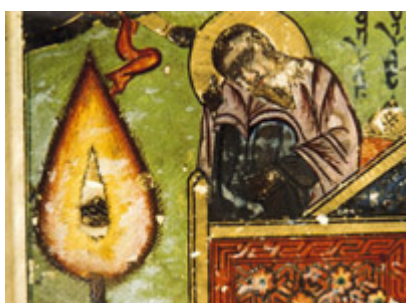


# Raman Microscopy Of A 13th-Century Illuminated Text

*A study of a rare manuscript demonstrates a promising technique for the nondestructive, in situ analysis of historical artifacts.*

[Robin J. H. Clark and Peter J. Gibbs](#)

*University College London (U.K.)*



Many analytical techniques can be used to identify pigments on historical artifacts. Recently, Raman microscopy has emerged as an analytical procedure that satisfies most of the important criteria for the archaeometric analysis of pigments. The technique is sensitive, spatially refined, and immune to interference. It also offers the possibility of in situ and nondestructive analyses. The Raman spectrum for a given pigment is also highly specific. For example, the principal band of interest for lead white (basic lead(II) carbonate) and chalk (calcium carbonate) arises from the  $\nu_1(a_1)$  mode of  $\text{CO}_3^{2-}$ . For lead white, this band is found at  $\sim 1050 \text{ cm}^{-1}$ ; for chalk, the wavenumber is  $\sim 1088 \text{ cm}^{-1}$ . Table 1 compares the effectiveness of Raman microscopy for pigment analysis with that of each technique (1). Difficulties with Raman microscopy may arise if the pigment scatters light weakly or if the laser light leads to either fluorescence or photodegradation.

## [Table 1. Strengths and weaknesses of the main techniques for pigment analysis](#)

To date, the use of Raman microscopy in the field of manuscript analysis has focused on the study of illuminated manuscripts--originally described as manuscripts embellished with luminous colors (especially gold and silver), but the category also includes colored manuscripts. Typically, these studies characterize the artist's palette (1-9). [Related studies have also been done recently on Egyptian faience (10)--glazed earthenware and porcelain--and Italian pottery (11, 12).]

Raman microscopy has enormous potential to provide information that will assist the conservator in preserving manuscripts for future generations. For example, if light-sensitive pigments, or pigments susceptible to other forms of deterioration, were identified on a painting or manuscript, the conservator could make the necessary arrangements to store and display the artifacts in such a way to prevent damage. If deterioration had already occurred, Raman

microscopy could be used to identify the decomposition products and, thus, enable the conservator to consider carefully any treatments that halt or reverse the process.

The effectiveness of Raman microscopy as a tool for archaeometric analysis is illustrated in this article by a case study, undertaken at the request of the British Library, of a rare early 13th-century Byzantine/Syriac Gospel lectionary. The work illustrates how Raman microscopy can be used to identify the palette, establish the nature of the conservation problem, and provide data for informed comment on proposed treatments for reversing the degradation.

### **A rare and fragile manuscript**

The Byzantine/Syriac Gospel lectionary studied here dates from 1216-20 A.D. and consists of 264 folios with text, 114 verso, 115 recto, and 60 illuminations. It is valued at more than \$1 million (U.S.). The relatively large number of illuminations distributed throughout a manuscript of this type is unusual and implies that the lectionary was made for an important person (see box on "[The Byzantine Empire](#)"). Reportedly, the only other manuscript of similar age, style, illumination, and importance is in the Vatican collection.

### **[The Byzantine Empire](#)**

The illuminations on the lectionary are of good quality and have a full palette, but some have suffered serious deterioration of a white pigment that has turned black. The deterioration is mainly around the edges of the illuminations, but the whole picture is affected in other places. Fortunately, unaffected areas provide comparison. The phenomenon is most striking where the figures' faces--apparently initially colored with a mixture of a white and a red pigment--are affected, creating blackened areas devoid of features (Figures 1 and 2).



**Figure 1. Detail of the illumination on f. 231v of the lectionary.**



**Figure 2. Additional detail of the illumination on f. 231v of the lectionary.**

The condition of the manuscript is poor. In addition to the deteriorating white pigment, the brown/black ink that the scribe used for the bulk of the text is clearly visible on the reverse of the thin paper and appears to be corroding it

Also, a considerable amount of calligraphy was done in red ink and in gold leaf with a red border, which does not show through the paper.

### **The analytical technique**

Raman microscopy involves the illumination of a sample with monochromatic light and the analysis of the components that are inelastically scattered--that is, scattered with wavenumbers different from that of the light incident upon the sample. Under the experimental conditions used, the exciting radiation is focused to a spot with  $\sim 1\text{-}\mu\text{m}$  diameter. These conditions define the spatial resolution of the experiment. The Raman spectrum--a plot of the intensity of scattered radiation as a function of the wavenumber shift--is characteristic of the composition and the sample structure. The spectrum is sufficient, when observed with reasonable definition (typically  $S/N \geq 5$ ), to permit unambiguous identification of the sample. In a typical setup, an optical microscope is coupled to a spectrometer with an intensified photodiode array or charge-coupled detector. Laser radiation is brought to focus on each pigment grain on the artifact via the microscope objective. The Raman scattering by the sample initially retraces the path of the incident beam, and is then collected by the same objective and directed to the monochromator and the detector (Figure 3).



**Figure 3. Optical configuration of a Raman microscope.**

Individual grains of the pigments in the inks and illuminations of the lectionary were examined, nondestructively and in situ, with a Raman microscope with a 50x or 100x objective and a 10x eyepiece. The microscope was coupled to an X-Y triple-grating spectrometer with a photodiode array detector, which has a spectral resolution of  $3.5\text{-}7.5\text{ cm}^{-1}$ , depending on the laser beam wavelength. An  $\text{Ar}^+$  laser, operating at excitation wavelengths of 488.0 and 514.5 nm and a power of 5 mW, and a  $\text{Kr}^+$  laser, operating at an excitation wavelength of 647.1 nm and a power of 5 mW, were the light sources. A 10% neutral density filter, which decreased the laser power at the surface to 0.5 mW, was introduced where necessary to reduce the risk of damage from laser light. Integration times of 1-10 s for 10-100 accumulations were used to obtain spectra of sufficient quality for the current study.

Because of the size restrictions of the microscope, only some of the pages--and a limited area of each--could be studied. Despite these constraints, certain areas of 14 of the 60 illuminations could be analyzed. This capability sufficiently covered the full palette of pigments on the manuscript and confirmed all of the observations when compared with the results obtained from studies of several illuminations.

## Analyzing the pigments

Analysis of the inks and illuminations of the lectionary revealed seven pigments, or compounds. The most important observation was that the black compound that seemed to come from the deterioration of a white pigment (Figures 1 and 2) was identified unambiguously to be lead(II) sulfide (Figure 4). The white pigment on the manuscript was identified as basic lead(II) carbonate,  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ , commonly known as "lead white" (or sometimes "white lead"). This compound was discovered in its pure form (Figure 4) and also mixed with red, blue, purple, and brown pigments. These mixtures were prone to degradation, the white pigment being the component that degraded. The blue and red pigments, for example, could sometimes still be detected in areas that were heavily discolored.

The red pigment, identified as mercury(II) sulfide, is known as vermilion (if synthetic) or the mineral cinnabar. Vermilion and lead white together are known as flesh tone (14). Vermilion was the most common pigment used throughout this manuscript and is the only red pigment identified. It was found in the red ink, the red borders of the gold leaf ink, the borders of the illuminations, and in the illuminations themselves. Vermilion was mixed with a black or a yellow pigment, depending on whether the artist required a dark red or an orange color. Raman spectra obtained for vermilion on the manuscript and for a standard are illustrated in Figure 4.

The sole blue pigment identified on the lectionary was lazurite,  $[\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})]\text{S}_n$ , the sulfur-containing sodium aluminum silicate that can be extracted from the mineral lapis lazuli. Its synthetic equivalent is ultramarine blue. Although this pigment is rare and would have been expensive, it was used widely throughout the manuscript. Lazurite was also mixed with lead white to create shades of blue. Figure 4 shows a spectrum of lapis lazuli obtained from the lectionary and a comparison with that of a standard sample. The purple, green, and brown pigments on the lectionary, which were often mixed with lead white, did not give useful Raman spectra and could not be identified. They were almost certainly organic pigments.



**Figure 4. Raman microscope spectra of various pigments.**

The analysis of yellow pigments on this manuscript provided the most interesting results. Orpiment, arsenic(III) sulfide ( $\text{As}_2\text{S}_3$ ), was found throughout the manuscript (15). Occasionally, it was used as a pure pigment to cover a large area, especially in the patterns at the beginning of the manuscript. The pigment, however, was mainly found in the pure form, adding small highlights to the green or red cloaks of the figures in the illuminations. Examples of both occurrences appear in the angel's cloak in Figure 1.

Orpiment was not the only yellow pigment used on this manuscript. Examples of a rich yellow coloration (see, for example, Figure 2), the hue of which is much deeper than that of orpiment, appear in 32 of the 60 illuminations. When viewed through the microscope, the pigment seemed to be dominated by yellow crystals with a significant number of orange ones. Recent analysis by Raman microscopy revealed (15) that the latter are realgar,  $\text{As}_4\text{S}_4$ , and that the yellow crystals are pararealgar, a light-induced transformation product of realgar first identified in 1980 (16). For the first time, pararealgar was observed (in situ or otherwise) on a manuscript; it was identified unambiguously by comparison with a genuine sample.

## The palette

The most extensive, recent study of illuminations on Byzantine manuscripts appeared in a treatise on Armenian manuscripts (17). The authors of the relevant section tabulated the results of studies on nine Byzantine manuscripts, all from the University of Chicago and dating from the 10th to late 13th centuries, principally to compare them with Armenian material. The pigments were identified primarily by microscopy (i.e., by viewing down a microscope) or by X-ray crystallography. Nevertheless, numerous findings shared commonalities, such as lapis lazuli and vermilion on five of the nine manuscripts (although these two pigments were both present on only four) and orpiment on one manuscript. In general, however, they noted that Byzantine illuminations tended to be rather dull and lifeless.

The lectionary is, therefore, a rare example of a surviving manuscript illuminated in the Byzantine style that still has a vibrant coloration. This finding emphasizes the significance of fully understanding the nature of the degradation problem, which has had such a devastating effect on many areas of the illuminations. The free use of lapis lazuli and gold leaf throughout the lectionary suggests that little expense was spared in its creation. Yet, this assumption is seemingly contradicted by the use of crude paper as a supporting medium. Paper, however, was commonly used at that time and in that region in preference to the typical medium, vellum, for important manuscripts of this age and type.

## Pararealgar

When natural realgar ( $\alpha\text{-As}_4\text{S}_4$ )--an orange-red pigment derived from the natural mineral of the same name--is exposed to light, a friable yellow material develops on the surface. Until recently, this material was mistakenly identified by mineralogists and conservation scientists as orpiment. In 1980, Roberts et al. (16) reported that the friable yellow material, which they characterized by X-ray diffraction (XRD), is pararealgar, a polymorph of realgar.

Several polymorphs of  $\text{As}_4\text{S}_4$  are known: A natural low-temperature phase,  $\alpha\text{-As}_4\text{S}_4$ , and a metastable high-temperature phase,  $\beta\text{-As}_4\text{S}_4$ , can be produced synthetically (18). Pararealgar is the light-induced polymorph of the low- and high-temperature phases (19). The structural differences among the known

polymorphs of  $\text{As}_4\text{S}_4$ , along with their XRD data and Raman spectra, have been reported. The conversion of natural realgar to pararealgar is believed to involve the breaking and reforming of As-As bonds (20). A paper on the spectroscopic investigation and normal-mode analysis of  $\alpha$ - $\text{As}_4\text{S}_4$ ,  $\beta$ - $\text{As}_4\text{S}_4$ , and pararealgar was published almost simultaneously (21), in which the transformation of realgar to pararealgar by absorption of laser radiation was monitored. The compound  $\alpha$ - $\text{As}_4\text{S}_4$  absorbs poorly at 647.1 nm-- the wavelength used in this study--and the transformation is slow (21). Radiation of longer wavelengths is scarcely absorbed by  $\alpha$ - $\text{As}_4\text{S}_4$ . Radiation of shorter wavelengths (optimally 530-560 nm), however, is readily absorbed. In this study, the conditions of irradiation at 647.1 nm (0.5 mW for ~1 min) were insufficient for a light-induced transformation of  $\alpha$ - $\text{As}_4\text{S}_4$ . (Trentelman et al. (20) also reported the results of the identification of pararealgar on a sample removed from a painting by the Renaissance master Tintoretto.)

Another question must be considered as a result of this discovery: Was the pararealgar on this manuscript applied by the artist as one of the original pigments, or was it the light-induced transformation product of realgar? Certainly, the rich hue of the yellow pigment in which pararealgar was identified on the lectionary is enhanced by the minority presence of natural realgar (also identified). However, the pararealgar is thought to have been applied deliberately by the artist. First, the rich yellow pigment always appears in the correct context. When the artist required an orange-red color, which could have been obtained by applying unaltered realgar, the pigment used was identified by Raman microscopy to be either plain vermilion or vermilion mixed with orpiment, as seen on the angel's cloak in Figure 1. As the rich yellow color of pararealgar is often found adjacent to the red and orange pigments of vermilion or vermilion and orpiment, it is more likely that the artist intended the original color to be yellow. In any case, realgar is not widely documented as having been used as an original pigment (20, 22). One can envisage the medieval pigment as having been scraped from the surface of a lump of realgar that had been left in sunlight, leaving a small amount of natural realgar behind as an impurity.

The second reason, and perhaps the more conclusive, is that usage of this particular shade of yellow throughout the manuscript is widespread. It was identified visibly on 32 of the 60 illuminations. It is unlikely that, had natural realgar been applied to all 32 illuminations, each page would have been subjected to identical light conditions, and thus a similar degree of transformation to pararealgar for each illumination would not have occurred.

Also interesting to note is that the artist did not mistake pararealgar for orpiment and that the rich yellow of pararealgar was clearly preferred over the paler yellow of orpiment for large areas. Orpiment was instead preferred for highlighting and mixing. This distinction is illustrated by the artist's frequent use of pararealgar and orpiment on the same illumination, thus demonstrating the artist's simultaneous access to both compounds as distinct yellow pigments.

## Degradation problem

Lead white, used as a pure pigment and in admixture with other pigments such as vermilion and lapis lazuli to illuminate this manuscript, is historically the most important of all lead pigments. Its dominance as a white pigment was not broken until the introduction of zinc oxide in the 19th century (14). Although lead white is a carbonate, hence reactive to acids, it has a good record for permanence and is unaffected by light. The most serious conservation problem associated with lead white is blackening, which has most often been observed on paintings in which the pigment was applied as a watercolor. When lead white was applied in other media, such as egg tempera or linseed oil, however, it has often remained apparently unaffected for centuries (14). One theory is that the blackening effect is caused by an interaction of the lead white with atmospheric hydrogen sulfide to form the compound lead(II) sulfide. This interaction may be prevented by an oil medium or a coat of varnish.

Unambiguously proven is that the black compound found in the deteriorated areas of the lectionary is, indeed, lead(II) sulfide. Potential sources of sulfur, such as vermilion (HgS), orpiment (As<sub>2</sub>S<sub>3</sub>), realgar, and pararealgar (both As<sub>4</sub>S<sub>4</sub>), are among the pigments on the manuscript. Yet, flesh tones have survived for centuries on paintings, with no recorded sign of deterioration (14). The flesh tone used on the lectionary is stable in many areas. Orpiment, realgar, and pararealgar apparently do not react with lead white, even though the pigments are adjacent to one another on many areas of the manuscript. The most likely sources of sulfur, as H<sub>2</sub>S, are the polluted London atmosphere of the late 19th century and the town-gas lighting used in the British Museum until the 1880s.

A recognized conservation treatment, using hydrogen peroxide to oxidize the black lead(II) sulfide to lead(II) sulfate (14), can "reverse" the effects of lead darkening on paintings and illuminated manuscripts. Though this treatment is often credited with reversing lead white blackening (23, 24), "reversal" is not an accurate term; the final product is a sulfate, whereas the original pigment was a carbonate. The original pigment will have undergone two chemical reactions in situ on the paper, and this process is likely to affect the pigment binding (through volume expansion or contraction) to the paper fibers. Hence, the conservator must consider whether the extensive treatment described previously would result in a friable white pigment, which could then crumble from the paper.

## Conclusion

This article illustrates the effective use of Raman microscopy to determine the nature of a serious conservation problem affecting a valuable manuscript. Evidence reveals that deterioration of the illuminations is caused by a transformation of the lead white pigment to black lead(II) sulfide. Five pigments have also been detected: vermilion, lapis lazuli, orpiment, realgar, and pararealgar. The last has not been detected previously on any manuscript nor has it been identified previously in situ and noninvasively on any historical

artifact. These results show that Raman microscopy is one of the most useful analytical tools currently available for archaeometric analysis and one that provides, by in situ and nonintrusive study, invaluable information for conservators.

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*Robin J. H. Clark is Sir William Ramsay Professor and Head, Department of Chemistry, University College London. His research has embraced many aspects of inorganic chemistry and spectroscopy, notably the chemistry of mixed-valence compounds and electronic, IR, Raman, and resonance Raman spectroscopy. Peter J. Gibbs is a postdoctoral fellow at University College London. He specializes in the application of analytical techniques, particularly Raman microscopy, to the analysis of historical artifacts with conservation problems. Address correspondence to Clark at Dept. of Chemistry, University College London, 20 Gordon St., London WC1H 0AJ, U.K. ([r.j.h.clark@ucl.ac.uk](mailto:r.j.h.clark@ucl.ac.uk)).*