Studies in Conservation

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/ysic20

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To cite this article: Tea Ghigo, Daniel Bone, David Howell, Kelly Domoney, Michele Gironda & Andy Beeby (2022): Material Characterisation of William Burges' *Great Bookcase* within the Disruption of a Global Pandemic, Studies in Conservation, DOI: 10.1080/00393630.2022.2153463

To link to this article: https://doi.org/10.1080/00393630.2022.2153463

STUDIES IN CONSERVATION
https://doi.org/10.1080/00393630.2022.2153463

ORIGINAL RESEARCH OR TREATMENT PAPER

OPEN ACCESS

Material Characterisation of William Burges' *Great Bookcase* within the Disruption of a Global Pandemic

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ABSTRACT

This contribution presents the results of a technical investigation on the pigments of William Burges' *Great Bookcase* (1859–62), preserved at the Ashmolean Museum. It is the first thorough material investigation of a remarkable piece of Gothic Revival painted furniture, notably an artwork by Burges, whose work has so far received little attention from a technical point of view. This study was developed during the Covid-19 pandemic, which significantly affected the planned research activities since the investigation relied extensively on collaborations with institutions within and beyond the University of Oxford. The disruption caused by the lockdown and other restrictions went far beyond any prediction and led us to redefine the project's outcome and methodology 'on the fly' while maintaining its overall vision. However, thanks to the timeliness of a substantial research grant received from the Capability for Collection Fund (CapCo, Art and Humanities Research Council), we could ultimately turn this research into a unique opportunity to test the potential of recently acquired instruments, namely the Opus Apollo infrared camera and the Bruker CRONO XRF mapping spectrometer. Therefore, besides reporting on the findings, this contribution outlines the strategy adopted and assesses the new equipment's capability for the non-invasive analysis of complex polychromies.

ARTICLE HISTORY
Received May 2022
Accepted November 2022

KEYWORDS
Pigment analysis; Victorian painting; Gothic Revival style; William Burges; macro-XRF mapping; multi-analytical approach; project management

Introduction

The *Great Bookcase* (h x w x d 317.5 × 173.9 × 49.5 cm) is a striking piece of painted furniture designed by the architect William Burges and painted by 13 young artists between 1859 and 1862. Made to hold Burges' collection of art and architecture books, the *Bookcase* is a rare and supreme example of Gothic Revival painting style, and as such, it formed the centrepiece of the Medieval Court at the London International Exhibition in 1862. Acquired by the Ashmolean Museum in the early 1930s, it was initially deemed 'not acceptable to present taste' and was exhibited at the museum only 80 years after the purchase. The *Bookcase* measures roughly two metres wide and three metres high and is lavishly decorated with a sophisticated iconographical programme from top to bottom, including on the inside doors (Figure 1). The middle section displays a mosaic of eight panels depicting Christian themes on the left and pagan themes on the right, floating over alternating monochrome backgrounds in gold and blue (Winterbottom 2017; Ribeyrol Forthcoming).

The Conservation Department at the Ashmolean Museum conducted material analyses of this Bookcase as part of the European Research Council project *Chromotope* (building on preliminary investigations by Thistlewood (2017)). This ongoing project aims to investigate how the nineteenth-century 'Colour Revolution' that stemmed from industrial progress mapped out new ways of thinking about colour in literature, art, science, and technology throughout Europe. Painted in the middle of the nineteenth century, the *Great Bookcase* represented an ideal case study to acquire some perspective on a masterpiece of Victorian art that was created by several artists. The material investigation aimed primarily to reveal the palette(s) the artists used, to understand the material choices made to paint a Medievalising *Bookcase* in the midst of the Industrial Revolution when the market of painting materials underwent a significant transformation. Furthermore, it initially sought to reconstruct the manufacturing process of the *Bookcase* and determine, for instance, whether the artists painted the different sections while working in the same workshop (thus, using the same materials) or whether they each used their own colours.

The primary aim of this contribution is to present the results obtained during this technical investigation, which is, to our best knowledge, the first in-depth material characterisation of Gothic Revival painted furniture and of a work designed by William Burges that has been carried out so far. The Covid-19 pandemic

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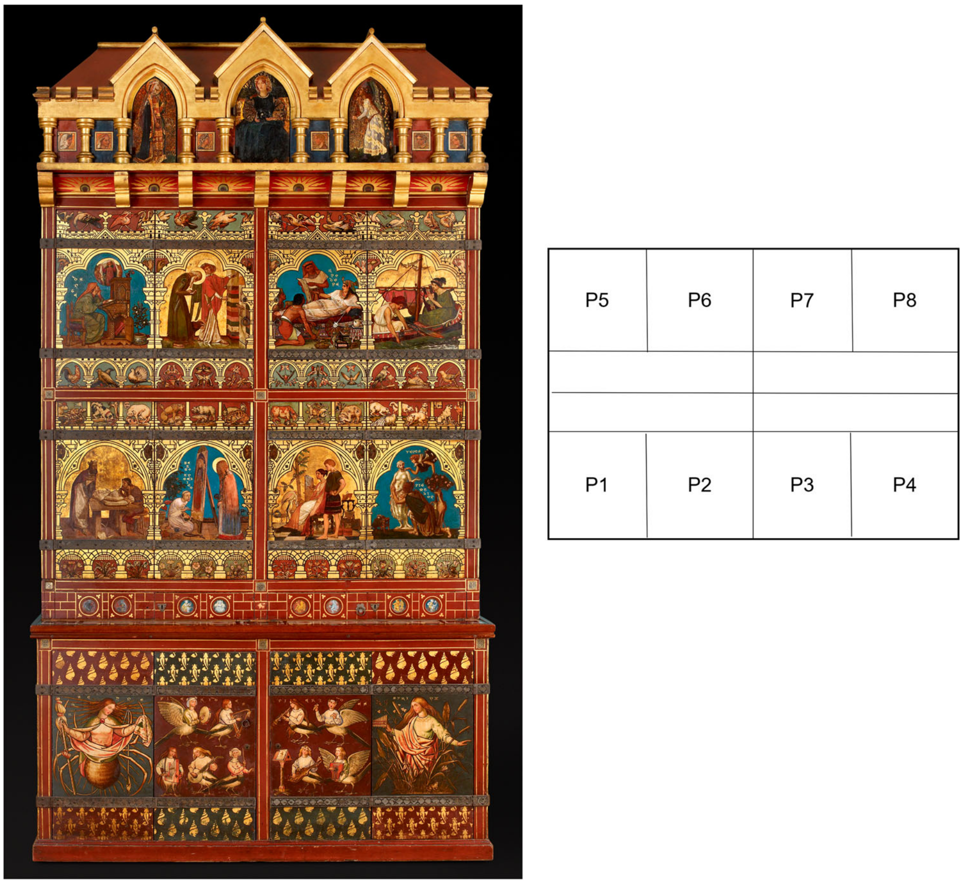


Figure 1. The *Great Bookcase* (left) and a diagram of its middle section with the eight painted panels (right). P1: Albert Moore, *Edward I and William Torrel*, P2: Thomas Morten, *Fra Angelico painting the Virgin*, P3: Frederick Smallfield, *The origin of painting*, P4: Simeon Solomon, *Pygmalion and Galatea*, P5: Edward Poynter and (possibly) Dante Gabriel Rossetti, *The apparition of Beatrice to Dante*, P6: Simeon Solomon, *St John and the New Jerusalem*, P7: Edward Poynter, *Rhodopis commissioning a pyramid*, P8: Henry Holiday, *Sappho serenading Phaon*.

repeatedly disrupted the development of research activities which began on the verge of the second wave of infections in the UK (November 2020). This extraordinary situation forced us to re-adapt the project's strategy multiple times in response to the challenges imposed by pandemic restrictions and conservation concerns. Thanks to the timeliness of the Art and Humanities Research Council 'Capability for Collections' grant, the investigation of the *Bookcase* was ultimately turned into a unique opportunity to test the technology acquired, notably the Bruker CRONO XRF mapping spectrometer with ESPRIT Reveal software and the Opus Apollo infrared camera. Therefore, in presenting the methodology adopted to investigate the *Bookcase* and its outcome, this article also describes the decision-making process underlying the management strategy and assesses the capability of the recently acquired equipment in the investigation of painted surfaces.

Original plan versus an unpredictable unfolding of events: shaping a new route

The planning of the project *Chromotrope* initially allocated 12 months of research to fully characterise and contextualise the pigments of the *Great Bookcase*, starting in November 2020. The envisioned strategy was built on the use of non-invasive techniques supplemented by invasive analytical methods where necessary, which is widely recognised as an effective approach to characterise composite heritage objects. The initial plan was to commence with a further inspection of the painted surface built on previous examinations (Thistlewood 2017) during the first three months, which included observing the surface with a Dinolite digital microscope, examining it using ultraviolet (UV) light to track possible repainting and localised fluorescence of pigments, and performing preliminary analyses with hand-held XRF. This last method would have provided helpful information to map out the next analytical steps. However, alone it would not have been sufficient to elucidate the composition of the pigments used on the *Bookcase*, considering the potentially diverse elaboration of the stratigraphy over such a lavishly painted surface and the material complexity of nineteenth-century commercial colours (Carlyle 1993; Townsend et al. 1995; Townsend 1995; Carlyle 2001).

The following stage, which would have led to the identification of most pigments, included investigation using FORS and Raman spectroscopy in collaboration with the University of Durham, was planned to occur between months 4 and 6 of the project's timeline. Furthermore, an in-depth analysis of selected micro samples mounted in cross-sections would have integrated the results obtained with non-invasive methods. It was planned for months 7–9 using instruments available across different laboratories at the University of Oxford and Durham. The overall evaluation, interpretation, and dissemination of the results would have occupied the last trimester of this timeline.

In November 2020, the investigation on the *Bookcase* started with the initial inspection, which was successfully completed in the first trimester. However, in January 2021, the pandemic forced the UK government to implement heavier restrictions, with northern England being in total lockdown due to a rise in the number of infections. This turn of events impeded the collaboration with the University of Durham, postponing the examination with FORS and Raman spectroscopy until further notice.

We decided to move up the analysis of samples, having at our disposal eight cross-sections prepared in 2016, when the *Bookcase* underwent conservation treatment (Thistlewood 2017). These samples had previously been analysed with optical microscopy, which we complemented with SEM-EDX and micro-Raman analyses. However, six out of these eight samples derived from the red monochrome decoration of the framework and therefore did not represent the *Bookcase*'s diverse polychromy. By the time the analysis of samples was completed, the project had reached its mid-point, and due to the constraints imposed by the pandemic, there was still no concrete plan to apply FORS and Raman spectroscopy. Therefore, we considered the possibility to collect further samples.

The curatorial department promptly agreed to sample collection, as the results from the analysis would have cast light on the morphology and composition of pigments' particles of each paint layer, which could have been used to infer their origin. However, when our painting conservators inspected the surface before sampling, they observed no obvious access points for discrete and successful extraction and that the chosen sites were all of significant aesthetic importance. The physical condition and adhesion of the paint in these areas are very good, and the new incisions required would have probably incurred additional paint damage beyond the extraction of the samples themselves. Furthermore, logistic challenges were added to conservation concerns. Since the university's analytical laboratories at Oxford had been inactive for a long time due to the pandemic, they were now overwhelmed with a long list of urgent pending tasks. This would have certainly slowed down sample analysis, which might not have been thoroughly completed before the end of the project. As there was a chance that the outcome might not have been worth the sacrifice, we decided not to proceed to extract other samples.

Due to this choice, the development of this project was now counting almost exclusively on non-invasive analysis, but FORS and Raman spectroscopy were not immediately available. Therefore, the overall strategy of the project had to be revised. We decided to redefine the expected outcome while maintaining the project's broad vision. Although the combination of invasive and non-invasive analysis would have allowed us to reach a higher level of information and granularity and clarify, for instance, whether the artists worked using the same colours, non-invasive analysis alone would have still identified a number of pigments and provided insight into the materials used. However, non-invasive examination of such a big object typically requires a team of several people to move around the instruments and perform the analysis, especially considering that the investigation of the top part of the *Bookcase* had to be carried out at a height, since the Covid-19 risk assessment precluded enough people working together to dismantle it into its three structural parts. During those months, such a workforce was not consistently available at the museum due to furlough and work-from-home triggered by school closures. To make the most of the time left and resources available, we restricted the investigated area to the eight painted panels of the middle section since they display the most chromatic variety.

The project finally saw a positive turnaround in spring 2021, when the museum expanded its analytical suite thanks to the grant received from the Capability for Collection Fund (CapCo, Art and Humanities Research Council). Two new instruments for infrared reflectography and macro-XRF mapping were acquired. The new equipment was planned to be implemented starting from the end of 2021, once the Conservation Department would have been back operating at standard capacity after the reincorporation of different staff members. However, we opted for immediate implementation since we foresaw that these methods could provide invaluable insight into the *Bookcase*'s elaborate polychromy. This way, we optimised the time gained by reducing the area under investigation.

Infrared reflectography was applied on the *Bookcase* in spring, quickly leading to outstanding results.[1] On the other hand, implementing macro-XRF mapping was somewhat energy – and time-demanding. Nonetheless, we decided to prioritise this operation over any other activity, as the analyses conducted up to that moment had shown a diversified and elaborated stratigraphy with colours that often resulted from complex mixtures of pigments and additives. This suggested that macro-XRF mapping would be better suited to investigate the pigments on the

Bookcase, since it would allow us to virtually 'peel off' different layers of paint. By contrast, we expected FORS to yield spectra of difficult interpretation without comparative tests on mock-up samples, and Raman spectroscopy to provide limited insight due to fluorescence phenomena. These two methods were finally applied on the *Bookcase* in September 2021 and macro-XRF mapping in October 2021.

During this investigation, the European Research Council acknowledged that the pandemic largely hampered the development of the project's main research activities. However, no extra funds were available to cover an extension. Two additional months of work were funded by the Ashmolean, which acknowledged the job done during this investigation to implement new facilities for heritage science at the museum. This time was dedicated to the overall interpretation of the results and initiating the academic dissemination.

Figure 2 compares the Gantt charts of the project's management as initially planned (left) and finally developed (right). In blue are represented milestones (M) and deliverables (D) as planned initially, while in red are milestones and deliverables which resulted from changes in the strategy adopted. The exclamation marks represent events that promoted revision of the overall approach: the missed application of Raman and FORS in month 4 and the decision not to extract other samples made in month 7, as sampling was logistically not possible.

Analytical methods

The analyses were performed primarily *in situ* in Gallery 66 at the Ashmolean Museum, where the *Bookcase* is currently preserved. A scaffolding tower and a tailor-made aluminium frame were used to reach the top part.

DinoLite

The micro-photographs presented in this article were captured with this USB digital microscope using 50x magnification.

Apollo camera, Opus

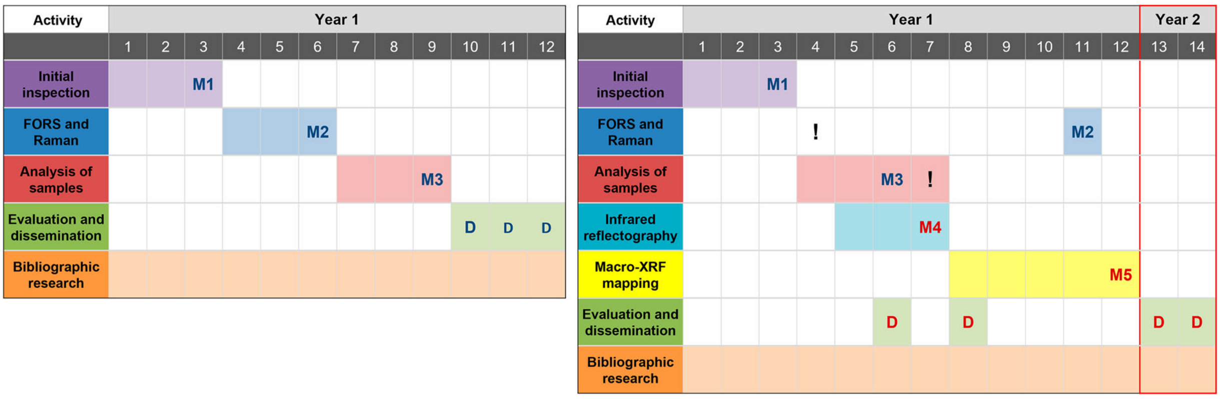
This infrared camera features a cooled indium gallium arsenide sensor with a spatial resolution of 128 × 128 pixels. The infrared images were acquired by scanning the paintings in the full spectral range of the sensor (900–1700nm).

CRONO, Bruker

This X-rays fluorescence spectrometer features a rhodium target tube and a 50 mm^2 SDD detector with energy resolution <140 eV for Mn Kα with input count rate of up to 500,000 cps. It allows for a fast collection of elemental maps on up to 600 × 450 mm areas for elements in the range $11 < Z < 92$ (Na in single point measurement only). The maps and line-scans presented in this article were obtained with a 0.5 mm collimator operating at 50 keV and 200 μA. The data collected were processed using the ESPRIT Reveal software by Bruker.

FORS

A custom-built fibre optic reflectance spectrometer that operates in the range 400–2500 nm and designed specifically for the safe study of fragile works of art was used to record the FORS spectra (Beeby et al. 2018). Light is delivered by a bifurcated fibre and two collimating lens to illuminate the sample, with a beam diameter of 2.5 mm and a total power of < 0.5 mW, and a working distance of 3 cm. The reflected light is collected and analysed by a combination of a CCD-spectrograph (Ocen Optics Maya 2000Pro) and an FT-NIR spectrometer (Arcoptix OEM) equipped with a cooled InGaAs detector. In the range 400–1000 nm the bandwith of the system is 3.5 nm, whilst in the SWIR, 900–2500 nm, the bandwidth is 8 cm^{-1}, corresponding to 2.5 nm at 1750nm. Spectra were recorded relative to a Spectralon standard and took 1 second per measurement.



Activity	Year 1											
	1	2	3	4	5	6	7	8	9	10	11	12
Initial inspection	▨	▨	M1									
FORS and Raman				▨	▨	M2						
Analysis of samples							▨	▨	M3			
Evaluation and dissemination										D	D	D
Bibliographic research	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨

Activity	Year 1												Year 2	
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Initial inspection	▨	▨	M1											
FORS and Raman				!							M2			
Analysis of samples				▨	▨	M3	!							
Infrared reflectography					▨	▨	M4							
Macro-XRF mapping								▨	▨	▨	▨	M5		
Evaluation and dissemination						D		D					D	D
Bibliographic research	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨

Figure 2. Gantt charts showing the main changes in the project's strategy.

Portable Raman

A custom-made Raman spectrometer was used for the *in situ* analysis. This employs a 633 nm diode laser delivered to a custom-made Raman probe via a fibre-optic cable, and equipped with an ultra-long working distance × 40 microscope lens. The head was mounted on a micrometer-controlled stage on a gantry assembled in front of the cabinet. The laser spot on the sample is estimated ca. 50 µm diameter and the power at the sample was maintained at 0.4 mW. The Raman signal is collected by the same lens and scattered laser light removed by an edge filter (Semrock Razor-edge) and passed down a second fibre optic cable to a spectrograph and cooled CCD camera (Andor Shamrock-163 and iDus416). The spectra acquired resulted from the sum of 100 × 1 second acquisitions.

Benchtop Raman

Spectra of the paint flakes were recorded using a benchtop confocal Ramam microscope (Horiba LabRAM-HR) equipped with a 633 nm laser and a 50x LWD lens. Spectra were typically acquired using a 4 × 2 s acquisitions.

EVO LS15, Zeiss

This flexible variable pressure electron microscope has an image resolution of 4.5 nm at 30 kV and features an EDX detector with a 35° take-off angle. Elemental analyses were performed at 10 Pa and 15 keV, at a working distance of about 10 mm from the sample.

Results and discussion

Underdrawing and underpainting

The macroscopic examination of all eight painted panels revealed the typical craquelure pattern throughout the surface. Further investigation of the cracks of the blue and gold backgrounds showed evidence of underlying colours. Figure 3 shows two micro-photographs captured on the panels of *The origin of painting* on the left and *The apparition of Beatrice to Dante* on the right. The surface of the gold background on the left presents a superficial brownish deposition suggesting that a substance was used to treat the gold and simulate an antique effect. Beneath the gold layer, it is possible to see a horizontal dark line appearing through the cracks. Similarly, the image on the right shows that the blue background that we observe was painted over a red field.

Previous analyses using an infrared camera with a spectral range up to 900 nm had revealed several underdrawings, showing a hidden virgin with the baby in the panel *The apparition of Beatrice to Dante* and some notes on the colours to be used in *St. John and the New Jerusalem* (Thistlewood 2017). With the new Apollo camera, we had the opportunity to investigate the panels with a wider spectral range of up to 1700nm. This instrument recovered a significant portion of hidden iconography, especially for the panels of *Fra Angelico painting the Virgin* and *Pygmalion and Galatea*. Figure 4 shows the visible and infrared pictures (spectral range up to 900 nm on the left and 900–1700nm on the right) of Fra Angelico's (a) and Pygmalion's (b) panels, respectively. The top images reveal that the scene of Fra Angelico was initially set in an outdoor space, rather than floating within an abstract blue ground, as evidenced by the wall stone with ivy visible between the painting and the Virgin in the infrared picture. By contrast, the bottom images reveal that Pygmalion and Galatea were initially placed against what seems to be a theatre curtain, hanging from a horizontal bar visible between the statue and the tree.

Furthermore, we recovered the underpaintings on the panels with a golden background by using macro-XRF mapping. Figure 5 shows the elemental maps obtained on the panels of *The origin of painting* (a) and *Sappho serenading Phaon* (b). The spatial distribution of copper (green), cobalt (blue), and mercury (red) show that some abstract patterns, possibly belonging to a wallpaper decoration, were initially filling the background on the right of the man

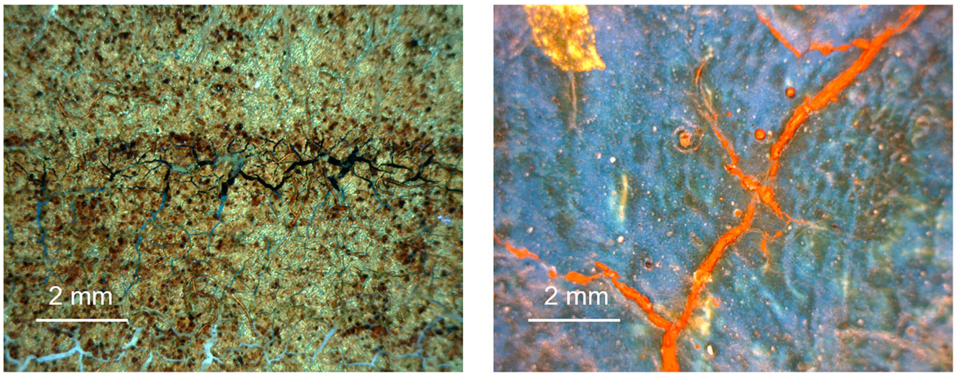


Figure 3. Two areas on the background of the panel *The origin of painting* (left) and *The apparition of Beatrice to Dante* (right).

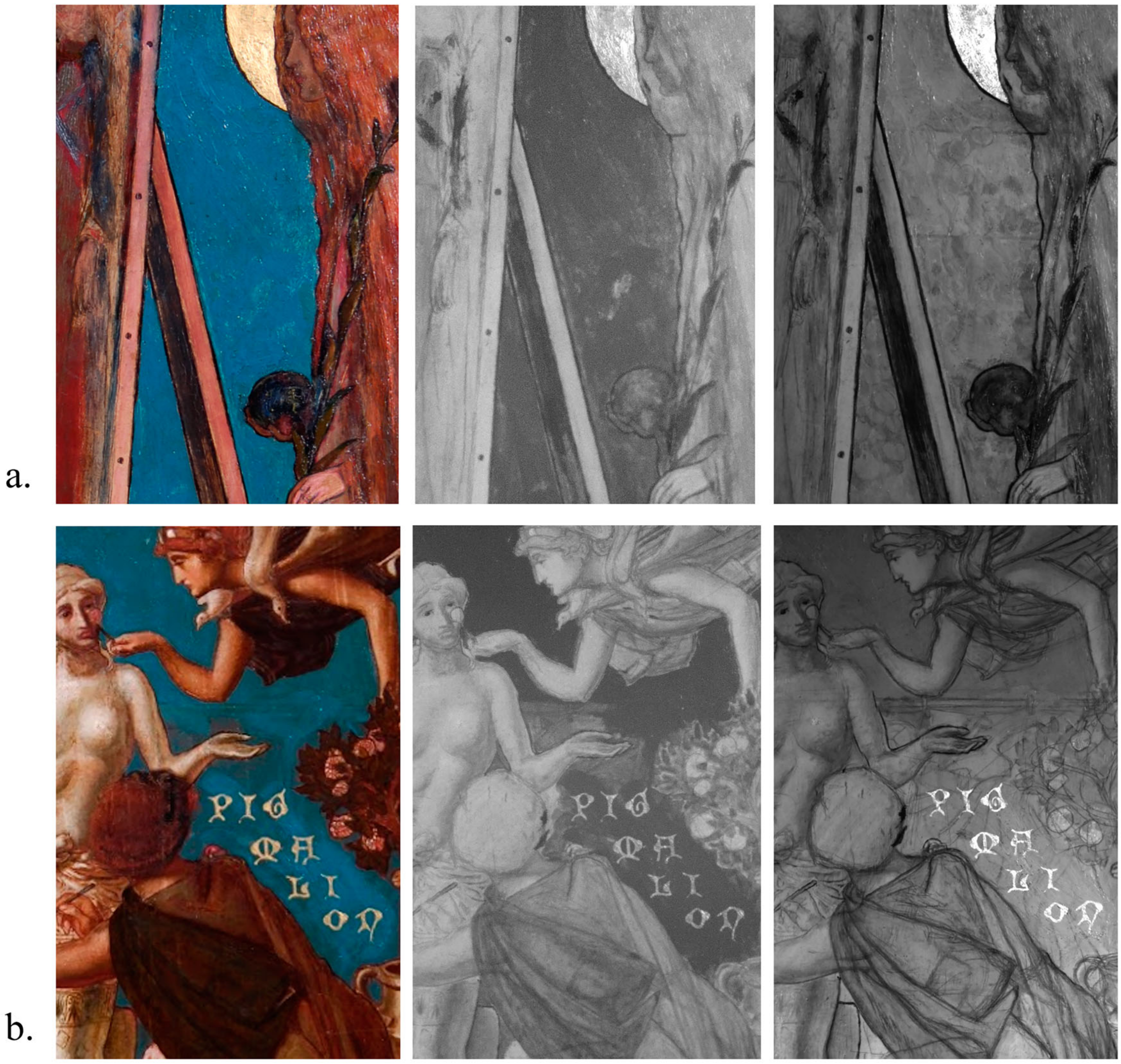


Figure 4. Visible and infrared images (up to 900 nm on the left and 900–1700nm on the right) of the panels *Fra Angelico painting the Virgin* (a.) and *Pygmalion and Galatea* (b.).

depicted in *The origin of painting*. Furthermore, we observed that the red sail in the panel of Sappho was originally occupying a broader area of the background, running beneath Phaon, all the way to the left border of the composition. A few black and white pictures taken at the London International Exhibition in 1862 seem to show that the original settings of the Pygmalion and Sappho panels had already been covered, although the quality of the image is rather poor.[2] This suggests the original backgrounds were covered soon after the *Bookcase* had been completed, perhaps seeking to achieve a sense of uniformity across the panels before presenting it at the International Exhibition in 1862.

The images recovered beneath the gold and blue backgrounds sparked new research across art history and literature aimed to further the significance of the original settings. For instance, the iconography unveiled on the Pygmalion panel cast light on the influence of Ovid and Shakespeare's plays and Botticelli's art on Burges (Ribeyrol Forthcoming, 151–73). The golden background was laid both in gold leaf and shell gold. The gold leaf covered most of the background across the scenes, while shell gold was used to touch up a few minor details around the figures. The gilded background presents the same surface treatment with a superficial brownish deposition across the four panels, and the blue background is consistently characterised by a 'clumsy application', as the conservator Jevon Thistlewood noted when he treated the *Bookcase* (Thistlewood 2017). The consistency of the execution suggests that gold and blue were applied over the previous iconography by the same person. The fact that the artistic quality of the blue background is not as refined as it appears on the rest of the *Bookcase* seems to indicate that it was Burges rather than one of the artists who painted over the original backgrounds.

Pigments and binder

Since only two samples were available for examination, most of the information on the composition of pigments was obtained with macro-XRF mapping. In

Figure 5. Visible images and false colour XRF maps of cobalt (blue), mercury (red), and copper (green) on two areas from the panels *The origin of painting* (a.) and *Sappho serenading Phaon* (b.).

fact, FORS produced spectra that were often inconclusive or challenging to interpret without comparative analysis on mock-up samples, while portable Raman spectroscopy often yielded inconclusive spectra. This was due to the limitation of the portable instrument used together with interference from the paint's organic compounds. This interference increased the fluorescence intensity that often covered the Raman signal. By contrast, macro-XRF mapping produced high-resolution elemental maps of the polychromies depicted over almost the entire surface of the painted panels. The combination of elemental composition and spatial distribution obtained was very effective in gaining insight into pigments used across the stratigraphy, notably due to the versatility of the software used for data processing (Bruker, ESPRIT Reveal).

Furthermore, in interpreting the elemental maps, we considered the existing literature on English nineteenth-century painting materials, including both archival sources and technical studies. For instance, arsenic has been associated with the yellow/orange pigments orpiment and realgar throughout recorded history. However, these rarely appear in nineteenth-century English colourmen's account books or artists' handbooks, nor are they often reported in technical studies. Instead, Victorian artists used, among others, lead chromate, Naples yellow, gamboge, or strontium chromate for the yellow tones, while arsenic is typically associated with green areas painted with emerald green (copper acetoarsenite, Cu(CH3COO)2·3Cu(AsO2)2), one of the favourite pigments of the Pre-Raphaelites, the main artistic movement of that period (Field 1835; Carlyle 1993; Townsend 1993; Katz 1995; Townsend 1995; Townsend et al. 1995; Katz 1998; Carlyle 2001; Townsend, Ridge, and Hackney 2004). Figure 6 shows a typical false colour elemental map obtained on an area of the panel *Rhodopis commissioning a pyramid*, where mercury is displayed in red, cobalt in blue, copper in dark green, and arsenic in yellow. By comparing the visible image and the false colour map, we infer that the different sections of the peacock-headdress were painted using vermilion, cobalt-based blue, and emerald green (the light green area in the false colour image resulting by displaying both copper and arsenic).

Reds

Iron oxides and vermilion were the pigments most abundantly used for the red and orange tones. Portable Raman spectroscopy detected in a few cases a peak at around 260 cm^{-1}, assigned to the symmetric stretching of the bond Hg-S (Figure 7). Furthermore, FORS spectra showed the typical fingerprint of vermilion in a couple of cases. However, the use of this pigment was mostly inferred by observing the distribution of mercury revealed with macro-XRF mapping

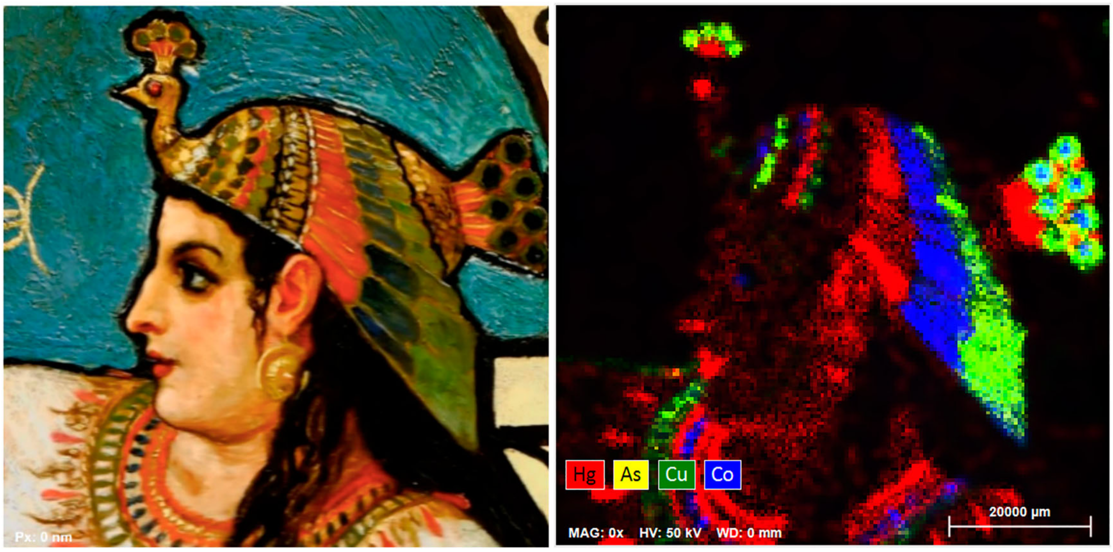


Figure 6. Visible image and false colour XRF map of mercury (red), arsenic (yellow), copper (green), and cobalt (blue) on an area from the panel *Rhodopis commissioning a pyramid*.

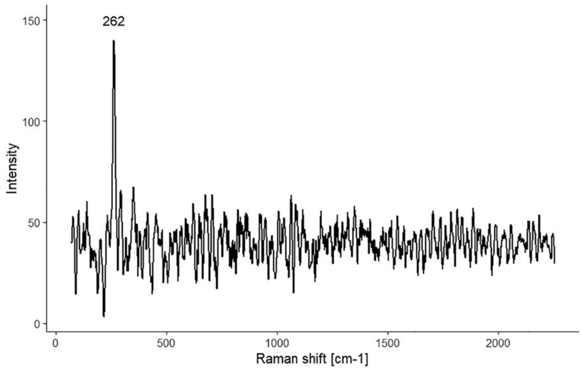


Figure 7. Raman spectra of a red area on the panel *Pygmalion and Galatea*.

(Figure 6), and the knowledge that no other red pigment except iodine red (mercuric iodide, known to fade rapidly by sublimation even in the dark (Daniels 1987)), contains mercury. Similarly, we inferred the presence of iron oxides and, in few cases, red lead by observing the distribution of iron and lead, respectively. Furthermore, the use of organic reds was deduced by the absence of XRF signal from the elements traditionally associated with red pigments and, in few cases, UV fluorescence was observed in these areas.

When different elements traditionally associated with several pigments were detected in the same area using macro-XRF mapping, in addition to the elemental maps, we observed the profiles of elements along a line scan. Figure 8 shows the elemental profile of lead (Mα), mercury, and chromium along a line scan moving from the blue background to the orange fruit. The co-presence of these elements in the fruit initially led us to think that a mixture of chrome yellow (lead chromate, $PbCrO_4$) and vermilion was used. However, the plot shows that while the profile of chromium and mercury are relatively similar, with the intensity of emission increasing sharply at the interface between background and fruit, the profile of lead shows no sharp increase. This indicates that the lead is not associated with the orange pigment but probably with the binder. An orange pigment composed of mercury and chromium has never been reported in previous technical studies of Victorian paintings. However, in his treatise *Chromatography*, the nineteenth-century chemist George Field mentions mercury chromate (without specifying any chemical formulation) among the orange pigments (Field 1835, 218). Therefore, this might be the first recognised and documented occurrence of mercury chromate as a pigment. If this result were confirmed via sample analysis, it would provide further evidence that mercury-based pigments might historically have been more common than we tend to think. Recent studies highlighted the use of calomel (Hg_2Cl_2) as a white pigment on manuscripts, paintings, and decorative objects from Britain and South America dating from the fifteenth century onwards (Burgio et al. 2018; Crippa et al. 2021).

Yellows

The golden background on four of the eight panels makes up most of the yellow tone on the *Bookcase*. Apart from that, few areas are yellow in colour, and they were mostly painted using iron oxides. Only on the panel *Rhodopis commissioning a pyramid*, XRF analysis revealed the presence of both lead and chromium, pointing to the use of chrome yellow. Furthermore, we found evidence suggesting that the artists blended yellow and green pigments to obtain a particular colour shade. Figure 9 shows the false colour maps of the lily stem held by the Virgin in the panel of Fra Angelico. The distribution of strontium and

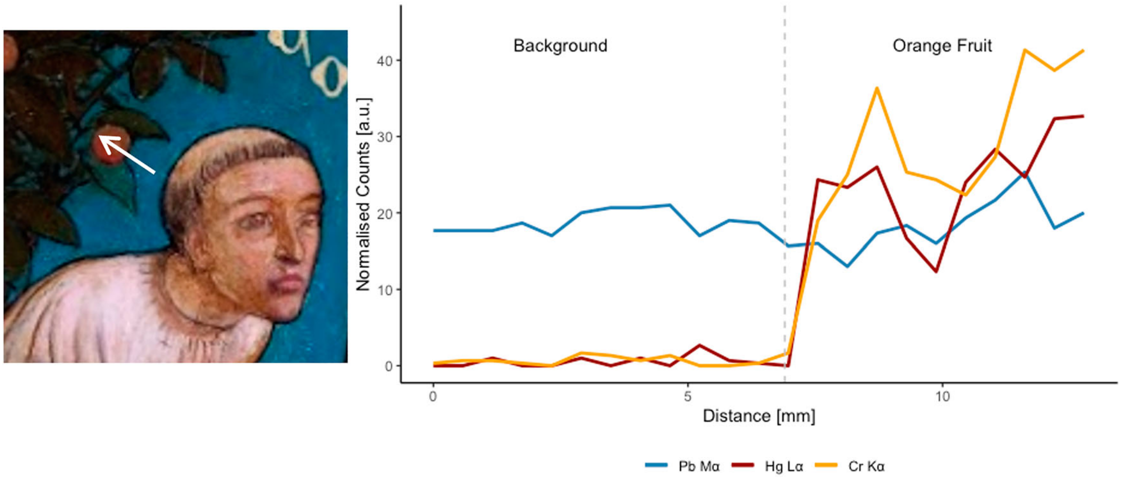


Figure 8. On the left, visible image of a section of the panel *Fra Angelico painting the Virgin*. On the right, XRF elemental intensity profile along a linescan at the interface between a blue and an orange area (white arrow shown on the visible image).

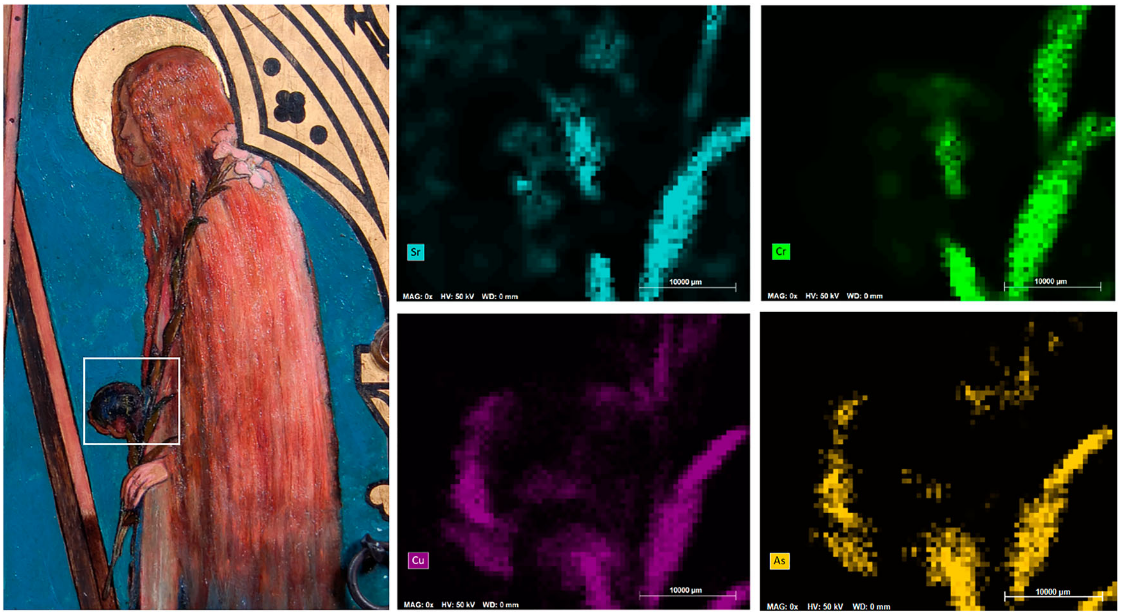


Figure 9. XRF false colour maps of strontium (turquoise), chromium (green), copper (purple), and arsenic (yellow) on an area on the panel *Fra Angelico and the Virgin*.

chromium (turquoise and green, respectively) suggests that strontium chromate, sold in the nineteenth century as 'lemon yellow', was used. This pigment was probably mixed with emerald green, as indicated by the distribution of copper and arsenic (in purple and yellow, respectively). Chromium and copper-based greens might also have been used to paint this green area.

Greens

Emerald green was extensively used to paint the *Bookcase*, as shown, for instance, on the elemental map in Figure 6. This pigment was sometimes found together with cobalt-based blues. Figure 10 shows the XRF elemental profile collected along a line moving from Beatrice's white veil to her blue garment. The line chart shows that the elements cobalt, probably from cobalt blue, copper, and arsenic, very likely coming from emerald green, have a very similar profile, suggesting that these two pigments were mixed to paint the vest.

Furthermore, chromium-based greens were found. During the nineteenth-century these greens were available in transparent and opaque forms: Cr_2O_3 and $Cr_2O_3{\cdot}2H_2O$. Figure 11 shows the false colour map of an area from the panel *The origin of painting*. The spatial distribution of chromium, copper, and arsenic shows that both chromium-based green and emerald green were used to paint the gecko, the former for the head, the latter for the body. Once again, the false colour map was crucial to observe colour modulations on the body of the gecko that is nowadays partially lost due to deterioration.

Besides emerald green and chromium-based greens, copper-based greens were also found. Figure 12 shows

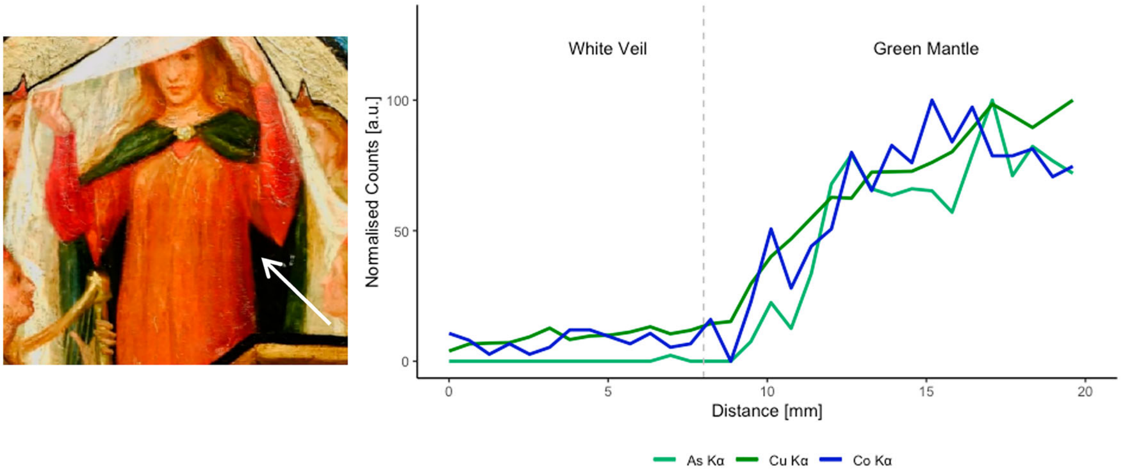


Figure 10. On the left, visible image of a section of the panel *The apparition of Beatrice to Dante*. On the right, XRF elemental intensity profile along a linescan at the interface between a white and a green area (white arrow shown on the visible image).

Figure 11. Visible images and false colour XRF map of chromium (green), copper (purple), and arsenic (yellow) on an area from the panel *The origin of painting*.

the blouse worn by the man depicted in *The origin of painting*. The first two elemental maps show the distribution of copper and arsenic, respectively, indicating that they are both present in the blouse and suggesting that emerald green was used in this area. The third elemental map results from the subtraction of arsenic to copper. Suppose the blouse had been painted solely with emerald green. In that case, this area should be completely black as the pigment contains a ratio of copper to arsenic 2:3 and the atomic cross-section of interaction with X-rays is higher for arsenic, which would result in a much higher intensity detected. However, the subtraction map clearly shows that much of the blouse remains coloured, thus indicating that the green colour contains a mixture of copper-based green pigments and emerald green.

Blues

Many of the blue areas covering the *Bookcase* are cobalt-based (see, for instance, Figure 6). In some

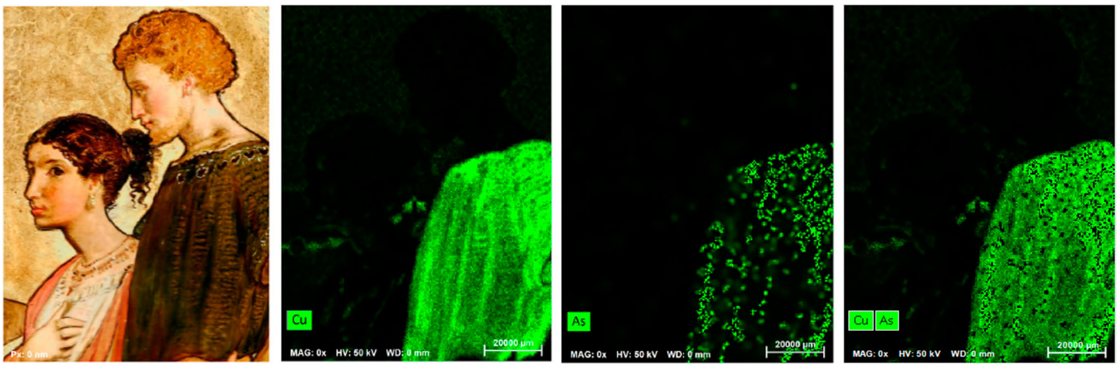


Figure 12. Visible image and XRF false colour maps of an area from the panel *The origin of painting*.

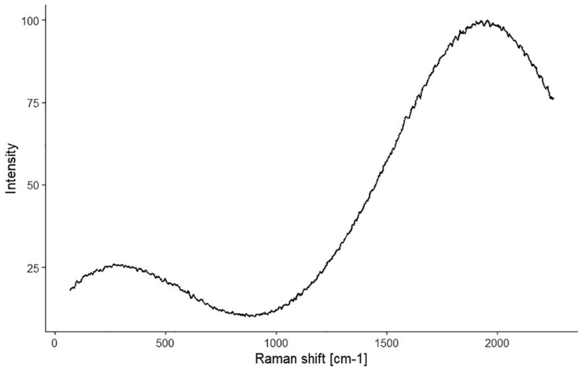


Figure 14. Raman spectrum of a blue area on the panel *Rhodopis commissioning a pyramid*.

cases, XRF detected aluminium together with cobalt, thus hinting cobalt aluminate ($CoAl_2O_4$) was used. This pigment was also identified on one of the samples using SEM-EDX. Furthermore, elemental maps showed the use of Prussian blue ($Fe_4[Fe(CN)_6]_3$) for the mantel of the Venus depicted on the panel of Pygmalion, as shown by the distribution of iron (Figure 13). This same false colour map shows that the painter initially used a different pigment for the highlights, revealing modulations of colours that we cannot appreciate today. Deterioration and ageing mechanisms turned this *chiaroscuro* into a flat, dull dark blue coating.

Indigo was identified in the pillow used on the panel of *Rhodopis commissioning a pyramid* using portable Raman spectroscopy that revealed its fluorescence spectrum: a broad fluorescence band characteristically centred around 1700cm^{-1} (Figure 14). Besides, the presence of an organic blue in the panel of *St John and the new Jerusalem*, whose composition was not possible to elucidate, was inferred by the absence of XRF signal from the elements traditionally associated with blue pigments in the false colour maps.

Most of the blue surface covering the *Bookcase* corresponds to the background on four of the eight panels. The initial inspection with hand-held XRF showed that iron, zinc, and barium are present in the blue background of all four panels and that this composition is unique across the *Bookcase*. This evidence further indicates that the blue backgrounds on the four panels were laid together after the Bookcase was completed.

A sample of this blue background (BUR-D) was extracted in 2016 from the panel *The apparition of Beatrice to Dante* and was analysed thoroughly during this study. The stratigraphy of the cross-section is relatively simple, as only a paint flake corresponding to the outmost blue layer was collected. Figure 15 shows the images under the stereo and electron microscopes, along with the elemental spectrum and maps obtained on two different areas with EDX. Spectrum 1, collected on a deep blue particle in area 1, shows intense peaks at 1.04, 1.48, 1.74, and 2.31 keV, corresponding to sodium, aluminium, silicon, and sulphur. This elemental composition is typical of artificial ultramarine blue ($Al_6Na_8O_{24}S_3Si_6$), as can be inferred from the absence of calcium, which is present in the mineral lazurite. This deep blue particle is embedded into a heterogeneous light blue matrix whose elemental distribution is better shown in area 2. Here, zinc appears to be evenly distributed across the section, while iron is localised in correspondence with small particles (about 4 µm size) and barium with bigger particles. The presence of small particles containing zinc with bigger particles containing barium suggests the use of lithopone, a white pigment consisting of an intimate mixture of barium sulphate and zinc sulphide (Eastaugh et al. 2008, 809). Figure 16 shows the Raman spectra obtained on the light blue matrix of sample BUR-D. The peaks around 280, 540 cm^{-1}, and those

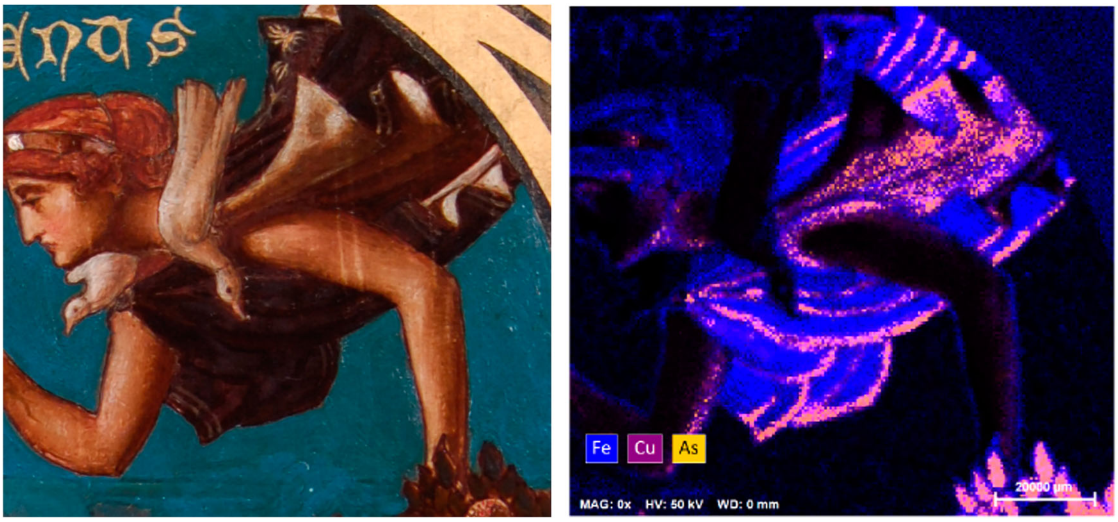


Figure 13. Visible images and false colour XRF maps of iron (blue), copper (purple), and arsenic (yellow) on an area from the *Pygmalion and Galatea panel*.

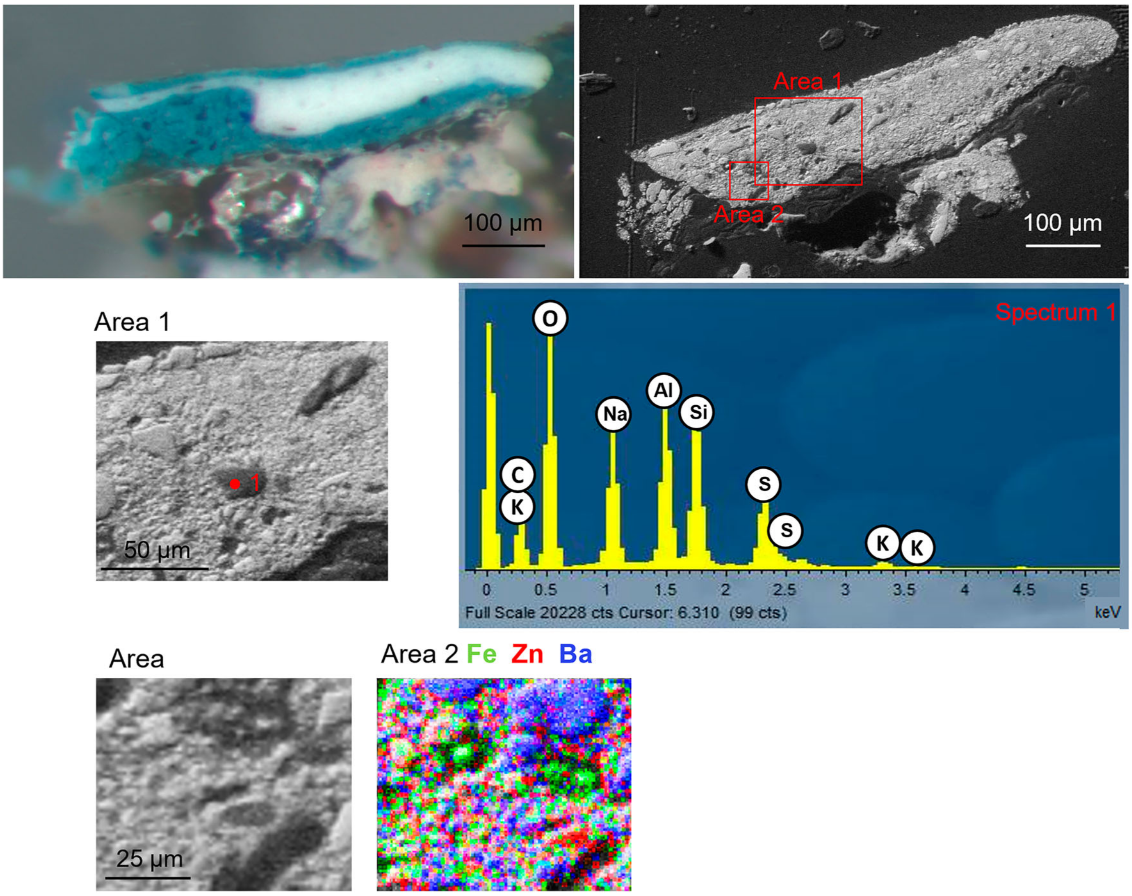


Figure 15. Visible and BSE images of the sample BUR-D, with elemental maps and EDX spectra.

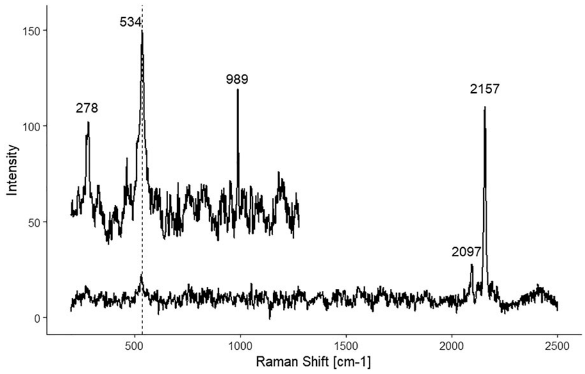


Figure 16. Raman spectra of the blue layer from the sample BUR-D.

at 2097 and 2157 cm^{-1} are all consistent with Prussian blue, which typically presents relatively small particles. In the lower area of the spectrum, the peak at 278 cm^{-1} corresponds to the Fe-CN-Fe bond deformation, while those around 540 cm^{-1} to the Fe-C stretching vibration. Furthermore, the peaks between 2097 and 2157 cm^{-1} correspond to the stretching of the triple bond C–N (Moretti and Gervais 2018). Finally, the sharp peak at 989 cm^{-1} is associated with barium sulphate, consistent with the observed larger particles.

It seems unlikely that Burges intentionally mixed colour with such a material composition on his palette. First of all, ultramarine was acknowledged as the most precious pigment in the medieval palette. Therefore, it seems unlikely that an artist whose work was inspired by the Middle Ages intentionally mixed it with Prussian blue, especially since the introduction of artificial ultramarine turned it into a much more affordable pigment. Furthermore, should an artist choose to combine these two pigments, the ratio of the two would be likely more balanced than what we observed in sample BUR-D, where very few particles of ultramarine are dispersed in a matrix that is mainly made of Prussian blue and lithopone. Burges most likely purchased this colour as a prepared mixture. The 'clumsy application' of the blue ground indicates that Burges worked relatively quickly and suggests that he might not have bothered mixing the pigments himself but used a ready-made colour instead, perhaps purchased in a paint tube. To pay tribute to medieval icons, he might have bought a colour labelled 'ultramarine blue' and fallen prey to deceit since industrially produced pigments were abundantly adulterated (Carlyle 1993). Previous research reported the nineteenth-century adulteration of ultramarine with Prussian blue and barium sulphate, among other materials (Townsend et al. 1995). Since lithopone was commercialised in the 1870s, these blue backgrounds could not have been painted before presenting the *Bookcase* at the International Exhibition in 1862. Therefore, the monochrome backgrounds we see today do not correspond to those that seem to be visible in the aforementioned black and white photographs from 1862.[3]

Purple

Since the *Bookcase* presents several repaintings, we often compared the fluorescence emissions of different lines for elements such as lead and mercury. This way, we observed the elemental distribution across the stratigraphy, with M lines showing emissions from outmost layers and L lines from innermost layers. Figure 17 shows the king's purple garment in the panel *Edward I and William Torrel*. The elemental maps show that cobalt (in violet) is associated with the garment, indicating that purple was obtained as a mixture of blue and red pigments. The map of mercury's Lα line (red, on the left) shows this element is mainly contained in the background, with some of it being associated with the garment. However, the map of mercury's Mα line (red, on the right) shows that no emissions are coming from this area, indicating that the red pigment vermilion is present in the innermost layer rather than in the superficial coating used for the king's garment. Instead, cobalt blue (cobalt aluminate, $CoAl_2O_4$, as the garment was found to contain both cobalt and aluminium) was likely mixed with an organic red pigment. Mixtures of cobalt blue and madder have been reported in pre-Raphaelites and coeval paintings[4] (Townsend, Ridge, and Hackney 2004, 62–63). A different purple pigment was found in the panel of *St John and the new Jerusalem*. Here, the mapped area showed a lack of XRF signal from elements associated with blue or red pigments, thus suggesting the use of an organic purple.

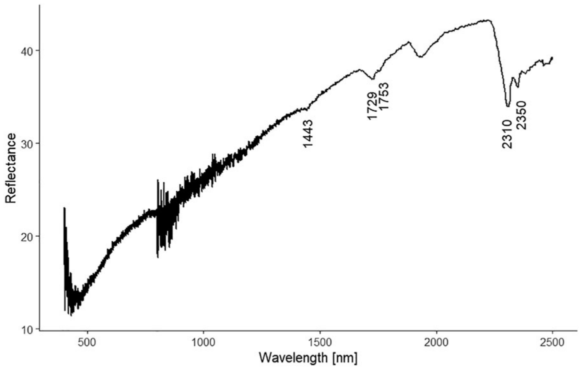


Figure 18. Reflectance spectrum of a greenish area on the panel *The origin of painting*.

Binder

MA-XRF detected intense emissions for Pb Lα and Mα lines across the entire surface of the *Bookcase*, suggesting that lead white ((PbCO3)2·Pb(OH)2) was used for the preparation ground and, possibly, a lead-treated oil was employed as a binder, as it is often reported in nineteenth-century painting handbooks (Carlyle 1999). These results were corroborated by FORS analysis. Figure 18 shows the spectrum obtained on a greenish area on the panel *The origin of painting*. The spectral region between 400 and 900 nm, which is usually diagnostic of the pigment examined, shows a trend where no maximums and minimums are observed and suggests that the colour used resulted from elaborate materials' mixtures. This was the case for many of the spectra acquired. On the other hand, the spectral region between 1200 and 2400 nm was more insightful. For almost the totality of the spectra collected, we observed peaks between 1720 and 1750nm, which have been assigned to the first-overtone bands of methylene (–CH2–), methyl (–CH3), and alkenyl (–CH = CH–) stretching modes, and peaks between 2300 and 2490 nm, assigned to the combination bands of (–CH2–) and (–CH3) stretching modes (Pallipurath et al. 2013). These bands are compatible with the use of oil as a binder. Furthermore, a peak positioned between 1440 and 1450 nm, assigned to the first overtone of OH stretching, and a combination band at 2310 nm were observed in this and many other spectra, suggesting

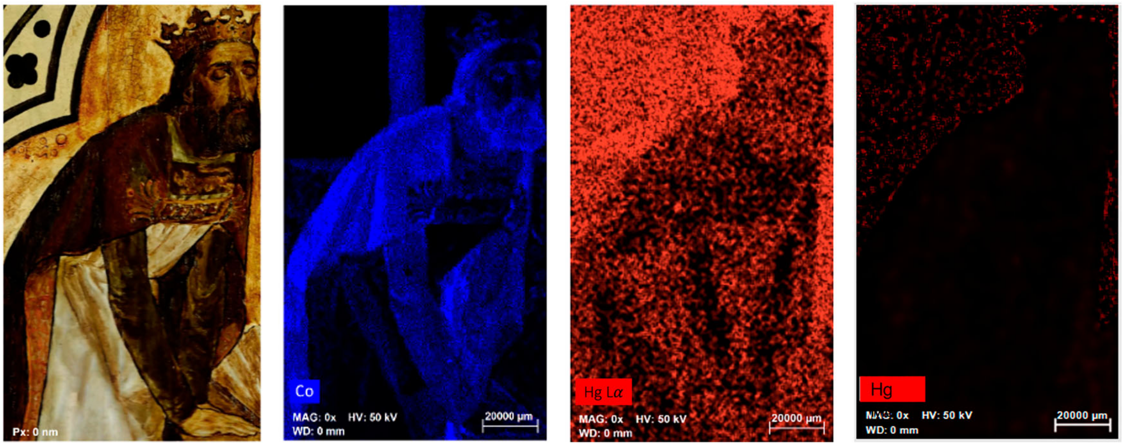


Figure 17. Visible image and elemental maps of cobalt (blue), mercury L alpha lines (red, on the left), and mercury M alpha lines (red, on the right) of an area on the panel *King Edward and William Torrel*.

Table 1. Summary of pigments identified on the *Great Bookcase* and their distribution across the different panels. The labels P1-P8 correspond to the painted panels as listed in Figure 1.

	P1	P2	P3	P4	P5	P6	P7	P8	Methods
Iron oxides	✓	✓	✓	✓	✓	✓	✓	✓	XRF (Fe)
Mercury chromate (?) [unknown chemical formula]		✓							XRF (Hg, Cr)
Organic red	✓	✓	✓						XRF (no elements detected) UV fluorescence (in some areas)
Red lead [Pb_3O_4]					✓				XRF (Pb)
Vermilion [HgS]		✓	✓	✓	✓	✓	✓	✓	XRF (Hg) Portable Raman FORS
Chrome yellow [$PbCrO_4$]							✓		XRF (Pb, Cr)
Gold	✓	✓	✓	✓	✓	✓	✓	✓	XRF FORS SEM-EDX
Lemon yellow [$SrCrO_4$]		✓							XRF (Sr, Cr)
Chromium-based green		✓	✓		✓			✓	XRF (Cr)
Copper-based green	✓		✓			✓		✓	XRF (Cu)
Emerald green [$Cu(CH_3COO)_2{\cdot}3Cu(AsO_2)_2$]		✓	✓	✓	✓	✓	✓	✓	XRF (Cu, As) SEM-EDX (Cu, As)
Cobalt blue [$CoAl_2O_4$]	✓	✓			✓		✓		XRF (Co, Al) SEM-EDX (Co, Al)
Cobalt-based blue					✓		✓	✓	XRF (Co)
Indigo [$C_{16}H_{10}N_2O_2$]							✓		Portable Raman
Synthetic ultramarine* [$Al_6Na_8O_{24}S_3Si_6$]					✓				SEM-EDX (Al, Na, S, Si)
Organic blue						✓			XRF (no elements detected)
Prussian blue [$Fe_4[Fe(CN)_6]_3$]				✓	✓				XRF (Fe) Raman on a sample
Organic violet						✓	✓		XRF (no elements detected)
Barium white [$BaSO_4$]					✓				SEM-EDX (Ba, S) Raman on a sample
Lead white [(PbCO3)2·Pb(OH)2]	✓	✓	✓	✓	✓	✓	✓	✓	XRF (Pb) FORS
Zinc white [ZnO]		✓							XRF (Zn)

that lead white was used for the preparation ground (Viguerie et al. 2020).

Table 1 summarises the pigments identified on the *Bookcase*. Where the material composition of a pigment could not be fully elucidated, the table indicates the main element, such as 'copper-based green'.

Conclusions

This investigation cast new light on William Burges' *Great Bookcase* and furthered our understanding of this object by characterising the materials involved in its making. The use of an infrared camera with a spectral range of 900–1700nm revealed the original iconography hidden beneath the monochrome blue backgrounds of the painted panels, which had remained uncovered during the preliminary study conducted in 2016 (Thistlewood 2017). The images recovered inspired new research across art history and literature that furthered the significance of the iconographic programme. The analyses revealed most of the palette used by the artists, showing that the *Bookcase* was extensively painted using nineteenth-century pigments introduced thanks to the progress brought about by the Industrial Revolution, such as cobalt blue, emerald green, and lemon yellow. However, the peculiar composition of the blue colour used for the background on four of the eight panels suggests that Burges might have tried to imitate medieval materials by purchasing a misleadingly labelled 'ultramarine blue' pigment that turned out to be heavily adulterated. The insight obtained helped to understand better Victorian artists' attitudes towards newly introduced pigments, which is discussed in detail in a different contribution (Ghigo Forthcoming). The results obtained will serve as a foundation for further technical research on Burges' artworks and Victorian painted furniture, both of which have never systematically been addressed.

From a technical point of view, this study showed that macro-XRF mapping was very effective to retrieve information on pigments' composition, notably because it was supported by recently developed software technology and combined with archival research on nineteenth-century painting materials. This method was, in this case, far more efficient than portable Raman spectroscopy and FORS, which provided limited insight due to the complexity of the colours used on the *Bookcase* and its elaborate painting stratigraphy.

The use of infrared reflectography and macro-XRF mapping was not initially planned. These methods were applied on the *Bookcase* thanks to the timeliness of the funding received to upgrade the museum's analytical suite and because the Covid-19 pandemic disrupted the access to other equipment. Therefore, the outcome of this study would not have been possible without the opportunities offered by the funding received and the management strategy that succeeded in redefining goals, redirecting resources, and making enough time to implement the new equipment.

Notes

1. Part of the outcome from this analysis was turned into a podcast episode for the series *Museum Secrets*. Available at: https://museumsecretspodcast.buzzsprout.com/1557707/8253429-beneath-the-blue.
2. Available at: collections.vam.ac.uk.
3. Available at: collections.vam.ac.uk.
4. Personal communication with Joyce H. Townsend, December 2021.

Acknowledgements

The authors would like to acknowledge Charlotte Ribeyrol, PI of the *Chromotrope* project, Matthew Winterbottom, Curator of Decorative Arts, and the colleagues from the Conservation Department at the Ashmolean Museum who supported this project. Special thanks to our Exhibition Technicians Tim Crowley, Kevin Jacques, and David Orwell for their professional assistance while building and moving the scaffolding towers around Gallery 66. Warm thanks also go to Paul Kayente, Radiation Protection Officer, for offering his help and insight while implementing macro-XRF mapping in the gallery and to Calum Smythe for the technical assistance in preparing the images of this article. Thanks to Kalin Dragnevski from the Engineering department and Owen Green from Earth Sciences, who assisted during optical microscopy and SEM-EDX analyses. Warm thanks to Ivan Shevchuck from the University of Hamburg for the training provided in using the Apollo camera. Last but not least, thanks to Joyce H. Townsend for the fruitful discussion that helped shape this work.

Funding

This research received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No. 818563 – CHROMOTROPE).

Disclosure statement

No potential conflict of interest was reported by the author(s).

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