1(b), but importantly, without the bathochromic shift (vide supra). Minium and litharge have been shown to be highly stable during Raman analysis with red excitation lines (632.8 and 647.1 nm) and have Raman spectra that are distinctly different from that observed by Andalò et al [1]. Therefore, the most probable lead component in the mixture would be one of the species formed by degradation of lead white, viz. $PbO_2$ or PbS, each of which degrades at even modest laser power when using 632.8 nm excitation radiation. The Raman spectrum of the degraded species in each case is nearly identical to that shown in Fig. 1(b). The presence of PbS can sometimes be distinguished by its further degradation to form an assortment of basic lead(II) sulfates [8], whose characteristic Raman bands appear in the region of 950–970 $\text{cm}^{-1}$, i.e. well outside the range studied by Andalò et al. However, if the lead compound present on the drawing is due to degradation of lead white, then it is curious that no residual traces of this pigment were detected either visually or by Raman microscopy.

It is interesting that massicot is reported to be present in the blue areas of the *Trionfo d'Amore* which are painted with lapis lazuli [1]. However, the spectrum from this area of the painting appears to be the same as that reported for the brown area discussed above, though the latter has a larger fluorescence background. Furthermore, the key bands of the spectrum from the blue area are slightly red-shifted and broader than those from a commercial sample of orthorhombic PbO used as a reference. Although the authors comment that massicot was commonly painted over other pigments during the Italian Renaissance, and so its identification over lapis lazuli is plausible, the results which Andalò et al. present do not establish this to be the case. The massicot-like spectrum recorded from this area of the drawing almost certainly arises from the thermal degradation of $PbO_2$ or PbS produced by the degradation of lead white as discussed for the brown areas above. However, without the indication of peak wave number on the spectrum of the blue area, it is not possible to make a final decision on this matter.

## 2. Conclusion

The misidentification of $PbO_2$ due to laser-induced degradation highlights the care that must be taken when analysing lead pigments and pigment degradation products in artwork using Raman microscopy. In this instance, the unambiguous identification of the pigment component in the brown and blue areas of *Trionfo d'Amore* could be quite revealing, either enhancing our understanding of the artistic techniques of Botticelli or potentially indicating a serious conservation problem that has greatly changed the intended effect of the drawing. Moreover, if the compound derives from degradation of lead white, then the positive identification of the contaminant as either $PbO_2$ or PbS could potentially change the treatment used to restore the drawing. Unfortunately, none of these possibilities can be established unless a re-examination of the drawing is undertaken using much lower laser excitation powers. As more collaborations are created at the Arts–Science interface, it is imperative that spectroscopists undertaking Raman analyses of artwork understand the sensitivities of the materials used in the creation of the objects so as to gain the most information from them without causing any damage.

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