

SUMMARY REPORT: 171.09

Subject: Analysis of a paint sample from a mural of *St Christopher*
Location: St John the Baptist Church (Lound, Suffolk)
Client: Fiona Johnson, Cliveden Conservation
Date: November 2022

1. INTRODUCTION

A sample of paint from a 1920s mural of *St Christopher* at St John the Baptist Church (Lound, Suffolk) has been provided for analysis in order to determine the composition of the materials present and establish possible reasons for the observed delamination of the paint; restoration work to the mural in the mid-20th century which included overpainting may have had an effect (Figure 1). The following report presents a summary of the findings with details of the analytical techniques used provided in Appendix I.

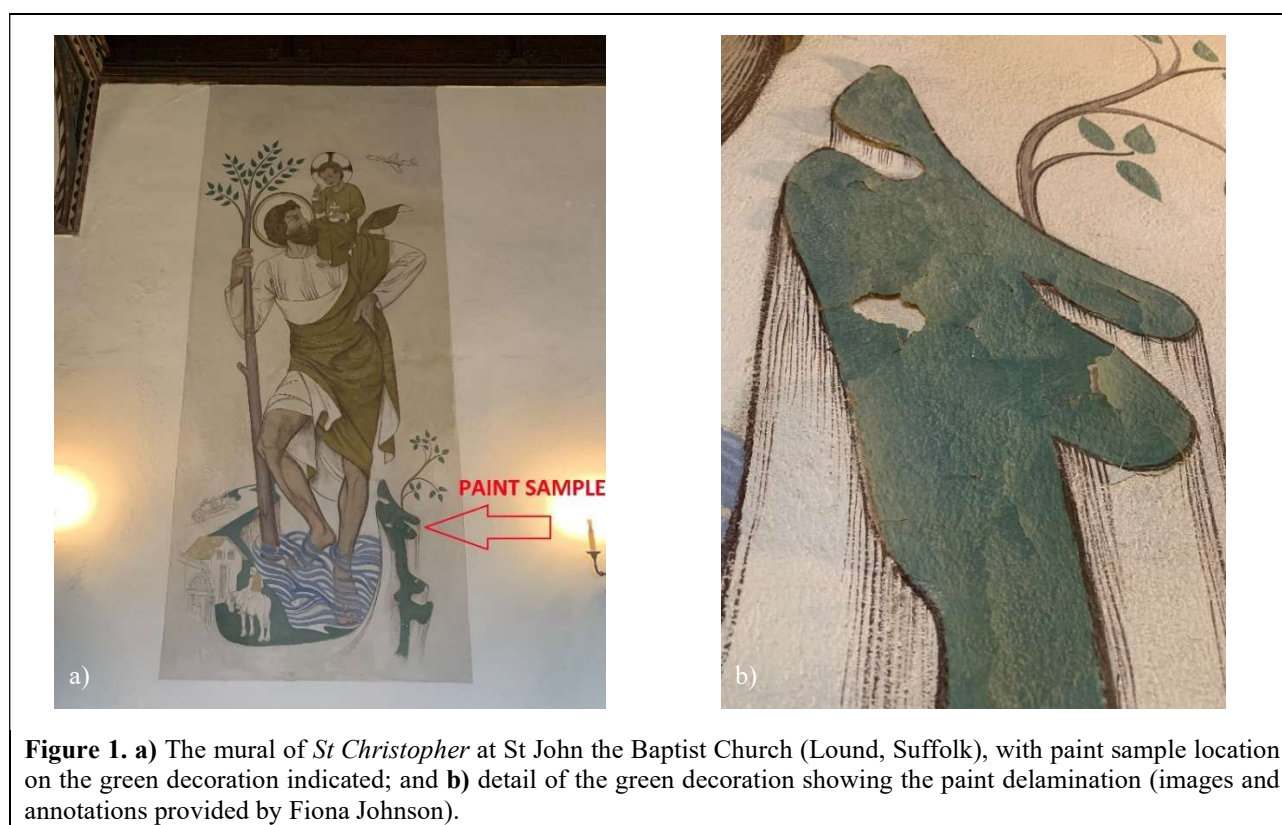


Figure 1. a) The mural of *St Christopher* at St John the Baptist Church (Lound, Suffolk), with paint sample location on the green decoration indicated; and **b)** detail of the green decoration showing the paint delamination (images and annotations provided by Fiona Johnson).

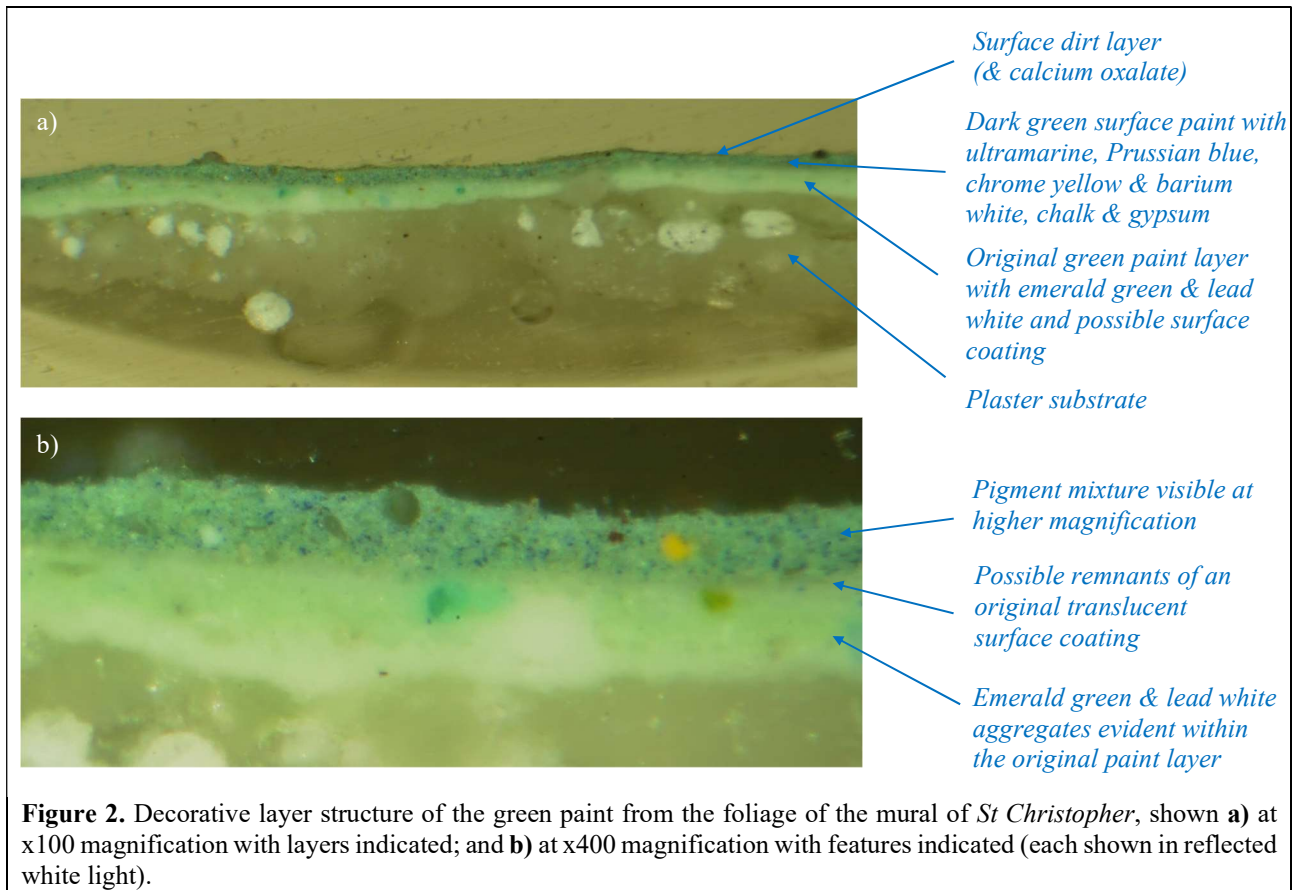
2. RESULTS

The decorative layer structure of the green paint used for the foliage decoration on the mural consists of a green paint layer composed of *emerald green*¹ and *lead white*² applied to the plaster substrate;

¹ *Emerald green* is a synthetic copper-arsenic compound ($\text{Cu}[\text{C}_2\text{H}_3\text{O}_2] \cdot 3\text{Cu}[\text{AsO}_2]_2$); it was sold commercially from 1814 under the name *Schweinfurt green* after its manufacturing location in Germany, and under names such as *Mitis green* and *Vienna green* where it was also first produced in Austria in 1814. It appears to have been used more widely from in paints from c.1830 onwards (Fiedler, I. & Bayard, M.A. 'Emerald Green and Scheele's Green' in *Artists' Pigments. A Handbook of their History and Characteristics* 3 (ed: E.W. FitzHugh) Oxford University Press (1997) 219-271).

² *Lead white* is an umbrella term that encompasses a wide range of white lead-based paints but typically refers to the more common basic lead carbonate pigment ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$), used almost routinely from antiquity until the 1970s (although its use declined with the introduction of less toxic pigments such as zinc white, barium white and the titanium dioxide whites (Gettens, R.J., Kuhn, H. & Chase, W.T. 'Lead White' in *Artists' Pigments. A Handbook of their History and Characteristics* 2 (ed: A. Roy) Oxford University Press (1993) 67-82).

the paint may have been added as two layers applied in rapid succession with only weak evidence for any boundary between them. Remnants of a translucent coating are apparent at the surface of the original green paint in some areas of the sample. A darker green surface paint was subsequently added which contains *ultramarine blue*, *Prussian blue*, *chrome yellow*, *barium white* and *chalk*^{3,4,5,6,7}; a small amount of *titanium white* may also be present.⁸ A dirt layer has since accumulated at the paint surface, with calcium oxalate deposits also formed (Figure 2). No evidence for paint delamination within the layer structure was observed.



3 *Ultramarine blue* $[(\text{Na,Ca})_8[(\text{Al,Si})_{12}\text{O}_{24}](\text{S},\text{SO}_4)]$, the synthetic form of the mineral lazurite derived from lapis lazuli, was discovered in France in 1787 and became widely commercially available from c.1828 onwards. It is distinguished from its natural counterpart by its smaller grain size, its narrower grain size distribution and complete colouration across the particles (Plesters, J. ‘Ultramarine Blue, Natural and Artificial’ in *Artists’ Pigments 2* (1993) *op. cit.* p37-66).

4 *Prussian blue* is considered to be the first modern synthetic pigment (iron hexacyanoferrate, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot 14\text{-}16\text{H}_2\text{O}$); it was first produced between 1704 and 1707 in Berlin, Germany, with rapid and widespread use reported in Europe thereafter (Berrie, B.H. ‘Prussian blue’ in *Artists’ Pigments 3* (1997) *op. cit.* p191-217).

5 *Chrome yellow* is a synthetic pigment based on lead chromate ($\text{PbCrO}_4 \cdot \text{PbO}$), produced since the early 19th century (c.1804-1809), with variations in the shade of yellow/orange created by altering the synthesis conditions (Kühn, H. & Curran, M. ‘Chrome Yellow and Other Chromate Pigments’ in *Artists’ Pigments. A Handbook of their History and Characteristics 1* (ed: R.L. Feller) Cambridge University Press (1986) 187-218).

6 *Barium white* is a synthetic barium sulphate pigment (BaSO_4), introduced c. 1810-1820 and used as a white pigment, extender, lake base and component in various co-precipitated pigments such as *Lithopone* (Feller, R.L. ‘Barium Sulfate – Natural and Synthetic’ in *Artists’ Pigments 1* (1986) *op. cit.* p47-64).

7 Chalk is a soft white sedimentary rock formed entirely from microscopic fossilised phytoplankton. It has been ground and widely used as an artist’s material since ancient times (Eastaugh, N., Walsh, V., Chaplin, T.D. & Siddall, R. *The Pigment Compendium – A Dictionary of Historical Pigments* Elsevier Science (2004) p92-93). Chalk has been identified here both by the presence of coccoliths, the fossilised remains of the phytoplankton (see Appendix I).

8 Titanium dioxide white paints (*titanium whites*) have been manufactured since the early 20th century. The early form (known as the ‘anatase-type’) was produced from c.1919 onwards and contained pigment grains with the crystal structure of anatase, one of the natural mineral forms of titanium dioxide; later formulations of titanium white (post-1940) were produced comprising pigment grains with the rutile mineral structure (known as the ‘rutile-type’; Laver, M. ‘Titanium Dioxide Whites’ in *Artists’ Pigments 3* (1997) *op. cit.* p295-355).

The binding medium of the surface dark green paint layer contains a *seed oil* (such as linseed oil). Due to the varied pigment content of the paint layer it is difficult to establish whether the oil has been used alone or is present as part of an *alkyd resin*; however the latter seems less likely with significant characteristic bands in the FTIR spectrum absent (Figure 3a). The lower paint layer also contains a *seed oil*-based medium (Figure 3b).

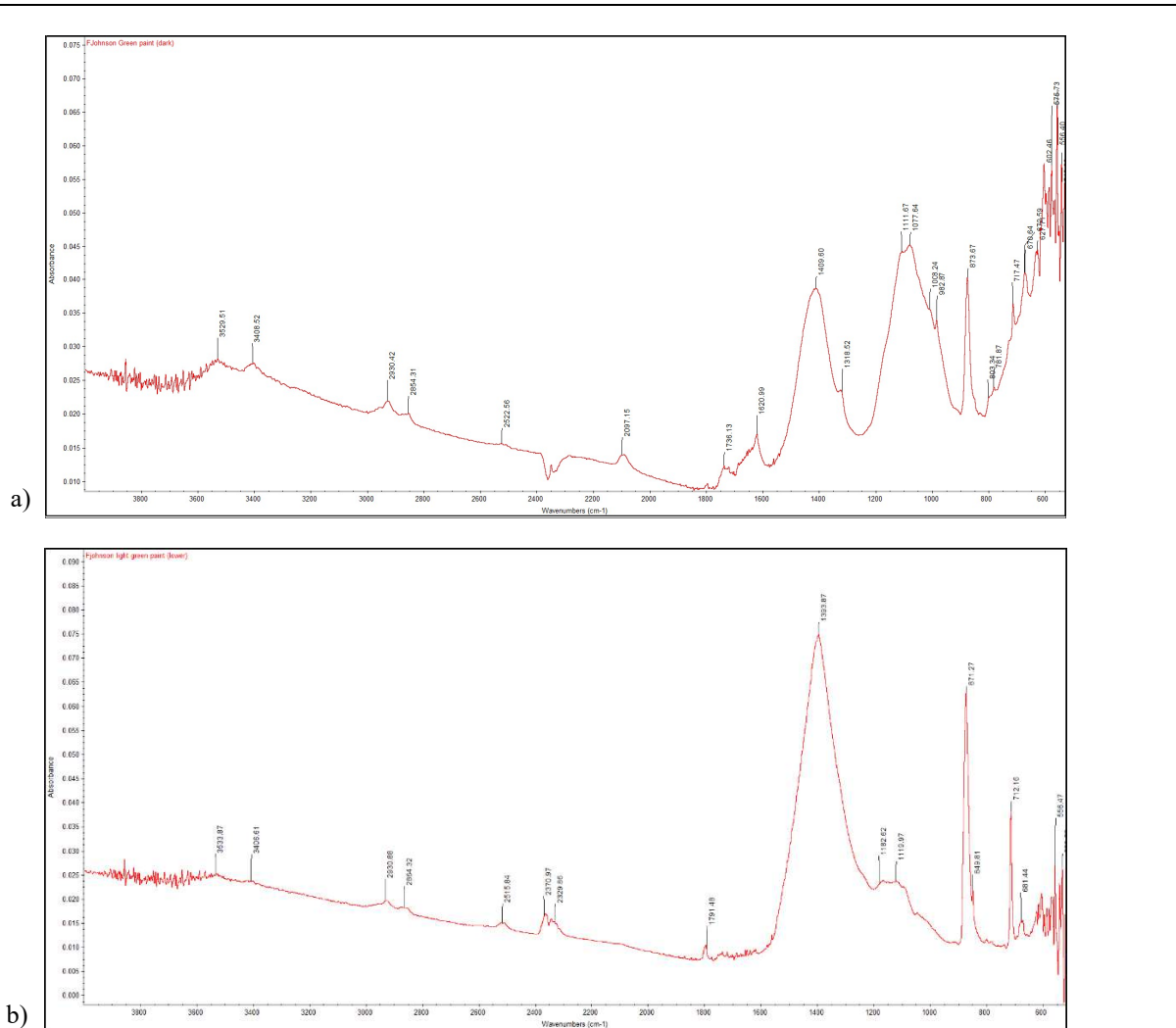


Figure 3. FTIR spectra obtained for the green paint layers, showing the spectrum for **a)** the dark green surface paint, with bands at c. 2930, 2854, 1736, 1715, 1700 & 717 cm^{-1} associated with a seed oil or seed oil-based modern coating such as an alkyd⁹; however, the bands which would permit distinction between these materials are obscured by the inorganic pigment/extender components in the paint, although the expected band at 1254 cm^{-1} is absent. The bands at c. 2097, 983 & 602 cm^{-1} indicate that Prussian blue is present, with bands at c. 1078, 983, 627 & 602 cm^{-1} characteristic of barium sulphate; the bands at c. 2523, 1410, 874 & 711 cm^{-1} are indicative of calcium carbonate (CaCO_3) and the bands at c. 3530, 3409, 1621, 1112, 1008 & 670 cm^{-1} are associated with gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), with the bands at c. 1620, 1318 & 781 cm^{-1} attributable to calcium oxalate. The pigment content and the absence of a strong band at c. 1254 cm^{-1} suggests that the use of an alkyd paint may be less likely; and **b)** the lower paler green paint layer, also with bands at c. 2931, 2864, 1740 & 712 cm^{-1} associated with a seed oil; the bands at 2516, 1791, 1394, 871 & 712 cm^{-1} are associated with *calcium carbonate* (possibly from the underlying plaster layer), with the bands at 3534, 1394, 1041, 840, 691 & 604 cm^{-1} associated with *lead white*; the bands at c. 3534, 3407 & 1120 cm^{-1} may be due to *gypsum*.

⁹ Alkyd resins are a special class of synthetic polyester polymers which have been corrected with natural or synthetic fatty acids or oils to allow them to be air-cured. Alkyd resins were introduced primarily as binders for household paints and for industrial paints and coatings in the very late 1920s due to their rapid drying and good film hardness in comparison with earlier paints based on stand oils, although they were not widely used in household paints the UK until the late 1940s (Heitkamp, A. & Pellowe, D. "Alkyd and Polyesters" in *Paint and Coating Testing Manual* (ed: J.V. Koleske; 1995, 14th edition) ASTM International, p53-59; Stoye, D. "Alkyd resins" in *Resins for Coatings: Chemistry, Properties and Applications* (1996) Stoye, D. & Freitag, W. (eds) Hanser Gardner Publications, pp60-80).

The development of calcium oxalates at painted surfaces has been more widely described in the literature in the context of oil paints that have a significant calcium carbonate/chalk component; the subject is discussed less widely for alkyd paints (although this may be because research on the degradation of such materials is comparatively understudied).¹⁰ However, the differing pigment content of the adjacent paint layers may be more significant in terms of the observed delamination effects on the mural. Paints containing *lead white* and copper-based pigments typically form more durable layers in which mechanical strength increases over time; *chalk* and *barium white* reportedly provide little strength in oil-based paints, with lead-based *chrome yellows* also imparting less strength compared with *lead white*. Fluctuations in temperature and relative humidity will also affect the properties of applied paints, and layers containing *chalk* and *barium white* are known to be more adversely affected by moisture.^{11,12} The differing mechanical strengths of the adjacent paint layers and their different responses to ageing and environmental changes may therefore be a factor in the observed delamination of the paint on the mural.

3. CONCLUSIONS

The decorative layer structure of the green foliage of the mural of *St Christopher* consists of the original green paint layer containing *emerald green* and *lead white* applied to the plaster substrate; the green paint may have been applied as two layers but the boundary between them is only weakly defined indicating that the layers are well adhered. A translucent surface coating was then added, of which only remnants are observable. The surface dark green paint was subsequently added which contains a mixture of *ultramarine blue*, *Prussian blue*, *chrome yellow*, *barium white* and *titanium white* pigments; calcium oxalates have developed thinly at the surface and a dirt layer has also accumulated. Both paint layers appear to contain an oil-based medium; the FTIR spectrum obtained for the upper layer suggests that the oil could be part of an alkyd resin but no strong evidence was found to support this (due to the complexity of the pigment content). *In situ*, the painted surface of the mural shows delamination in some areas although this was not observed in the sample provided. The very different pigment contents of the adjacent paint layers will affect the mechanical behaviour of the individual layers: the original paint containing *lead white* and copper-based *emerald green* is more likely to form a more durable and stronger layer; the more recent paint layer contains pigments which impart little mechanical strength and may promote a greater adverse response to moisture content changes. Thus, with continued ageing and in response to fluctuations in temperature and relative humidity, the adjacent paint layers are likely to behave differently causing them to detach at the weakest boundary.

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10 Otero, V., Vilarigues, M., Carlyle, L., Cotte, M., de Nolf, W. & Melo, M.J. "A little key to oxalate formation in oil paints: protective patina or chemical reactor" *Photochemical and Photobiological Science* 17 (2018) 266-270.

11 Mecklenburg, M.F. "Methods and materials and the durability of canvas paintings: a preface to the topical collection failure mechanisms in Picasso's paintings" *SN Applied Sciences* 2 (2020) and references therein.

12 Weldon, D.G. *Failure Analysis of Paints and Coatings* Wiley (2009) pp362.

4. APPENDIX I

The following appendix provides details of the analytical methods used during the examination of the paint layer structure.

4.1 Cross-section analysis

Cross-sectional analysis allows the layer structure of any item or object to be examined. In the current study, the sample was embedded in Polylite clear polyester setting resin and upon hardening of the resin, the sample was ground and polished using abrasive papers (180 to 12,000 grade MicroMesh) to reveal the layer structure. The sample was examined under reflected white light on a Brunel Instruments SP300-XP microscope which provided magnifications of up to 1000x.

4.2 Fourier transform infrared (FTIR) spectroscopy

To characterise the organic content of the paint, FTIR analysis was carried out using a ThermoScientific Nicolet iS10 infrared spectrometer equipped with a Smart Orbit accessory and diamond cell. Each sample was placed onto the diamond window and pressed onto it using a metal anvil. Each sample was scanned 160 times in the range 4000-400 cm^{-1} and the background spectrum automatically subtracted, with the scans averaged to produce an FTIR spectrum. The resultant spectra (shown in Figure 3 in the main body of the report) were compared with those obtained from standard reference materials,^{13,14,15,16} with interpretative support provided by Dr Brian Singer (Analysis for Conservation).

4.3 Scanning Electron Microscopy with Energy Dispersive X-Ray (SEM-EDX) Analysis

To establish the elemental content of the layers in the sample, a Zeiss EVO 25 scanning electron microscope coupled with an Oxford Instruments x-max 80 energy-dispersive spectrometer was used; the accelerating voltage was set at 20 kV and the working distance at 8.5 mm. The sample was carbon coated with a Leica EM ACE200 carbon thread evaporation coater to aid analysis and several areas on the surface were analysed by this technique; the elemental content determined at each site was recorded and the resultant peaks in the spectra were compared with those of reference standards using Aztec software (Oxford Instruments Ltd; see Figures A1 & A2).

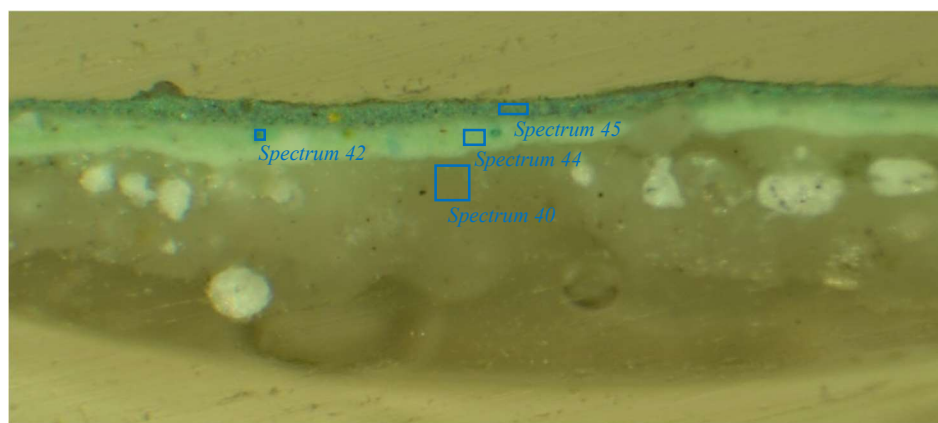


Figure A1. Decorative layer structure of the green paint from the foliage of the *St Christopher* mural (shown at x100 magnification in reflected white light), with SEM-EDX analysis sites shown; see Figure A2 for the spectra obtained.

13 Derrick, M.R., Stulik, D. & Landry, J.M *Infrared Spectroscopy in Conservation Science* The Getty Conservation Institute (1999)

14 Infrared users group database (www.irug.org)

15 Vahur, S., Teearu, A., Peets, P., Joosu, L. & Leito, I. "ATR-FT-IR spectral collection of conservation materials in the extended region of 4000-80 cm^{-1} " *Analytical and Bioanalytical Chemistry* 408 (2016) 3373–3379.

16 E-visart database (<http://www.ehu.es/udps/database/index1.html>)

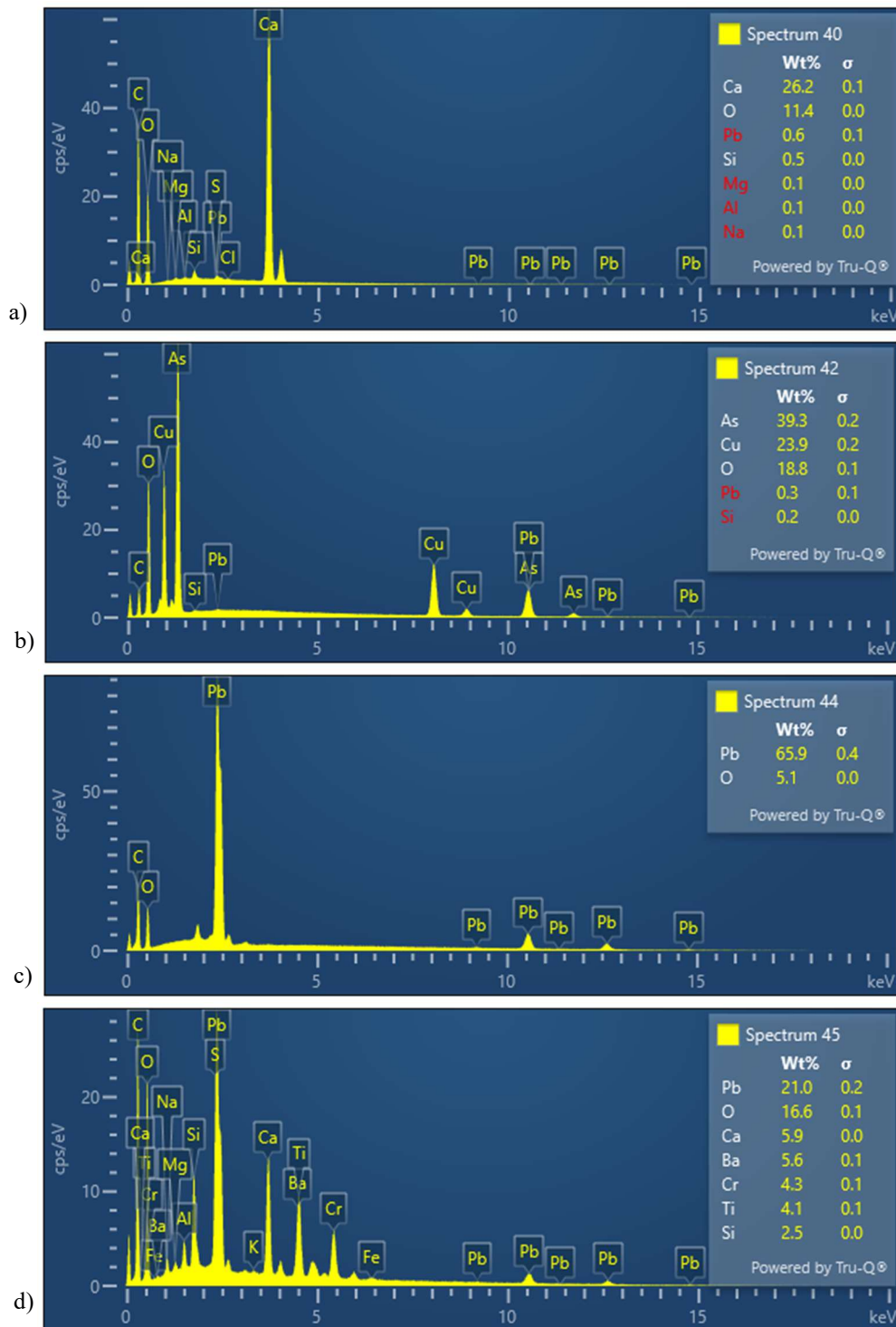


Figure A2. EDX spectra obtained for the layer structure of the foliage of the *St Christopher* mural (see Figure A1), showing the spectrum for the **a**) white substrate (*Spectrum 40*), dominated by peaks for calcium (Ca) most likely due to *calcium carbonate/lime plaster* (CaCO_3); the weak peaks for sodium (Na), magnesium (Mg), aluminium (Al), silicon (S), sulphur (S) & chlorine (Cl) may be due to impurities in the plaster; the weak peaks for lead (Pb) are likely to be associated with material in the overlying paint; **b**) green grains in the original paint layer (*Spectrum 42*) with strong peaks for arsenic (As) & copper (Cu) associated with *emerald green* ($\text{Cu}[\text{C}_2\text{H}_3\text{O}_2] \cdot 3\text{Cu}[\text{AsO}_2]_2$); the weak peaks for lead (Pb) indicate that *lead white* ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$) is present; **c**) general area of the original green paint (*Spectrum 44*), dominated by peaks for lead (Pb) most likely due to *lead white*; **d**) surface green paint (*Spectrum 45*), with peaks for lead (Pb) & chromium (Cr) attributable to *chrome yellow* ($\text{PbCrO}_4 \cdot \text{PbO}$); the peaks for barium (Ba) & sulphur (S) are due to *barium white* (BaSO_4); barium could also be associated with *barium chromate* (BaCrO_4); the peaks for sodium (Na), aluminium (Al), silicon (Si), sulphur (S) & calcium (Ca) suggest that *ultramarine* has been used ($[(\text{Na},\text{Ca})_8[(\text{Al},\text{Si})_{12}\text{O}_{24}](\text{S},\text{SO}_4)]$); the relatively strong peak for calcium (Ca) may also indicate that *calcium carbonate/chalk* is present and the peaks for titanium (Ti) suggest that *titanium white* pigment (TiO_2) is included.

4.4 Polarised light microscopy (PLM)

In this technique, individual samples are dispersed on a glass slide in a mounting medium of known refractive index (RI) which allows comparison with other known materials dispersed in the same medium. Here Cargille Meltmount with an RI of 1.66 was used as the medium. Dispersions were made from the samples provided and examined using a Brunel Instruments SP300-XP microscope with magnifications of up to x1000. The optical properties of the materials were examined and compared with those of known materials previously examined by the author and colleagues.¹⁷ The analysis showed the presence of *ultramarine blue*, *Prussian blue*, *chrome yellow*, *barium white* and coccolith plates associated with *chalk*.

4.5 Microchemical testing

The sample was tested for the presence of protein binding media by the application of acid fuchsin dye (prepared as a 1% solution in ethanol) to the cross-section surface for 30s-60s; this was then removed using a swab dampened with deionised water. Areas of a sample which take up the pink-red stain are those which contain protein. The current sample did not test positive for the presence of protein indicating that no proteinaceous binder (such as that found in soft distemper paint) had been used in the decorative layer structure.

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¹⁷ Eastaugh, N., Walsh, V., Chaplin, T.D. & Siddall, R. *The Pigment Compendium – Optical Microscopy of Historical Pigments* Elsevier Science (2004).

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