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Interpreting technical evidence from spectral imaging of paintings by Édouard Manet in the Courtauld Gallery

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The paintings by Édouard Manet in The Courtauld Gallery *Déjeuner sur l'herbe* (1863–68), *Marguerite de Conflans en Toilette de Bal* (1870–1880), *Banks of the Seine at Argenteuil* (1874), and *A Bar at the Folies-Bergère* (1882) were investigated for the first time using a range of non-invasive in situ analyses.

The aims of the study were to investigate the painting techniques and materials used for this group of works and to critically evaluate the technical evidence derived from the integrated use of imaging techniques and portable spectroscopic methods in this context.

The paintings were investigated by means of macro X-ray fluorescence (MA-XRF), reflection spectral imaging, portable UV-Vis-NIR spectroscopy, portable Raman spectroscopy, and reflection FTIR. MA-XRF and reflection spectral imaging allowed visualising elements in the compositions that were not visible using traditional methods of technical study. For example, MA-XRF analysis of *Déjeuner sur l'herbe* revealed elements of the development of the composition that provided new evidence to consider its relationship to other versions of the composition. The study also highlighted questions about the interpretation of elemental distribution maps and spectral images that did not correspond to the reworking visible in X-radiographs. For example, in *A Bar at the Folies-Bergère* Manet made numerous changes during painting, which were not clearly visualised with any of the techniques used.

The research has wider implications for the study of Impressionist paintings, as the results will support technical studies of works by other artists of the period who used similar materials and painting methods.

1 | INTRODUCTION

The Courtauld Gallery in London displays four important works by Édouard Manet (Figure 1). These are *Déjeuner sur l'herbe* (1863–68 [?], 89.5 × 116.5 cm), a version of the large work in the Musée d'Orsay in Paris; *Au Bal* -

Marguerite de Conflans en Toilette de Bal (55.7 × 35.5 cm), a rapidly executed sketch painted between 1870 and 1880, which remained in Manet's studio until his death; *Banks of the Seine at Argenteuil* (62.3 × 103 cm) one of the very few outdoor scenes painted partly *en plein-air* by Manet in 1874, which was

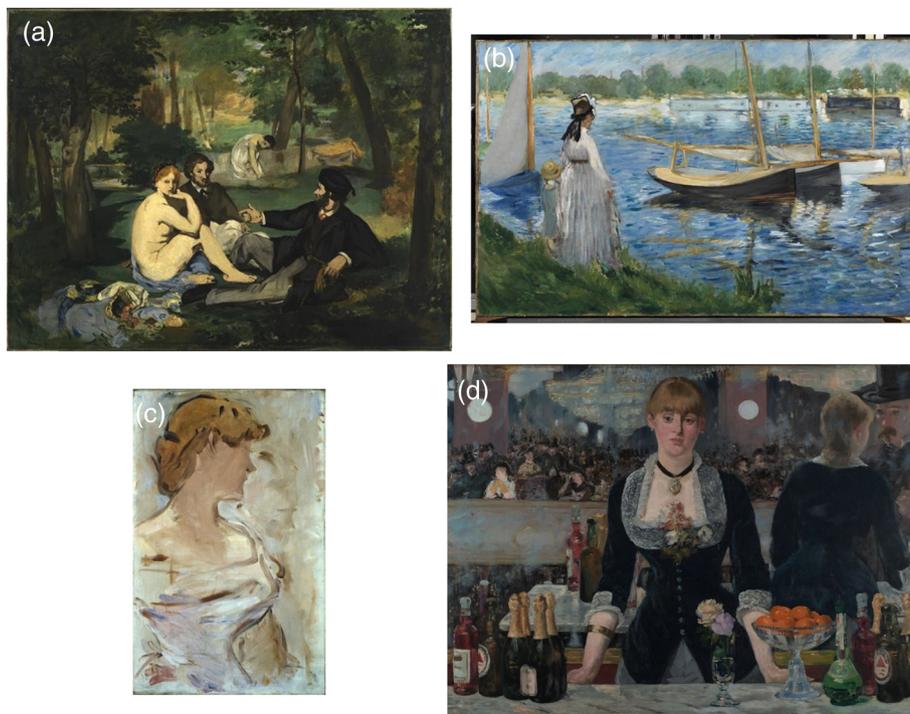


FIGURE 1 The paintings by Édouard Manet in the Courtauld Gallery. (a) *Déjeuner sur l'Herbe*, 1863 (?), 89.5 × 116.5 cm ©the Samuel Courtauld Trust, the Courtauld Gallery, London; (b) *Banks of the Seine at Argenteuil*, 1874, 62.3 × 103 cm ©private collection, on extended loan to the Courtauld Gallery, London; (c) *Au Bal - Marguerite de Conflans en Toilette de Bal*, 1870–80, 55.7 × 35.5 cm, ©the Samuel Courtauld Trust, the Courtauld Gallery, London; (d) *A Bar at the Folies-Bergère*, 1882, 96 × 130 cm, ©the Samuel Courtauld Trust, the Courtauld Gallery, London

on long-term loan from a private collection; and the iconic *A Bar at the Folies-Bergère* (96 × 130 cm) painted in 1882 and exhibited at the Paris Salon in the same year.

None of the above works had previously been subjected to full technical examination. The works represent a range of the artist's genres, different subject matter, date, and painting methods, thus representing the ideal set of case studies to critically evaluate the evidence derived from the application of spatially resolved imaging techniques with non-invasive site-specific chemical analyses.

The paintings were investigated for the first time using a combination of non-invasive in situ analytical methods including multispectral and hyperspectral imaging (400–2,400 and 400–2,500 nm spectral range, respectively), macro X-ray fluorescence (MA-XRF), portable ultraviolet, visible, and near-infrared (UV-Vis-NIR) reflection spectroscopy, portable Raman spectroscopy, and portable reflection Fourier transform infrared (FTIR) spectroscopy, provided by collaboration with the University of Delft, University of Antwerp and the European mobile platform MOLAB (<http://www.iperionch.eu/molab/>).^[1]

The choice of analytical techniques used in this study is based on the potential for each method to yield different

and complementary information.^[1,2] Recent studies have shown that the application of a combination of reflection spectral imaging and MA-XRF with portable spectroscopic methods is particularly suited to study those paintings whose material heterogeneity and compositional complexity present a challenge for other methods of technical examination.^[3–5] Visualisation of changes in composition, including features in underlying paint layers, and areas of conservation intervention can be characterised including non-invasive identification of inorganic and organic pigments and binding medium. This technical information may inform specific art historical questions. In the context of a comparative study of Manet's painting methods, this research aimed at maximising the potential of such a non-invasive multitechnique analytical approach in relation to the interpretation of painting materials and techniques used for works that exhibit typical features of the Impressionist painting technique. These are, for example, changes made by the artist during the painting stage and complex paint mixtures applied in layers, which may represent a challenge for data interpretation.

This paper presents a selection of results from this ongoing study and outlines the next phase of the research.

2 | METHODS

The four paintings by Édouard Manet in The Courtauld Gallery were analysed in the Department of Conservation and Technology of The Courtauld Institute of Art. At first, each painting was investigated using MA-XRF as well as multispectral and hyperspectral imaging (400–2,400 and 400–2,500 nm spectral range, respectively). Then, based on the information gathered, different site-specific analyses were carried out on a selected number of areas for the chemical identification of specific painting materials. In the case of *A Bar at the Folies-Bergère*, the focus of the investigation was the reworking of the female figure and her reflection in the mirror behind her, therefore MA-XRF measurements were only performed in these two areas of the painting, and no point analyses were carried out. The analytical findings of the present study were sufficient for characterising most of the pigments used in each of the paintings investigated, and the results gathered will be discussed in the following section.

2.1 | Macro X-ray fluorescence (MA-XRF)

MA-XRF measurements were carried out using two different instruments. Elemental mapping of the entire surface of the paintings was performed with the MA-XRF scanner M6 Jetstream from Bruker Nano GmbH (Berlin, Germany). This instrument consists of a 30 W Rh-target microfocus X-ray tube equipped with a polycapillary X-ray lens for beam focusing, with a maximum voltage of 50 kV and a maximum current of 0.6 mA, and a 30 mm² Silicon-Drift detector (with energy resolution of <145 eV for Mn K α) mounted on an X–Y–Z motorised stage with a maximum travel range of 80 × 60 cm.^[6] The elemental distribution maps of the paintings were collected with a dwell time of 50 ms/step and a step size of 1 mm. The X-ray fluorescence (XRF) spectra acquired were fitted and the elemental distribution maps produced using the data analysis software packages Datamuncher and PyMca.^[7]

Details of the paintings were scanned using the MA-XRF scanner CRONO from XGlab (Milan, Italy). This instrument consists of a high efficiency X-ray generator source with an Rh anode (maximum voltage of 50 kV and maximum current of 0.2 mA), 3 software selectable collimators (typical 0.5, 1 and 2 mm), and a 50 mm² Silicon-Drift detector (with energy resolution of 130 eV for Mn K α) mounted on an X–Y–Z motorised stage that enables a scan area of 45 × 60 cm².^[8] The elemental distribution maps of details of the paintings were collected with a dwell time of 50 ms/step and a step size of 0.5 mm. Region of interest images were obtained using the data analysis software package PyMca.

2.2 | Multispectral Vis–NIR imaging

Multispectral data of the paintings were gathered using a computer-controlled scanning system that allows for the collection of metrically and optically corrected sets of 32 images registered at different wavelengths: 16 in the visible (400–800 nm) and 16 in the near-infrared (NIR; 800–2,400 nm) spectral region. The detection unit is a photo-detector array composed of Si (400–1,000 nm) and InGaAs (1,050–2,400 nm) photodiodes, each equipped with an interferential filter. The lighting system is composed of two low-voltage current-stabilised halogen lamps and two high-power narrow-spot white LEDs. The spectral resolution ranges between 20 and 30 nm in the visible range and 50 and 100 nm in the NIR range, the spatial sampling is 250 μ m and the acquisition time is 3 hr per square meter.^[9] The monochromatic images acquired were analysed separately and collectively. Based on the reflectance variations of different pigments in different spectral regions, false colour composites in trichromatic red–green–blue (RGB) were produced to examine and facilitate visualisation of painting features varying with wavelengths, and to visualise information from more than one spectral band simultaneously.^[10]

2.3 | Hyperspectral Vis–NIR imaging

Hyperspectral imaging of the paintings in the visible spectral range was performed using the SOC710 Hyperspectral Imaging System consisting of a grating-based spectrometer with a high-speed, low-noise silicon-based CCD sensor. The instrument covers the 400–1,000 nm spectral range, featuring ~5 nm spectral resolution and 128 spectral bands. The camera has a 12-bit dynamic range and speed of 30 spatial lines per second and 23.2 s per cube (696 lines per cube). Two halogen lamps were used as illumination sources; the camera was radiometrically calibrated and a diffuse reflectance grey standard, included in the scene, was used to convert the image cubes to reflectance factor. False colour images in trichromatic RGB were produced by ENVI software (Harris Geospatial) to visualise simultaneously the distributions of different pigments on the basis of their diagnostic spectral bands.^[11]

Hyperspectral imaging of the paintings in the NIR spectral range was carried out using the line-scan imaging device ImSpector N25E, with a Peltier-cooled MCT detector. The camera operates in the 1,000–2,500 nm range, with 10 nm spectral resolution and 256 spectral bands. Six halogen lamps were used as illumination sources, and the camera was calibrated with white reference (99% reflectance–Spectralon®). The data analysis was performed with ENVI software (Harris Geospatial).

A telecentric lens with focal length of 15 mm was used to collect images of the paintings with 1 mm spatial resolution, whereas details with 0.3 mm spatial resolution were taken using a macroscopic lens with a 1:1 magnification.

2.4 | UV–Vis–NIR reflection spectroscopy

Reflection spectroscopy was performed using a portable instrument designed for non-invasive in situ investigation of paintings.^[12] The instrument is coupled with a fibre optic system that allows directing the excitation light (a deuterium-halogen lamp) to the painting surface under examination and capture the reflected light by means of a sensitive CCD spectrometer (200–1,100 nm range with a spectra resolution of 8 nm) and an InGaAs spectrometer (950–1,600 nm range with a spectral resolution of 24 nm).

2.5 | Portable Raman spectroscopy

Raman measurements of *Bank of the Seine at Argenteuil* were carried out using the portable spectrometer Rigaku Xantus-2, which is equipped with two lasers operating at 785 and 1,064 nm, respectively. The first laser excitation works with a Peltier-cooled CCD detector and the spectral resolution is between 7 and 10 cm^{-1} . The 1,064 nm excitation laser uses an InGaAs detector and the spectral resolution is between 15 and 18 cm^{-1} . In both cases, the laser power at the sample can be software adjusted, while the spatial resolution is about 4 mm^2 . Spectra were successfully recorded with the 785 nm laser line in the 2,000–200 cm^{-1} range with a maximum laser power of 7 mW with variable exposure times and accumulations (generally 3 s and 3 accumulations).

2.6 | Portable reflection FTIR spectroscopy

Reflection FTIR spectra were recorded in the range 7,500–400 cm^{-1} using the portable spectrometer ALPHA-R Bruker Optics, which is equipped with a Globar radiation source, a modified Michelson interferometer and a DLaTGS detector. Measurements were acquired with a spectral resolution of 4 cm^{-1} , spatial resolution of about 28 mm^2 , and 180 scans.

3 | RESULTS

3.1 | Blue paints

The blue pigments used for the four paintings were identified by combining the information obtained with

portable reflection FTIR, UV–Vis–NIR reflection spectroscopy and MA-XRF. Prussian blue and cobalt blue were detected in many of the blue-painted passages in all the works. In addition, cerulean blue was identified in *Banks of the Seine at Argenteuil*, where it was used together with cobalt blue to paint the water—both in juxtaposed dabs of pure pigment and mixed together—and in the upper portion of the waitress' dress in *A Bar at the Folies-Bergère*. Cobalt blue was the only blue pigment detected in the sketch, *Au Bal*, that was made using a limited palette.

The distribution of cerulean blue, cobalt stannate, was visualised using MA-XRF based on the colocalised XRF detection of cobalt and tin (CoK α line at 6.9 keV and SnL α line at 3.4 keV; Figure 2b), while the pigment cobalt blue, cobalt aluminium oxide, was conclusively assigned by reflection spectroscopy (absorption bands in the 550–650 nm range due to ligand field d-d electronic transitions).^[13] Because the reflectance spectra of cobalt and cerulean blue are also characterised by strong absorption bands in the 1,200–1,500 nm range and in the 1,400–1,800 nm range, respectively, false colour composites in trichromatic RGB using NIR images at 950, 1,230, and 1,705 nm were produced, which allowed visualisation of the distribution of both pigments in the paintings. Cobalt blue is shown in pink, and cerulean blue is shown in orange (Figure 2c).^[14]

The distribution of iron-containing pigments was visualised by MA-XRF (Supporting Information). The detection of iron (FeK α line at 6.4 keV) is usually related to both the presence of iron oxide pigments, which can be present in both the ground and paint layers, and Prussian blue, which is usually present only in the paint layers.

Prussian blue, iron-hexacyanoferrate, has a very high tinting strength, and consequently a low concentration of pigment is needed to achieve a deep dark blue shade that looks almost black if not mixed with white or another opaque pigment. Thus, the XRF signal for the iron present in this pigment is generally not very strong and the question of whether it can be detected in paints that contain a low proportion of Prussian blue requires further study. In the present study, Prussian blue was positively identified using portable reflection FTIR (absorption band at 2,093 cm^{-1} assigned to CN stretching, Figure 3a).^[15]

Although Prussian blue does not feature specific bands in the NIR region, it strongly absorbs up to 1,000 nm, in contrast with other blue pigments that are highly reflective in the same spectral region.^[13] Thus, its presence in this group of paintings could be highlighted using false-colour images at 950 nm, where Prussian blue and the cobalt blue pigments are imaged in dark blue and dark pink, respectively. This is shown for the painting *Déjeuner sur l'herbe* in Figure 4a,b, where the presence of cobalt blue in the false-colour image corresponds to the distribution of Co in the XRF map.

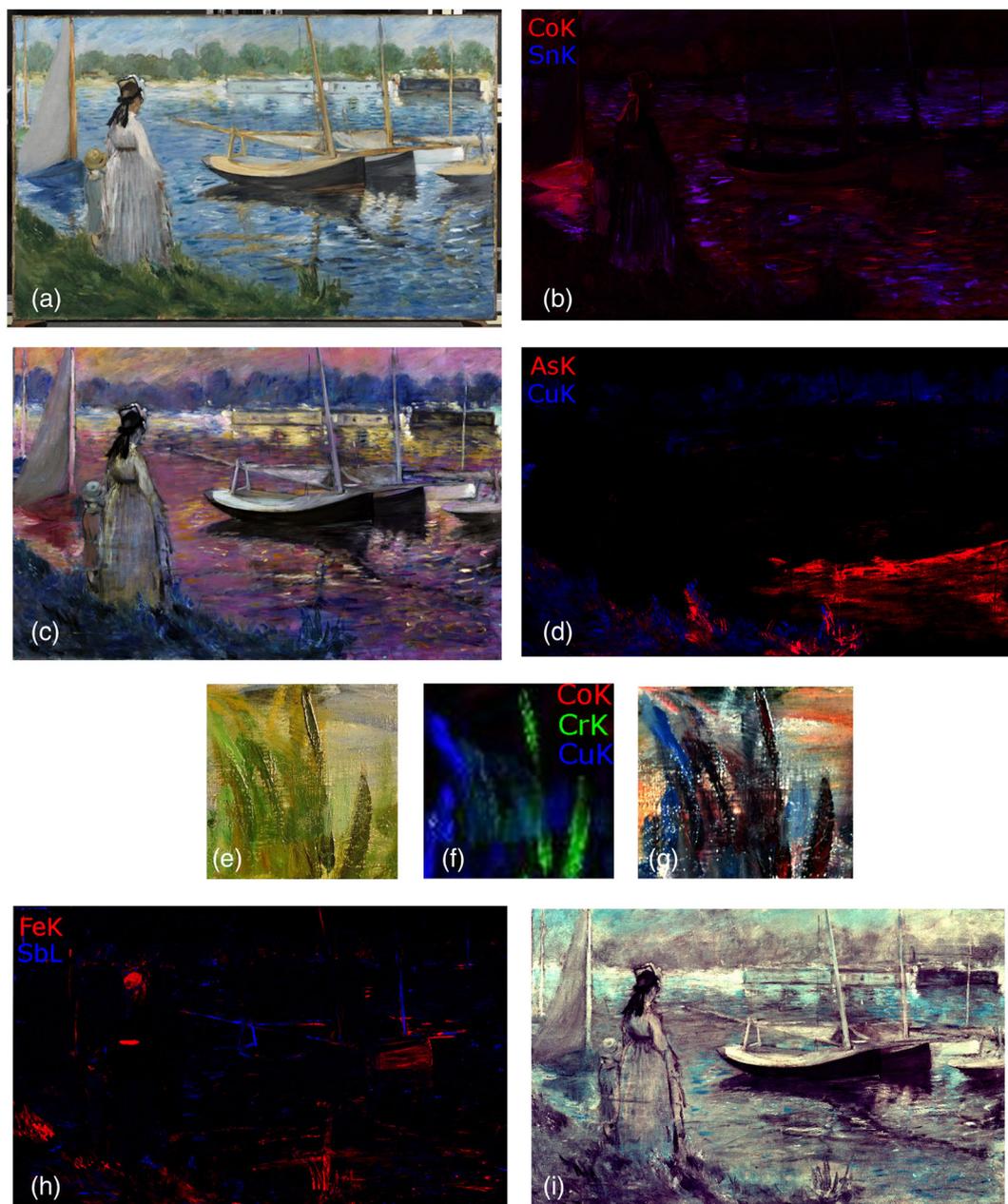


FIGURE 2 (a) *Banks of the Seine at Argenteuil* (1874, the Courtauld Gallery, 62.3×103 , ©private collection. On long-term loan to the Courtauld Gallery, London); (b) false-colour image showing the distribution of cobalt (red) and tin (blue); (c) false-colour image ($R = 950$ nm, $G = 1,230$ nm, $B = 1,705$ nm) showing cobalt blue in pink and cerulean blue in orange; (d) false-colour image showing the distribution of arsenic (red) and copper (blue); (e) detail of the grass in the foreground showing that different green pigments were used; (f) false-colour image showing the distribution of cobalt (red), chromium (green), and copper (blue); (g) false-colour detail of the grass in the foreground ($R = 835$ nm, $G = 653$ nm, $B = 582$ nm) showing the spatial distribution of a copper-based pigment (blue), viridian (red), and cobalt blue (orange); (h) false-colour image showing the distribution of iron (red) and antimony (blue); (i) false-colour image ($R = 1,705$ nm, $G = 1,940$ nm, $B = 2,100$ nm) highlighting the outline of the two figures in paint and the change in the pose of the woman

3.2 | Green paints

The analytical results showed differences in the pigments used by Manet to paint the green passages within this group of works.

The reflectance peak at about 520–540 nm and the broad absorption between 600 and 1,000 nm in the

reflectance spectra collected from some of the green areas in the grass in the foreground and the trees in the background of *Banks of the Seine at Argenteuil* suggested the presence of copper containing green pigments (data not shown).^[16] The colocalisation of the copper and arsenic XRF signals ($\text{CuK}\alpha$ line at 8 keV and $\text{AsK}\alpha$ line at 10.5 keV, Figure 2d) in the grass in the foreground

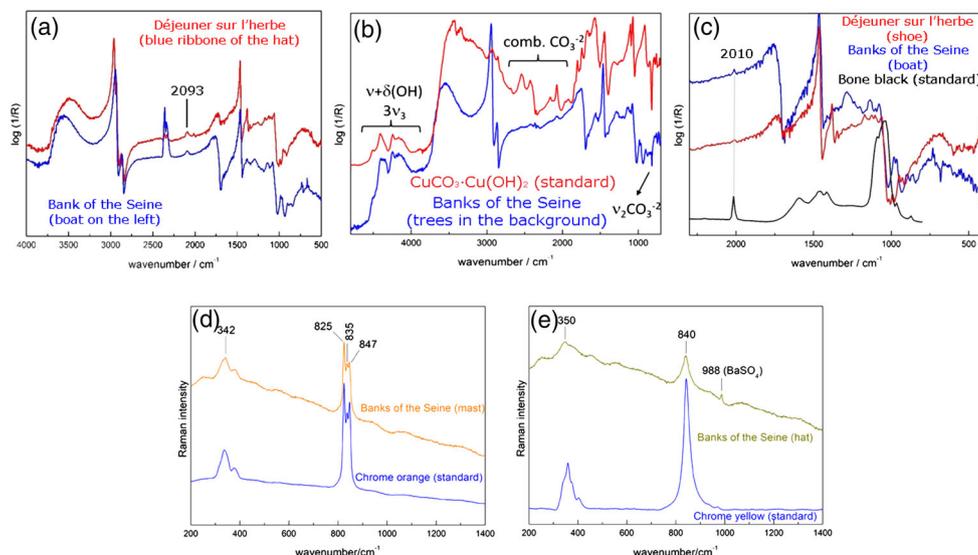


FIGURE 3 Fourier transform infrared reflection spectra of blue (a), green (b), and black (c) painted areas compared to the reference spectra of Prussian blue, $\text{CuCO}_3\text{-Cu(OH)}_2$ (malachite or green verditer), and bone black; Raman spectra recorded on an orange (d) and yellow (e) area of *Banks of the Seine at Argenteuil*, compared to the reference spectra of chrome orange and chrome yellow

suggested the use of either Scheele's green (copper arsenite) or emerald green (copper acetoarsenite). Reflection FTIR can usually be used to detect the acetate group in emerald green (inverted antisymmetric stretching of COO^- between 1,558 and 1,570 cm^{-1}), thus differentiating the two pigments.^[17] In the present study, however, the overlapping signal for organic materials in the paint and varnish coatings in reflection FTIR measurements hampered the identification of the copper and arsenic-based pigment. Nevertheless, considering that *Banks of the Seine at Argenteuil* was painted in 1874, emerald green is more likely to have been used, because its introduction in the early 19th century led to a decrease in the use of Scheele's green due to its relatively dull hue.^[18]

In the same painting, elemental copper was present alone in the trees in the background, suggesting the use of a copper-based green pigment different from emerald green. Reflection FTIR measurements revealed features consistent with either malachite or green verditer (basic copper carbonate and its synthetic version, respectively). These were identified by absorption bands for CO_3^{2-} at 900 cm^{-1} , combination band of CO_3^{2-} in the 2,600–2,000 cm^{-1} range; a weak 2δ (O–H) band at 2075 cm^{-1} , a weak $\nu_1 + \nu_3$ combination band at 2421 cm^{-1} , second-order overtone of ν_3 CO_3^{2-} at 4425 cm^{-1} , and combination of O–H bending and stretching at 4,425 cm^{-1} (Figure 3b).^[17]

Chromium XRF signals (CrK α line at 5.4 keV) were recorded in both the grass in the foreground and the trees in the background, which can be related to the use of chrome green (a mixture of chrome yellow and Prussian blue), chromium oxide, or viridian (hydrated chromium oxide).^[15] Viridian was confirmed by reflectance vis spectroscopy (absorption band between 580 and 650 nm due

to Cr(III) d^3 configuration) and its distribution was visualised by MA-XRF (showed in green in the map, Figure 2f) and vis hyperspectral imaging (showed in red in the map, Figure 2g).^[19,20]

In addition, light microscopy and SEM–EDX analysis of a sample from the grass taken from the lower left edge of the painting suggested the presence of a yellow chromium-based pigment that was not detected using the other methods, although no copper-based pigments were identified (Supporting Information). Non-invasive point analyses and MA-XRF analysis of the painting were useful for identifying and mapping copper-containing pigments used in the area of sampling that were not present in the sample itself, underpinning the point that inferences based only on the analysis of samples may be limited. Conversely, pigments present in low concentration may be difficult to detect by non-invasive methods, in which case analysis of samples can provide additional information.

Admixtures of Prussian blue, emerald green, viridian, lead, and zinc white were used to paint the green leafy setting of *Déjeuner sur l'herbe*. Characterisation of the paint mixtures was achieved again using a combination of portable reflection FTIR (data not shown), MA-XRF (Figure 4d, where the leaves painted in emerald green are shown in purple, in contrast with those painted using viridian, which are shown in green), and reflectance vis spectroscopy (data not shown). MA-XRF also detected tin in the same green passages (XRF elemental maps in Supporting Information). To the best of the authors' knowledge, this element can be related to a limited range of paint materials, which include cerulean blue, lead-tin yellow, and a tin-based substrate for an organic dyestuff.^[21] The presence of cerulean blue in this area is excluded on the basis

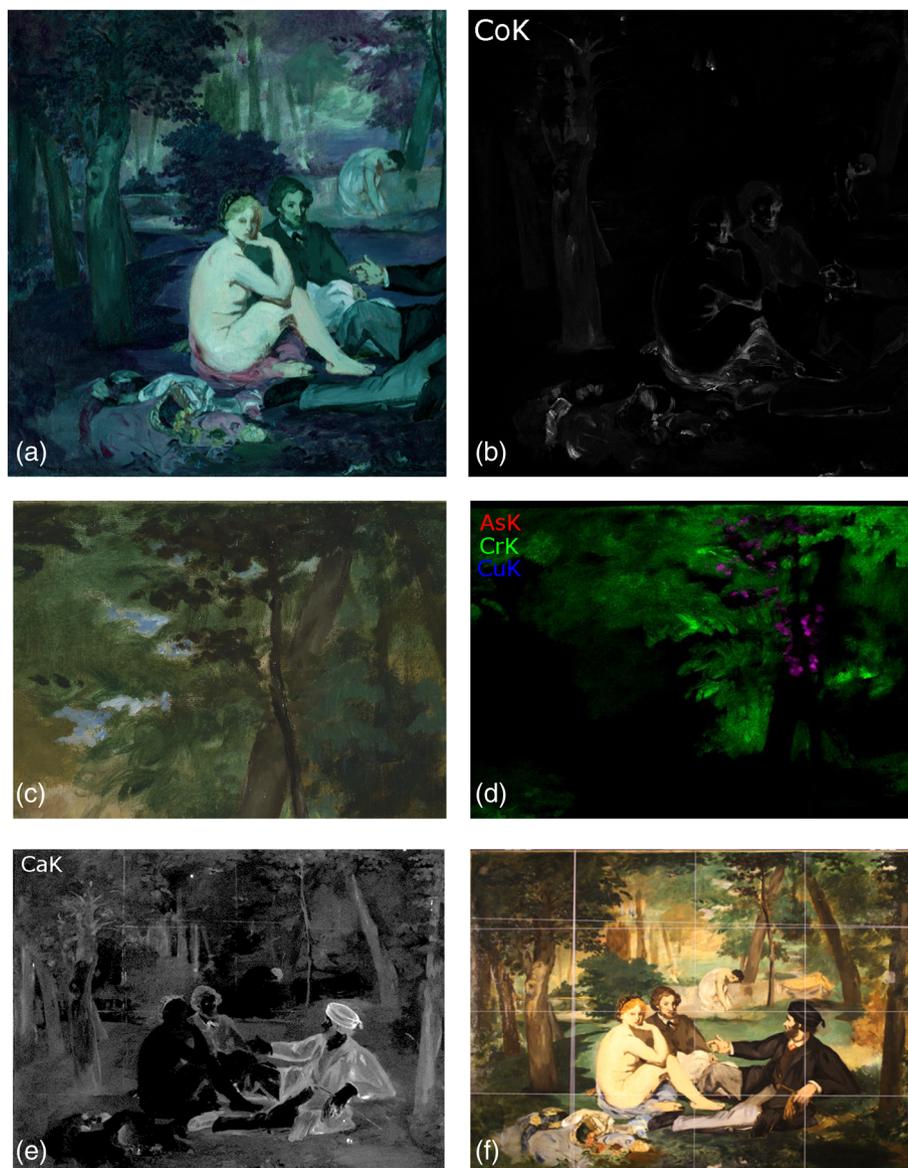


FIGURE 4 (a) False-colour image of *Déjeuner sur l'Herbe*, (950 nm, R, G), detail; (b) X-ray fluorescence scanning distribution map of cobalt; (c) detail of the trees in background, in the upper area of the painting; (d) false-colour image showing the distribution of arsenic (red), chromium (green), and copper (blue); (e) X-ray fluorescence scanning distribution map of calcium; (f) reconstruction of the grid lines on the Courtauld picture based on the distribution image of calcium

of the absence of the XRF signal of cobalt which, when detected together with tin, allows to conclusively assign this pigment; the use of lead-tin yellow is unlikely because such a pigment was not used for paintings after 1,750, when it was replaced by Naples yellow.^[22] The presence of a tin-based substrate for an organic dyestuff could not be confirmed nor excluded in this study. Thus, further research is required to explain the presence of tin in the green painted areas of *Déjeuner sur l'herbe*.

3.3 | Orange, yellow, and red paints

Because some of the orange and yellow pigments used in the paintings do not have characteristic absorptions in the

spectral ranges explored in this study, and the overlapping signal of organic material such as the varnish in the Raman and reflection FTIR measurements often hampered their molecular identification, their assignment was mainly hypothesised based on the elements detected by MA-XRF.

An exception is represented by *Banks of the Seine at Argenteuil*, where Raman measurements of some orange and yellow paints allowed to reveal features consistent with lead chromate pigments such as chrome orange (825, 835, and 847 cm^{-1}), and in one case with chrome yellow (840 and 350 cm^{-1} assigned to the chromate symmetric stretching [ν_1] and symmetric bending [ν_4] modes, respectively, and sulphate symmetric stretching

mode [ν_1] at 988 cm^{-1} assigned to barium sulphate BaSO_4 , Figure 3d,e).^[23,24]

The antimony and iron XRF signals (SbL α line at 3.6 keV and FeK α line at 6.4 keV) recorded in the same yellow details would lead to the hypothesis that either Naples yellow and iron-oxide containing pigments were used in addition to chromium-based pigments, or that iron is present in Naples yellow as an additional element due to the manufacturing process of the pigment (Figure 2h).^[25] A similar paint mixture is also likely to be used for the brown–yellow painted areas of *A Bar at the Folies-Bergère* (Figure 6e). In this case, the antimony, chromium and zinc (ZnK α line at 8.6 keV) colocalised XRF signals in the bright orange tangerines could be related to either a mixture of Naples yellow and both zinc and chromium-based pigments, or to the use of a mixture of chromium-based pigments and Naples yellow, where zinc might be indicative of an extender.^[25,26] In contrast, iron oxide-containing pigments (identified by reflection vis spectroscopy) mixed with zinc and lead white were used for different brown–yellow passages of *Déjeuner sur l'herbe* (XRF elemental maps in Supporting Information).^[27]

Vermilion, which was used for the red passages and mixed with lead white to render the flesh tones, was identified using MA-XRF (HgL α line at 9.9 keV, XRF elemental maps in Supporting Information).^[28]

3.4 | Dark brown and black paints

The dark-brown passages were painted using either a mixture of Prussian blue, iron oxide-containing pigments and bone black in *Banks of the Seine at Argenteuil*, or a mixture of cobalt and iron-based pigments for *Au Bal* and *Déjeuner sur l'herbe*. Bone black was identified by FTIR and visualised on the painting surface by MA-XRF. All

the black painted areas of the works showed high XRF signals for calcium (CaK α line at 3.7 keV, Figure 4e). Calcium is the main element present in bone black, which is made by charring bones and thus contains calcium hydroxyapatite. Reflection FT-IR showed a weak absorption at $2,010\text{ cm}^{-1}$, which is related to the phosphate content of the pigment, thus confirming the presence of bone black (Figure 3c).^[29]

3.5 | Visualisation of sketches, paint changes, and preparatory squaring

Both multispectral and hyperspectral imaging in the NIR range highlighted features in underlying paint layers of some of the paintings investigated within the present study. For example, imaging of *Au bal* at 1,000 nm enhanced the visibility of an inverted earlier sketch of a figure, possibly drawn with graphite, as suggested by the fact that the sketch is also visible at longer wavelengths (Figure 5a–c). Imaging of *Banks of the Seine at Argenteuil* in the range 1,700–2,500 nm allowed the visualisation of the outline of the two figures in paint. The figures were painted over the water and their pose was altered during the painting stage (Figure 2i).

The study also highlighted questions in relation to the interpretation of elemental distribution maps and spectral images that did not correspond to the reworking visible in X-radiographs. This question is exemplified in the study of the iconic *A Bar at the Folies-Bergère* that Manet reworked during painting, making numerous changes directly on the canvas. The artist initially painted the barmaid with her arms crossed across her waist and altered her reflected image in the mirror twice (as visible in X-ray radiography in Figure 6b). Such compositional changes were not visualised in the Pb distribution map of the

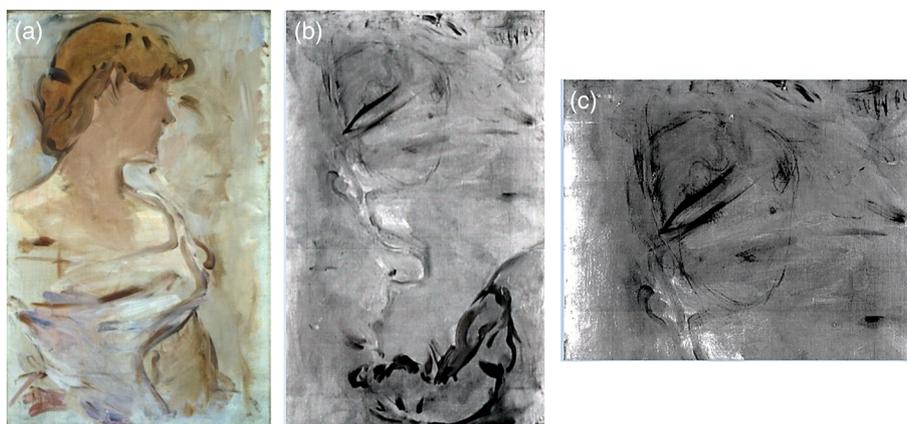


FIGURE 5 (a) *Au Bal - Marguerite de Conflans en Toilette de Bal* (1870–80, the Courtauld Gallery, 55.7 × 35.5 cm, ©the Samuel Courtauld Trust, the Courtauld Gallery, London); (b) image at 1000 nm, ~6 nm spectral resolution, 1 mm spatial resolution, (c) detail at 0.3 mm spatial resolution



FIGURE 6 (a) *A Bar at the Folies-Bergère* (1882, the Courtauld Gallery, 96 × 130 cm, ©the Samuel Courtauld Trust, the Courtauld Gallery, London); (b) X-radiograph; (c) X-ray fluorescence scanning distribution map of zinc; (d) near-infrared image at 2,100 nm; (e) X-ray fluorescence scanning distribution maps of various elements present in the painting

painting (PbL α line at 10.5 keV, XRF map in Supporting Information), whereas the early positions of the reflected head were just barely visible in the Zn distribution map (ZnK α line 8.6 keV, Figure 6c).

Distribution maps of chromium, arsenic, copper, cobalt, tin, and iron suggested the presence of a chromium-based pigment, emerald green, cobalt blue, cerulean blue, and Prussian blue in the thickly applied overpaint concealing the early position of the hands (Figure 6e). As MA-XRF is

not depth-selective, contributions from the pigments present at and below the painting surface are included in the elemental distribution maps produced, thus making it difficult to assess whether the range of pigments identified is present as a mixture or in overlying layers. NIR spectral imaging of this area showed faint traces of the original position of the hands over 1,700 nm, where the pigments in the overpaint become more transparent (Figure 6d). The thick complex overlying paint may absorb the XRF emission

from the underlying layers, which may explain why the changes in composition of *A Bar at the Folies-Bergère* are not clearly visualised using MA-XRF.

MA-XRF analysis of *Déjeuner sur l'herbe* revealed elements of the development of the composition that were not clearly visualised with any of the other techniques used. The distribution map of calcium revealed a grid that is likely to have been drawn on the ground and used to transfer the design to the canvas (Figure 4e). The grid lines, which divide the scene into 16 squares, are not perfectly straight and their somewhat irregular pattern suggests that they may have been laid out without the use of a ruler, possibly traced freehand or by means of a string web. It remains unclear, whether the grid was used to produce a copy after the Paris painting in the Musée d'Orsay painted in 1863 or whether Manet used it to work out the composition in a preliminary sketch that he would have later scaled up to paint the larger version. The calcium content of the grid lines suggested the use of either bone black or chalk (calcium carbonate). However, MA-XRF alone was not sufficient for discriminating between these two pigments, as calcium is the only element detectable in both cases. Bone black contains about 15–20% carbon, therefore underdrawings made with such pigment would generally be possible to detect by infrared reflectography, while chalk, which is reflective in the IR range, would be difficult to register.^[30] Neither multispectral nor hyperspectral imaging in the IR range allowed recording the grid lines, which would lead to the hypotheses that they may have been traced using chalk.

4 | DISCUSSION

The analytical methods used in this study proved to be complementary and provided data that allowed the characterisation of many of the pigments used in the works by Édouard Manet in The Courtauld Gallery. The non-invasive approach proved to be well suited to study the material heterogeneity and compositional complexity of such a group of paintings, providing the opportunity to examine all the areas of the paintings, and allowing the visualisation of the distribution of elements indicative of pigments used.

The interpretation of the analytical findings highlighted some key points that require further research. These included the mapping of tin in the green paint passages of *Déjeuner sur l'herbe*; the identification of Prussian blue by elemental analysis, when present in low proportion; the inability of visualising changes in composition concealed by thick and complex overlying layers using MA-XRF, in the case of *A Bar at the Folies-Bergère*. These issues will be further supported by the analysis of a set of

reference samples produced using known materials and techniques characteristic of Manet's painting methods. Analysing this reference samples using the same methods as the paintings will allow direct comparison of the analytical data gathered from the paintings and will provide the opportunity for a critical evaluation of the analytical methods used, including their detection limits. Other areas not addressed in the present study include the characterisation of lake pigments that were used by Manet, that are beyond the scope of the current research, and the detailed characterisation of paint binding media used for these works. The research has wider implications for the study of Impressionist paintings, as the results of this study will also inform technical studies of works by other artists of the period who used similar materials and painterly methods.

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SUPPORTING INFORMATION

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