

# The Identification of Pigments Used on Illuminated Plates from 'Flora Danica' by Raman Microscopy

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Six plates in folio format, made from copper engravings, from the collection 'Flora Danica', have been studied by Raman microscopy in order to obtain information about the palette in use in Denmark at the end of the 18th and the beginning of the 19th centuries. The folios examined had been first printed, and subsequently illuminated by hand. The following pigments have been identified: vermilion, red lead, massicot, orpiment, Prussian blue, white lead, chalk, a carbon-based black pigment (probably ivory black or lamp black) and possibly green earth. No information could be obtained regarding the green pigments, the brilliant yellow pigment or the two orange pigments. No problems of degradation were detected, and the pigments identified are consistent with those found on other European artworks produced at the turn of the 18th century, no synthetic pigments of a later period being identified. Scanning electron microscopy and elemental analysis studies have also been performed in a few cases.

Our cultural heritage is enshrined in manuscripts, paintings, pottery, china, enamels, faience, papyri, icons and other works of art which have, in some cases, been preserved for thousands of years. The analysis and identification of pigments on such artefacts and the interpretation given to the presence of particular pigments on items from a particular place and of a particular age encompasses many disciplines. An important role of the scientific disciplines is to identify the techniques and materials used to produce an artefact and hence to provide information on the development and spread of chemical technology, on artistic styles and techniques, and on trading routes. Being at the interface of the Arts and Sciences, this subject attracts as much interest from art historians, librarians, palaeographers and historians as from research scientists, since the information obtainable bears upon matters to do with restoration, conservation, dating and authentication of artefacts.

*Flora Danica.* *Flora Danica* is a comprehensive record of the plants of the Scandinavian region which, at the time of the compilation, included Norway and Iceland then under Danish domination, and territories such as Schleswig-Holstein now belonging to Germany. It consists of 18 folio volumes, with 3240 coloured illustrations of Scandinavian plants.<sup>1,2</sup> Six of these illustrations have been examined by Raman microscopy in order to estab-

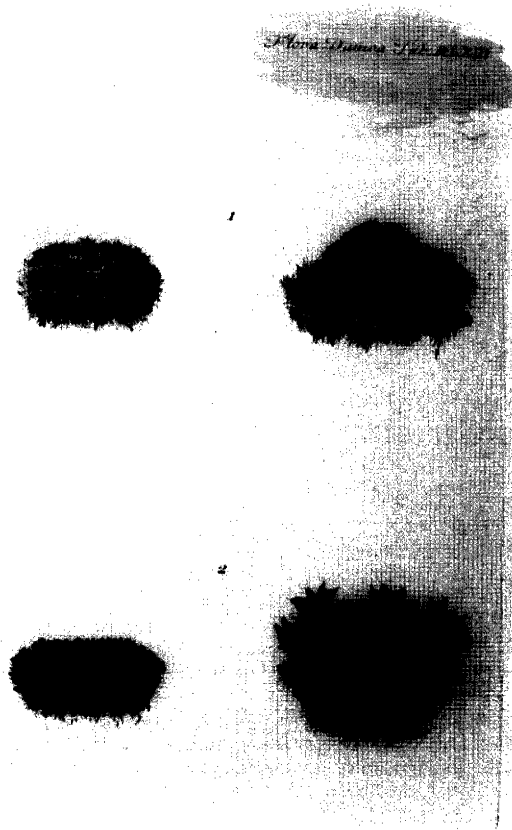
lish the palette in use at the time of the illumination (Figs. 1 and 2).

The *Flora Danica* issues came in two versions, one black and white, and the other coloured. Pages which were intended to be illuminated were printed with a light brownish ink. The colouring varies from copy to copy, but it is generally superb, and even minute details are accurately coloured. Technically the illumination is done with body colours which are sufficiently opaque to conceal most of the engraved lines.†

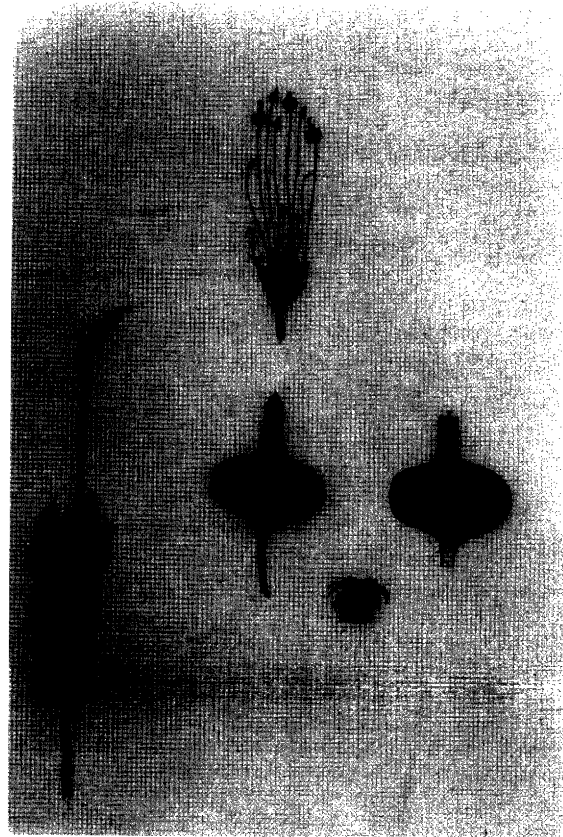
† As stated by Dunthorne,<sup>3</sup> *Flora Danica* is 'a beautiful but not a decorative work'. The intention was that it should serve persons interested in botany and therefore be scientifically correct. However, 'this magnificent work never fulfilled its purpose in this respect; time has overtaken it, and now it is regarded mostly as a beautiful memorial of a time of great initiative in the natural sciences in Denmark'.<sup>4</sup> According to one of the publishers, Hornemann, it is possible that botanists would have been better off with the cheaper plain versions because colouring was sometimes unsuccessful. Nevertheless, the coloured versions were the more in demand. In most cases people who obtained the uncoloured versions made their own arrangements for the illuminations. Illumination of copper plates is an art which had not been developed in Denmark in the middle of the 18th century. The King did not want the work to be done abroad, so the Royal Academy of Arts was commissioned to create a school of art illumination. The pupils were poor girls and the teacher a skilled lady, J. A. Seizberg, from Augsburg. She was paid a salary of 50 rixdollars a year, which was also the amount spent on the materials used in the illuminations. A skilled artist could colour four plates by hand every day but, as the salary they could earn was so small, the illuminators were always women.

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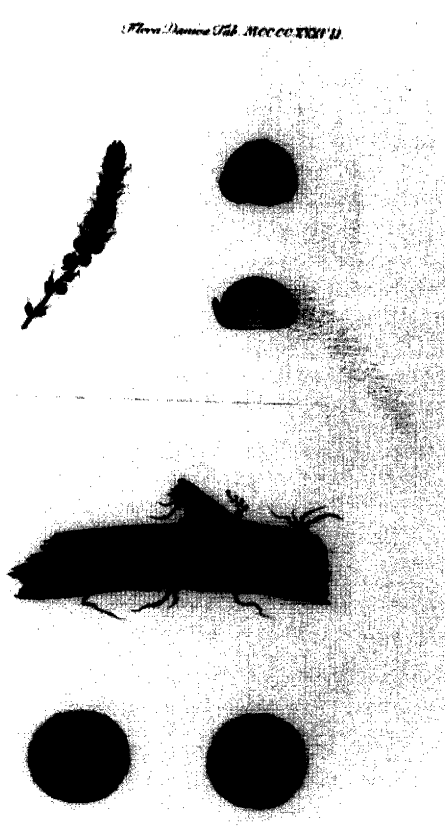
(a)



(b)



(c)



(d)

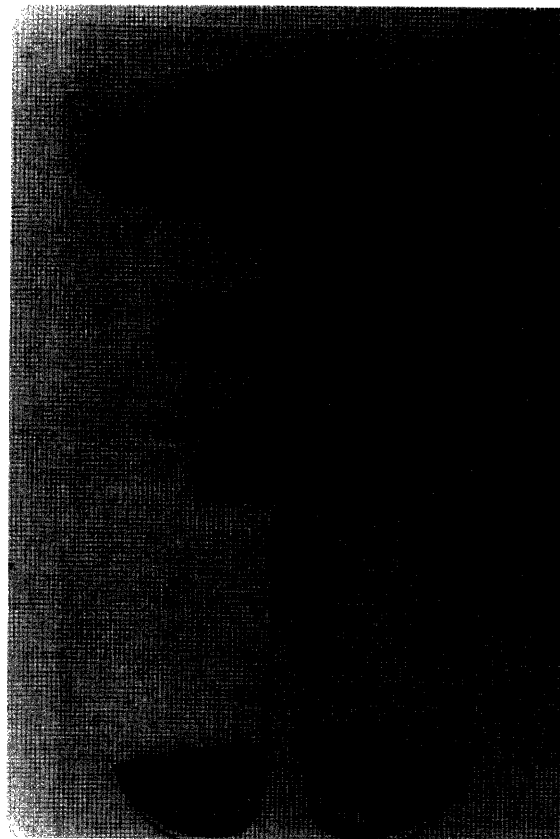
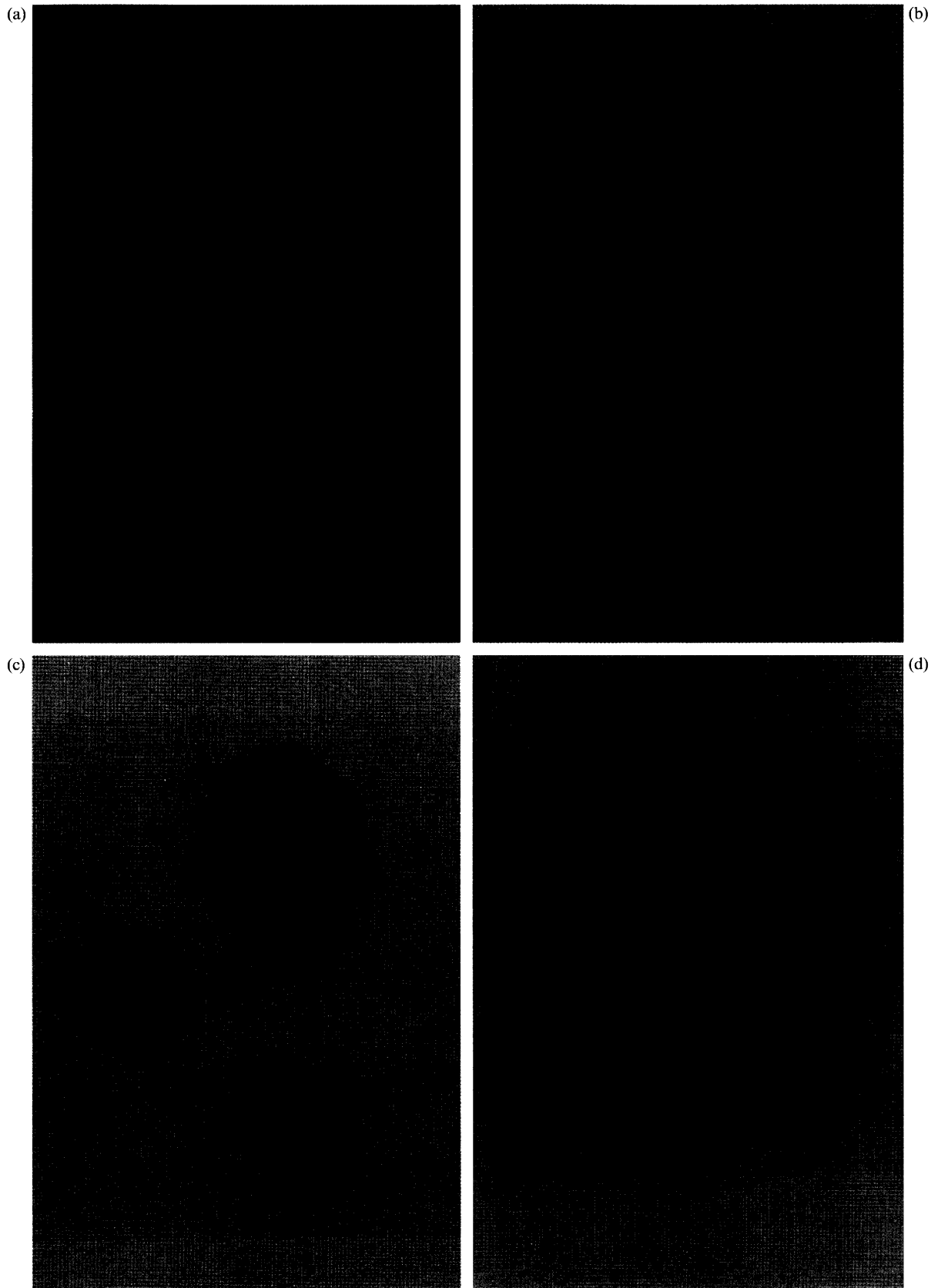


Fig. 1. (a) Top left, Plate MLXIII; (b) top right, Plate MCCCCXIII; (c) bottom left, Plate MCCCCXXXVII; (d) bottom right, Plate MCCCCLXXXVII.



*Fig. 2.* (a) Top left, Plate MCCCCLXXI (detail); (b) top right, Plate MCCCCLXXI (detail); (c) bottom left, Plate MCCCCXXXVII (detail); (d) bottom right, Plate MCCCCXXXVII (detail).

It has not been possible to trace either the origin or the identity of the pigments used in the illuminations. Although recipes for the preparation of watercolours can be found in both old and contemporary handbooks,<sup>5</sup> it is more likely that the pigment mixtures were imported from Germany, with which country a trade in watercolours had been established by the end of the 18th century. Although the illuminations were usually done shortly after the prints were issued, the exact date of this is difficult to establish.‡

**Raman microscopy.** Raman microscopy<sup>6–23</sup> is now considered to be the best single technique for the identification of pigment grains on manuscripts, paintings and other artefacts in that it combines the required attributes of being reliable, sensitive, non-destructive and largely immune to interference from other pigments, binder and fluorescence, with that of being applicable *in situ*. Moreover, the spatial resolution possible is  $\leq 1 \mu\text{m}$ , important when the components of a pigment mixture are to be identified. Such studies are of immense value in helping to establish the authenticity of artefacts.<sup>19</sup>

The weakness of the Raman effect in the absence of resonance effects and the only moderate sensitivity of the early detection systems (semiconductor or diode) originally available were unattractive features of Raman microscopy. Many of these problems have now been solved by the introduction of CCD detectors to modern spectrometers, which thereby allow poorly scattering pigments, notably fluorescent organic dyes, to be studied with near-infrared, low-power lasers and long integration times.

It is also now realised that there is enormous potential for Raman microscopy to provide information that will assist the conservator to preserve manuscripts for future generations. For example, if deterioration had already occurred, Raman studies may lead to the identification of decomposition products and thus enable the conservator to consider treatments to either halt or reverse the process.

## Experimental

**Instrumentation.** All the pigments on the six leaves have been analysed non-destructively and *in situ* using three different Raman microscopes. The first was a Dilor XY triple-grating spectrometer, configured with an Olympus BH-2 microscope, a water-cooled Coherent Innova 300 1 W krypton-ion laser light source (647.1 nm) and a

photodiode-array detector operating at  $-38^\circ\text{C}$ . The second was a Renishaw Ramascope, configured with an Olympus BH-2 confocal microscope, an air-cooled Spectraphysics 21 mW argon-ion laser light source (514.5 nm), and an air-cooled CCD detector operating at  $-70^\circ\text{C}$ . The third instrument was a Kaiser Hololab 5000 spectrometer, configured with an Olympus BX60 microscope, an air-cooled SDL-8530 50 mW AlGaInAs diode-laser light source (784.8 nm) and an air-cooled CCD detector operating at  $-70^\circ\text{C}$ .

The scanning electron microscope used to determine the atomic composition of a few crystal samples removed from the Flora Danica prints was a JEOL 733 Superprobe with an ATW (atmospheric thin window) detector at Birkbeck College, London. Data were collected with an accelerating voltage of 15 kV (the areas examined were approximately  $2 \mu\text{m}$  across) using an Oxford Instrument ISIS energy dispersive system.

**Experimental details.** For the Raman analyses the pigment grains were examined using a  $50\times$  objective in conjunction with a  $10\times$  eyepiece, thus achieving a spatial resolution of  $2 \mu\text{m}$ : in a few cases only, a  $100\times$  objective was used when performing an analysis with the Dilor XY instrument.

The laser power was carefully controlled in order to avoid any possible modification of the pigments examined by local overheating. Therefore, when using the Renishaw Ramascope, each sample was first examined by setting the power to the lowest value possible (0.04 mW). Once it was evident that the sample was not affected, the power was increased to the value of 0.4 mW. Only in a few cases was a power of 1 mW used. A similar procedure was adopted when using the Dilor XY microscope and the Kaiser spectrometer – the initial power being ca. 1 mW. This cautious procedure was necessary especially when examining red or orange pigments which might absorb the green  $\text{Ar}^+$  line of the Renishaw spectrometer. It was found to be necessary with this spectrometer to use very low power (up to 25 times less than that used for the Dilor XY) to avoid partial degradation.

In order to examine the effect of the laser power (514.5 nm) on the orange and red pigments, the single crystal referred to in Table 1 was chosen, and its spectrum recorded under the same conditions (number of scans, and duration of each scan), except for the incident power. It was possible to see that in fact increasing the power did affect the crystal, whose appearance changed from orange to yellow. The relative intensities of the bands in the spectra changed extensively, consistent with the conversion of  $\text{Pb}_3\text{O}_4$  into  $\text{PbO}$  (massicot) in the beam.<sup>24,25</sup>

## Discussion

The six plates from Flora Danica show a rich palette, eight pigments of which were identified by Raman microscopy (Fig. 3): vermilion,  $\text{HgS}$ ; red lead,  $\text{Pb}_3\text{O}_4$ ; massicot,  $\text{PbO}$ ; orpiment,  $\text{As}_2\text{S}_3$ ; Prussian blue, iron(III)

‡ There is only one important exception, namely the set made by Seizberg. This was kept at Christiansborg Palace, but unfortunately all these prints, except the 60 in Fascicle 12, were burned during a fire in 1888. Sometimes documents in the archives give valuable information. As an example it is mentioned in a letter from the King's librarian that the tenth volume of the set, now kept at the University Library of Odense, was illuminated by one of Professor Hornemann's daughters in 1814, so in this case the delay was only one year.

*Table 1.* Pigments identified by Raman microscopy (those in *italics* have been identified by SEM-EDX analysis).

Colour	Pigment	Instrument <sup>a</sup>
Plate MLXIII		
Red and orange	Red lead	D, K
Black	Carbon	R
White	Lead white	K
Blue	Phthalocyanine blue <sup>b</sup>	R
Plate MCCCCXIII		
Red and orange	Vermilion and red lead	R, K
Blue	Prussian blue	R
Purple	<i>Unidentified lake</i>	<i>SEM-EDX</i>
Plate MCCCCXXXVII		
Red and orange	Red lead, vermilion and massicot	D, R, K
Black	Carbon	R
Blue	Prussian blue	R
Plate MCCCCLXXI		
Red and orange	Vermilion	D
Black	Carbon	R
White	Chalk and lead white	R
Green and yellow	Earth	R
Plate MCCCCLXXXVII		
Red and orange	Vermilion	D, K
White	Lead white	R, K
Blue	Prussian blue	R
Plate MCCCCLXXV		
Orange and yellow	Red lead and orpiment	K
Green	<i>Atacamite</i>	<i>SEM-EDX</i>

<sup>a</sup>The letters D, K and R mean respectively: D, experiment carried out using the Dilor XY spectrometer; R, experiment carried out using Renishaw Ramascope; K, experiment carried out using the Kaiser spectrometer. <sup>b</sup>Adventitious impurity.

hexacyanoferrate(II)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot 14\text{--}16\text{H}_2\text{O}$ ; white lead,  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ ; chalk,  $\text{CaCO}_3$ ; a carbon-based black pigment (possibly ivory black or lamp black); and probably green earth (hydrated aluminosilicate of magnesium, iron and potassium). Phthalocyanine blue has been also detected, but this is considered to be an adventitious impurity because only a single crystal was found. Its presence as a single crystal on Plate MLXIII is probably due to contamination of the illustration after it was painted, since the crystal examined was the only one of its kind, and phthalocyanine blue is a modern synthetic pigment dating from 1936.<sup>26</sup>

On Plate MCCCCXIII a purple pigment has been found which, viewed down the microscope, turns out to be a mixture of blue and brilliant crimson crystals. The blue crystals are Prussian blue; the crimson crystals failed to give a Raman spectrum, and they also failed to fluoresce under a UV lamp, suggesting that they are not madder. A few crystals from the purple areas have been analysed by SEM-EDX, and the results are consistent with the presence of alumina and aluminium hydroxide, which are compounds typically employed as lake substrates.

Some pigments scattered too poorly to give a Raman spectrum, notably two further green ones, a brilliant yellow and two orange pigments. A few crystals from a green area on Plate MCCCCLXXV were examined by SEM-EDX. The elements detected were copper, chlorine and oxygen, suggesting that the pigment is a basic copper chloride, possibly atacamite  $[\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2]$ .

Attempts to obtain further information by using an FTIR microscope non-destructively, i.e. in transmittance, were unsuccessful, since the water absorbed on the surface of the pigments always obscured the signals of the compounds underneath.

In all the plates examined red lead has been found, and the spectra collected were typical of this pigment. However, in Plate MCCCCXXXVII something different can be seen; all the spectra showing the characteristic peaks of red lead also exhibit further peaks that are typical of massicot. Massicot is lead(II) oxide,  $\text{PbO}$ , and although it can be used as a pigment in its own right or in admixture with other compounds, it could also appear either as a decomposition product of red lead  $\text{Pb}_3\text{O}_4$  or as an indicator of insufficient heating during the synthesis of  $\text{Pb}_3\text{O}_4$  (Refs. 24 and 27) from  $\text{PbO}$  or white lead. In the process which leads to the formation of red lead the furnace temperature has to be controlled very accurately (450–470 °C when the starting material is  $\text{PbO}$ , 425–430 °C when the starting material is white lead) in order to produce pure red lead.<sup>24,25</sup>

Several observations exclude the possibility that the eventual decomposition took place during the analysis: the pattern of red lead and massicot in the same spectra was found only for orange crystals on the red and yellow parts of the illustrations referred to in Plate MCCCCXXXVII, but not on those in the other plates. Several crystals were examined in different illustrations on the same day under the same experimental conditions (laser power, number of accumulations and accumulation time). The laser line used for collecting the spectra ( $\lambda_0 = 647.1 \text{ nm}$ ) is the most appropriate for examining red and orange crystals, since it minimises the risks of decomposition of the sample due to local overheating because of absorption. The selection of a shorter wavelength (514.5 nm) and higher power laser line does indeed give rise to changes indicating conversion of  $\text{Pb}_3\text{O}_4$  to  $\text{PbO}$  in the beam. The power actually used at 647.1 nm was very low and, even when it was gradually increased (from 0.2 to 5 mW), no changes in the relative intensities of the peaks in a spectrum were seen. If any decomposition had occurred due to the use of excessive power, the massicot peaks would have intensified relative to those of red lead. This did not happen.

The possible explanation of the peculiar pattern shown by these orange crystals in Plate MCCCCXXXVII is that the artist had used a sample of impure red lead.

## Conclusion

The technique of Raman microscopy for the identification of pigments has previously been applied to oil

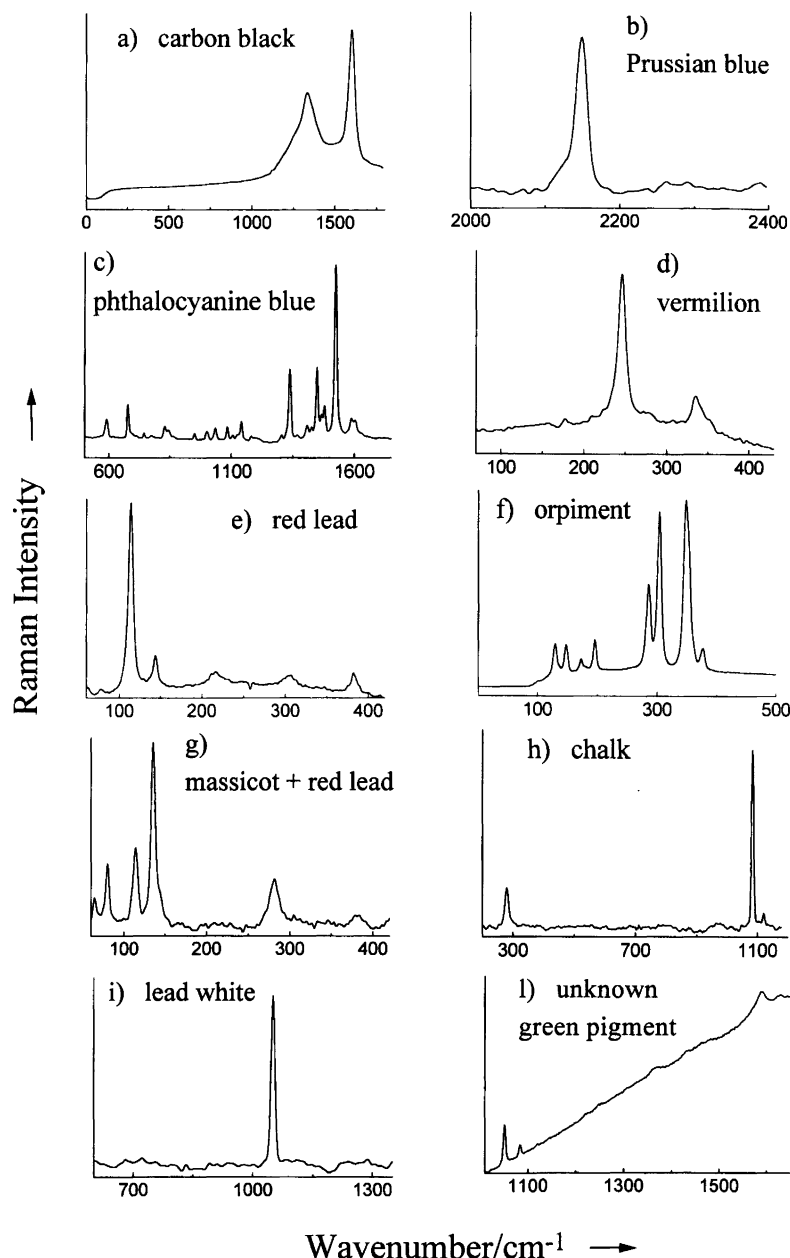


Fig. 3. (a) Raman spectrum of carbon black,  $\lambda_0=514.5$  nm, Plate MLXIII, bottom right bush. (b) Raman spectrum of Prussian blue,  $\lambda_0=514.5$  nm, Plate MCCCCLXXXVII, grass under yellow mushroom. (c) Raman spectrum of phthalocyanine blue,  $\lambda_0=514.5$  nm, Plate MLXIII, bottom right bush. (d) Raman spectrum of vermilion,  $\lambda_0=647.1$  nm, Plate MCCCCLXXI, red stalks. (e) Raman spectrum of red lead,  $\lambda_0=647.1$  nm, Plate MCCCXXXVII, yellow ball bottom right. (f) Raman spectrum of orpiment,  $\lambda_0=784.8$  nm, Plate MCCCCLXXV, bottom figure. (g) Raman spectrum of massicot,  $\lambda_0=647.1$  nm, Plate MCCCXXXVII, yellow ball bottom right. (h) Raman spectrum of chalk,  $\lambda_0=514.5$  nm, Plate MCCCCLXXI. (i) Raman spectrum of white lead,  $\lambda_0=514.5$  nm, Plate MCCCCLXXXVII, yellow mushroom. (j) Raman spectrum of an unknown green pigment,  $\lambda_0=514.5$  nm, Plate MCCCCLXXXVII, grass under yellow mushroom.

paintings<sup>18</sup> and illuminated manuscripts.<sup>6-16,22,23</sup> It has now been shown that the technique can also be used non-destructively and *in situ* to identify pigments in watercolours used on the illuminated prints made from copper plates.

Much of the palette of the folios has been established, being consistent with that of other early 19th century

European artworks. No synthetic pigments of a later period have been identified.

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