Identification of lead(II) sulfide and pararealgar on a 13th century manuscript by Raman microscopy

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The *in situ* non-intrusive chemical analysis by Raman microscopy of a very rare, early 13th century, Byzantine/Syriac Gospel lectionary implies that the serious pigment blackening of many hues and affecting most of the illuminations is caused by the degradation of lead white to lead(II) sulfide, and that pararealgar (As_4S_4) never previously identified on any manuscript was used throughout as a deep yellow pigment.

Raman microscopy is now established as the analytical procedure which is the most specific, sensitive, spatially refined and immune to interference for the *in situ* analysis of inorganic pigments on manuscripts.[1] The use of Raman microscopy in the field of manuscript analysis has been dominated by the study of illuminated manuscripts in order to characterize the artist's palette,[1–10] but, as shown in this article, this technique can now be used to provide critical information for conservation of a manuscript.

The 13th century Byzantine/Syriac Gospel lectionary, from the British Library Oriental and India Office Collection, dates from 1216–1220 AD and is a heavy (10 kg), large (470 × 395 × 107 mm) volume. It consists of 264 folios with text and sixty illuminations and is valued at more than US$1 million. The large number of illuminations distributed throughout a manuscript of this type is very unusual; they are of high quality and have a rich palette which includes vermilion, lazurite, orpiment, lead white, realgar and pararealgar. Some of the illuminations have suffered serious deterioration of the white pigment, which has turned black in parts. The deterioration is mainly around the edges of the illuminations, and while there are often unaffected central areas for comparison, there are also places where the whole picture is affected. The phenomenon is most striking where the faces of the figures, apparently initially coloured with a mixture of white and red pigments, are affected, creating blackened areas devoid of features (Fig. 1).
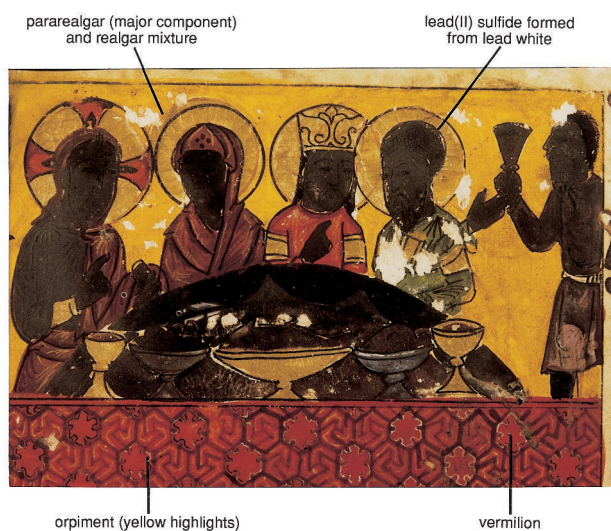
The size of the microscope constricted the study to some of the pages and to only a limited area of each page; nevertheless, it was still possible to analyse certain areas of fourteen of the sixty illuminations, sufficient to cover the full palette. Analysis of the inks and illuminations of the lectionary by Raman microscopy revealed unambiguously the presence of seven pigments.

The most important observation was that the black compound which appears to result from the deterioration of a white pigment, basic lead(II) carbonate $2PbCO_3 \cdot Pb(OH)_2$, commonly known as 'lead white' (Fig. 1), was identified unambiguously to be lead(II) sulfide by comparison of its Raman spectrum with that of a standard sample (Fig. 2). Lead white was identified both pure and mixed with red, blue, purple and brown pigments. All of these mixtures were prone to degradation, but it was invariably the lead white that had degraded whereas the intact blue and red pigments, for example, could sometimes still be detected in areas which were heavily discoloured.

The most likely source of sulfur (as H_2S) causing the deterioration was the polluted London atmosphere of the latter half of the 19th century and first half of this century.[11] The town-gas lighting in use in the British Museum until the 1880s may also have contributed to the problem.

The only recognized conservation treatment for 'reversing' the darkening of lead white on illuminated manuscripts and paintings involves treatment with hydrogen peroxide.[11] Although such a procedure leads to an aesthetic improvement, the white pigment so generated is lead(II) sulfate. The worry about this procedure is that, since two chemical transformations have been carried out *in situ* on the paper [basic lead(II) carbonate → lead(II) sulfide → lead(II) sulfate], the binding of the pigment (through volume expansion/contraction) could deteriorate, and the lead(II) sulfate become friable and crumble from the paper.

The study of the palette of the lectionary also led to the identification of vermilion [mercury(II) sulfide] and lazurite [$Na_8(Al_6Si_6O_{24})]S_n$, a sulfur-containing sodium aluminium silicate extracted from the mineral lapis lazuli. The analysis of the yellow pigments was especially interesting. The well known
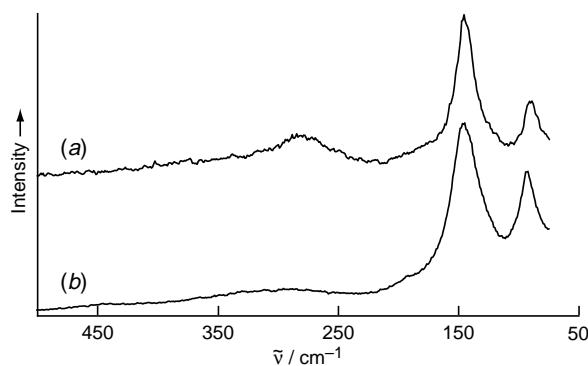

Fig. 1 A detail of the illumination of *f.67r*

pararealgar (major component) and realgar mixture

lead(II) sulfide formed from lead white

orpiment (yellow highlights)

vermilion

Fig. 2 Raman spectra (by Raman microscopy, $\lambda_0 = 514.5$ nm) of (*a*) discoloured area of the illumination of *f.67r* and (*b*) a standard sample of lead(II) sulfide

throughout the manuscript, but it was not the only yellow pigment used. In thirty-two of the sixty illuminations there are examples of a very rich yellow colouration (see, for example, Fig. 1) which differs significantly in appearance from that of orpiment, which has a much lighter hue. Viewed through the microscope, the pigment appears to be dominated by yellow crystals with a significant number of orange ones. Analysis by Raman microscopy revealed that the orange crystals were realgar,[12] arsenic(II) sulfide (As_4S_4), and that the yellow crystals were pararealgar,[13,14] a light-induced transformation product of realgar first identified in 1980 (Fig. 3).[15] There are
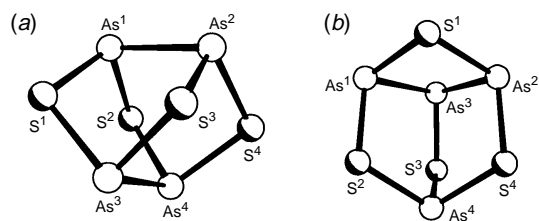

Fig. 3 Structures of (*a*) realar (both α- and β-polymorphs)[12] and (*b*) pararealgar[13]
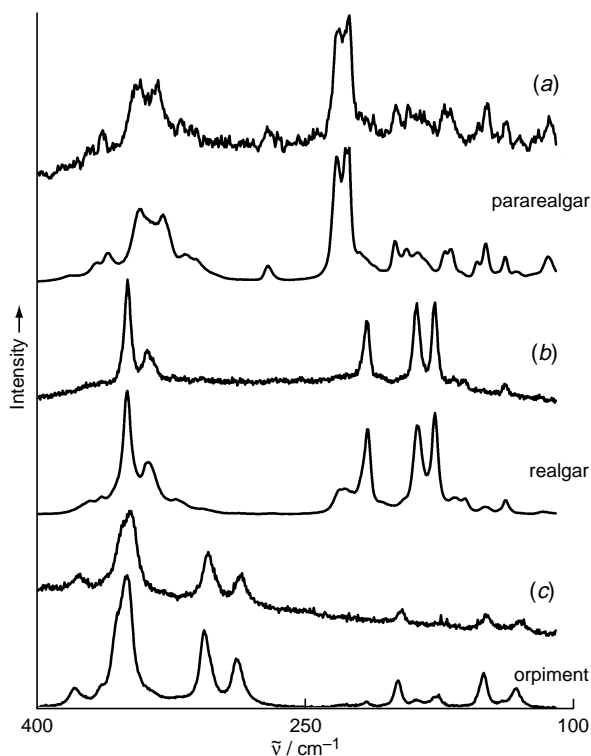

Fig. 4 Raman spectra (by Raman microscopy, $\lambda_0 = 647.1$ nm) of (*a*) the major component of the yellow–orange pigment on *f*.67*r*, (*b*) the minor component of the yellow–orange pigment on *f*.67*r* and (*c*) the yellow pigment used for highlighting the base of the illumination on *f*.67*r*, and of pararealgar, realgar and orpiment

phase, α-As_4S_4, a metastable high-temperature phase, β-As_4S_4, and a light-induced form, χ-realgar. All transform to pararealgar on irradiation with light of wavelengths in the range 500–670 nm, most rapidly with those in the range 530–560 nm.[16] The mechanism of transformation is believed to involve photo-induced breakage and reformation of As–As bonds.[14–16] The rich yellow hue of the pigment always appears in the correct context, and the usage of this particular shade of yellow is widespread throughout the manuscript.

It is clear that the artist did not mistake pararealgar for the more common yellow pigment, orpiment: the artist often used both pigments on the same illumination, showing that he had access to and had used them both as distinct yellow pigments. This is the first time that pararealgar has been observed (*in situ* or otherwise) on any manuscript and it was identified unambiguously by comparison with a genuine sample. The Raman spectra of orpiment, realgar and pararealgar are illustrated in Fig. 4, together with spectra obtained from the yellow pigments used in the illumination on *f*.67*r* of the lectionary (Fig. 1).

This study has resulted in the first effective use of Raman microscopy to determine the nature of a serious conservation problem affecting a very valuable manuscript, and also in the first identification of pararealgar on an illuminated manuscript. These results confirm that Raman microscopy is one of the most useful analytical tools for *in situ* and non-intrusive archaeometric analysis, and one that can provide invaluable information for both scientists and conservators alike.

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