JOURNAL OF RAMAN SPECTROSCOPY
J. Raman Spectrosc. **30**, 307–311 (1999)

Spanish Mediaeval Frescoes at Basconcillos del Tozo: a Fourier Transform Raman Spectroscopic Study

H. G. M. Edwards,[1]* D. W. Farwell,[1] F. Rull Perez[2] and S. Jorge Villar[3]
[1] Chemical and Forensic Sciences, University of Bradford, Bradford BD7 1DP, UK
[2] Cristalografia y Mineralogia, Facultad de Ciencias, Universidad de Valladolid, Prado de la Magdalena s/n, 47011 Valladolid, Spain
[3] Area de Geodinamica, Facultad de Humanidades y Educacion, Universidad de Burgos, Calle Villadiego s/n, 09006 Burgos, Spain

The late mediaeval frescoes in the Church of SS Cosmo and Damian at Basconcillos del Tozo, Castille y Léon, Spain, were studied using Fourier transform Raman spectroscopy. The paintings were only discovered about 3 years ago and afforded a rare opportunity for spectroscopic analysis of pigments and substrata which have not been subjected to cleaning or re-touching over the last 600 years. Although in a polychrome palette, the most common pigments were reds, followed by black, yellow and blue; 20 samples were taken for analysis. The red pigments were identified spectroscopically and a hierarchical application is evident, with pure cinnabar being used for only the most important biblical figures. There is evidence in two of the samples taken of hydrated calcium oxalate, probably arising from lichen colonization, but it is not possible to infer whether this is pre- or post-mural painting. The substrate shows no evidence for the presence of a gypsum plaster. The difference between the red pigments in the paintings is associated spectroscopically with mixtures of red ochre and cinnabar in the figures and also organic coloured resins in the background. There is also some spectroscopic evidence for the inclusion of red lead in figures in the lower panels.

INTRODUCTION

Mediaeval wall paintings in churches were fairly common between the twelfth and fifteenth centuries, but very few have survived the ravages of time and environmental exposure; often, fragments are discovered during structural repair work, when later applications of paint or limewash are removed. The scenes commonly depict religious and moral subjects and details from the lives of popular saints; the paintings probably had some importance as reminders of important biblical events, and are usually accompanied by geometrical patterns and decoration.

Conservation of mediaeval wall paintings is subject to the same basic principles as other branches of conservation: preservation is the prime objective.[1] However, one of the main difficulties with mural paintings is that they have been executed as part of a standing building and have, in effect, become part of the archaeology of the structure. It is therefore of primary importance to determine both the chemical and physical nature of the materials employed and the substrate in the formulation of a satisfactory conservation strategy.

The very close association between the wall painting, its substrate and the masonry of the ecclesiastical or other structure raises several problems for conservators and heritage scientists, since air pollution,[2] biological organism invasion,[3] changes in temperature and humidity[4] and natural phenomena such as earthquakes can have disastrous effects on the stability and integrity of the artwork. More subtle changes arising from the presence of human beings, e.g. soot and hydrocarbons from smoking lamps and candles, reactivity of body vapours and perspiration and the instability of the pigments or pigment mixtures with time, also produce dramatic deterioration in wall paintings. For example, even though it was recognized by Roman artists that *minium*, mercury(II) sulphide (HgS), and *minium secondarium*, lead tetraoxide (Pb_3O_4), were unstable in admixture,[5] there are reported instances of adulterated pigments being used for presumably economic reasons; an example of this was found in our laboratories during a Raman spectroscopic study of the mediaeval wall painting of the 'Entombment of Christ' in Winchester Cathedral, UK, where a significant dilution of expensive cinnabar with cheaper red ochre had been undertaken.[6]

Although there is a substantial body of work which describes the application of Raman spectroscopic techniques to pigment analysis on ancient manuscripts, many of which have been preserved in scriptoria or libraries under special conditions, the situation with regard to wall paintings is less well defined. Some early work has been reviewed recently by Coupry and Brissaud[7] and we have reported Raman spectroscopic studies of Italian Renaissance frescoes,[8] American Indian prehistoric cave art[9,10] and Islamic-influenced frescoes at the Convento de la

* Correspondence to: H. G. M. Edwards, Chemical and Forensic Sciences, University of Bradford, Bradford BD7 1DP, UK.
Contract/grant sponsor: British Council.
Contract/grant sponsor: Spanish Ministry of Education and Science.

CCC 0377–0486/99/040307–05 $17.50

Received 25 June 1998
Accepted 4 December 1998

(a)

(b)

(c)

Plate 4. Mediaeval wall paintings in the Church of SS Cosmo and Damian at Basconcillos del Tozo, Castilla y Léon, Spain. (a) The Central figure is Christ supported by St John at the right and Virgin Mary at the left; (b) St Peter occupies the lower panel along with scenes depicting Adam and the Garden of Eden: (c) the lower panel on the right of the window shows a demonic figure and Purgatory (see 'Spanish Mediaeval Frescoes at Basconcillos del Tozo: a Fourier Transform Raman Spectroscopic Study' by Edwards, Farewell, Rull Perez and Villar)

Peregrina (Sahagún) (H. G. M. Edwards, F. Rull Perez, A. Rivas and L. Drummond, to be published).

In this paper, we report the results of our Raman spectroscopic study of 20 specimens of pigment and substrate from the Church of SS Cosmo and Damian in Basconcillos del Tozo, Castille y Léon, Spain. During removal of a fifteenth century carved reredos 3 years ago, mediaeval wall paintings were discovered which had been covered for about 600 years. This important discovery afforded an excellent opportunity for the application of the Raman spectroscopic technique to the characterization of these paintings, which were in fine condition and had obviously not been re-touched or cleaned in the intervening time. Historically, therefore, we were looking at an original mediaeval work of art which has not been modified in any way to suit later tastes.[11,12]

EXPERIMENTAL

Samples

Twenty specimens of pigment and limestone substrate were taken from the recently discovered wall paintings in the Church of SS Cosmo and Damian in Basconcillos del Tozo, Castille y Léon, Spain. The paintings covered the whole eastern wall of the church (Fig. 1 and Plate 4) from a height of about 2 m to the roof beams, and also extended part way along the side walls; they were contained by a geometric border in red and black. The scenes were biblical in origin; the centrepiece above the window consisted of Christ flanked by St John and the Virgin Mary with attendant angels. At lower left, a panel depicted St Peter and Adam, and a lower right panel showed demonic scenes from Purgatory. The predominant palette consisted of reds, followed by black, yellow and one blue (that of the cape of the Virgin Mary). The paintings are of considerable importance because of their seclusion, which means that they have not been subject to re-touching or modification since the fifteenth century.

Raman spectra

Fourier transform (FT) Raman spectra were excited at 1064 nm using an Nd:YAG laser and a Bruker IFS 66 optical bench with an FRA 106 Raman accessory. To avoid any possible thermal degradation of the highly coloured pigments, the laser was operated with a maximum power of 100 mW and up to 2000 scans at 8 cm^{-1} resolution were accumulated. For some specimens, the use of a Raman microscope attachment was dictated; a Nikon Optiphot microscope with 40× or 100× objective lenses gave sampling areas of 20 and 8 μm, respectively, for which a reduced laser power of *ca* 20 mW maximum was used.

It is important to emphasize that the FT-Raman analysis carried out in this study was non-destructive of the specimens taken.

Figure 1. The Church of SS Cosmo and Damian at Basconcillos del Tozo, Castille y Léon, Spain.

RESULTS AND DISCUSSION

Visually, the red pigmentation in particular changed in depth of colour over different regions of the wall paintings, from dark red in the main central scene to lighter red for the bottom panels and a deep orange red for the window surrounds. The following conclusions can be drawn.

The cloak of Christ, the tunic of St John and the hem of the Virgin Mary's tunic all contain cinnabar, mercury(II) sulphide (HgS), with characteristic Raman bands at 253, 285 and 343 cm^{-1}. An example is shown in Fig. 2, which is the FT-Raman spectrum of the specimen from St John's cloak (the figure to the right of Christ in Plate 4). The absence of features due to calcite (1086, 712 cm^{-1}) and gypsum plaster (1007 cm^{-1}) in this spectrum are noteworthy;[8] no 'dilution' of the cinnabar pigment by calcite or gypsum was therefore undertaken by the artists and there has been no adulteration by cheaper red pigments such as red lead or red ochre. The latter was found spectroscopically in the early mediaeval wall paintings at Winchester Cathedral in the UK.[6]

A weak band at 464 cm^{-1} appears in the Raman spectrum of the specimen from Christ's cloak only (Fig. 3; expanded wavenumber scale); this is of great interest since the two major natural sources of cinnabar in Spain in mediaeval times were the mines at Almaden and Tarna. In a previous study, we demonstrated that natural cinnabar pigments from the volcanic Almaden mines[5] always contain α-quartz. We therefore assert that the cinnabar pigment for Christ's cloak probably came from an Almaden source, whereas the cinnabar for the other central figures of importance was obtained from another non-volcanic source; a good local candidate for the latter would be the mines at Tarna in Léon, which are close to the Church in Basconcillos del Tozo. The hierarchical religious significance of the different sources for such pigments is conjectural but perhaps Almaden cinnabar was more highly regarded than the local product, which nevertheless was still used for the other important figures in the central scene.

The red pigments used for the other characters in the wall paintings also provide scope for discussion. The red-pigmented important figure of St Peter holding the key to the Kingdom on the lower left panel has a complex spectrum (Fig. 4; St Peter's cloak). Here, there is evidence not only of a small amount of cinnabar, but also significant amounts of calcite (1086, 712, 280 cm^{-1}), a broad feature near 780 cm^{-1} assigned to limewash or silicate,[5] quartz (465 cm^{-1}) and much weaker features near 1525 (not shown) and 1150 cm^{-1}, which we have previously assigned to carotenoids.[13] A weaker feature near 400 cm^{-1} is characteristic of red ochre, perhaps used as a diluent pigment. The angel's cloak in the right hand part of the central scene also has a complex spectrum (Fig. 5) which contains a broad limewash or silicate feature near 800 cm^{-1}, some cinnabar and red

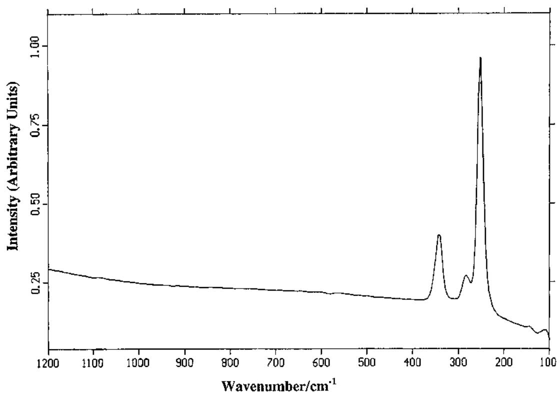

Figure 2. FT-Raman spectrum of red pigment from the cloak of St John, central scene; 1064 nm excitation, 8 cm^{-1} spectral resolution, 1000 scans accumulated over the wavenumber range 100–1200 cm^{-1}. The spectrum is that of pure cinnabar.

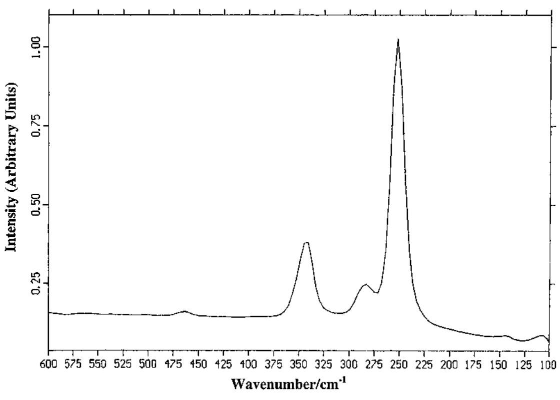

Figure 3. FT-Raman spectrum of red pigment from the cloak of Christ, central figure; conditions as in Fig. 2, but expanded wavenumber scale, 100–600 cm^{-1}.

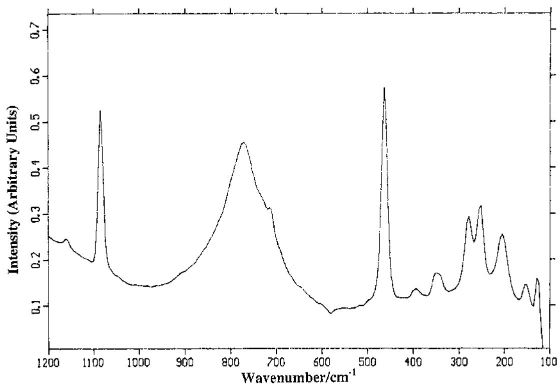

Figure 4. FT-Raman spectrum of red pigment from St Peter's cloak, lower scene at left of wall painting; conditions as in Fig. 2. The complexity of the spectrum relative to those of Figs 2 and 3 should be noted.

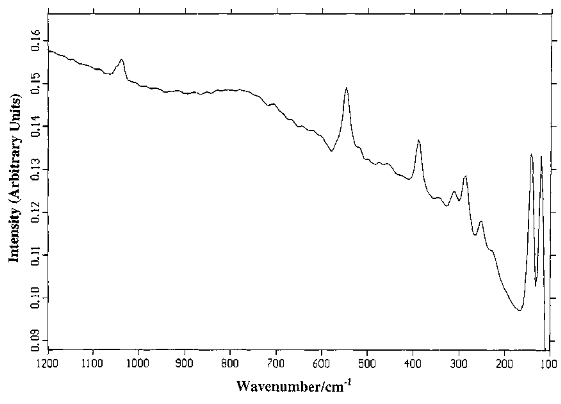

Figure 5. FT-Raman spectrum of red pigment from angel's cloak at right hand of main scene; conditions as in Fig. 2.

lead (550 cm^{-1}), but also a medium-weak intensity band at 1050 cm^{-1} which is characteristic of white lead, a lead carbonate. Impure red lead manufacture in antiquity would be expected to have some carbonate present. However, the red pigment constituting the trumpet of the other angel in the same central scene comprises red ochre, quartz, calcite and limewash/silicate and there is no evidence for cinnabar. In contrast, the pigment constituting the cloak of the angel in the left-hand panel of the same central scene can be described as mainly cinnabar with some red ochre and calcite, but no limewash!

The red pigments which depict blood from Adam (lower left) and the demonic creature (lower right) are also complex mixtures spectroscopically (Fig. 6). Both contain significant amounts of calcite and limewash/silicate, with some quartz, and clearly contain cinnabar. The presence of lead tetraoxide (Pb_3O_4) in these figures is clearly indicated by the bands at 550 and 390 cm^{-1}; significant adulteration of the red pigments has occurred for these figures, bearing in mind the obviously larger molecular scattering factor for cinnabar over red ochre and red lead.

The 'structural' pigment colours comprising the background surrounds to the central window and the wall on the left-hand side are also visually distinct from the red pigments used for the figures described above. These are unique in the current study in showing no evidence for red ochre, red lead or cinnabar in their Raman spectra (Fig. 7). However, there is evidence for significant proportions of calcite and limewash of silicate, with some quartz; we have been unable to identify the colouring material from organic dyes, with unsaturation in the region of 1600, 1440 and 1340 cm^{-1}; earlier Raman spectroscopic studies of archaeologically degraded coloured resins such as dragon's blood, shellac and rosin[14,15] give credence to this statement with C=C, aromatic rings and CH_2 groups being present. Perhaps of even greater significance, however, is the observation in Fig. 7, for the first time in the current series of specimens, Raman bands at 1007 cm^{-1} due to gypsum and a band at 1476 cm^{-1}, which we have seen in biodegraded rock substrata and earlier fresco studies and assigned to the ν(CO) stretching mode of calcium oxalate dihydrate (weddelite). The significance of the observation of this band in these particular locations on the wall paintings is borne out with its attribution to biodeteriorative lichen invasion.[3,16] Oxalic acid produced in the mycobiont of invading, colonizing organisms reacts with calcareous substrata and forms hydrated calcium oxalate; the extent of the hydration depends critically on the local environment;[4] under cold, damp conditions the dihydrate is favoured and we have shown that lichens are able to control strategically their water uptake using calcium oxalate under environmentally stressed conditions.[17,18] Obviously, the regions near the central window and the outer church wall are prone to airborne invasion by lichen spores and conservators of these paintings must monitor the damage. In earlier papers from our laboratory, we have shown that such a lichen colonization can irreparably destroy important wall paintings and architectural surfaces.[3,8,13,19]

The black pigment in the wall paintings, which we sampled from the geometric designs and Latin inscription, is carbon from soot or lamp-black, as expected.[10]

The yellow pigment did not yield good-quality spectra, but we were able to identify it as yellow ochre and eliminate the alternatives massicot, realgar and orpiment.[20] The presence of quartz is evident and may have been incorporated possibly as an aid to grinding with the use of silver sand; calcite is also present.

Finally, blue pigment is found in only one location on the paintings, namely the Virgin's cape. This has been identified as lapis lazuli, a semi-precious pigment which again lends credence to its use only for the most important historical figure(s) in the scene (Fig. 8).[20]

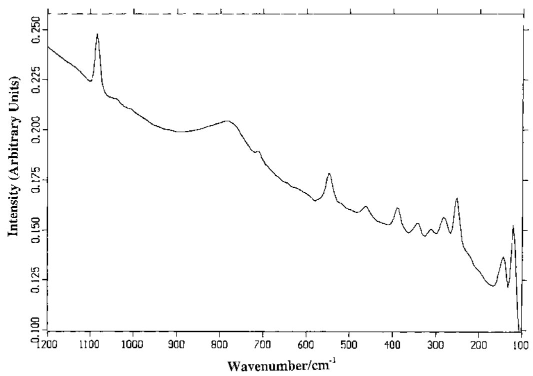

Figure 6. FT-Raman spectrum of sample of blood from Adam figure (Plate 4); the pigment is a mixture of red lead and cinnabar, with calcite and limewash/silicate.

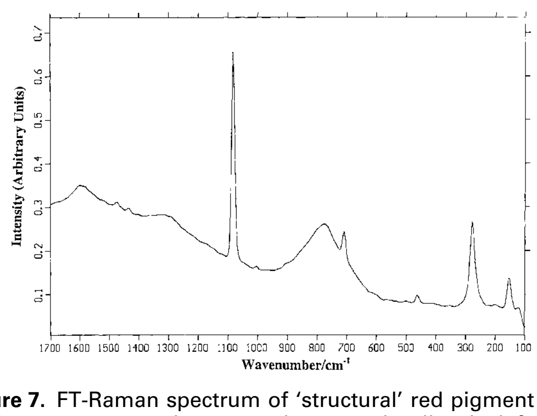

Figure 7. FT-Raman spectrum of 'structural' red pigment from window recess, central scene, and structural wall to the left of the murals; conditions as in Fig. 2 but 3000 scans accumulated over the wavenumber range 100–1700 cm^{-1}. The absence of cinnabar and red ochre is to be noted, as is the presence of a feature at 1476 cm^{-1} indicative of calcium oxalate dihydrate (weddelite) which we ascribe to lichen colonization. Another unique feature in this study is the band due to $\nu(SO_4{}^{2-})$ of gypsum at 1007 cm^{-1}.

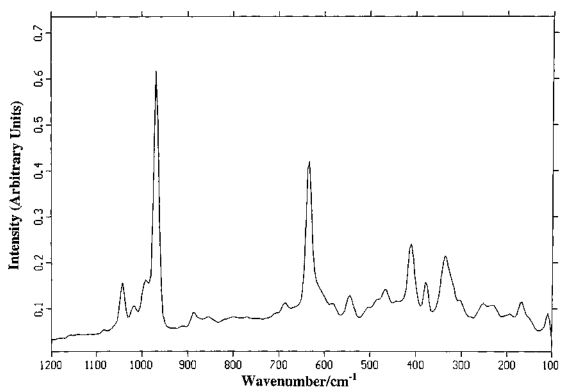

Figure 8. FT-Raman spectrum of lapis lazuli, the semi-precious pigment used for the cap of the Virgin Mary; conditions as in Fig. 2.

Without a detailed knowledge of artistic techniques used in this period in northern Spain, we are currently unable to provide information of a more precise nature concerning the broad feature near 800 cm^{-1} assigned to limewash or silicate, both of which were used as pre-mural treatment or inorganic binding agents.

CONCLUSIONS

The Raman spectroscopic study of the 20 specimens of pigment from the Church of SS Cosmo and Damian in Basconcillos del Tozo has provided some unique information which has hitherto been unsuspected. A hierarchical use of pigments is suggested—only the most important biblical figures have been painted with the most precious pigments. This has previously been noted[20] with historiated mediaeval manuscripts, but this is the first time that it has been observed spectroscopically in wall paintings. In other cases, adulteration of pigments has been practised in common with other studies we have made of mediaeval wall painting. Of some additional interest is the identification of cinnabar from an Almaden source which has been used only for the figure of Christ and we accord this some special significance. The almost haphazard use of mixtures of pigments and diluents for other figures in the scenes is possibly explicable on the basis of several groups of artisans working on the project, each having their individual technology for local pigment preparation.

The use of a natural, coloured resin akin to 'Dragon's Blood' but as yet unidentified for the background colours on larger areas of the murals is also suggested; the pigment coloration is certainly very different from the others used in this art-work.

We have identified the presence of hydrated calcium oxalate in two locations of the 20 samples on the wall paintings; whereas this could have remained from lichen or fungal hyphae after the initial wall preparation for the paintings in the fourteenth century, it is equally likely that there could be evidence here for more recent lichen or fungal invasion. We advise that this should be monitored and subjected to closer examination by art conservators, with more comprehensive sampling at the site.

Acknowledgements

We are grateful for the assistance and generosity of F. Jose Valdavida Lobo in the taking of samples for our analysis, to the Junta of Castille y Léon for sanctioning our investigation and to the British Council/Spanish Ministry of Education and Science 'Accion Integrada' scheme for support in this international research collaboration.

REFERENCES

1. P. M. Schwartzbaum, in *Conservation of Wall Paintings*, edited by P. Burman, pp. 13–16. Council for the Care of Churches, London (1986).
2. M. Del Monte, C. Sabbioni and G. Zappia, *Sci. Total Environ.* **67**, 17 (1987).
3. M. R. D. Seaward and H. G. M. Edwards, *J. Raman Spectrosc.*, **28**, 691 (1997).
4. H. G. M. Edwards, N. C. Russell, M. R. D. Seaward and D. Slarke, *Spectrochim. Acta, Part A* **51**, 2091 (1995).
5. H. G. M. Edwards, D. W. Farwell and S. Rozenberg, *J. Raman Spectrosc.* in press.
6. H. G. M. Edwards, C. J. Brooke and J. K. F. Tait, *J. Raman Spectrosc.* **28**, 95 (1997).
7. C. Coupry and D. Brissaud, in *Raman Microscopy: Developments and Applications*, edited by G. Turrell and J. Corset, Chapt. 10. Academic Press, London (1996).
8. H. G. M. Edwards, E. R. Gwyer and J. K. F. Tait, *J. Raman Spectrosc.* **28**, 677 (1997).
9. J. Russ, L. Palma, D. H. Loyd, D. W. Farwell and H. G. M. Edwards, *Geoarchaeology*, **10**, 43 (1995).
10. J. Russ, H. G. M. Edwards and L. Drummond, *Stud. Conserv.* in press.
11. S. Hughes, *New Sci.* **128**, 21 (1990).
12. A. E. A. Werner, *The Scientific Examination of Paintings*. Royal Institute of Chemistry Monograph No. 4, Royal Institute of Chemistry, London (1952).
13. H. G. M. Edwards, *Microsc. Anal.* **59**, 5 (1997).
14. H. G. M. Edwards, D. W. Farwell and A. Quye, *J. Raman Spectrosc.* **28**, 243 (1997).
15. H. G. M. Edwards, D. W. Farwell and L. Daffner, *Spectrochim. Acta, Part A* **52**, 1639 (1996).
16. H. G. M. Edwards, N. C. Russell and M. R. D. Seaward, *Spectrochim. Acta, Part A* **53**, 99 (1997).
17. D. D. Wynn-Williams, N. C. Russell and H. G. M. Edwards, in *Ecosystem Processes in Antarctic Ice-Free Landscapes*, edited by W. B. Lyons, C. Howard-Williams and I. Hawes, pp. 77–88. Balkema Press, Amsterdam (1997).
18. H. G. M. Edwards, D. W. Farwell and M. R. D. Seaward, *Lichenologist* **29**, 83 (1997).
19. M. R. D. Seaward and H. G. M. Edwards, *Cryptogamic Bot.* **5**, 282 (1995).
20. R. J. H. Clark, *Chem. Soc. Rev.* **24**, 187 (1995).

