Raman spectroscopic study of the pigments in a putative John Constable oil sketch

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Abstract
Raman has long been established as a nondestructive and noninvasive technique that has found increasing application in the area of cultural heritage and the study of works of art. Here, we present a further application of Raman spectroscopy in the study of an oil painting belonging to the de Brecey Trust. In the work presented, Raman microscopy has been employed to spectroscopically study minute fragments of excised pigments from a small oil painting bearing the hallmarks of a study sketch by the famous English landscape artist John Constable. Raman spectra were collected from 18 discrete areas of the work, chosen due to their colour in order to potentially cover all of the pigments used in this work. Of the 18, six positive identifications were made, confirming that the painting contained pigments and minerals known to be favoured by the artist. Whilst the remaining 12 sample sites were complicated by the fluorescence effects observed from the applied varnish, this can be useful in providing evidence to support the application of the ‘scumbling’ technique known to be favoured by Constable. We have positively identified the pigments: ultramarine/lapis lazuli, lead white, red lead, Prussian blue, chrome yellow and ivory black. We have also identified amorphous carbon and gypsum. These positively identified pigments link into Constable’s existing colour box and four palettes, providing evidence that could lead to the painting being attributed to Constable.

KEYWORDS
de Brecey Trust, John Constable, pigment analysis, Raman application in art

1 | INTRODUCTION
The opportunity arose recently for the undertaking of a limited Raman spectroscopic analysis of a small oil painting, which has the hallmarks of being a study sketch in oils by John Constable, the famous English landscape artist who painted in the early 19th century. Due to the condition of the painting, we were able to excise small fragments of pigment before the painting was taken for restoration.

The picture was acquired by the late collector George Lester Winward (1933–97) on 17 June 1988 at a Cheshire Auction House sale of oil paintings and watercolours, the catalogue describing it as ‘Norwich School - Locking-up..."
with a horse drawn barge, oil on oak panel’. On 29 August 1995, he transferred the work, together with his picture collection, into the ownership of the de Brécy Trust.

John Constable was born on the 11 June 1776 to Golding and Ann Constable at East Bergholt Suffolk. His father was a miller and John spent his early years growing up in Flatford Mill and later at Dedham Mill on the River Stour, in an area which later became known as ‘Constable country’, where he spent most of his life painting scenes that he knew well: he is quoted as saying to his friend John Fisher of Salisbury in 1821, “I should paint my own places best”, and he put this into practice, depicting scenes of rural life from his own childhood on the banks of the Stour and it is claimed that he was inspired by the artistry of the French painter Claud Lorrain. It may come as a surprise now, realising the esteem in which John Constable is held nowadays, that his painting in the first quarter of the 19th century was considered rather unfashionable in an age that demanded romantic views of wild landscapes and Gothic ruins rather than tranquil scenes such as those he depicted. Constable was therefore more appreciated and popular in France, admired by Delacroix particularly for the rendering of his green colours, where he sold 20 paintings in only a few years compared with another 20 sold in England in his whole lifetime. His painting inspired the formation of the Barbizon School in France. He married Maria Bicknell in 1816, who pre-deceased him, and he died in 1837, aged 61 years. He left four pallets and a paint box with his favourite pigments contained in small pigs’ bladders tied with twine to prevent their drying out. He favoured vermilion, emerald green, chrome yellow, cobalt blue, lead white and madder, and he ground his pigments with linseed oil, pine resin and poppy oil, the latter being a favourite of his as it was slow drying and allowed him to make amendments and work continually with his brush strokes.

A particular technique favoured by John Constable was ‘scumbling’, whereby pigment was applied thickly and relatively dry to an already glazed area of the painting, so that the glaze showed through in patches and afforded an interesting layered effect on clouds and vegetation. This is certainly evident in the painting under investigation here as is the rather curious effect of white highlights which appear on the painting which was another favourite signature of Constable to simulate the dappling effect of light across the landscape and especially near running water. The latter effect engendered some adverse criticism at the time: an art critic of The Times wrote in May 1831, of Constable’s Salisbury Cathedral from the Meadows “somebody has spoiled this landscape by spotting the foreground all over with whitewash. It is quite impossible that this offence can have been committed with the consent of the artist” and “The numerous patches of dead white intended for the lights and drops of rain after a shower have all a chilling coldness after a snowstorm on a winter’s morn”.

2 THE PAINTING

The painting, illustrated in Figure 1, in oils on a wooden panel, measuring 228 × 292 mm, depicts a barge with two containers, which is awaiting the opening of a lock gate, drawn by a Suffolk Punch horse and manned by a
single bargee. It is signed ‘J.C’ on the freeboard of the barge to the left of the bargee. It is probably early afternoon in late summer and the towpath bends around to the right beyond the harnessed horse, following the curve of the river around the lock-keeper’s cottage with a dilapidated lean to a scene that is typical. It is untitled, but a visit by one of us to rural Suffolk a few years ago established that the modern scene shown in the Supporting Information almost exactly matches the setting of the painting, which if by John Constable would be dateable to the period 1815–1825. The modern photograph depicts a stretch of the River Stour near Stratford St. Mary, which was a favourite location for John Constable’s works in this period. Although the lock-keeper’s cottage has been demolished along with the lock gates, the photograph shows the presence of the remains of a lock stanchion still standing with the appropriate bend of the river and the distant hills. It is likely, therefore, that this location is that which is featured in the painting under study here. Constable favoured large canvases for his exhibition works, particularly at the Royal Academy, which he termed his ‘six footers’. He made number of small oil sketches of his scenes of about this size which formed the basis of his larger and more well-known works. One of his first ‘six footers’, <i>Stratford Mill</i>, was purchased in 1820, by Dr. John Fisher, along with his famous <i>Hay Wain</i>, who became his lifelong friend, and it is quite possible that the present sketch represents a working study for this picture.

In 1900, his family released over a 100 of his previously unseen oil sketches and pictures and re-kindled the interest in the work of this wonderful landscape artist, who was contemporary with that other great English landscape painter, James Mallord William Turner. Constable has been much copied, especially in late Victorian times, and it will be interesting to see what analytical spectroscopy can reveal about the pigments used in this painting.

### 3 | EXPERIMENTAL

Samples were excised from regions of the painting, shown in Figure 1, using a scalpel and needle tweezers. The samples were examined with a Renishaw <i>InVia</i> Reflex Raman microscope with a diode laser operating at 785 nm using a 50× microscope objective lens; each specimen was placed on a gold-coated microscope slide and a calibration check was made against silica. The spectra were collected at 1% of total laser power (approximately 0.628 mW at sample), using a 10-s exposure time and with 10 accumulations to enhance the signal-to-noise ratio.

Of the 18 samples collected, Raman spectra were only collected from six of them because of the very high levels of background fluorescence, which was attributed to the degradation of aged varnish covering the painting. Also, the technique known as ‘scumbling’ described earlier involved the intimate mixing together of the pigment and varnish, and this would tend to also mask the Raman pigment signature bands when the varnish is fluorescing strongly. Table 1 lists the major Raman features observed in six samples and their pigment assignment. Stack plots of the spectra can be seen as Figures 2 and 3.

### 4 | DISCUSSION OF RESULTS

The law of large numbers tells us that the number of sampling sites was statistically low in this study based on the size of the painting and the variety of colours used. Furthermore, of the samples analysed, only six unique sampling sites displayed any peaks of significance due to the high levels of background fluorescence. The number of samples we were able to excise was limited by the destructive nature of the sampling method, requiring us to excise samples from discreet areas whilst excising as many unique colours as possible. Due to the need to preserve the artwork, this low sample number is common in the analysis of art works, particularly where destructive sampling is employed.[10,11]

| Sample number | Peak position (cm⁻¹) | Assignment                  |
|---------------|----------------------|-----------------------------|
| 4             | 539                  | Ultramarine/lapis lazuli[5–7]|
| 6             | 1049, 257            | Lead white[6,8]              |
| 8             | 547                  | Ultramarine/lapis lazuli[5–7]|
| 9             | 2152, 2120, 2091, 279, 216 | Prussian blue[6,8]         |
|               | 1594, 1338           | amorphous carbon[6,9]        |
|               | 1007                 | gypsum[7]                    |
|               | 838, 532             | chrome yellow[6,8]           |
|               | 986, 602             | bone/ivory black[6,9]        |
| 12            | 629, 544, 438, 381, 328 | Red lead[5–8]               |
| 17            | 1074, 545, 252       | Gypsum[7]                    |
| 17            | 1074                 | Ultramarine/lapis lazuli[5–7]|
|               | 545                  | Red lead[5–8]                |

### TABLE 1 The list of major Raman features and their pigment assignment
FIGURE 2  A stack plot of spectra generated from samples (a) 4, (b) 6, (c) 8 and (d) 17

FIGURE 3  A stack plot of spectra generated from samples (a) 12, and (b) 9
Although most of the specimens failed to yield definitive Raman bands on account of the extremely strong background fluorescence, which was attributed to the degraded varnish, the intimate association between the varnish and the pigment is strongly indicative that the scumbling technique has been used in the construction of this painting. Since this technique was definitively used by John Constable in his earlier work on local scenes, this in itself is a positive conclusion to be drawn from the negative Raman data for several of these samples.

The identification of ultramarine/lapis lazuli, red lead, lead white, Prussian blue and chrome yellow is all positive attributes for this artist: it is known that Constable favoured chrome green and emerald green for his green pigments. It does need noting that the Raman analysis excited at 785 nm remains resonant for the Sn chromophore and therefore does not make it possible to discriminate between ultramarine or lapis lazuli.[12] However, ultramarine is a known pigment used by John Constable. Chrome green was a mixture of chrome yellow (lead chromate, PbCrO₄, synthesised by Louis Vauquelin in 1809) and either Prussian blue or ultramarine, and emerald green (also known as Schweinfurt green, Paris green and Vienna green) is a copper acetotriarsenite, Cu₄(As₃O₆/Cₒ)₂(CH₃CO₂)₂, which was synthesised by Justus von Leibig in 1814. Both chrome yellow and emerald green are strong colours and much favoured replacements by Constable’s time for the weaker yellow ochre and verdigris, respectively.

The use of carbon black in the form of bone or ivory black is also interesting: some artists preferred the deeper more glossy black colour afforded by the bone or ivory black compared with the simple soot or charcoal blacks for darkening the colour tones of their pigments and clearly this was the case here, too.

Gypsum was detected in two of the spectra, and this could have been used as a lightening agent in addition to the lead white. The adoption of red lead as a colourant is also interesting as it was detected in area are that was not predominantly red: however, it is known that Constable did favour using a red coloured base to some green vegetation and also some skies to give a greater depth of colour: in sample 12, where the red lead signatures were detected, the riverside vegetation is distinctly brown and reflects the presence of large dock leaved plants growing by the water’s edge.

Much has been written about Constable’s production of oil sketches in his early career, and a related topic of relevance to the sketch being analysed here is a study made of ‘Anglers at Stratford Mill’, painted in 1811 and numbered 97. Generally, the panels he used were quite small, ranging in size from 190 x 146 mm to 190 x 360 mm. Generally, no ground preparation was undertaken on the panels unlike the canvases, and Constable used the natural reddish colour of the wood to show through into the painting. It is known that he liked to prepare his own oil paints fresh from dry powdered pigments and preferred poppy seed oil as it gave him more time to work his painting before the paint dried; he was also aware that in the early 19th century, it was quite prevalent for unscrupulous ‘colour men’ suppliers of artists’ pigments to adulterate their pigments, which could lead to their premature fading and degradation. Constable’s colour box and four palettes exist which has enabled art historians to study his favourite pigments. He is known to have used vermilion, red ochre, red lake, madder, Naples yellow, yellow ochre, Prussian blue, ultramarine, burnt umber, lead white and charcoal black early in his career from 1802, these being the preferred choice of Bardwellm, but that he changed his selection of pigments when stronger and more desirable ones became available synthetically in the first two decades of the 19th century. In particular, he favoured Prussian blue, which is detected in all of Constable’s paintings, which he mixed with lead white and charcoal black for his blue and grey skies. A comment exists that he went over to ivory black later and developed the use of smalt (a synthetic cobalt aluminosilicate glass, also known as cobalt blue) and that he used a red lake to add warmth to his backgrounds. He was especially particular about using ultramarine, which was synthesised in 1828, but Constable still preferred the use of the natural variety, the chromophore in the precious gemstone lapis lazuli, even though that was significantly more expensive in comparison with the synthetic version, which he felt was of a much poorer tonal quality. He reserved ultramarine pigment particularly for his ‘scumbles’ and did not substitute anything else here. He favoured the use of Prussian blue with ivory black for his tonal darkening adjustment and his colour box found after his death in 1837 contained a piece of gypsum which he liked to use as a lightening agent and for delineating some sketches.[13]

5 | CONCLUSIONS

Science alone cannot be used to identify the artist behind a particular work. However, what science can provide is the identity of the pigments used in that work to provide evidence as to who the artist may have been. In this work, we are able to demonstrate the presence of ultramarine, lead white (hydrocerussite), Prussian blue, amorphous carbon, gypsum, bone/ivory black and red lead. These are all pigments known to be a part of Constable’s colour palette and lend evidence to this oil painting being
one of John Constables. Furthermore, the often perceived ‘negative’ results attributed to degraded varnish may actually be a positive result in attributing this work to John Constable. The use of varnish could be associated with the scumbling technique which is in clear evidence in the early works of John Constable.

DATA AVAILABILITY STATEMENT
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION
Additional supporting information may be found online in the Supporting Information section at the end of this article.

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