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"The Best Painter of Still Life that Ever Existed": Deconstructing the Materials and Techniques of William Henry Hunt in the Ruskin Teaching Collection, Ashmolean Museum, Oxford

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ABSTRACT

This study presents the first in-depth analysis of the pigments and techniques employed by William Henry Hunt, the pioneering nineteenth-century watercolourist renowned for his vibrant realism and innovative 'pure colour over pure colour' technique. Through a multidisciplinary investigation incorporating MA-XRF, single-point XRF, XRD, FORS, and high-resolution microscopy, this research identifies the pigments and methods that enabled Hunt to achieve his extraordinary lifelike effects. The examination of eight works, held in the Ruskin Teaching Collection at the Ashmolean Museum, reflect the range of techniques employed by Hunt, including layering colour washes, stippling pure pigment onto zinc white bodycolour, and the strategic using of unpainted paper for lighting effects. The pigments identified are consistent with those available during Hunt's era, but also confirm his careful curation of materials to maximise the vibrancy and longevity of his artwork. Notably, the identification of cerulean blue and cadmium pigments in *Peach and Grapes* suggests a later creation date than previously assigned. The works held in the Ruskin Teaching Collection at the Ashmolean Museum, University of Oxford, span approximately thirty years of Hunt's 58 year career as an artist, hence intersecting one of the most critical periods in material art history. This research emphasises the value of integrating multidisciplinary scientific analysis with historical context to provide further insights into nineteenth-century art practices amid the industrial revolution.

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Pigment; watercolour; elemental analysis; X-ray fluorescence; X-ray diffraction; FORS; nineteenth century; multispectral imaging; William Henry Hunt

Introduction

The Ruskin Teaching Collection housed at the Ashmolean Museum, University of Oxford, is a unique resource of 1470 diverse works of nineteenth-century art assembled by the influential Victorian artist, polymath and art critic John Ruskin (1819-1900) for his School of Drawing and Fine Art at Oxford. The collection comprises of watercolours, drawings, prints, lithographs and photographs and was used by Ruskin to teach the rudiments of artistic technique – outline, shading, colour – through lessons in copying works of art and natural specimens. Many of the works were made by Ruskin or commissioned from his disciples and contemporaries such as Edward Burne-Jones (1833-1898), Henry Stacy Marks (1829-1898) and J. M. W. Turner (1775-1851). Included among the collection are paintings by the pioneering English watercolourist, William Henry Hunt (1790-1864). Hunt is recognised as one of the nineteenth-century's foremost still life painters and is renowned for developing ground-breaking techniques to achieve prodigious realism, which he termed 'pure colour over pure colour' (Roget 1891, 197). This method used gouache or 'Chinese white' to create a base over which pure watercolour pigment was applied using a stippling-like effect. The near three-dimensional effects accomplished by this technique created lifelike still life paintings that were previously unknown in the watercolour medium. Hunt's exceptional skill was deeply admired by Ruskin who selected eight of Hunt's still life works to teach his 'Rudimentary' and 'Educational' lessons (Ruskin 1908, xlvi). Although Hunt was a successful and popular artist in his time, relatively little written documentation about his artistic material choices exist; traditional archival records such as purchasing accounts, personal correspondence or preserved artists supplies which may elucidate Hunt's material choices as a painter are scarce when compared with contemporary artists such as J.M.W. Turner, James Whistler and William Holman Hunt discussed in Townsend (1993), Townsend (1994), and Katz (1998). Therefore, most of what is known comes from anecdotal accounts by friends and associates and published in biographical accounts by Stephens (1891), Roget (1891) and referrals by Ruskin himself.

The Ruskin Teaching Collection is the focus of a four-year analytical research project (2022-2026)

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funded by the Leverhulme Trust, which seeks to examine the material choices of Ruskin and his contemporaries through a research forensic programme of non-destructive pigment characterisation. The project provided the authors with a unique opportunity to examine the materiality of Hunt's works and technical approach. Through a programme of surface imaging and non-destructive chemical characterisation this research aims to identify the specific pigments Hunt used and the method in which these were applied to create the vibrant effects and enhanced realism. Furthermore, given the widespread concern by Ruskin and his contemporaries over pigment substitution and adulteration in the nineteenth-century art market, this research aims to investigate whether the pigments identified in Hunt's works reveal his views on pigment selection and permanence. Finally, as Hunt rarely dated his work this research aims to determine if pigment identification could aid in refining the dates of production.

William Henry Hunt, background and career

Born to a tin-plate worker, Hunt was described by family members as a sickly child and his weak physical disposition and limited mobility likely contributed to his partial schooling; as a consequence he dedicated his time to painting and drawing at home (Roget 1891, 191; Witt 1982, 31). In 1806, Hunt's father fortuitously apprenticed his sixteen-year-old son to the artist John Varley (1778–1842) for seven years, believing this to be the correct amount of time needed to become proficient in the tin trade, and paying Varley £200 for the term (Stephens 1891). Varley was an influential figure in the London artists' circle and in every way an excellent mentor for Hunt: he was a founding member of the Old Water-Colour Society and generously supported his fellow artists through practical and financial means. Not only would Hunt have benefitted from his mentor's teachings and connections, but also from Varley's fanatical dedication to artistic realism (Cormack 1979).

Hunt's career, which spanned approximately fifty-eight years, is typically divided into three distinct periods based on the development of his technique and choice of subjects, though biographers F.G. Stephens and John Witt differ slightly in their interpretation of these phases. Period one encompasses Hunt's early years, from his apprenticeship under Varley until 1830. During this time, Hunt worked in both oil and watercolour, producing landscapes, 'Sketches from Nature,' and 'rustic figures.' He followed the standard eighteenth-century practice, likely learned from Varley, of outlining in pen or pencil and then applying pure watercolour on top. Hunt's talent in his early works earned him the attention of prestigious early patrons, including the 5th Earl of Wessex, and the 6th Duke of Devonshire (Witt 1982, 40). Period two is generally defined as the years between 1830 and 1845 in which Hunt began to employ more varied techniques, such as using a knife to scrape paint from the paper to create patches of light (observable in *Farm Boys*) and experimenting with a form of stippling. Notably, Hunt increased his production of fruit studies, conspicuously of grapes and began using three brothers from the Swain family as models. These works, which often exhibited a warm, humorous element, became a successful series for Hunt. The third period spans the years of approximately 1845/50–1864 (the artist's death) and is characterised by a decline in still life works, often portraying his daughter Emma, the Swain boys, and an increase in flowers, bird's nests and fruit.

Hunt was an exceptionally prolific artist, exhibiting 153 drawings between 1824 and 1831 and showcasing nearly 800 works during his four-decade membership with the Old Watercolour Society. Although he was not a fast worker, Hunt was disciplined and dedicated long hours to his works, taking between fourteen to eighteen days to complete (Stephens 1891, 14). In addition to his exhibited pieces, he completed numerous commissions and sold many works directly to patrons. Though skilled in several techniques including oil paints, the reed pen and washes of transparent colour, Hunt devoted himself exclusively to watercolours by 1826, the year he was elected a full member of the Watercolour Society. His most productive years were from 1831 to 1851, during which he created approximately 25 works annually. While he earned the nickname 'Bird's Nest Hunt' due to the numerous paintings featuring this subject, Hunt demonstrated remarkable versatility, capturing a wide array of themes. However, he was best known for his vibrant and realistic still life scenes, particularly those depicting fruits, hedgerow flowers, and, most famously, birds' nests. It is for these works that Hunt developed his unique and innovative 'pure colour over pure colour' approach to watercolour painting which cemented his reputation as a watercolour virtuoso. After 1851, Hunt's artistic output slowed to approximately eleven works per year, but as an established master of watercolour, the value of his work had significantly increased (Roget 1891, 201). Early biographer Stephens notes that, as a burgeoning artist, Hunt was satisfied with receiving two or three pounds for a small drawing and considered ten pounds generous for a larger work (Stephens 1934-1935, 53). However, by 1862, Hunt's modestly sized works measuring eleven by ten inches (28 x 25 cm) were selling at Christie's for £117. Roget recounts an incident that well illustrates Hunt's desirability as an artist. Believing that a collection of rough sketches and drawings piled up in his Marchmont Street studio were of little value, Hunt was convinced to sell them to a visiting art dealer named Roberts. Hunt, unwilling to part with the sketches for nothing, readily accepted Roberts' offer of £200; Roberts then had the works prepared and mounted for sale, ultimately making a considerable profit from them (Roget 1891, 194). During his lifetime, Hunt was widely recognised as one of the most technically skilled and accomplished practitioners of watercolour painting in addition to being credited not only as a source of inspiration for the contemporary Pre-Raphaelite movement but also as an influence on the development of the pointillist movement (Witt 1982, 67).

William Henry Hunt and John Ruskin

Ruskin was likely introduced to Hunt's work through his own father, who was a collector of Hunt's paintings. One of the earliest mentions of Hunt in Ruskin's writings appears in the third edition of *Modern Painters* Volume 1, published in 1846. Ruskin acknowledged Hunt's limited subject matter but praised his exceptional skill, stating, 'I do not think that there is another man in the Old Water-Colour Society with so keen an eye for truth or with power so universal.' (Ruskin 1886, 616). He further admired Hunt's ability to adequately capture the beauty of nature, remarking, 'Hunt is the only man we have who can paint the real leaf-green under sunlight.' (Ruskin 1886, 604). Ruskin not only held Hunt in high regard as an artist but also had a personal fondness for him, taking lessons from the artist in 1854 (Ruskin 1979, 76) and again in 1861 (Boyce 1981, 32). In 1859, Ruskin lauded Hunt's mastery of colour, declaring him to be 'the best painter of still life that ever existed' (Ruskin 1908, 220). Hunt's meticulous attention to detail and his vibrant use of colour resonated deeply with Ruskin's fundamental belief in the artistic representation of truth and beauty. Upon Hunt's death in 1864, Ruskin was deeply affected, writing to Hunt's daughter that '… no one living of your father's friends will mourn him more deeply than I: – it was my pride that I could recognise his unrivalled powers in art.'

Works analysed in this study

Ruskin included the following eight watercolour studies by Hunt in his Teaching Collection: *Still Life with Earthenware Pitcher* (1820), *Coffee Pot and Basket* (1820), *Study of Two Woodcock* (1825), *Study of a Copper Pot and a Horn Mug* (1825), *Study of a Woodcock* (1825), *Farm Boys* (1833), *Grapes and a Yellow Snail Shell* (1845), *Peach and Grapes* (also referred to as *'Grapes and Peach'* by Ruskin in his notes) (1845) and *Dead Game* (1854). All eight works were examined in this research and are described below in Table 1. Two of the still life works *Grapes and a Yellow Snail Shell, and Peach and Grapes* were produced using the 'pure colour over pure colour' technique, and were specifically chosen by Ruskin to illustrate 'several matters of importance', including the management of 'retiring' and 'advancing' colours and shadow by using mixed tints and touches of pure colour to produce vibrant effects (Ruskin 1908, 139). The still life compositions of utilitarian objects and dead game were selected by Ruskin to demonstrate the techniques of providing depth to shadows, local and reflected colour (Ruskin 1908, 182–3) and the figure study of children (*Farm Boys*), demonstrated 'force and quality of entirely pure water-colour, now seldom used in figure-painting' (Ruskin 1908, 211). All works are painted on either laid paper or wove paper, three works were mounted in a window mount, made out of conservation grade archival board. Five works were supported by conservation grade archival board during analysis.

Methods

The works were analysed using a standardised programme of imaging techniques and non-destructive chemical characterisation used in combination at the museum specifically for works on paper. Imaging techniques, including reflectance transformation imaging (RTI), infrared reflectography (IRR), multispectral imaging (MSI) and 3D microscopy allowed us to examine the surface topography, layering techniques and map the process of application. Chemical techniques, macro X-ray fluorescence mapping (MA-XRF), X-ray diffraction and fibre optics reflectance spectroscopy (FORS), then allowed us to identify and map the specific pigments used throughout each work.

Surface imaging

Multispectral images were recorded by a digital camera (Canon-EOS-90D) with both the IR and Bayer filters removed (by MaxMax Llc) through an apochromatic lens (Jenanoptik 60 mm) and a custom made, computer-controlled 16-position filter-wheel equipped with 15 bandpass filters, with centre wavelengths (and bandwidths) at 365(25), 400(25), 450(25), 475(25), 500(25), 525(25), 550(25), 575(25), 600(25), 625(25), 650(25), 700(25), 750(25), 825(50) and 925(50) nm (Edmund Optics Ltd). An additional position has a 400 nm long-pass filter that allow direct imaging of the sample, and was the filter used for 1050 nm imaging reported herein. A colour-reference card (Image Science Associates) is placed alongside the picture being imaged to allow colour correction if required. Images were recorded as both JPG and as raw files to allow post-processing using a range of tools written in MATLAB. The works were illuminated by a bank of LEDs which allow selective illumination, whilst minimising the exposure to light. For a

Table 1. Collection of works by William Henry Hunt in the Teaching Collection.

	Accession number	Title	Material and technique	Date	Size (mm)
	WA.RS.RUD.059	*Still Life with Earthenware Pitcher, Coffee Pot and Basket*	Watercolour and bodycolour over graphite on paper	1820	170 × 252
	WA.RS.RUD.180	*Study of Two Woodcock*	Watercolour over graphite on wove paper	1820	154 × 232
	WA.RS.RUD.060	*Study of a Copper Pot and a Horn Mug*	Watercolour and bodycolour on paper	1825	107 × 134
	WA.RS.RUD.179	*Study of a Woodcock*	Watercolour and bodycolour over graphite on wove paper	1825 (dated by the artist)	129 × 221
	WA.RS.RUD.143	*Farm Boys*	Watercolour and bodycolour over graphite on wove paper	1833 (dated by the artist)	279 × 203
	WA.RS.ED.192	*Grapes and a Yellow Snail Shell*	Watercolour and bodycolour on wove paper	1845	138 × 93
	WA.RS.ED.213	*Peach and Grapes*	Watercolour and bodycolour over graphite on paper	1845	124 × 175
	WA.RS.ED.168	*Dead Game*	Watercolour and bodycolour on wove paper	1854	122 × 217

typical exposure, the light level at the page is < 1 mW cm-2. With this system it is possible to record both reflectance images and UV or visible light induced florescence images using any combination of the excitation LEDs and/or emission filters. For imaging at 1050 nm the picture was illuminated using 1045 nm LED's (Roithner Laser, GD35N-1045DL) (See Supplementary Material for MSI set-up).

RTI was performed on all artworks to help identify watermarks, characterise paper types and paint layering depths. The RTI dome, designed by the University of Southampton is equipped with a Nikon Z6 camera, an AF-S Nikkor 50 mm f/1.8G lens, and the images were analysed with the RTIViewer software, developed by the Visual Computing Laboratory at the Institute for Information Science and Technology (ISTI), part of the Italian National Research Council (CNR) (http://vcg.isti.cnr.it) (See Supplementary Material for RTI set-up).

Additional infrared reflectography was undertaken using an Opus Instruments Apollo camera in order to ascertain underdrawing materials and technique.

The camera is fitted with a 128 × 128 px InGaAs area sensor and has an operational wavelength of 0.9–1.7 µm. Lens specification – 6 element 150 mm focal length F/8–11. Works were illuminated by ELIO Halogen lamp (240 V) (VIS to IRR range) from chsopensource.org.

A Keyence VHX-7000 digital 3D microscope was used to visualise and measure depth of pigment layers and help target XRF point analyses at x20, x100 and x200 magnification.

Chemical characterisation techniques

A Bruker CRONO MA-XRF spectrometer was used as the first step in characterising pigments in each painting by mapping the distribution of chemical elements across each surface and identifying elements specific to individual colours. The system has a rhodium target X-ray tube and a 50 mm^2 SDD detector providing an energy resolution <140 eV for Mn Kα with input count rate of up to 500,000 cps. The maps were run in the 'automatic acquisition' mode, speed 13.89 mm/s, spectra time 30 ms, an analysis range of Mg ($Z = 12$) to U ($Z = 92$) with a 0.5 mm collimator. A map of each object was undertaken in order to determine the single point analysis strategy. Single point analyses were taken using a 0.5 mm collimator using operating conditions 50 kV, 200µA, 100 s per analysis. Data was processed using the Bruker ESPRIT Reveal software.

XRD analysis was conducted using a Bruker HYDRA system in order to identify chemical compounds specific to each pigment colour. The HYDRA features a 30W micro-focus X-ray generator with a Cu anode and parallelising poly-optics, and a 50mm^2 SDD detector. The system is equipped with a photon-counting 2D detector for XRD measurements, carried out at angles between 20° and 40° 2-theta in the first run, and 40° to 60° 2-theta in the second. The XRD measurements used a 220 µm collimator with an acquisition time of 300 s per run, resulting in a total measurement time of 10 min per analysis. Diffraction patterns were processed and characterised using Panalytical High-Score Plus software, in conjunction with the International Centre for Diffraction Data (ICDD) database (https://www.icdd.com/) for phase identification and comparison with known Powder Diffraction Files.

FORS analysis was conducted to detect and identify organic pigments using a custom-built fibre optics reflectance spectrometer, custom designed by Andrew Beeby (Gameson et al. 2023). Operating in the 400–2500 nm range, this equipment delivers a 2.5 mm diameter light beam with a total power of less than 0.5 mW to the target surface, at a working distance of 3 cm. The system has a bandwidth of 3.5 nm in the 400–1000 nm range and 8 cm^{-1} in the SWIR region (900–2500 nm), equivalent to 2.5 nm at 1750nm. Spectra were recorded relative to a Spectralon standard, with each measurement taking 1 s. Pigments were identified by comparing the reflectance spectra to published data, reference samples and online databases provided by CNR-IFAC (https://spectradb.ifac.cnr.it/) (See Supplementary Material for example FORS spectra).

Results and discussion

The full set of results of MA-XRF, XRD and FORS analysis are presented in the Supplementary Materials. Results are discussed here by materials and techniques, from paper supports, under sketching and colour application through to pigment characterisation, selection and dating.

Paper support

Of the eight works, one is painted on laid paper (*Study of a Woodcock* (1825)) and the remaining seven are painted on wove paper, all of which are standard nineteenth-century artists materials. Several features of laid paper are observed in RTI including striations from the frame used in the manufacturing process (Figure 1). This work contains a watermark with entwined letters J and W, likely the insignia of J. Whatman, one of the primary paper manufacturers of the time. The support used for *Study of Two Woodcock* and *Farm boys* (described by Ruskin as a 'finished study on white paper' (1908, p211)) is constructed from more than one piece of paper which could indicate the artist's resourcefulness using leftover pieces of paper for study works rather than pieces to be formally exhibited and sold.[1]

Under sketching

Examination using IRR revealed a fine IR absorbing medium, most likely carbon or graphite pencil, beneath the paint layers was used to roughly sketch outlines of composition using a grid. Figure 2 illustrates the under sketching technique used in *Study of Two Woodcock*. This is in agreement with the account given by James Orrock, a fellow watercolourist, who describes Hunt's process as roughly pencilling an outline before applying the paint layer (Webber 1903, 149).

Application of colour and manipulation techniques

Once the outline had been sketched, Hunt used pigment in a variety of ways to create a range of effects. Washes of multiple colours were delicately applied by brush in strokes or stippled to define and add depth to his subjects. This can be readily observed under digital microscopy, for example in *Farm Boys* blues, reds and oranges are applied over a base of

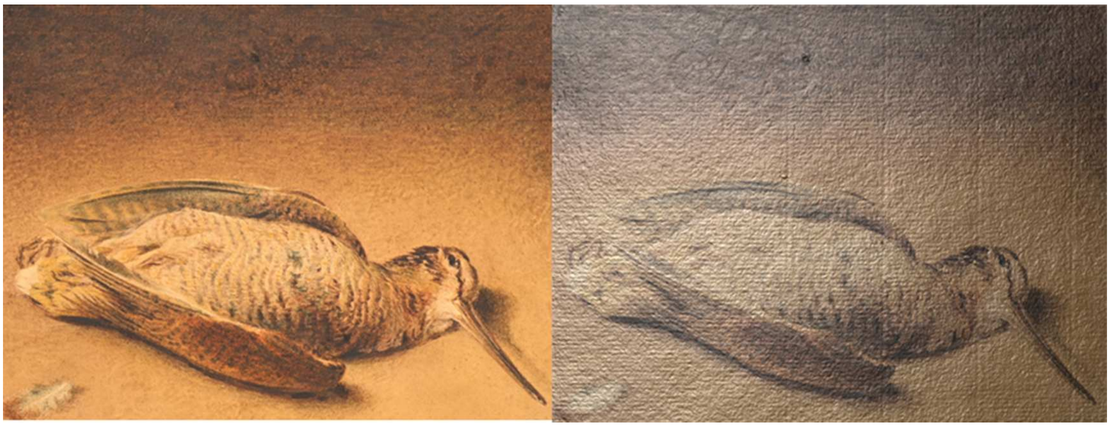

Figure 1. (Left) Image of *Study of a Woodcock* using default rendering in the RTI viewer. (Right) Image using the Specular Enhancement mode indicating the watermark above the body of the woodcock.

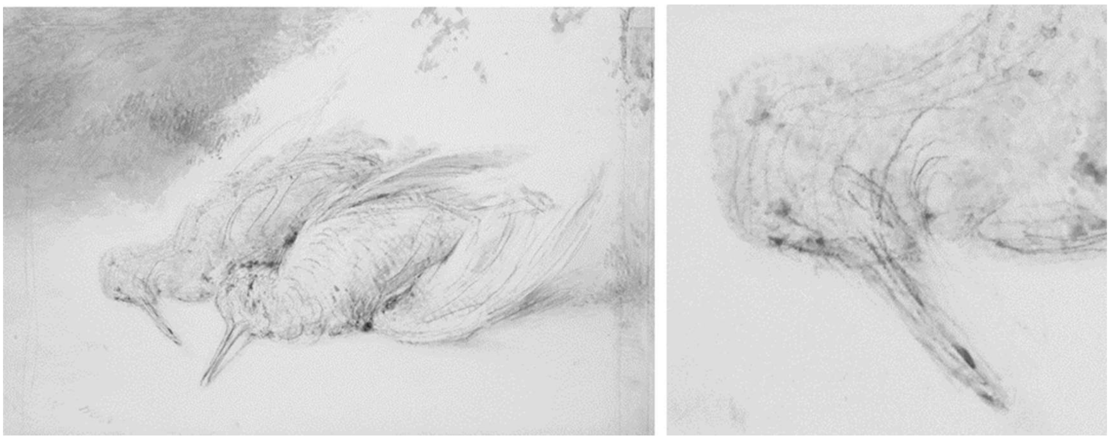

Figure 2. (Left) Multispectral image of *Study of Two Woodcock (*WA.RS.RUD.180). (Right) Detail of beak. Both images were acquired at a wavelength of 925 nm.

yellow to create a vibrancy and depth to the apple and to the face of the children (Figure 3). Hunt also used the unpainted paper substrate, known as 'reserving', within his composition as a means to create lighting effects, for example in *Farm Boys* the clouds are rendered as unpainted spaces (Figure 3) and as areas of light in *Peach and Grapes,* specifically the body peach itself (Figure 4). From early on, Hunt also employed the use of a scraping knife to 'pick out' areas of light (Witt 1982, 65). This scraping technique can be seen in *Farm Boys* to define the left edge of the jug. Hunt often enhanced his art by abrading the surface of the paper to mimic the textured surfaces of his subjects. However, the RTI and digital microscopy imaging techniques used in this study did not reveal any evidence of him employing this method in these particular works.

'Pure colour over pure colour'

Hunt was renowned for his use of Chinese white, or zinc white, to create texture and relief in his still life paintings, a technique that is exemplified in *Peach and Grapes* and *Grapes and a Yellow Snail Shell* (Figures 4 (top) and 5 (top left)). In this approach, zinc white was applied in thick layers to achieve a textured background, onto which was stippled pure pigment. Orrock described observing Hunt at work, noting that Hunt would 'roughly pencil out a group of plums or grapes and thickly coat each one with Chinese White and leave [it] to harden. On this brilliant china-like ground he would put his colours (i.e. pure watercolour), not in washes, but solid and sure so as not to disturb the ground which he had prepared.'. Orrock further explained that Hunt intentionally developed this method to achieve the utmost 'strength and brilliancy' of colours, ensuring the longevity of the vibrant hues (Webber 1903, 149). XRD analysis of areas of white on both *Peach and Grapes* and *Grapes and a Yellow Snail* provided a strong diffraction pattern match with zinc oxide (ZnO), confirming the use of this pigment for the colour on colour technique. Mapping MA-XRF illustrates how zinc white was applied across the surface of both works to create each composition (Figure 5). The Zn Kα map of *Peach and Grapes* reveals the distribution of zinc white in varying concentrations, with brighter areas indicating higher levels of detected zinc. This pigment was

Figure 3. (Left) *Farm Boys* by William Henry Hunt (1833), dated by the artist (279 mm x 203 mm). (Top right) Detail of the proper left eye. (Bottom right) Detail of the colours used to render the apple held by the child on the right.

strategically applied to enhance specific features of the painting, serving as a base for the moss and grape stem. Additionally, significant quantities were identified in the beige-coloured ground layer. The maps also showed that the artist used zinc white to create the relief for the stalks of the grapes and the green and brown leaves above.

The texture and relief achieved by the artist is further observed under RTI and measured using digital microscopy; in *Grapes and a Yellow Snail*, the RTI image shows how zinc white body colour was used to create texture and highlights in the foliage, in addition to creating definition and relief to the stalks of the grapes and creating the thick ridge in the lip of the shell. Measurements using digital microscopy show that Hunt achieved relief of approximately 170 μm on the lip of the yellow shell creating a convincing three-dimensional effect (Figure 6).

Pigments

Blues

The preliminary MA-XRF elemental maps identified the presence of cobalt in five of the eight works examined. Cobalt blue was introduced as an alternative to the expensive ultramarine, however, it became popular with nineteenth-century artists as a superior colour in its own right. Its discovery as a pigment was published in late 1803 and commercial manufacture was instigated in 1807 in France, becoming more widely available in England from approximately 1815 (Harley 2001, 54). Hunt's mentor, Varley, recommended it in his work 'List of Colours' as a good alternative for ultramarine to render skies in 1816 (Varley 1816) and although relatively expensive, it was widely adopted by artists as a watercolour pigment owing to its stability, lightfastness and compatibility with other pigments (Field 1841, 204; Harley 2001, 54). It was sold under several names, including Thenard's Blue (a cobalt phosphate with alumina) and Leithner's Blue (cobalt arsenate) (Church 1901, 210–11), the nomenclature of which distinguished the variations in composition and '… degrees of purity' (Field 1841, 204), however contemporary writers generally referred to the pigment as cobalt blue, and Salter classifies cobalt blue into the class 'aluminous cobalt blues' (Salter 1869, 190). Single point XRF undertaken on the cobalt-rich areas of works *Still Life with Earthenware Pitcher, Coffee Pot and Basket, Study of Two Woodcock, Farm Boys* and *Grapes and a Yellow Snail Shell* detected the presence of cobalt with elevated levels of aluminium; the correlation of aluminium to cobalt was also confirmed on the XRF elemental map. XRD analysis was conducted on the same points examined by XRF, consistently producing diffractograms matching the pattern for cobalt aluminium oxide ($CoAl_2O_4$), confirming the presence of the pigment cobalt blue in these works. Single point

Figure 4. (Top) *Peach and Grapes* by William Henry Hunt, dated by Witt as being painted in 1845 (124 mm x 175 mm). (Bottom left) Detail of the stem end of the peach. (Middle) Detail illustrating the colour use of blue, purple and red tones to render the grapes. (Right) Detail of the green leaf above the grape stalk, showing the use of green and yellow tones and zinc white.

XRF on all cobalt rich areas also confirmed the lack of arsenic, thereby excluding cobalt arsenate formulations of cobalt blue from Hunt's material choices (Roy 2007, 152).

Smalt, traditionally made by grinding potash-rich cobalt blue glass, is also classified as an aluminous cobalt blue (Eastaugh 2008, 351). Although widely available as an artist's pigment since the fifteenth century, Smalt was considered difficult to work with, with both Field and Salter describing it as inferior to cobalt blue (Field 1841, 197; Salter 1869, 205). Nevertheless, Smalt remained in use as a blue watercolour pigment into the nineteenth century, often sold under different names based on quality, with the finest known as 'Dumont's Blue' Field (1841, 205). The darker areas and shading of the grapes in *Grapes and a Yellow Snail Shell* exhibit a high concentration of potassium and phosphorus correlating with cobalt; XRF analysis on watercolour charts dating from 1887 to 1923, issued by Winsor and Newton, indicates that the formulation of the 'smalt' pigment also contains high levels of cobalt, potassium, phosphorus, and aluminium, but is notably low in silicon, hence aligning with the composition of the cobalt-based pigment used in this work (Taylor 1887; Krotova and Filatova 2022). FORS analysis matched the resulting spectra with those in the FORS spectral database for smalt (by reference to samples of modern paints (Cornelissen), and the colour reference panel (Cultural Heritage Science Open Source: chsopensource.org)) and Winsor and Newton watercolour samples (Taylor 1887). The elevated calcium content, and the IRR images taken from the corresponding areas indicates that a black pigment was combined with smalt to achieve the darker blue hues of the grapes, such as bone black which is produced by carbonising animal bones, resulting in a basic calcium phosphate composition ($Ca_5(OH)(PO_4)_3$) (Winter and Fitzhugh 2007, 16). The magnified images of the grapes reveal blue, purple, and red-purple hues, with the elemental maps

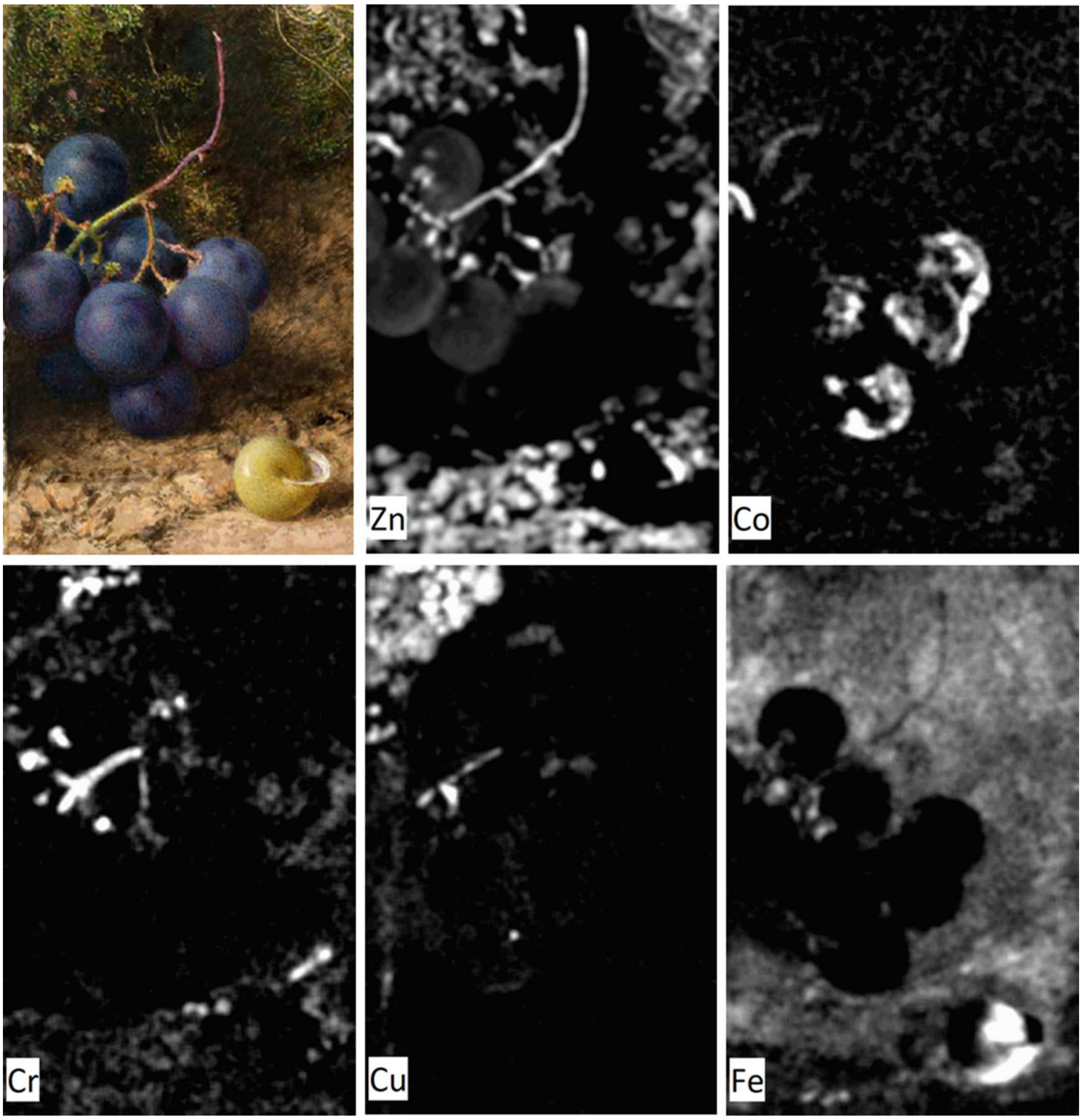

Figure 5. (Top left) *Grapes and a Yellow Snail Shell* by William Henry Hunt, dated to 1845. (Top middle – right) XRF maps showing the spatial distribution of zinc (Zn) and cobalt containing pigments (Co). (Bottom left to right) XRF maps showing the spatial distribution of pigments containing chromium (Cr), copper (Cu), and iron (Fe).

detecting an elevated sulphur content corresponding with the shape of the grapes and the background foliage, suggesting the use of a red lake pigment (Kirby, Spring, and Higgitt 2005; Kirby, Spring, and Higgitt 2007).

The elemental map of *Peach and Grapes* identified tin in precise correlation with cobalt, this was further confirmed by XRD analysis which identically correlated with the diffraction pattern of the cerulean blue pigment standard, Kremer pigment 45730 (colour index PB35, CHSopensource.org). Cerulean blue, classified under the cobalt stannate pigment group, appears to have had a more convoluted progress to widespread use in England. First synthesised in 1789 by Swiss chemist Albrecht Höpfner by roasting cobalt and tin oxides to create a cobalt stannate, the pigment had limited production in Germany under the name 'Cölinblau' (Höpfner 1789). Cerulean blue was later released as 'Höpfner blue' during the first half of the nineteenth century, however the pigment was not widely available and remained largely obscure in England until the 1850s-1860s (Eastaugh 2008, 96) with colourman George Rowney being credited by some sources for the re-introduction (Coffignier 1924). The pigment was reintroduced under the name 'Cerulean blue' and appeared in artist suppliers' catalogues in the second half of the century, however the exact date of introduction is debated (Gettens and Stout 1966, 103; Mayer and Smith 1991, 46). The German origin is consistent with comments by Salter (1869, 190) that 'Under the name Coelin there has of late years been imported from Germany the cobalt blue with a tin base … which likewise contains or is mixed with gypsum, silica and sometimes magnesia'. Coffiegnier states this took place 'around 1850', but Carlyle differs, noting that this did not likely happen before 1862-1863, being immediately prior to the British firm Roberson purchasing 'Blue No. 58

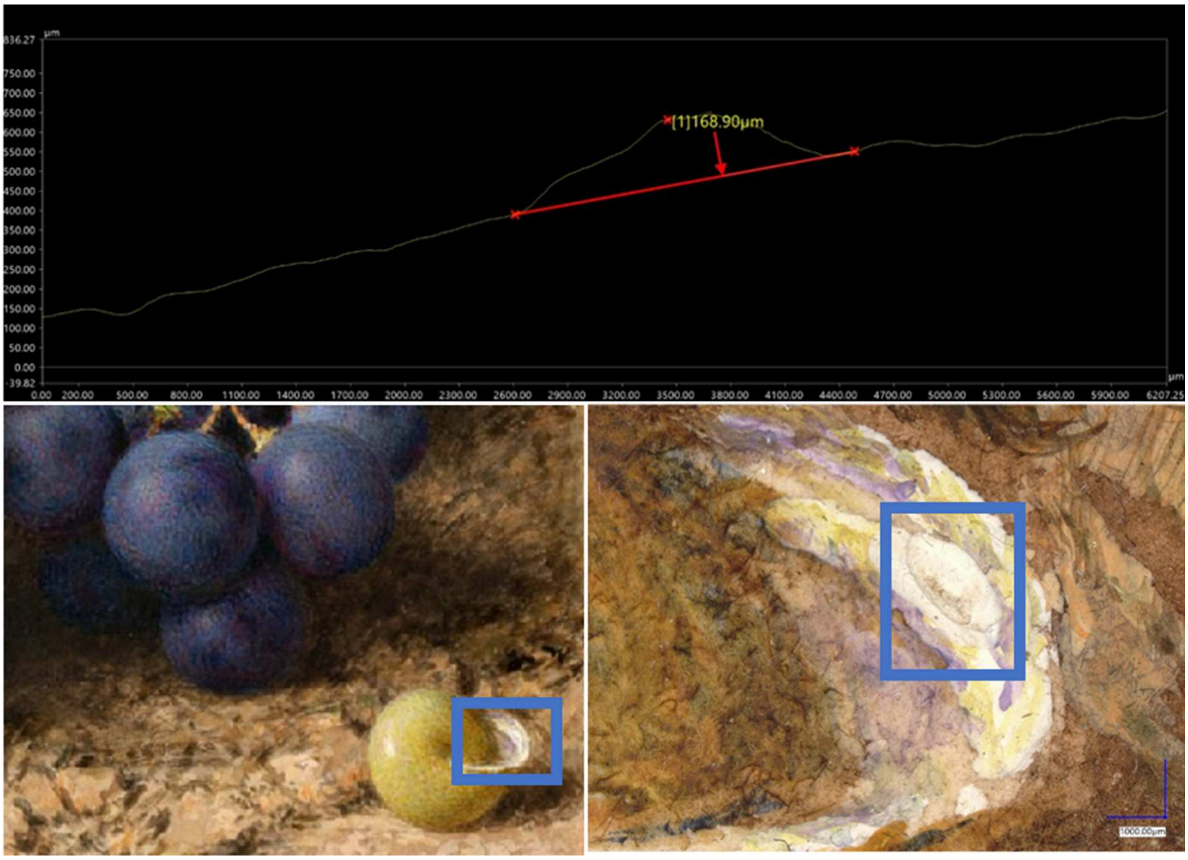

Figure 6. (Top) Digital microscope measurement of the shell lip, where zinc white was used, in *Grapes and a Yellow Snail Shell*. (Bottom left) Marker indicating the specific region of the watercolour examined. (Bottom right) Macro image of the shell lip, with marker denoting the measured area.

(Cerulium)' from German firm Frauenknecht and Stotz (Coffignier 1924; Carlyle 2001, 96). The Ashmolean Museum dates both *Grapes and a Yellow Snail Shell* and *Peach and Grapes* to 1845, however, Witt dates the latter work to slightly later, circa 1850. This becomes pertinent as the blue pigments used for the grapes in each painting are subtly different; cobalt based blues are primarily used for the grapes in *Grapes and a Yellow Snail Shell*, whereas cerulean blue is used for *Peach and Grapes*. Therefore, the use of cerulean blue in *Peach and Grapes* may suggest that it is a later work, created after the pigment became available to artists in England. Alternatively, it could indicate that Hunt was both aware of, and had access to, European materials, although it is unlikely that he acquired them personally as his limited mobility impacted his travel ability.

Nickel is commonly present in cobalt ores as an associated element, and this can be observed in the varying levels of nickel concentration found in the cobalt pigments used in works by Hunt in the Teaching Collection. In *Farm Boys* and *Peach and Grapes* a relatively high concentration of nickel can be seen to correlate with the cobalt based pigments, indicating that this particular cobalt pigment was likely refined from a high Ni-ore to create the smalt, such as the Erzebirge mining region in Germany and the Valais region in Switzerland (Gratuze et al. 1996). *Study of Two Woodcock* also shows correlation between nickel and cobalt, albeit at a lower concentration than observed in *Farm Boys*. In opposition, areas of cobalt-rich pigment in *Grapes and a Yellow Snail Shell* does not show the same correlation, indicating that the pigment used for this work was produced from an ore with relatively low nickel.

In addition to the cobalt-based pigments, FORS analysis indicated that Hunt employed other blues in his work; ultramarine was suggested as being used to render the grapes in *Grapes and a Yellow Snail Shell*. Owing to the extraordinary high cost of natural ultramarine, it is likely that synthetic ultramarine was used as it was largely available and considered to be of adequate quality as a blue pigment (Field 1841, 202; Field 1858, 56). Prussian blue was indicated by XRF in high Fe-areas of blue in the works and was confirmed using FORS as being present on the lighter areas of the grapes in *Grapes and a Yellow Snail Shell,* and for the blue smock in *Farm Boys* with cobalt blue applied to the darker folds of the garment. Prussian blue was discovered in Berlin between 1704 and 1710, it quickly gained popularity due to its deep blue hue, closely resembling ultramarine but a much lower cost (Berrie 1997, 193). The manufacturing process remained a closely guarded secret until 1724, but was disclosed as the preparation of sulphate of iron with nitric and sulphuric acid to create persulphate of iron (Kirby 1993). Ferrocyanide of potassium (yellow prussiate of potash) was added to form a precipitate which was then washed and dried thoroughly giving the chemical formula $KFe[Fe(CN)_6].xH_2O$ or $Fe_4[Fe(CN)_6]_3.xH_2O$ and crystalline structure $Fe_4[Fe(CN)_6]_3 \cdot xH_2O$ (x = 14-16) (Buser et al. 1977; Berrie 1997, 201).

The organic blue pigment, indigo, was confirmed using FORS analysis on the works *Still Life with Earthenware Pitcher, Coffee Pot and Basket, Study of Two Woodcock,* and *Dead Game*, Hunt used indigo for the lighter areas of the blue cloth and to tint the 'grey' feathers on the latter two works. It is interesting to note that in his book, *Varley's list of colours (1816),* the author advises that indigo will create a purple grey; a visibly similar to the hue applied to the feathers are observed on his pupil's work *Study of Two Woodcock* and *Dead Game*.

Reds and oranges

Nineteenth-century artists had access to a variety of red pigments, each with distinct compositional qualities, origins, and uses. In the period that Hunt was active, traditional red pigments used for watercolour paints were often iron based such as red ochre (Fe_2O_3), a naturally occurring iron oxide commonly found in England, particularly in Oxfordshire (Harley 2001, 108). Common ochres comprise a mixture of mineral components, including oxides, oxide-hydroxides, quartz, carbonates micas and clays which can be rich in silica and aluminium (Helwig 2007). Other red iron oxide pigments and their derivatives were known by various names, such as Venetian red, which was composed of partially hydrated ferric oxide. Mars red, was a manufactured iron oxide with the same chemical composition (Fe_2O_3) and was synthesised by oxidising iron sulphate, combining it with alum, and precipitating it using an alkali. Conversely, the absence of primary elements like iron, lead, chrome, or mercury in areas where red pigment is used suggests the presence of an organic rather than inorganic red pigment. The detection of elements involved in the processing of organic pigments can help identify which organic pigment was likely used. For example, madder pigments were often precipitated with barium sulphate, alum and potassium carbonate or applied using a tin – or copper-based substrate (Schweppe and Winter 1997; Kirby, Spring, and Higgitt 2007). Elevated levels of aluminium, potassium and sulphur indicate that the base used was aluminium hydroxide alum, $AlK(SO_4) \cdot 12H_2O$, a common base for natural red dyes (Schweppe and Winter 1997). Tin was also detected in *Study of Two Woodcock* in the darker brown plumage shades which did not correlate with other primary elements detected in the MA-XRF map. This indicates that a red lake pigment was used with a tin substrate. The lack of correlation between the tin and mercury in *Study of Two Woodcock* suggests that the red pigment is not 'scarlet lake', which is defined as a combination of crimson lake and vermillion (Eastaugh 2008, 340).

Two red pigments were identified in *Farm Boys*: XRF analysis revealed an iron-based pigment on the figures' cheeks, which was confirmed as red ochre using FORS. In examining finer red details, such as the hat's band, the apple, and the edging of the trousers, XRF detected high sulphur levels rather than iron, with single-point XRF analysis further confirming elevated levels of both aluminium and sulphur, indicating the use of a red lake pigment.

Mercury was detected with a corresponding high concentration of sulphur in three of the Hunt works, suggesting the use of the mercuric sulphide pigment vermillion (Gettens, Feller, and Chase 1993, 160; Eastaugh 2008, 392). Hunt appears to use vermillion in conjunction with other pigments to achieve a red hue to brown pigments in these works, rather than using the vermillion as the primary red pigment. This is observed using the elemental mapping of mercury on the *Study of Two Woodcock* where mercury is detected in the dark brown hue between the two birds (Figure 7), in the red-brown pot behind the coffee pot in *Still Life with Earthenware Pitcher, Coffee Pot and Basket* and two small discrete brown and beige areas in *Farm Boys*. One of Hunt's students, William Collingwood, recounts his teacher's skill employing complementary colours to create startling vibrancy, specifically the combined use of emerald green and vermillion (Collingwood 1898), offering a rare first-hand account of Hunt's selection of vermillion as one of the red pigments he specifically chose to achieve his vibrant effects.

The notable discovery of the element cadmium by Stromeyer in 1817 and the subsequent invention of cadmium yellow during Hunt's lifetime are significant topics of discussion specifically in relation to pigments. Although the pigment cadmium yellow was available as early as 1840, its production was limited due to the scarcity of the metal (Fiedler and Bayard 1986, 65). Cadmium yellows were produced by precipitating a cadmium salt from an acid solution using either hydrogen sulphide gas or an alkali sulphide, however, Salter (1869, 88) reports that early versions of cadmium yellow were manufactured abroad and were often heavily adulterated with orpiment, chromate, and lead; this finding has also been confirmed with modern day analysis (Townsend et al. 1995). The resulting precipitate can vary in colour from lemon yellow to deep orange, depending on the particle size and whether the particles are amorphous or crystalline. In his 1841 work, Field noted that the behaviour

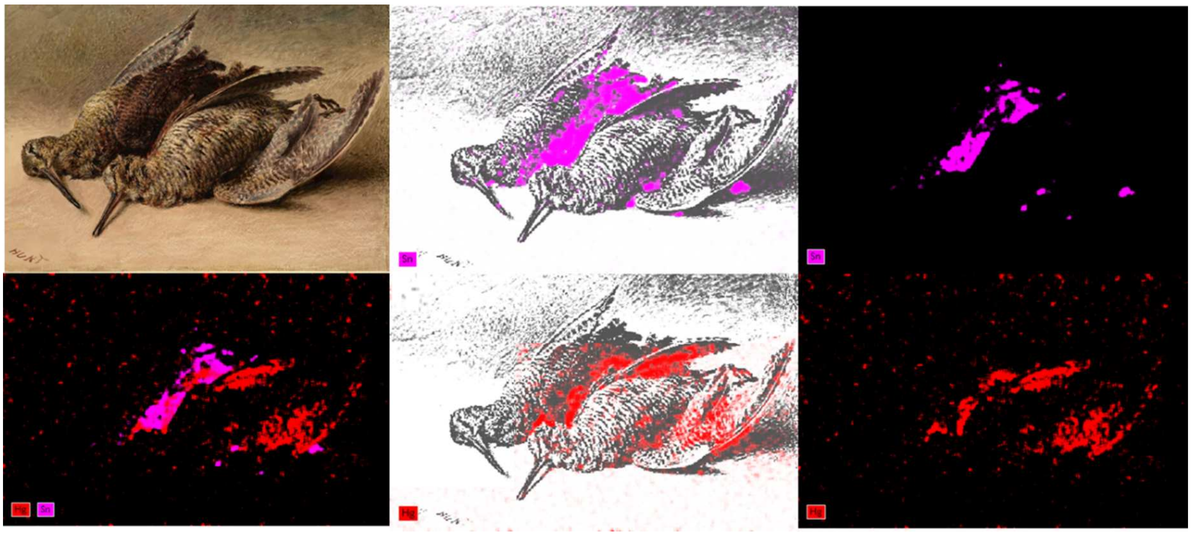

Figure 7. MA-XRF mapping reveals the distribution of tin (Sn Lα) (top middle and right) and mercury (Hg Lα) (bottom middle and right) in *Study of Two Woodcock*, confirming the use of two distinct pigments: vermilion and a probable madder pigment with a copper substrate.

of this new pigment was not yet well understood due to its recent introduction (Field 1841, 153), however, by 1869, it was reported that cadmium orange had been officially introduced at the International Exhibition of 1862 (Salter 1869, 244).

Notably, the popular pigment cadmium red was discovered after the death of Hunt, with the patent only being filed in 1892 (Eastaugh 2008, 76), nearly 30 years later. Therefore, it is interesting that cadmium is detected using single point XRF analysis in the red/pink hue area of the peach in Hunt's *Peach and Grapes,* but not detected in the yellow portions of the peach. Additionally, small concentrations of cadmium were detected in the brown/orange leaf above the grapes, further suggesting that Hunt used a cadmium pigment with a more orange hue. The pink area of the peach also shows a strong correlation between the elements aluminium, sulphur, and potassium consistent with bases used for organic red pigments. Hunt also used cerulean blue to define the outside of the peach, creating a lifelike texture, whilst also toning the pink/red of the peach with cerulean blue and emerald green. The same application of several colours can be seen to create the indentation of the peach stem (Figure 4, bottom left).

Yellows

During the course of Hunt's active years of painting, a series of new yellows was released onto the artists market. Traditional yellow pigments such as yellow ochre were still widely in use, but many artists became concerned with the longevity of their pigments, and the impact that larger scale manufacturing had on the quality of their materials. Field wrote at length about the negative qualities of several of these pigments available by 1840 (Field 1841), however, Hunt's selection of yellow pigments for the works in the teaching collection appear to be well curated, avoiding those which were reported to blacken, fade or to require careful handling due to their extreme toxicity. Yellow ochre was identified in five of the eight works in the collection. Notably the yellow ochre used in *Farm Boys* and the shell in *Grapes and a Yellow Snail Shell* contained a high silica content correlating with iron observed in both the elemental map and single point analysis.

The elemental analysis of the yellow peach area in *Peach and Grapes* detected elevated levels of sulphur, barium, chromium and lead with some potassium. The XRD data returned a low matching diffraction pattern for lead chromium oxide and potassium barium chromium oxide ($K_3Ba_2Cr_3O_8$). This combined data indicates that the artist likely used a combination of chrome yellow pigments including chrome yellow ($PbCrO_4$) and lemon yellow ($BaCrO_4$) to render the peach (Kühn and Curran 1986, 187; Eastaugh 2008, 105, p242). Although chrome yellow was considered to be a robust pigment, Field stated that the pigment was too bright and did not 'accord with the modest hues of nature' (Field 1841, 143), perhaps indicating why Hunt also employed the lighter hue of yellow in this work. The zinc elemental map shows that a ZnO pigment was not used in the area of the peach itself, demonstrating that Hunt used the white surface of the paper to create the lighting in this work, a standard watercolour technique that his mentor Varley would have instilled during the earliest stages of Hunt's apprenticeship (Witt 1982, 65). It is also possible that Hunt believed he had purchased pale cadmium yellow for use in *Peach and Grapes*, as this pigment was often adulterated with other yellow pigments due to its high cost (Townsend et al. 1995). However, the use of multiple pigments is consistent with Hunt's painting technique.

Greens

MA-XRF on *Grapes and a Yellow Snail Shell* and *Peach and Grapes* identified the presence of lead, chromium, arsenic and copper correlating with areas of green hues on both works. As the Kα peak at 10.54 keV for arsenic overlaps the Lα peak for lead at 10.55 keV, the presence of the respective Kβ peak at 11.73 keV and Lβ peak at 12.61 keV was used to indicate the presence or absence of these elements. Arsenic and lead can be differentiated by fitting the observed XRF spectra and further defining the distribution of these elements using the deconvolution function on the software spectra. The redefined maps were then used to determine areas for single point analysis. In addition to the differentiation of elements, the identification of elemental correlation using the redefined elemental maps were key in directing an informed strategy for single XRF and XRD readings which would optimise the number of positively identified pigments.

Areas with high concentrations of correlating copper and arsenic were identified through MA-XRF and confirmed by single-point XRF analysis. XRD analysis on the same single point areas returned diffractograms identifying the arsenate compound $Cu_3(AsO_4)_2$ (Figure 8), thereby confirming the pigment as emerald green, which is consistent with the report of Hunt's use of this pigment in the account by Collingwood (1898). The consistent detection of the phase $Cu_3(AsO_4)_2$, also known as lammerite, is a degradation product of emerald green $3Cu(AsO_2)_2{\bullet}Cu(CH_3OO)_2$ (Fiedler and Bayard 1997), therefore may indicate some degradation of the pigment (Holakooei, Karimy, and Nafisi 2018). Notably, the XRD analysis on areas containing copper arsenate consistently retrieved the same diffraction pattern code for each instance, suggesting compositional consistency of the emerald green pigment used by Hunt across the two works. Hunt used a combination of chrome green (chromium oxide) and a copper arsenate green to achieve the stalks and green foliage in his 'pure colour over pure colour' technique. Where the presence of both pigments was indicated as being present by XRF data, XRD analysis effectively identified diffraction patterns for the yellow pigment lead chromium oxide ($PbCrO_4$), and the green pigment chromium oxide (Cr_2O_3) (Newman 1997, 273). Emerald green, created in the early 1800s, was praised by Field as being opaque and the most durable pigment of its class, however he recommended chrome green as being the 'true hue' of emerald green (Field 1841, 236). It is interesting to note that Field does not discuss the toxicity of the arsenic greens, emerald or Scheele's green in the revised 1841 version however the 1869 version does elaborate on the dangers of the arsenic content of copper arsenic pigments (Salter 1869, 273). Similar to the yellow pigments, the XRF maps provide insights into Hunt's technique; by analysing the distribution of copper, arsenic, and chromium, the elemental maps reveal that the two greens were applied in overlapping areas, yet it can be seen that they were predominantly used in discrete regions rather than being uniformly mixed prior to application.

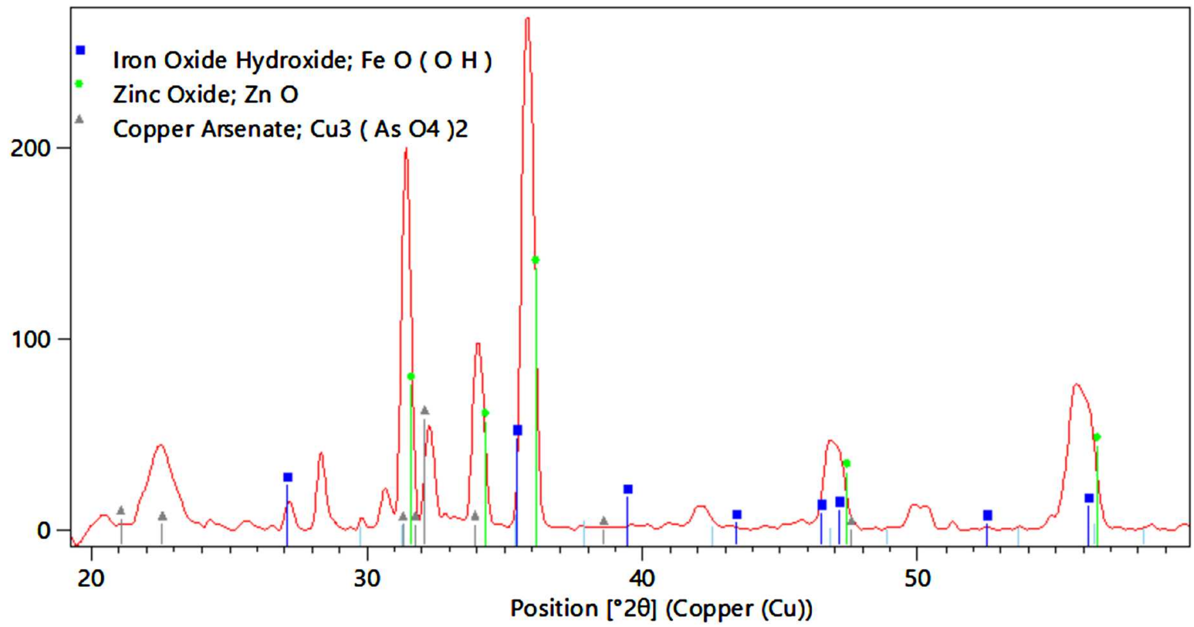

Figure 8. XRD Diffractogram of the green leaf in *Peach and Grapes* indicating the presence of zinc white, emerald green (copper arsenate, mineral name lammerite), and an iron-based pigment. Paper support peaks are labelled with *.

Browns

Brown pigments have been used in art from the beginning of art history, specifically iron-based pigments in the form of ochre, sienna and umber composed of manganese-rich clay. Brown pigments were considered 'main' colours, but artists commonly achieved brown, earthy hues by mixing black or blue paints with red. Several brown pigments appear in the Winsor and Newton catalogue from 1835, available in both tube and as a powder, including Cologne earth, Vandyke brown and asphaltum (Carlyle 2001, 533), Later, however, these renowned pigments, along with newly formulated brown pigments, were simultaneously produced by other manufacturers, including Reeves and Rowney, and were marketed with varying compositions and under different names (Townsend et al. 1995; Eastaugh 2008, 484). However, the practice of creating brown by combining excess pigments, or the deliberate combination of black or blue paints with red, is a longstanding artistic tradition. Therefore, the identification of explicit brown pigments used in Hunt's works, and other contemporary artists is accepted as challenging for several reasons.

Of the eight works by Hunt in the Ruskin Teaching Collection, four are painted using primarily brown hues: *Study of Two Woodcock*, *Study of Copper Pot and a Horn Mug*, *Study of a Woodcock* and *Dead Game*. *Still Life with Earthenware Pitcher, Coffee Pot and Basket* is also created using brown hues but the artist has included a blue cloth which is also shown reflected in the silver-coloured coffee pot. The combined analysis confirmed that Hunt used iron-based pigments in these works, and indicated that he also created brown hues by mixing pigments, in addition to applying red and blue pigments to create warm and cool hues in his paintings. The iron-based brown pigments used in *Study of Two Woodcock* show a high presence of silica correlating with the iron, but no significant arsenic or manganese, and only relatively low levels of calcium. This suggests that brown ochre was used for both the birds and the beige-brown background (Helwig 2007, 62). Cobalt blue was applied in the plumage of the woodcock on the upper left, while the presence of mercury and sulphur indicates that vermilion was used in the darker areas to create a rich red-brown tone. Tin and potassium were detected together in the darker area between the two birds in the MA-XRF map and without correlation to other elements, suggesting the use of a lake pigment (Schweppe and Winter 1997, 131). Additionally, high levels of calcium in the refined dark shading imply the use of bone black (Winter and Fitzhugh 2007, 16). Since the painting was executed on what appears to be two pieces of substrate bonded together, *Study of Two Woodcock* may have been a preliminary study, never intended for sale or display as a finished piece. In *Study of a Woodcock*, the background exhibits a relatively high iron content without associated elements, suggesting the use of ochre. Arsenic was detected in the red hue of the lower wing, correlating with iron, indicating the use of a sienna pigment (Manasse and Mellini 2006). Additionally, high concentrations of manganese in the single spectra, along with the corresponding manganese and iron distributions in the XRF maps, confirm the use of brown umber in the work. Similarly, the elemental distribution of iron, calcium and phosphorous in *Dead Game* indicates that this work was painted using primarily brown ochre and bone black.

A high concentration of copper was detected in the copper mug in the 1825 work *Study of a Copper Pot and a Horn Mug* with FORS detecting the use of an organic red pigment in these areas. The absence of correlating elements, such as arsenic, indicates that the copper is introduced from an organic red pigment, such as madder, produced using a copper-based substrate. At the time of Hunt's artistic career, relatively few pigments derived from copper had been created (Eastaugh 2008, 127–37), and even fewer copper-based brown pigments. Copper brown was only later described in Salter's volume released in 1869 and he provides an uncharacteristically short and unfavourable description of the pigment, stating that the pigment is 'varying in hue, is obtainable in the form of prussiate, &c., but cannot be recommended, however made.' (Salter 1869, 355). Therefore, this later pigment of poor reputation likely did not feature in Hunt's material choices. Overall, the analysis of the brown pigments in *Study of Copper Pot and a Horn Mug* is consistent with ochres and umbers due to the high iron content, despite the FORS analysis signifying that the brown pigments did not match the characteristic signatures of primarily iron-based brown pigments.

Pigment choice

The pursuit of vibrant realism was a fundamental aspect of Hunt's work, making the selection of permanent pigments a critical consideration. This is corroborated by Orrock's account, which highlights Hunt's deliberate choices to ensure the longevity of the colours in his paintings. This is particularly true for those pigments chosen for his 'pure colour over pure colour' works, a technique specifically designed to achieve exceptional vibrancy. As outlined in Supplementary Material Table S2, Hunt's material choices identified in his works from the Ruskin Teaching Collection exhibit significant overlap with the 'permanent' colours recommended by his mentor, Varley, in 1818, including cobalt blue, Prussian blue, indigo, lake, yellow ochre, and sienna. Hunt's preference for cobalt based pigments indicates that he was willing to pay for quality goods – cobalt blue was priced at five shillings per ounce, three times more expensive than the cobalt stannate pigment cerulean blue, and five times more expensive than synthetic ultramarine (Roy 2007, 159–60). The results of this study show that Hunt consistently favoured traditional permanent pigments like red, brown, and yellow ochres over the newer products available at the time. His preference for vibrant greens, described by George Field, and subsequently Salter, as some of the most stable and long-lasting pigments with brilliant hues, further underscores his deliberate selection of materials. These choices reflect Hunt's intentional effort to use pigments that would maintain their brightness and vibrancy over time, ensuring the durability of his works.

Date refinement

The pigments used by Hunt in seven of the eight examined works align with those commonly associated with the periods in which they were created. The exception is *Peach and Grapes*, dated to 1845, which features cerulean blue and a cadmium pigment with a yellow-orange hue. While both cerulean blue and cadmium pigments were developed prior to 1845, their introduction to the English art market for widespread use followed a convoluted journey with undefined timelines. As a result, the presence of these materials suggests that *Peach and Grapes* may have been created at a later date.

Conclusion

The non-destructive, multidisciplinary approach combining MA-XRF, XRD, and FORS (FORS) successfully identified over 20 pigments across a range of hues in the works of Hunt. This comprehensive methodology demonstrates its robustness for pigment identification in nineteenth-century artworks. The pigments detected suggest that Hunt deliberately selected materials to ensure the durability and vibrancy of his works over time. Notably, several pigments used by Hunt were described in published works by his mentor, Varley, suggesting his preference for traditionally proven colourfast materials. The pigments identified are consistent with the date of the works, except for the presence of cerulean blue in *Peach and Grapes*, which suggests that this piece was created at a later date. The smalt pigment used in the same work shows elevated phosphorus content, consistent with formulations documented in Winsor & Newton's nineteenth-century catalogues. Macro XRF mapping was instrumental in visualising the spatial distribution of specific pigments, including the strategic use of zinc white in Hunt's 'pure colour over pure colour' technique. The analysis also revealed Hunt's adherence to traditional watercolour practices, such as utilising the paper substrate to create highlights rather than applying white pigment. XRD analysis was key for distinguishing between chemically similar pigments, such as chrome green and chrome yellow, enabling precise identification of pigments.

Digital microscopy was critical in identifying and documenting areas where the artist applied multiple pigments to produce vivid realism, with some hues indistinguishable to the naked eye. In addition, the use of RTI revealed a previously undocumented watermark, providing insights into the specific brand of paper Hunt employed. RTI further captured the three-dimensional texture created by Hunt with zinc white to as part of his 'pure colour over pure colour' method. MSI and IRR revealed undersketchings in the works, showing Hunt's preliminary sketching process before the application of watercolour paints and/or pure pigments. Despite limited historical accounts of Hunt's techniques, this combined analytical approach demonstrates that the examined works align with known aspects of his artistic practices, and also confirm the artists specific material choices over thirty years of his artistic career. Furthermore, this study underscores the value of combining scientific analysis with historical research to uncover the artistic and material practices of nineteenth-century artists, offering new insights into this significant period in art history.

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Note

1. Notably, *Grapes and a Yellow Snail Shell* in the collection's Educational Series was part of a larger work featuring more grapes and an apple that was cut in two by Ruskin and split up within the collection. The second section was housed in the Working Series but has since been lost (Cook and Wedderburn (XXI.92 n. 3)).

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