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Identifying eighteenth century pigments at the Bodleian library using in situ Raman spectroscopy, XRF and hyperspectral imaging

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Abstract

There are multiple challenges in analysing pigments in historic watercolour paintings on paper, and typically non-invasive, in situ methods are required. Recent developments in portable analytical instrumentation have made this more accessible to heritage institutions, but many commercial systems are not optimised for the specific requirements of manuscripts and works on paper. This paper describes the successful use of Raman spectroscopy, X-ray fluorescence spectroscopy (XRF) and hyperspectral imaging to identify and map watercolour pigments used by the eighteenth century botanical illustrator, Ferdinand Bauer, and demystify the unusual colour code system found in his sketches. The value, delicate nature and large size of these paintings necessitated the use of using in situ, non-contact methods of analysis. A portable, bespoke Raman spectrometer specifically designed for analysing pigments from works on paper was used together with a bespoke portable Fibre optic reflectance spectrometer, portable X-Ray Fluorescence spectrometer and a hyperspectral imaging sensor. The results demonstrate that although there is a significant compromise between achieving good Raman spectroscopic results from artists' pigments and using sufficiently low laser power densities so as not to cause damage to the pigments, good results could be obtained with this portable system, particularly when combined with XRF, fibre optic reflectance spectroscopy (FORS) and hyperspectral imaging. Eight pigments were identified unequivocally from 125 watercolour paintings analysed, suggesting that Bauer used a more traditional and more limited palette than previously considered, and that his palette changed significantly in his later paintings. Similar pigments identified by the authors on colour chart that was discovered in 1999 in Madrid and attributed to Bauer, add weight to the attribution of this chart to Bauer. The data provides a much deeper insight into Bauer's colour annotations, and how he was able to achieve such an impressive degree of colour fidelity in his work.

Keywords: Portable Raman spectroscopy, FORS, Portable XRF, Ferdinand Bauer, Watercolour painting, Pigment Analysis, Botanical illustration

Background

The remarkable story of the *Flora Graeca*, one of the most magnificent printed books of the eighteenth century and the work of its artist, Ferdinand Bauer, has been well documented [1–4]. However, the methods and materials Bauer utilised in order to reproduce colour with astonishing accuracy in the 966 paintings of plants and 293 paintings of animals he produced for the endeavour during the period 1788–1794 has not been scrutinised. In particular, Bauer's palette and his use of a complex numerical colour code system used for both the *Flora Graeca* and the lesser known and unpublished *Fauna Graeca* have not been extensively discussed. This study was undertaken to determine the effectiveness of non-destructive, in situ methods to identify pigments used in Bauer's watercolour paintings and gain insight into how the artist worked in the field. Part of a larger research project at the Bodleian Library, the study was instrumental in unravelling the artist's colour code

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and understanding how his palette evolved over time by comparing pigments from 125 paintings from the *Flora* and *Fauna Graeca* with those identified in both an early painted colour chart [1, 2, 5] and in a number of later paintings [6].

Previous studies have used Raman spectroscopy, XRF, FORS and imaging spectroscopy for the non-invasive study of watercolour pigments in both manuscripts and paintings on paper [7–13]. Although more interventive technologies such as Surface Enhanced Raman Spectroscopy (SERS) have yielded better results with watercolour pigments, [14] these require either sampling, or direct contact with the surface of the object, something that is often not permitted in heritage collections. Furthermore, portable analytical studies are generally reliant on commercial instruments designed for general analytical work, rarely optimised for works on paper. The following study involves the use of bespoke Raman spectrometer and FORS systems, which have built entirely for the purposes of analysing pigments in works on paper and manuscripts.

The reduction in cost, and wider availability of non-invasive, portable instrumentation have facilitated identification of artists' pigments in heritage objects for which it would have been otherwise impossible [7–9]. In addition to portable XRF, the availability of portable Raman systems has also increased in recent years. The relatively low cost of these systems have made them an attractive prospect for heritage institutions. However, the laser powers employed by many portable Raman systems are typically set at levels to provide the optimal signal-to-noise ratio for robust samples but often exceed the level at which photosensitive pigments can be damaged or the nature of the pigment altered [15, 16]. For example, exposure to even very low laser power (> 1 mW) has been shown to rapidly transform iron oxide minerals, especially where they were poorly crystallised [17]. A comparison of a number of portable Raman systems, commercially-available in 2016, demonstrated that laser powers between 30 and 500 mW minimum were common with many systems. The typical power densities used in these systems are therefore likely to significantly exceed the threshold for use with certain heritage objects [15]. Not all manufacturers of portable systems quote a spot size in their literature, and therefore power densities for these systems are not possible to state categorically. However, unless otherwise stated by the manufacturer, the spot size for any Raman microscope may be assumed to be diffraction limited (i.e.: $d = \lambda/2NA$).

A bespoke Raman spectroscopy system has been designed and built at Durham University and optimised specifically for the analysis of pigments on books, manuscripts and works of art on paper. The benefits of using the Raman system are manifold: it is sensitive enough to identify many artists' pigments at laser power densities low enough to prevent photodegradation of light sensitive materials (20 W cm^{-2}), it allows for the sampling of a very small area (ca. 50 μm) compared to that of commercial portable Raman spectrometers, and it has a modular design that allows for a wide variety of sampling configurations, including the use of several different laser wavelengths.

In recent years, hyperspectral imaging and imaging spectroscopy have found numerous applications in the study and analysis of works on paper. It has been used for, amongst other applications, identifying stains on paper [18] and monitoring the condition of historic documents over time [19]. For artists' pigments, the value of hyperspectral scanning is to provide a digital image of the entire surface of an object, from which multiple analytical approaches can be taken (pseudo-colour mapping, principle component analysis and spectral angle mapping etc.). Delaney and others [11–13] have demonstrated the value of using both fibre optic reflectance spectroscopy (FORS) together with imaging spectroscopy and hyper/multispectral imaging to visualise and map the location of pigments in objects as diverse as paintings by Picasso and medieval illuminated manuscripts. Hayem–Ghez et al. [13] have also successfully demonstrated the validity of using hyperspectral pseudo-colour composites to differentiate between visually similar pigments. Therefore, the combination of portable Raman spectroscopy, FORS and XRF analysis together with Hyperspectral imaging can be considered a valuable and non-invasive system for the identification of historic watercolour pigments.

Ferdinand Bauer and the Flora Graeca

An enormous publishing endeavour, the *Flora Graeca* epitomised a change in character in the illustrated botanical book in the eighteenth century. It took 34 years to publish in its entirety, and was one of the most lavish and expensive books of its age.[1] It is most remarkable however, for the magnificent illustrations that it contains, painted with astonishing beauty and accuracy by Ferdinand Bauer (1760–1826).

John Sibthorp, Professor of Botany at Oxford met Bauer in Vienna, where he was working with the Naturalist and physician, Nikolaus Joseph von Jacquin in 1786. Impressed with his skill, if not his temperament, he wrote to his travelling companion, John Hawkins, on the 3rd March 1786: 'My painter in each part of natural history is *Princeps Pictorum*. He joins to the Taste of

[1] Harris notes that in 1830, twenty-five subscribers paid 620 lb for a complete copy of the *Flora Graeca*, roughly twenty times the average annual wage in England at the time. [4].

the Painter the Knowledge of a Naturalist—and animal, plant and Fossil touched by his hand shew the Master.' [20] Travelling from place to place quickly, often in difficult circumstances, Bauer was not able to carry with him large quantities of watercolour paper and other materials, nor would he have had the time to stop and prepare his colours to create full colour watercolour paintings for the many hundreds of specimens that he and Sibthorp collected.

In order to work in an efficient manner therefore, Bauer made simple graphite pencil sketches in the field, which were transformed into almost 1300 full scale watercolour paintings in Oxford between 1788 and 1794. In the field, he was unable to paint or record colour of these specimens directly. Crucial colour information was recorded solely by means of a complex numerical code applied to the sketches (Fig. 1). Lack and others [1–3] have argued that it is highly likely that Bauer utilised a painted, numbered colour chart in conjunction with this code, while Mulholland [21, 22] has suggested that Bauer may have used the code rather more as a simple mnemonic device without the need for a physical chart.

No painted colour chart that can be reasonably attributed to Bauer exists (or has survived) for Bauer's numbered sketches after 1787. However, in 1999, Lack [1, 2] discovered what appears to be an early colour chart made by Ferdinand or his brother Franz Bauer in the archive of the Real Jardín Botánico in Madrid in which the numbered colours matched several early numbered sketches and paintings created by the brothers. The order of numbered colours on this chart however does not correlate to any of Bauer's paintings after 1787, and if painted colour charts ever existed for either the *Flora* and *Fauna Graeca* or the Bauer's later work, they have been lost.[2] The Madrid chart therefore may have simply been an early experiment by the brothers to explore the accurate mixing of colours during their apprenticeship in the 1770s. The astonishing accuracy of Bauer's numerical colour code and his memory for colour is observed in the remarkable fact noted by Lack [1], that all but one of the 966 species Bauer painted for the Flora Graeca are painted with perfectly colour accuracy, and all are identifiable without any doubt (p156).[3]

Fig. 1 Ferdinand Bauer, colour coded sketch for *Iris germanicus*, Graphite pencil on paper, 1786-7 (MS. Sherard 243/38) © Bodleian Libraries, University of Oxford, 2017

Bauer's colour code

Based on the evidence in the Madrid colour chart, Bauer may have developed a scheme of some 140 colours into one of at least 300 for the *Flora Graeca*, and from then into a considerably more complex scheme of 999 colours for his work on the Matthew Flinders expedition to Australia from 1801–1806, which was decoded by Mabberley in 1999 [5, 6]. How exactly Bauer used this colour system is unclear, but in the absence of a physical chart, by comparing the numerical codes to their painted versions of the sketches, the authors found that the codes for the *Flora Graeca* definitively corresponded to the same ordered scheme as his later Australian paintings. Table 1 shows the basic ranges of colour by number code used by Bauer during his two botanical expeditions and that of the Madrid chart. Although the codes do not follow exactly the same pattern, the ordering of the colours by hue is similar in both the Flinders and Sibthorp numbering systems, but is markedly different in the unattributed painted colour chart form Madrid. Prior to this study it was unknown whether the pigments in the Madrid chart correlated with those found in later paintings [1–3].

[2] HW Lack carried out extensive research on Bauer's work over a period of 40 years, and in this time no colour chart has been discovered and no written reference to Bauer's use of a colour chart in the field for either the Sibthorp expedition (1786–1787) or the Flinders expedition to Australia (1801–1806).

[3] After comprehensive analysis, Lack found only one minor colour error in the 966 Flora Graeca paintings. Bauer's depiction of *Anchusa cespitosa* (MS Sherard 244 f35), is coloured grey–blue where it should have been a deep, striking blue [1] p. 156.

Table 1 Sequence of colour codes used by Bauer from ca. 1775–1806

Madrid/Haenke colour chart (ca. 1775–1786)	
Number code	*Colour range present in chart*
1–40	Reds-oranges
41–80	Yellows
81–120	Blues/lilacs
121–140	Greens
Flinders/investigator expedition to Australia (1801–1806)	
Number code	*Colour range observed in paintings*
1–100	Reds-dark reds
101–200	Purples-pinks
201–300	Pinks-mauves
301–400	Lilacs-violets-blues
401–500	Pale greens-greens
501–600	Dark greens-yellow greens
601–700	Yellows
701–800	Oranges
801–900	Browns
901–999	Whites and blacks
Sibthorp expedition to eastern Mediterranean (1786–1787)	
Number code	*Colour range observed in paintings*
1–20	Whites, greys blacks
21–40	Orange reds-dark reds
41–80	Dark reds, lilacs to light purples
81–120	Blues
121–160	Dark greens to yellow-greens
161–200	Bright yellows to yellow-ochres
201–220	Orange-yellows to brown-yellows
221–260	Red-browns to dark-browns
261–280 (largely used in Fauna paintings)	Transparent dark reds and purples
281–300 + (largely used in Fauna paintings)	Transparent greys and browns

Methods

In order to identify the pigments used in Bauer's paintings, watercolour mock ups were created based on a typical eighteenth century watercolour palette. Listed in Table 2 (below), these were chosen based on the results of a survey of 73 painting manuals published from 1640 to 1860, which list pigments specifically recommended for watercolour and miniature painting. Pigments were obtained from Kremer Pigments GmBH, and were ground with a glass muller on a ground glass plate using gum Arabic, honey and water in an approximate 1:4 pigment binder ratio, depending on the pigment. The samples were painted out using a sable brush on a hand-made, gelatine-sized, off-white Barcham Green antique laid paper, similar to that originally used by Bauer for the *Flora Graeca* paintings, and a library of Raman and visible reflectance spectra was compiled. A number of 19th century pigments commonly used in watercolour (e.g. Alizarin crimson, ultramarine violet) were also added for comparison.

Raman spectroscopy

The watercolour mock ups were analysed using three laboratory-based commercial Raman spectrometers at Northumbria University, Durham University and at the Rutherford Appleton Lab at the Harwell Campus, Didcot. These systems allowed the evaluation of six different laser excitation wavelengths: 488, 532, 633, 785, 830 and 1064 nm, to ascertain the optimum conditions for the library-based work (Table 2).

For the 488 nm, 532 nm, 633 nm and 785 nm laser excitation wavelengths, a Horiba Jobin–Yvon LabRAM HR confocal Raman microscope, equipped with a Peltier-cooled CCD and 50 × LWD 0.55 NA Leica objective was used. The minimum sizes of the laser spot on the sample surface according to Abbe's law are 0.44, 0.48, 0.57, 0.71 μm respectively. The maximum power value of each laser source was reduced to approximately 0.4 mW at the sample using a neutral density filter. A 600 l/mm grating was used with all sources, except measurements made with the 488 nm laser. In this case, an 1800 l/mm grating was chosen to increase resolution. The minimum wavenumbers accessible were 200, 120, 70 and 100 cm^{-1} respectively for the 488, 532, 633 and 785 nm. Theses were determined by the edge filters used to inject the laser into the optical path of the spectrometer and remove the Rayleigh contribution. All acquisition operations were controlled by Lab Spec 6-Horiba Scientific software.

The 830 nm Raman spectra were recorded using a Renishaw micro-Raman spectrometer (Rutherford Appleton Laboratory, Harwell Campus, Didcot), equipped with a 830 nm diode laser, a silicon CCD detector and 50 × LWD Leica objective lens. The resulting laser spot at the sample was 0.75 μm and the spectral range was 70–1800 cm^{-1} with a 1200 l/mm grating. The maximum laser power was 55 mW, attenuated to 1.1 mW at the sample. A silicon wafer was used as reference for calibration at 520 cm^{-1}.

The 1064 nm Raman spectra were recorded using a Bruker MultiRam FT-Raman spectrometer at the Rutherford Appleton Laboratory, Harwell Campus, Didcot, equipped with a 1064 nm Nd.YAG laser. The resulting laser spot at the sample was 100 μM. To achieve better results, samples were taken using laser powers adjusted to 50, 100 and 150 mW at the sample site, resulting in power densities of 0.64, 1.27 and 1.91 kW/cm^{-2} respectively.

In-situ Raman spectra were recorded on site at the Bodleian Library, Oxford, Real Jardín Botánico, Madrid and Natural History Museum, London using a dedicated

Table 2 Laser activation wavelengths and laser power densities for laboratory-based Raman Spectrometers used

System	Wavelength (nm)	Laser power at sample (mW)	Beam diameter (μm)	Beam area (cm^2)	Power density (kW/cm^{-2})
Horiba LabRAM HR	488	0.4	0.44	1.5×10^{-9}	270
Horiba LabRAM HR	532	0.4	0.48	1.8×10^{-9}	220
Horiba LabRAM HR	633	0.4	0.57	2.6×10^{-9}	150
Horiba LabRAM HR	785	0.4	0.71	4.0×10^{-9}	100
Renishaw inVia micro Raman	830	1.1	0.75	4.5×10^{-9}	249
Bruker MultiRam	1064	50	100	7.9E−05	0.64
Bruker MultiRam	1064	100	100	7.9E−05	1.27
Bruker MultiRam	1064	150	100	7.9E−05	1.91
Durham bespoke system	633 and 532	0.4	50	1.96×10^{-5}	0.02

spectrometer system optimised for the study of works on paper. The system employs a HeNe laser (632.8 nm, JDSU, 1 mW) attenuated using a neutral density filter, and focused into a fibre-optic cable for delivery to a Horiba Superhead sampling accessory. This is equipped with an ultra-long working distance × 40 microscope lens which also collects the backscattered Raman signal and provides a working distance of ca. 10 mm from the surface of the painting. The laser power at the sample was measured before each run and was maintained at < 0.4 mW. The laser spot on the sample is estimated ca. 50 μm diameter. However the apparent spot size using the fibre-delivery system is made considerably larger due to specular reflection from the surface of the object. As noted above, laser power density was calculated at 20 W cm^{-2}. The Raman signal is collected and passed down a second fibre optic cable to a spectrograph and cooled CCD camera (Andor Shamrock-163 and iDus416). The spectrometer control software was used to correct for the spectral response of the system and the wavenumber calibrated using a neon lamp. Spectra were typically the sum of 20 × 1 s acquisitions. For many samples that fluoresce (e.g. indigo), 1 s was the maximum integration time that could be used without saturating the sensor. For this reason, and to simplify data acquisition, 20 acquisitions were co-added to increase the signal to noise ratio for both fluorescent and non-fluorescent samples. The Raman sampling head was mounted on a vertical translation stage, itself mounted on a sliding rail fitted to a gantry that holds the head vertically over a single painting, or open bound volume, as illustrated in Fig. 2.

Access to different regions of the object are achieved by sliding the head left and right along the gantry, or by moving the entire gantry backwards and forwards. Vertical adjustment of the sampling head allowed fine focus control of the sampling head to achieve optimum signal. A USB microscope (Veho) was also mounted on the sampling head, allowing an image of the area and the precise position of the laser spot on the painting to be captured. Raman spectra obtained from a green laser were recorded using a second Superhead, equipped with optics for operation at 532 nm and a fibre-coupled frequency doubled Nd:YAG laser (Roithner Laser). This delivered < 0.4 mW at the sample and had a spot of 50 μm diameter, giving an average power density of 20 W cm^{-2}. The same spectrograph/camera as used for the 633 nm Superhead system was used for the acquisition of the Raman spectra.

Hyperspectral imaging

Hyperspectral scanning and visible/VNIR imaging reflectance spectroscopy was carried out using a Headwall E-series VIS/VNIR push–broom system with a sensor covering a range of 380–1000 nm, and a scientific grade, non-UV filtered, $f = 35$ mm lens was used. The sensor has a spatial resolution of 1600 pixels, an optical spectral resolution of 2.5–3 nm, and a spectral sampling interval of 0.64 nm, capturing a maximum of 972 individual wavelength bands for each pixel. For certain scans, a Headwall E-series high-efficiency VIS–VNIR spectrograph was used, also covering the range 380–1000 nm, but capturing a maximum of 320 individual wavelength bands per pixel. The volumes were placed on a precision movable translation stage under a stationary quartz halogen EKE dichroic light source. The source emitted a maximum of 1000 lx at the surface, at average exposures of 3–4 s per cm and a typical total exposure per painting of 2 lx-hours at typical museum lighting conditions for the exhibition of works on paper (50 lx). A white and dark field calibration was carried out prior to every session. A diffuse white standard (Labsphere Inc.) was used to calibrate the instrument to apparent reflectance. Scanning was carried out at the highest spectral resolution so as to provide the highest quality data. Pseudo-colour rendering was carried out following the methodology published by Hayem-Ghez et al. [18], and three wavelengths were chosen that agreed with maximum differentiation between the particular pigments under consideration for each painting.

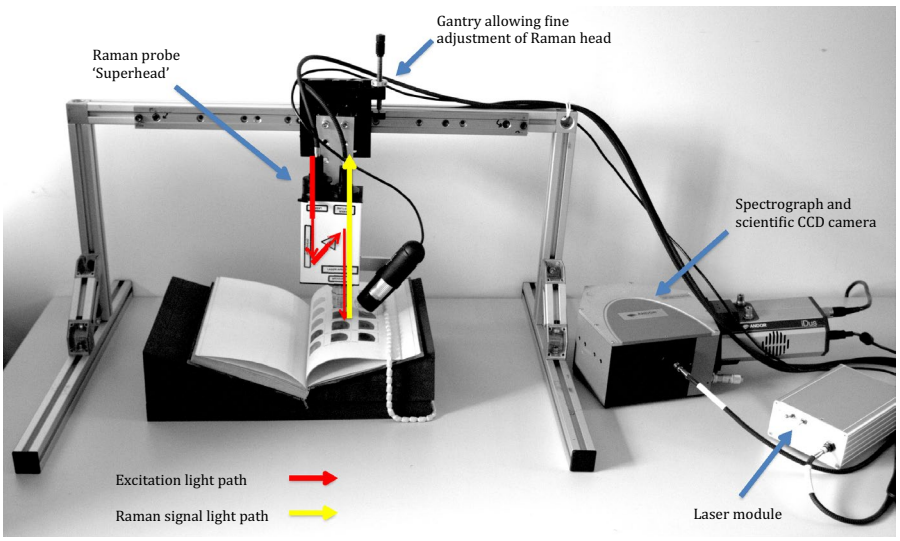

Fig. 2 Portable Raman Spectrometer, designed and built at Durham University © Durham University, 2017

Pseudo-colour rendering, spectral angle mapping and principle component analysis of hyperspectral images were carried out using two software packages: ENVI (Harris Geospatial Solutions) and Scyven (Scyllarus).

X-ray fluorescence

X-ray Fluorescence analysis on the bound *Flora Graeca* paintings was carried out using an Oxford Instruments X-MET 8000 series light element handheld XRF analyser with a 5 mm spot size. The instrument was run in air at 60 s acquisition times using the dual condition sets of 8, and 40 kV/8 μA so that a range of elements from magnesium to uranium could be detected. The same condition set and methodology was used for all analyses so that they are directly comparable. Longer exposure times were not possible due to the instrument being in handheld mode without a stand, and due to time restraints [23]. Analysis depth was in the region of 2 cm depending on the element, and therefore a non-fluorescing background plate was placed under the verso paper substrate so as not to pick up elements from the next painting in the volume. Due to the thin layer of the watercolour paint, elements from both the paint and paper substrate were inevitably included in the results. A measurement of the paper substrate from each page was taken and spectra from the paint and paper were overlaid in order to ascertain which elements derived from each component. Given the relatively large size of the beam, large areas of colour of measuring 5 mm in diameter or more were selected for analysis.

On site X-ray fluorescence of the unbound Madrid colour chart was carried out at the Real Jardín Botánico, Madrid by Dolores Gayo and Maite Jover de Celis from the Analytyical Laboratory, Museo Nacional Del Prado, Madrid using a Brüker Tracer III-SD handheld unit with a 3 mm spot size. Conditions were as noted above, with the exception that the instrument was run in a vacuum purge at 40 kV/20 μa with no filter and with an acquisition time of 60 s.

On site X-ray fluorescence on Bauer's unbound Australian orchid paintings was carried out by Robert McLeod at the Natural History Museum, London also using a Brüker Tracer III-SD handheld XRF unit. Conditions were as noted above, with the exception that the instrument was run in air using the dual condition set of 40 kV/10 μA with no filter and 40 kV/10 μA, and using a 12 mm Al + 1 mm Ti +1 mm Cu filter for higher sensitivity to heavier elements. Acquisition time was 60 s.

Vis/NIR fibre optic reflectance spectroscopy

For the analysis of pigments on the Bauer/Haenke chart, the mobile Raman spectrometer described above was transported from the Bodleian Library to the Real Jardín Botánico in Madrid in February 2017. Raman spectroscopy was carried out as described above. In this case however, analysis was supplemented with visible and near infrared fibre optic reflectance spectroscopy (FORS) for the identification of organic pigments and in particular for the presence of azurite. FORS was carried out using bespoke near infrared and visible FORS heads, designed and built at Durham University, which are attached to the adjustable Raman gantry described above together with the Raman Superhead. Both heads use a tungsten halogen light source. The visible FORS unit has a spectral range of 300–1100 nm, and the signal is acquired by an Ocean Optics

Maya 2000 Pro spectrophotometer. The FTIR-FORS unit equipped with a FR-NIR spectrometer (Si-Ware, Neospectra) and has a spectral range of 1300–2600 nm. The adjustable gantry allows for both heads to be attached at the same time and the FORS heads have a stand off from the object surface of 8 cm (visible) and 4 cm (infrared). A diffuse white standard (Labsphere Inc.) was used to calibrate the instrument to apparent reflectance.

Results and discussion

To determine the optimal parameters necessary for Raman spectroscopic analysis of the Bauer paintings, a range of pigment standards, described above, were investigated to determine which excitation wavelengths and laser power was most suitable for the paintings. Laboratory based instruments were utilised to establish optimum wavelength. Field spectra on the Bauer paintings were obtained using the 633 nm He-Ne laser as noted above. The study also established where the complimentary techniques (XRF, FORS and Hyperspectral imaging) could be best used to confirm the presence of pigments that had little or no Raman response at the power levels indicated.

The data in Table 3 shows the results obtained using laboratory-based commercial Raman spectrometers at Northumbria University, Durham University and at the Rutherford Appleton Lab at the Harwell Campus in Oxford. Although many pigments that exhibit good Raman scattering, such as vermillion, Prussian blue, red lead and ultramarine, yielded good spectra with all excitation wavelengths, the results confirmed that the green (532 nm) and the red (633 nm) lasers available in the Durham portable, in situ instrument produced consistently good results for a high proportion of the pigments (Table 3). The 830 and 785 nm lasers also produced good results, but were not considered further as, due to the need to use increased laser power to obtain acceptable signal to noise ratios, conditions under which they produced excessive damage to both pigment samples and paper substrate. The results of the survey were also useful in determining that many common eighteenth century watercolour pigments that Bauer may have used (e.g. Brazilwood, madder lakes, sap green, and copper blues and greens) did not produce Raman spectra using any of the excitation wavelengths tested at power levels acceptable for the study of the paintings. Both the 633 and 532 nm lasers used in the Durham portable system produced good results for the modern watercolour standards. However, the 633 nm laser was selected. It was found to perform better with historical watercolours, and allowed the identification of the maximum number of pigments whilst being used at power densities well below the damage thresholds for the materials under study (Table 4).

Identification of pigments in Ferdinand Bauer's watercolour paintings

A total of one hundred and twenty-five paintings were analysed, comprising of ninety-seven from a single volume of the *Flora Graeca* (Ms. Sherard 242) and twenty-eight from two volumes of the *Fauna Graeca* (MS. Sherard 239: *Pisces* and MS. Sherard 240: *Aves*). For comparison, several of Bauer's later paintings made in Australia between 1801 and 1806 were analysed by XRF and Raman spectroscopy at the Natural History Museum in London. Additionally, the painted colour chart held at the Real Jardín Botánico and likely created by Bauer in Madrid was analysed by Raman spectroscopy, Vis and FTIR FORS and XRF. Samples were selected that were representative of the wide spectrum of colours used by Bauer. The results were recorded and compared, where possible, to the numerical codes on the field sketches. Tables 5 and 6 show the pigments positively identified in all four sources. Results from the *Flora Graeca* were compared with those from the *Fauna Graeca* (Table 5), and with seven paintings of orchids painted by Bauer from sketches made during his Australian expedition (Table 6). Table 7 provides a representative sample of analytical data from all four sources.

Pigments identified in Bauer's *Flora* and *Fauna Graeca* paintings (1786–1794)

The identification of pigments by Raman spectroscopy were confirmed by XRF where possible, and demonstrated that Bauer's *Flora Graeca* palette was more limited than previously considered, was fairly consistent and traditional. Naturally, greens were present in almost all paintings, and in several of the *Fauna Graeca* paintings. Unlike many contemporary watercolour painters, Bauer seems to have favoured pure copper greens (often adulterated with organic lakes and indigo), rather than a mixture of blue and yellow such as Prussian blue and gamboge known as Hooker's Green in watercolour, and widely used by artists at the time for painting foliage [24, 25]. Positive identification and differentiation of the particular type of copper green used (for example, verdigris, bice, chrysocolla/cedar green, malachite etc.) is not trivial by Raman spectroscopy using the 633 nm laser employed by the portable system, and spectra were obscured by large bands of fluorescence. However, under visual examination, the vast majority of Bauer's greens absorbed strongly in the ultraviolet and near-infrared regions, characteristic of copper-based pigments, and XRF analysis of a number of representative areas of green pigment confirmed the presence of copper in all cases. Microscopic examination at 400× of the same examples indicated that Bauer rarely used a mixture of blue and yellow to provide green, so for example it is unlikely that he used a combination of copper blue

Table 3 Results of survey of six Raman excitation lasers on watercolour pigments

PIGMENT/Laser wavelength	488 nm Sapphire	532 nm Nd.YAG	633 nm HeNe	785 nm Diode	830 nm Diode	1064 nm Nd.YAG
REDS						
Alizarin Crimson						
Carmine/cochineal						
Alizarin crimson						
Lac						
Caput Mortuum						
Vermillion						
Cinnabar						
Brazilwood						
Madder lake						
Red lead						
Venetian red						
Haematite						
Red ochre						
Red ochre (deep)						
BROWNS						
Brown ochre						
Burnt umber						
Raw umber						
Burnt Siena						
Raw Siena						
Logwood						
Bistre						
Sepia						
BLACKS						
Ivory black						
Peach black						
BLUES						
Indigo						
Prussian blue						
Ultramarine (lapis lazuli)						
Lapis (Chilean)						
Smalt						
Blue verditer						
Blue bice						
Azurite						
Ultramarine violet						
GREENS						
Synthetic verdigris						
Egyptian green						
Malachite						
Chrysocolla (Cedar green)						
Green earth						
Sap green						
YELLOWS						
Yellow lake (buckthorn)						
Yellow ochre						
Gamboge						
Realgar						
Orpiment						

KEY	
	Good spectrum observed
	High level of fluorescence, but peaks observed
	High level of fluorescence obscuring peaks
	No spectrum observed

and a yellow pigment. Several green pigments could not be identified using Raman spectroscopy or XRF. In these cases, it is possible Bauer used a green lake pigment such as sap green or terre verte (green earth), both of which are recommended frequently in eighteenth century watercolour manuals [26–29].

Table 4 Number of pigments identified using different excitation wavelengths

Excitation wavelength (nm)	Pigments identified unequivocally	Pigments identified with weak peaks or peaks obscured by fluorescence
488	13	21
532	19	25
633	17	26
785	12	19
830	18	32
1064	10	15

Table 5 Instances of pigment use by Ferdinand Bauer in paintings for both the *Flora* and *Fauna Graeca* (1788–1794) from a total of 125 paintings

Pigments identified	*Flora Graeca* (MS. Sherard 242)	*Fauna Graeca* (MS. Sherard 239 and 240)	Total pigments identified
Indigo	51	21	72
Vermillion	36	16	52
Copper greens	17	6	23
Copper blues	6	10	16
Prussian blue	0	8	8
Red lakes	9	9	18
Vermillion and red lake	13	11	24
Red Lead	4	5	9
Madder	1	0	1
Yellow lake/gamboge/ ochre	21	10	31
Lead white	23	2	25

Table 6 Pigments identified in Madrid colour chart (c. 1780–86) and 6 painting of orchids by Bauer (1801–6)

Pigments identified	Bauer/Haenke colour chart (c 1780 s)	Orchid paintings (1801–06)
Indigo	Yes	Yes
Ultramarine/Lapis lazuli	No	Yes
Vermillion	Yes	No
Copper greens	Yes	No
Azurite/copper blues	Yes (Azurite)	No
Prussian blue	No	No
Red lakes	Yes	Likely
Vermillion and red lake	Yes	No
Red lead	No	No
Madder	Likely	No
Yellow lake/gamboge/ ochre	Likely	Likely
Lead white	Yes	No
Barium white	No	Yes
Iron oxide reds	Yes	No
Brown ochre	Yes	No

As expected, lead white is found throughout Bauer's work, both in white painted areas and, more commonly mixed with other pigments, identified using both Raman spectroscopy and XRF. Figures 3 and 4 show typical XRF spectra for the presence of lead in red and blue painted areas of the *Flora Graeca* paintings. Although zinc white was a popular replacement for lead white amongst watercolourists, it was not in common use until the early nineteenth century. As noted below, Bauer appears to have abandoned lead white for the more transparent barium white in some later paintings.

Both Raman spectroscopy and XRF results confirm that Bauer used vermillion almost exclusively for his red colours (Fig. 3), often tempered with an organic red lake, possibly cochineal/carmine or, less frequently, with red lead. Both vermillion and red lead were readily identified, but Raman spectroscopic results vary for the organic reds used, and in general identifiable peaks were obscured by fluorescence in all cases. However, visible reflectance spectra taken from the Madrid chart using FORS and from several *Flora Graeca* paintings using hyperspectral data produced characteristic absorbance bands for anthraquinones in several instances (500 and 560 nm with peak reflectance around 600 nm) [30], suggesting the presence of either madder or carmine, both recommended in most eighteenth century watercolour manuals [26–29]. Although it is occasionally possible to distinguish an insect (carmine, lac) or vegetable (madder) origin of anthraquinone-based red lake pigments in mock up samples, in this case the variation and quality of the spectra were not enough to identify these with confidence. However, the lack of madder's characteristic visible fluorescence under ultraviolet examination suggested carmine as the more likely. The few instances of pink colours analysed indicates that Bauer frequently used vermillion mixed with lead white or possibly madder mixed with lead white. Vermillion is present in almost all of Bauer's reds and also in mixture in many of his brown pigments. Red lead was identified in several orange colours but in general, when lighter reds/oranges were encountered, they were more commonly found to be a mixture of vermillion and an as yet unknown yellow pigment.

Yellow pigments from thirty-one paintings were analysed, but none produced a Raman spectrum. Inorganic yellows such as orpiment, realgar, massicot and Naples yellow were widely used in manuscript illumination, portrait miniature painting and botanical illustration prior to the

Table 7 Select results from the analysis of watercolour pigments used by Ferdinand Bauer ca. 1780–1806

Acc. no/colour	Major Raman peaks (cm^{-1})	XRF principle elements detected	Other	Inference
MS. Sherard 242: Flora Graeca				
Paper Background		Pb, Ca, Ba, Fe, Co, Ni, Cu, Al, Si, Mn, As, Zn	–	–
242/2: Yellow	Fluorescence covers peaks	–	–	–
242/6: Red	342, 251	–	–	Vermillion
242/6 Yellow	Fluorescence covers peaks	–	–	–
242/11: Brown	1576, 596, 544, 342, 251	–	–	Vermillion and indigo
242/12: Red	342 (s), 279, 252 (vs)		–	Vermillion
242/12: Green	1578 (m), 596, 544	–	Absorbs strongly in infrared	Copper green and Indigo
242/12: Brown	Fluorescence covers peaks	–	–	–
242/21: Green	1578, 596, 544	–	–	Indigo
242/21: Blue	Fluorescence covers peaks	–	–	–
242/24: Red	550, 342, 251, 121	–	–	Red lead and vermillion
242/24: Green	1575, 596, 544	–	Absorbs strongly in infrared	Copper green and indigo
242/29: Red	252 (m), 342 (m) and high degree of fluorescence	–	–	Vermillion and organic red
242/39: White	1048	–	–	Lead white
242/36: Blue outlines	1578, 595, 543	–	–	Indigo
242/36: Green	1577, 596, 542	–	Absorbs strongly in infrared	Copper green and indigo
242/27: Purple	Fluorescence covers peaks	–	–	–
242/27: Blue outlines	1578, 596, 544	–	–	Indigo
242/37: Blue outline	1577, 596, 544	–	–	Indigo
242/37: Yellow-green	1577, 1050 (s), 596, 544,	–	Absorbs strongly in infrared	Copper green, indigo and lead white
242/40: Yellow	Fluorescence covers peaks	Pb, Cu, Fe, Sb (similar level to paper background)	Cu likely from green outline	Unknown yellow and lead white
242/44: Purple	342, 280, 251	–	–	Vermillion and unknown blue
242/56: Red	342, 251	Hg, Cu	Cu likely from green outline	Vermillion
252/56: Purple	342, 250	–	–	Vermillion and unknown blue
252/62: White	1050	–	–	Lead white
252/62: Dark green	1577, 596, 544	–	Absorbs strongly in infrared	Copper green and Indigo
242/81: Dark red	342, 252	–	–	Vermillion
242/81: Dark green	1576, 596, 544	–	Absorbs strongly in infrared	Copper green and indigo
242/84: Green	1577, 596, 544	Cu, Pb, Ca, As (similar level to paper background)	Absorbs strongly in infrared	Copper green, indigo and lead white
242/84: Red	342, 252	Hg, Pb, Ca	–	Vermillion and lead white
242/115: Pink	1314, 341, 252	–	Fluoresces salmon pink under UV	Vermillion and madder lake
242/115: Red	1314	–	–	Carmine/Red lake/madder lake
242/115: Orange-red	550, 342, 252, 120	–	–	Vermillion and red lead
242/115: Orange	550, 120	–	–	Red lead
242/121: Red	342, 250	Hg, Pb, Cu		Vermillion and lead white
242/121: Green	1577, 596, 544	Cu, Pb, Hg	Absorbs strongly in infrared	Copper green, lead white and indigo
242/147: Dark blue	2152 (m), 1578, 544	Pb, Fe, Cu, Co (similar level to paper background)		Indigo, Prussian blue and lead white
242/147: White	1050 (w)	Pb, Cu	–	Lead white
MS. Sherard 239/240: Fauna Graeca				
239/23: Orange	342, 251	–	–	Vermillion
239/23: Dark blue	1576, 594, 543	–	–	Indigo
239/23: Orange	552, 121	–	–	Red lead

Table 7 continued

Acc. no/colour	Major Raman peaks (cm^{-1})	XRF principle elements detected	Other	Inference
239/24: Dark blue	2154 (vs)	–	–	Prussian blue
239/28: Blue	2153 (vs)			Prussian blue
240/19: Dark blue	2154, 342, 252	–	–	Vermillion and Prussian blue
240/66: Dark blue	2154, 342, 252			Vermillion and Prussian blue
Orchid Paintings				
Paper background	–	Pb, Ca, S, Fe, Co, Cu, Al, Si	–	–
166a: Dark red	–	Fe, Al, Ca, K		Madder/carmine/red lake
166a: Green	–	Ba, Ca, S, Al, K		Organic green lake and Barium white
166b: Blue	–	Ba, Ca, S, Al		Unknown blue and barium white
173b: Blue	539, 1096	Ba, Al, K, S, Fe	Orange ferrous deterioration products	Ultramarine/Lapis lazuli and barium white
173b: Dark Blue	1576,593, 543	–	–	Indigo
173b: Red	High degree of fluorescence	Fe, S, Si, K	Semi-opaque in infrared	Madder/carmine/red lake
173b: Green	High degree of fluorescence	Fe, K, Si, Al, S	Does not absorb strongly in infrared	Organic green lake
Madrid Colour chart				
Paper background	–	Pb, Ca, Fe, Co, Cu, Al, Si	–	–
Yellows (41–61)	Fluorescence covers peaks	Ca, Pb, Cu, Hg	–	–
Reds (1–10)	1314, 1312	Ca, Pb, Ca	FORS peaks at 500 and 560 nm with peak reflectance around 600 nm	Anthraquinones: Madder/carmine/red lake, some with lead white
Reds (11–21)	342, 252	Hg, Pb	–	Vermillion, some with lead white
Blue (80–100)	Fluorescence covers peaks	Cu, Pb, Fe	FORS-NIR absorbance bands at 2285 nm and 2352 nm	Azurite with lead white
Blues (100–120)	Fluorescence covers peaks	Cu (similar level to background), Pb, Fe	Several swatches with absorbance bands at 2285 nm and 2352 nm	Some azurite, together with swatches of an unknown blue and lead white
Greens (121–140)	1578, 596, 544	Cu, Pb	–	Copper green
Whites	–	Pb	–	Lead white
Brown 149	–	Hg, Fe, Mn	–	Brown ochre

late eighteenth century, and all four pigments are strong Raman scatterers. So the fact that no spectral evidence was found for any of these pigments strongly suggests that Bauer likely did not use them extensively. XRF analysis identified one instance where antimony was present (MS. Sherard 242/40) suggesting the use of Naples yellow (lead (II) antimonite) in at least one painting. However, it was not found in any other yellow pigment analysed from the *Flora Graeca*, *Fauna* Graeca, the Madrid chart or the Australian paintings. Traces of arsenic were also found in some examples suggesting the use of orpiment (arsenic (III) sulfide). However, the lack of the characteristic bands for orpiment in the Raman spectra, make this less likely. Furthermore, as Spring et al. [31] note, arsenic is frequently identified in conjunction with the blue pigment smalt, which was found to be present in significant amounts within the fibres of Bauer's paper substrate where it was used during the papermaking process as a 'blueing' agent, described below.[4]

Bauer's blues are dominated by two pigments: indigo and an unidentified copper blue. Analysis of several copper blue pigments identified with XRF in the Madrid colour chart confirmed the presence of azurite, characterized by NIR-FORS absorption bands at 2285 and 2352 nm. Indeed almost half of the blue swatches analysed in the chart were found to contain azurite. Although it is likely Bauer created this chart, there is no primary evidence to confirm this fact, and as NIR-FORS was not available at the time

[4] The physical appearance of Bauer's yellows with microscopy, and under ultraviolet and hyperspectral examination when compared to known standards, seems to indicate that he generally used two different yellows. The appearance of these under microscopy and with visual comparison under discrete hyperspectral wave bands, appears to be consistent with yellow ochre, yellow lake and gamboge.

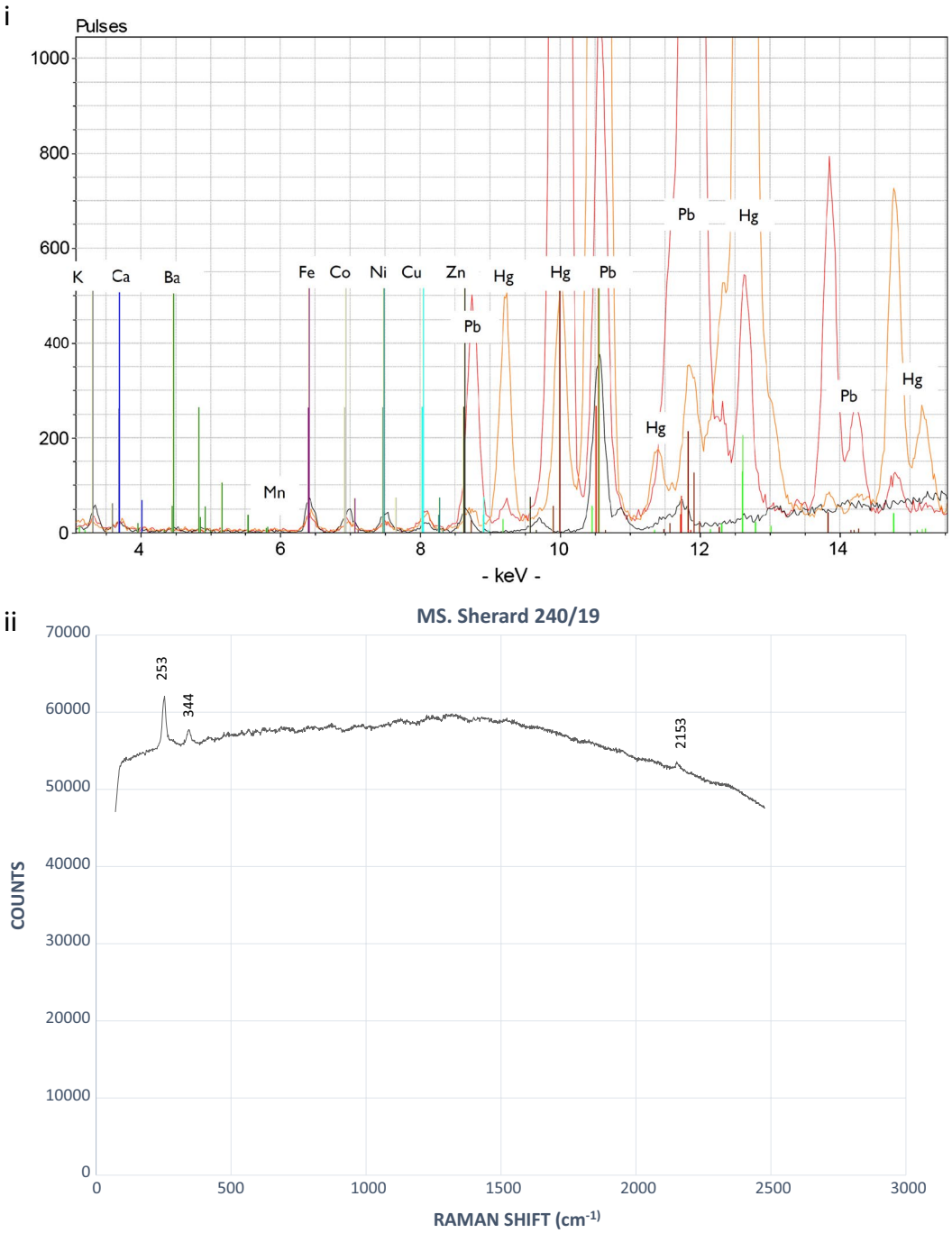

Fig. 3 **i**. XRF spectra of red and orange pigments from MS. Sherard 242/121, showing paper background (black line: Pb, Ca, Ba, Fe, Co, Ni, Cu, Al, Si, As, Zn), Red pigment (Red line: Pb, Hg, Cu) and orange pigment (orange line: Hg, Pb, Cu) indicating presence of vermillion © Bodleian Libraries, University of Oxford, 2017. **ii**. Raman spectrum of MS. Sherard 240/19 with characteristic peaks for vermillion and Prussian blue. © Bodleian Libraries, University of Oxford, 2017

of the *Flora Graeca* pigment analysis, azurite has as yet to be positively identified in known painted works by Bauer after 1786. Indigo was identified by Raman spectroscopy in 72 paintings, and, as a means to outline areas, in almost all of the *Flora* paintings analysed (Fig. 4ii). Bauer appears to have used indigo for particular purposes. He frequently used it to outline, delineate and define areas of a plant (he rarely used black pigments for this purpose), and he

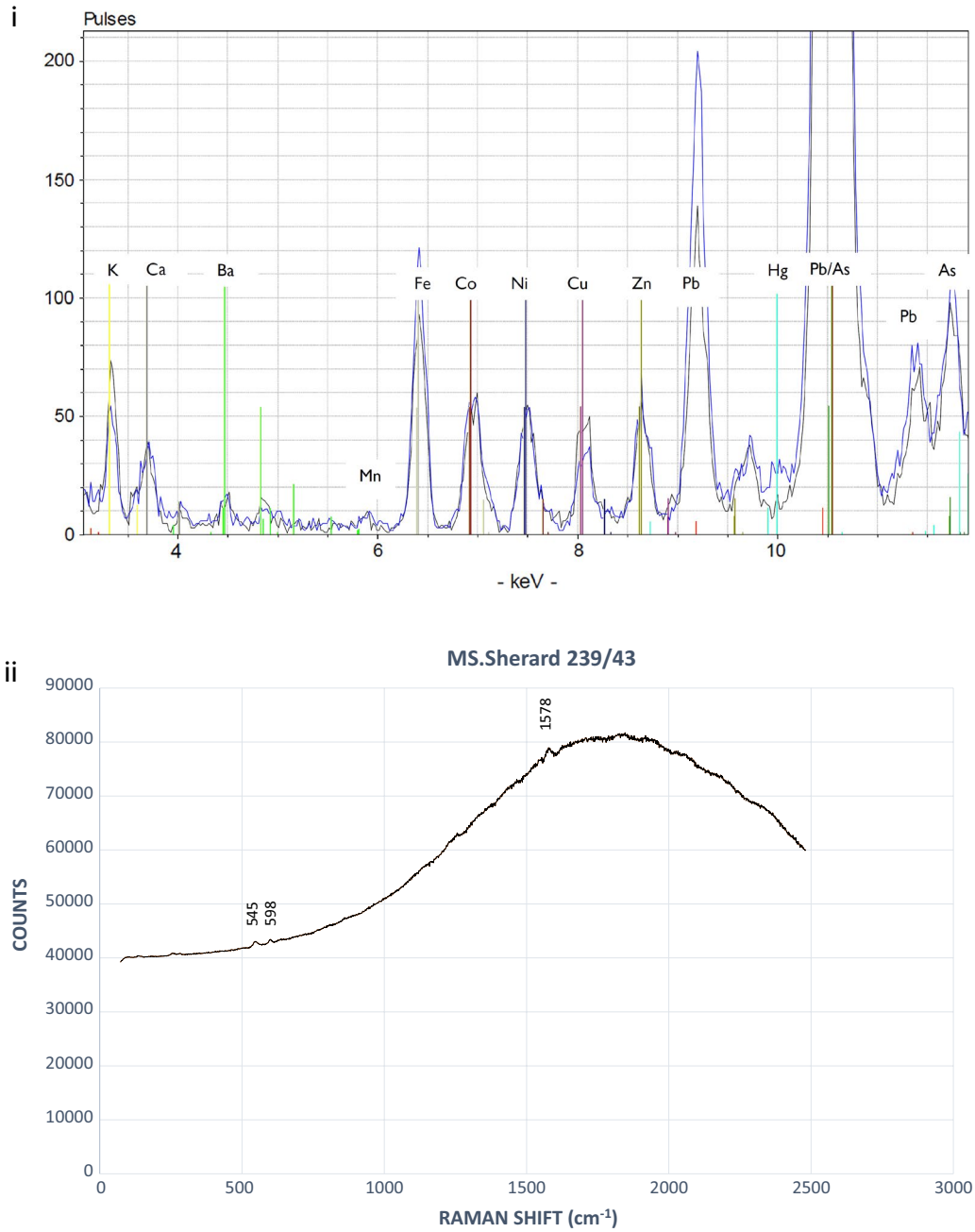

Fig. 4 **i**. XRF spectra of blue pigment from MS. Sherard 242/147 showing paper background (black line: Pb, Ca, Ba, Fe, Co, Ni, Cu, Mn, Al, Si, As, Zn) and Blue pigment (Blue line: Pb, Fe, Cu, Hg and Co at similar level to background). © Bodleian Libraries, University of Oxford, 2017. **ii**. Raman spectrum of MS. Sherard 239/43 with characteristic peaks for indigo. © Bodleian Libraries, University of Oxford, 2017

used it in admixture to manipulate the tone of other pigments. For example, indigo was identified as a component in almost all copper green pigments found in the *Flora Graeca* paintings and in several greens identified on the Madrid chart. Similarly, it was used together with vermillion or a red lake in most of Bauer's purples and in several of his browns.

Unsurprisingly perhaps, indigo was rarely used to paint the striking, vibrant blues in the flowering bodies of certain plants given its relative lack of brilliancy in watercolour. Although not confirmed, the results provided by the Madrid colour chart, and characteristic absorption in the infrared region makes it seem likely that this was a copper blue such as azurite, bice or

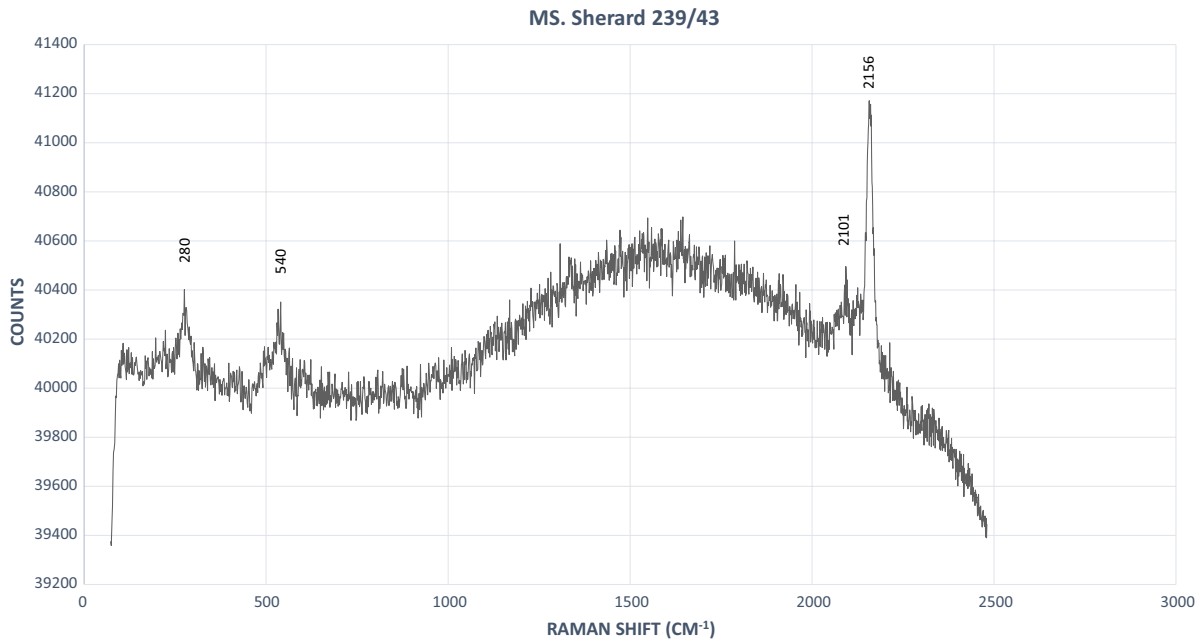

Fig. 5 Raman spectrum of MS. Sherard 239/43 with characteristic peaks for Prussian blue. © Bodleian Libraries, University of Oxford, 2017

verditer. Since Bauer was required to paint almost 1300 paintings in colour at a rapid pace, the widespread use of indigo, which was considerably less expensive than azurite, smalt and particularly ultramarine, and a pigment that was very workable in watercolour would be an obvious choice [32, 33]. For the volume of paintings that Bauer was commissioned to produce for Sibthorp between 1786 and 1794, it is understandable that he made as much use of it as he could.[5]

In the *Flora Graeca* paintings examined, none of the more vibrant blues produced a Raman spectrum at the levels described above. However the absence of results for Raman-active blue pigments such as Prussian blue or ultramarine suggests that neither was preferred by Bauer for this purpose. Ultramarine was discovered in discrete areas in two of Bauer's later orchid paintings, produced during his later (and considerably better-funded) Australian expedition. Given Bauer's complaints [1, 3] about the meagre compensation paid to him by Sibthorp during the expedition to the Levant, it is perhaps understandable that using the extremely expensive ultramarine for a project involving almost 1300 paintings that were ultimately intended to be reproduced in print would have been prohibitive. However, the relative absence of the comparatively inexpensive Prussian blue in the *Flora Graeca*, in use as an artists' pigment by the 1720s and recommended highly in manuals on watercolour painting published throughout the second half of the eighteenth century, is notable [27, 28].

Raman spectroscopy of several paintings of fish and birds from the *Fauna Graeca* paintings shows that Bauer used Prussian blue extensively in these works (Figs. 4ii, 5). XRF analysis performed on site at the Natural History Museum in 2016 on blue pigments used in six paintings of Australian orchids by Bauer from the museum's collection, found that they contained no copper, but that potassium, iron, phosphorus and sulphur were present. These are indicative, if not conclusive, of Prussian blue. Other aspects however, strongly suggested the use of Prussian blue. Orange-yellow iron ferrihydrite deterioration observed throughout the blue pigment used for *Epiblema grandiflorum* (NHM Botany 173b)[6] for example is consistent with the photo-oxidative deterioration of Prussian blue and with the results of artificial aging carried out on Prussian blue samples made according to traditional

[5] There are no extant records from either the Sibthorp or Flinders expeditions that document the purchase of artists' materials. However, it is highly likely that Bauer was responsible for purchasing his own materials from his own salary. The fact that very expensive pigments such as ultramarine or cochineal were not used or were used in very limited cases in the *Flora Graeca* paintings is likely due to Bauer's limited financial resources and the vast number of paintings he was required to produce within a very limited time period.

[6] Library and Archive, Natural History Museum, London: 'Forty-nine original water colour drawings of the Animals, and 252 of the Plants, which were collected when accompanying the Voyage under Capt. M. Flinders to Australia.'

eighteenth century recipes by Samain et al. [33].[7] Raman spectroscopy carried out on the same blue in 2017 however, confirmed only the presence of ultramarine, indigo and an unknown but highly fluorescent blue in these paintings (Table 7). Prussian blue was not found in any of the Orchid paintings analysed.

XRF analysis revealed that in the majority of blues used in the *Flora Graeca* paintings copper and cobalt were present, suggesting the use of either smalt or a copper blue (such as blue bice, verditer or azurite) (Fig. 4i). It is likely however, that the source of the cobalt in this instance was from the paper substrate itself. Under in situ microscopic examination at × 400, it was clear that the particle morphology of Bauer's blue pigments was not consistent with smalt, while that of the blue pigment within the paper structure was. Bauer's blue pigment appears as small, finely divided, rounded and semi-opaque particles, in contrast with smalt (amorphous, conchoidally-fractured, angular and transparent particles). As noted above, particles matching this description and containing cobalt were clearly visible within the fibres in all instances of Bauer's papers examined under microscopy, suggesting that the source of the cobalt was likely the paper itself, rather than the blue pigment.

A survey of Bauer's papers during the project demonstrated that he almost exclusively used high quality white, laid papers of Dutch origin. Almost all of these can be identified by their watermarks as papers from the mill of C&J Honig, imported in large quantities to England throughout the century.[8] As demand for white paper increased, so did demand for quality, white linen rags [35]. Cheaper, lower quality rags were used for efficiency, but resulted in papers with a yellow tinge. To visually counteract this, 'blueing' agents in the form of dyes, blue textile rags and pigments were added to the paper at the pulp stage [34–36]. The use of smalt for this purpose was widespread in the eighteenth century, as very little pigment was required to tint or neutralise the tone of the paper [35]. The practice likely originated in the Netherlands, whose mills were highly regarded for their blue papers [34], and smalt has been positively identified in Dutch eighteenth century white papers in a number of studies [34, 36, 37]. The source of cobalt in Bauer's paintings is therefore more indicative of this practice, rather than the presence of smalt as a pigment. Furthermore, the presence of copper in almost all examples analysed by XRF, together with the positive identification of azurite in the earlier Madrid chart, strongly suggests that in addition to indigo, Bauer's tendency was to use copper blue pigments in his work.

Pigments in Bauer's Later Paintings (1801–1806)

Bauer's painting style changed markedly during and after his expedition to Australia with Matthew Flinders (1801–1806), and he favoured a more delicate watercolour style in transparent watercolour [1, 6, 38]. After 1800, Bauer largely abandoned the opaque painting technique he had used for the *Flora Graeca* paintings. Having more time to paint these at his leisure in Australia and after he returned to England in 1806, it is likely that he was able to spend more time on the more technically complex transparent watercolour technique. To do so also required a change to his pigment palette. Opaque pigments used in the *Flora Graeca* paintings such as lead white, red lead and vermillion were perhaps more suited to the bodycolour painting traditionally used in both manuscript illumination and portrait miniature painting [22, 26, 38]. XRF analysis carried out at the Natural History Museum in 2016 revealed that, at least in the small sample of paintings analysed, lead, copper and mercury were absent from Bauer's palette during these years. Pigments in the later paintings contained iron, aluminium, sulphur, potassium and barium, suggesting that he abandoned the use of the opaque copper greens and blues, vermillion, red lead and lead white used throughout the *Flora Graeca* in favour of more transparent laked pigments. As noted above, ultramarine, indigo and an unknown, transparent blue were found in several instances, but no red pigment used in these paintings produced a Raman spectrum. Furthermore, levels of iron in these pigments were only slightly higher than the paper background, largely ruling out the iron oxide reds, and suggesting Bauer's preference for organic red lakes at this time.

The presence of barium and absence of lead in these samples is notable. It suggests that Bauer likely used barium white (barium sulphate, barytes, blanc fixe, constant white, permanent white) as a replacement for lead white or as a transparent extender for his coloured pigments. Rejected by oil painters due to its lack of opacity in oil, barium white found favour with watercolourists in the late eighteenth century [24]. It is notable that James Sowerby, the London engraver who printed Bauer's paintings for the published *Flora Graeca* lists it in his book on colours in 1809 [39]. Indeed, the use of barium white remain almost entirely limited to watercolour until the 1820s, when it began to be used as an adulterant in

[7] There are reports of the deterioration of Prussian blue from the nineteenth century onward. Samain et al. [32] found that a bright orange iron ferrihydrite was formed on prepared samples of Prussian blue after accelerated light aging at 400 h at 90,000 lux. Significantly this only occurred on samples prepared to traditional eighteenth century recipes. Modern, commercially available Prussian blue pigments were not affected in the same manner. An experiment carried out by the authors in 2016 in which modern Prussian blue watercolour mock ups were exposed to 6 months of daylight agreed with these findings.

[8] The Honig paper mill was formed in 1662 at Wormer by Cornelius Jan Honig. It was enlarged and moved to Zaandijk in 1668, becoming one of the most important paper mills in the Netherlands in the eighteenth century. It continued under successive generations of the Honig family until 1854, when it was sold to Gerbrand der Jong and enveloped into his company.

the production of lead white [40]. Harley [24] notes that barium white was first described as an artists' pigment by Scheele in 1775, although it was certainly in use sporadically since the sixteenth century.

In artists' manuals, it is recommended specifically as a translucent white for watercolour painting as early as 1783 [28], and is cited as an excellent white for watercolour in Field's influential manual, *Chromatography,* as late as 1841 [41]. Eastaugh et al. [42] also note that Prussian blue was precipitated onto a barium sulphate substrate and sold under the name 'Brunswick blue' in the eighteenth century. This seems a likely explanation for the presence of barium in the blue pigments in these works. In general XRF analysis of these later works suggest that Bauer abandoned the opaque pigments from his earlier work in favour of more transparent lake pigments. This would be entirely consistent with a move towards the more delicate, transparent watercolour painting observed in these later paintings.

Hyperspectral mapping and pseudo-colour composites of *Fauna Graeca* paintings

For pigments that produced inconclusive results from a combination of Raman spectroscopy and XRF analysis, hyperspectral imaging was employed to differentiate and map visually similar pigments. Pseudo-colour rendering was chosen as it provided simple and rapid differentiation and mapping of certain pigments for the entire painted surface. The results were compared with those from spectral angle mapping and principle component analysis algorithms in ENVI. Following the methodology in Hayem-Ghez et al. [13], hyperspectral pseudo-colour images of red and blue watercolour pigment standards from the samples discussed above were rendered by identifying areas of their Vis/VNIR reflectance spectra showing the most significant differences. These were then compared to the hyperspectral images of two paintings by Bauer rendered to the same three wavelength bands: 593, 629 and 859 nm. Using the Headwall sensor and Scyven software, these bands and the resultant pseudo-colours for the Bauer mock up paint standards were found to be in agreement with the findings for the same pigments in an oil medium in Hayem-Ghez et al. [13] The high spectral resolution of the Bodleian Headwall sensor enabled discrete wavelength bands to be chosen to within 1.3 nm. Figures 6 and 7 show the results of the hyperspectral pseudo-colour mapping of *Naucratus ductor* (MS. Sherard 239/43) and *Labrus carneus* (MS. Sherard 239/26) (Figs. 6 and 7).

Raman spectroscopic analysis of *Naucrates ductor* identified three different blues used in the image; indigo, Prussian blue and an as yet unidentified highly fluorescent pigment, likely a copper blue. However, due to the apparent visible laser spot size, not having the ability to image the area through a microscope lens, and the extremely finely painted lines of the blue scales over other areas of blue often made it difficult to isolate precise areas of blue from others, particularly where one blue was applied over another or where pigments may have been mixed. Maximising the difference in the reflectance spectra of known samples of copper blues (azurite, bice and verditer), indigo and Prussian blue, and comparing this to the hyperspectral pseudo-colour image of the painting

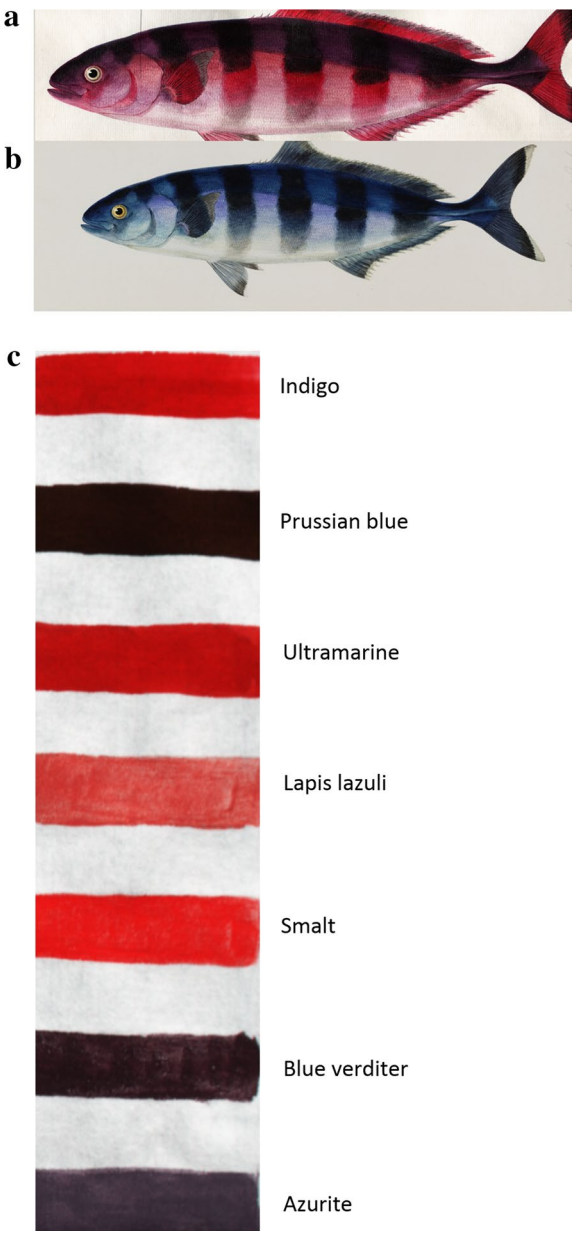

Fig. 6 Ferdinand Bauer, *Naucratus Ductor*, Original (below), and hyperspectral pseudo-colour composite at 593, 629, 859 nm (above). MS. Sherard 239/43. © Bodleian Libraries, University of Oxford, 2017

Fig. 7 Ferdinand Bauer, *Labrus carneus*, Original (above), and hyperspectral pseudo-colour composite at 593, 629, 859 nm (below). MS. Sherard 239/26. © Bodleian Libraries, University of Oxford, 2017

allowed the mapping of the locations of these three pigments. Figure 6 shows that in the pseudo-colour image, areas of indigo appear red, the copper blues appear purple and Prussian blue appear black. Principle component analysis and spectral angle mapping were performed, and provided results that were consistent with the pseudo-colour rendering, further suggesting that four different blues may have been used in the painting and providing much clearer visual map of the location of these paints.

Raman spectroscopic analysis of *Labrus carneus* identified vermillion and red lead, which were present throughout the painting together with another unidentified red pigment used to paint the scales throughout the body. The analysis also demonstrated that Bauer generally used red lead, red lead mixed with vermillion, red lead mixed with a yellow pigment or vermillion mixed with a yellow pigment in order to produce orange in the *Fauna Graeca* paintings. The oranges used in *Labrus carneus* all appear visually similar. However, as above, it was difficult to isolate the exact location of areas painted with each pigment with Raman spectroscopy and XRF alone.

The pseudo-colour image in Fig. 7 shows the mapping of areas of vermillion (appears yellow) and red lead (appears transparent). The main body of the fish appears to be painted in red lead alone with no vermillion. The dorsal and pectoral fins and areas of the gills and eye clearly contain vermillion, whereas the pelvic fin appears to be painted in red lead. The tips of the dorsal and pectoral fins appear purple in the pseudo-colour image, indicating a copper blue. The scales however appear to be painted in a red lake. The light red/pink colour of the red used in the delineation of the scales in the pseudo-colour image and subsequently confirmed by Raman spectroscopy suggests this contained neither vermillion nor red lead and was likely to be an organic lake pigment. In this case the pseudo-colour appears similar to that of lac, madder or brazilwood lakes, but not to that of carmine/cochineal. It is important to note that what was sold as 'red lake' by colourmen and apothecaries in the eighteenth century often referred to a number of materials—cochineal and brazilwood among them [27–29]. A 1738 manual states for example that "[Red] Lake is to be had in most colour shops ready prepared in shells for water-colours" [26].

Conclusion

This study has demonstrated through the analysis of approximately ten percent of Bauer's paintings for the *Flora Graeca* using non-invasive, in situ methods, that Bauer used a fairly simple and traditional palette for the period, and that together with his colour code system,

he used a relatively small number of pigments to achieve almost perfect colour fidelity in his work. It has determined that Bauer largely favoured a pure (copper-based) green adulterated with indigo for his foliage, rather than a mixture of blue and yellow pigments, unusual for the time It has also shown that the Madrid colour chart was created using a very similar palette, and although Bauer cannot be definitively credited as its creator, the pigment data adds to an existing body of historical information that provides convincing evidence that this is likely. From the limited analysis performed on his later paintings, it is clear that Bauer's pigment use changed as he evolved toward the more time consuming and technically challenging transparent watercolour painting style where he abandoned more opaque pigments such as vermillion, copper blues and greens, red lead and lead white in favour of more transparent pigments.

Finally, the study demonstrates that while there are clear limitations in using in situ, non-destructive analytical techniques to characterise the materials and techniques of an artists' oeuvre, portable Raman spectroscopy, FORS, portable XRF and hyperspectral imaging are valuable and complimentary techniques that can provide important data from watercolour paintings. It shows that good results can be obtained from Raman spectroscopy using laser powers that are well below the threshold that might otherwise damage photochemically sensitive pigments, and that hyperspectral pseudo-colour composites can be a useful technique for mapping areas of pigment use over a large area and for the differentiation of visually similar pigments, one that has much potential for future work. The data provides an insight into Bauer's technique, his process, and how he was able to achieve such an impressive degree of fidelity and accuracy in his work. Perhaps more importantly however, the results of this study enabled the creation of a physical reconstruction of Bauer's *Flora Graeca* colour chart. Recreated by the authors using traditional watercolour pigments that were identified in Bauer's work during the study, this chart was exhibited to the public at the Bodleian in the Summer of 2017, allowing visitors to see—for the first time—a visual representation of what Bauer's 'lost' colour chart may have looked like.

Abbreviations

FTIR: Fourier Transform infrared spectroscopy; FORS: fibre optic reflectance spectroscopy; XRF: X-ray fluorescence spectroscopy.

Authors' contributions

RM, DH, AB, CN and KD contributed to the conception of the study and acquisition and analysis of the data. All authors were involved in the interpretation of the results and in the editing and revising of the manuscript. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

Availability of datasets

The datasets supporting the conclusions of this study are available on request at the Heritage Science department, Bodleian Library, University of Oxford.

Consent for publication

Not applicable.

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