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'It's not easy being green': a spectroscopic study of green pigments used in illuminated manuscripts†

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This study explores the use of green pigments and mixtures in manuscript illumination, drawing upon experimental evidence derived from a non-invasive spectroscopic survey of green pigments used in 31 bound manuscripts and 23 manuscript cuttings or single folios in the collections of the Fitzwilliam Museum in Cambridge, UK. Analytical investigations were carried out on green-coloured areas by visible and near-infrared fibre optic reflectance spectroscopy (FORS), at times supplemented by X-ray fluorescence (XRF). FORS spectra can easily be acquired in great numbers and without subjecting the manuscripts to any physical strain, making this technique especially suitable for analytical surveys of valuable and fragile objects. Despite some drawbacks, its use in combination with XRF often provides a relatively complete characterisation of pigments and mixtures, particularly when FORS analysis is extended into the shortwave-infrared range (to 2500 nm). The experimental results are examined in light of the recipes for green pigments found in medieval technical treatises. The outcome is a contextualized study with a focus on French illumination between the 13th and the 16th century, but allowing for comparisons with contemporary materials of different geographic origin.

Introduction

This study explores the use of green pigments and mixtures in manuscript illumination, drawing upon experimental evidence derived from a non-invasive spectroscopic survey of green pigments used in 31 bound manuscripts and 23 manuscript cuttings or single folios in the collections of the Fitzwilliam Museum (FM) in Cambridge, UK. The survey was carried out within the context of a broader research project[1] which aims to combine the non-invasive technical analysis of pigments and other painting and drawing materials used on manuscripts with information on the historical, art-historical, social and political context in which the manuscripts were commissioned, executed and used. The non-invasive identification of artist's materials, carried out using methods which do not require contact with the object analysed, provides a powerful tool to further categorise and characterise manuscripts following stylistic analyses by art historians, thus enhancing the overall appreciation of this type of works of art.

The reasons for the specific interest in green, amongst all colours, are manifold. Firstly, green is a colour with multiple cultural, emotional and religious associations. It is no wonder, then, that so many shades of green have been used throughout history by artists, including illuminators. Secondly, and most importantly from the point of view of pigment analysis, illuminators have used a variety of green pigments, both natural and synthetic, organic and inorganic, as well as a wide range of mixtures of yellow and blue, to obtain their preferred shades of green. In many cases, these green pigments and mixtures present significant deterioration issues (Fig. S1†). These include damage caused by shadowing, strike-through and in severe cases, losses to the paper or parchment substrate. Copper-based metallic alloys, used to imitate gold, have at times deteriorated and now appear green to the eye (Fig. S1c†). In these cases, identification of the nature of the green pigments used by the artist is of paramount importance, because it enables conservators to carry out informed and sympathetic conservation treatments.

This analytical survey was undertaken with all these reasons in mind, and in parallel with a preliminary survey of recipes for green pigments and mixtures surviving in medieval technical treatises and artist's recipe books. The focus on 13th to 16th century French illumination was decided upon because of art-historical research currently being carried out on the French manuscripts in the FM collection.[2] The museum's wide-ranging manuscripts collection also allowed comparisons with contemporary manuscripts of different geographic origin.

During the past few decades, numerous analytical methods have been used to analyse manuscripts, with a preference for non-invasive approaches, due to the value and fragility of these

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† Electronic supplementary information (ESI) available: Fig. S1 shows deterioration of the painted surface in green areas, while Table S1 includes a list of the manuscripts analysed and a summary of the green pigments and mixtures identified. See DOI: 10.1039/c3ay40530c

objects.[3] Non-invasiveness of the analysis and portability of the scientific equipment are key characteristics which often determine the choice of analytical methods. In this study, the identification of pigments and paint mixtures was achieved mainly by means of fibre optic visible and near-infrared (vis-NIR) reflectance spectroscopy (FORS). FORS spectra can easily be acquired in great numbers and without subjecting the manuscripts to any physical strain, making this technique especially suitable for the analysis of such fragile objects, as demonstrated by an ever-increasing number of publications.[4,5] The advantages and drawbacks of this analytical method for the analysis of manuscripts and other art objects, including a discussion of the benefits of extending the range of analysis beyond the visible to include the near- and shortwave-infrared portion of the spectrum (NIR and SWIR), up to 2500 nm (4000 cm^{-1}), have already been addressed by several authors[6] and therefore won't be dealt with at length here. It is however worth underlining that the extension into the SWIR allows the identification of vibrational overtones and combinations which are characteristic of functional groups such as sulphates, hydroxyls and carbonates, facilitating the identification of a number of pigments.[7,8]

During this study, FORS analysis was in some cases supplemented with X-ray fluorescence (XRF) analysis. While FORS yields information about the chemical structure and the presence of certain functional groups for both inorganic and organic materials, XRF yields elemental information and so is mostly useful for the identification of inorganic materials. Both FORS and XRF can rely on portable instruments and are non-invasive and quick (FORS: ~8 seconds per spectrum, XRF: ~200 seconds per spectrum). Their efficient synergy for the identification of pigments on manuscripts has been well demonstrated in a number of recent studies.[4,5] Despite such good synergy, the combined use of these two analytical methods does not always provide a straightforward or complete characterisation of the materials under analysis. For example, Fig. 1 shows reflectance spectra of test samples obtained by painting green pigments and mixtures on a parchment support.[9] The spectra of malachite and verdigris can be distinguished with relative ease, mainly by their difference in slope between about 1000 and 1850 nm. Malachite usually also shows specific absorption bands in the 2200–2500 nm (4000–4545 cm^{-1}) region, due to combination and overtones of the fundamental vibrations of the O–H and CO_3^{2-} groups within its structure.[7] On the other hand, it would be hard to ascertain the presence of lead-tin yellow mixed with malachite by FORS alone. In this case the availability of a complementary technique, such as XRF or Raman spectroscopy, becomes indispensable for a complete and correct identification.

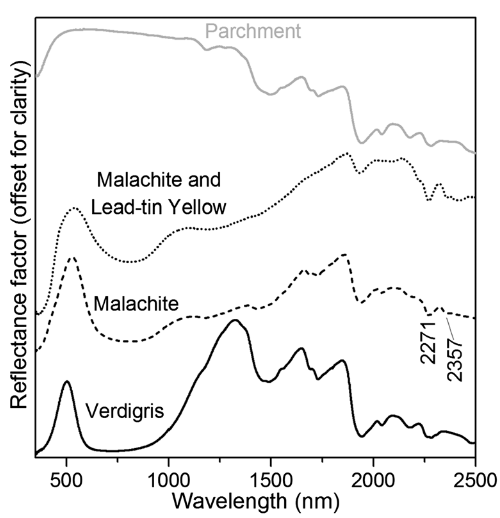

Fig. 1 FORS spectra of reference green pigments and mixtures, bound in gum Arabic and painted on a parchment support, whose spectrum is shown at the top for comparison.

The results presented here are mostly based on the analysis of FORS spectra. They represent an important, albeit preliminary, step towards the complete identification of green pigments, which we intend to refine by carrying out further investigations.

Green pigments and mixtures mentioned in medieval technical treatises: a brief survey

Dozens of medieval recipes for the manufacture of green pigments and mixtures survive in a number of technical treatises composed in various European regions,[10,11] and many more may have existed that are now lost. Our brief survey of recipes for green pigments and mixtures was restricted to those found in treatises which are known or thought to include instructions specifically related to manuscript illumination. The survey seems to indicate that throughout the Middle Ages and until the 18th century, when modern synthetic chemistry entered the artist's studio, the range of green materials used by Western European illuminators was relatively limited, at least in terms of general guidelines. Many variations exist, however, yielding a greater variety of green compounds than previously imagined, as a number of recent analytical studies have shown.[12,13]

Verdigris is mentioned in colour lists and in technical literature since antiquity and throughout the medieval and Renaissance period and beyond.[14] The term has been used historically to indicate a number of different copper-containing compounds, including basic or neutral copper acetates, copper chlorides, copper carbonates and other compounds.[13–15] It is in this broad sense that the term 'verdigris' will be used throughout this article. Verdigris is fundamentally the only green pigment widely mentioned in 12th and 13th century technical treatises, including the *Liber diversarum arcium*, composed probably c. 1300 in Northern Europe (Flanders, France or Germany), in addition to plant extracts, mostly added to verdigris to modify its colour, and to green earth.[16] The corrosive nature of verdigris was well known to medieval practitioners: the anonymous late 14th century author of *De Arte Illuminandi* mentions verdigris but does not provide a recipe for it, because of the potential damage it may cause to the parchment support.[11]

De Arte Illuminandi, similarly to other 14th and 15th century treatises, expands on the green palette available to illuminators:

it lists *terre-verte* (green earth), malachite,[17] sap green and other plant juices, to be potentially ground together with azurite to obtain 'a very lovely green'.[11] Mixtures of indigo and orpiment are also mentioned, but again the potentially damaging nature of orpiment results in the absence of a specific recipe.

Several other green pigments have been identified analytically on medieval illuminations, but no historic recipes are known that describe their preparation. Amongst them are various copper sulphates (mainly brochantite and posnjakite),[12,18] and copper proteinate.[12,19] However, as has been shown to be the case for copper resinate (mostly used in easel painting),[20] recent studies suggest that copper proteinate was not deliberately used as a pigment, but rather that its presence may derive from the interaction of verdigris with a proteinaceous binding medium.[12]

Experimental

Manuscripts analysed

The survey concerned the use of green pigments on 31 bound manuscripts (149 folios analysed) and 23 manuscript cuttings or single folios. Twenty-six manuscripts and fifteen cuttings are of French origin and date to the mid-13th through the 16th century, with the exception of an 11th century Gospel book. Among these are manuscripts produced at the Royal court in Paris as well as books illuminated in different French regions, most of them of exceptionally high quality. In order to provide a comparison with the French material, contemporary manuscripts and cuttings produced in Italy, Persia, and Silesia (a region in modern-day Poland) were also analysed. A detailed list of the materials analysed is presented in Table S1.†

Analytical methods

FORS spectra were acquired in the 350–2500 nm range using a FieldSpec4 fibre optic spectroradiometer (ASD Inc., Boulder, Colorado, USA). The instrument's resolution is 3 nm at 700 nm, and 10 nm at 1400 and 2100 nm, and the wavelength accuracy is 0.5 nm. The spectroradiometer includes a 512 element silicone array for signal detection in the 350–1000 nm range, as well as two graded index InGaAs photodiodes, TE cooled, for signal detection between 1000 and 2500 nm. Analysed areas were illuminated using ASD's Hi-Brite probe (halogen bulb, 2901 K colour temperature). Spectra were collected and processed using ASD's RS^3 and ViewSpec Pro software as well as Origin Pro 8.6 (OriginLab, Northampton, MA, USA). The following setup was used: 64 accumulations, light probe held normal to the manuscript page, 1.5 m glass optic fibre probe hand-held at approximately a 45° angle to minimise specular reflection.

Material identification was achieved *via* comparison with online and in-house spectral databases of reference pigments and mixtures painted on various grounds and bound in different media. The importance of having an extensive and reliable database of reference spectra is paramount. The presence of a certain material can in fact only really be hypothesized once its spectrum has been measured, or at least its spectral features predicted based on its chemical structure.

XRF spectra were acquired using a Tracer IV-SD handheld analyser (Bruker Elemental, Kennewick, WA, USA) at either 40 kV/16 μA or 15 kV/55 μA. Spectra were collected using Bruker's S1-PXRF software and processed using Origin Pro 8.6 (OriginLab, Northampton, MA, USA). The instrument was mounted on a tripod and the X-ray beam directed horizontally at the page to be analysed, at a distance of ~2 to 4 mm. Peaks in the XRF spectra were assigned to individual chemical elements, and the possible presence of specific pigments inferred by comparison to databases.

For both FORS and XRF analyses, the exact geometry of the experimental setup had to be adapted to each manuscript's size and physical constraints (*e.g.* cockled pages, impossibility to keep it open at a pre-determined angle). Therefore, no quantitative analysis of the XRF spectra was attempted. In the case of FORS, pigment identification relies on overall spectral shape, rather than on absolute reflectance values, as well as on the position of any characteristic absorption bands, which does not depend on measurement geometry.

Results and discussion

The analytical survey aimed at getting a sense of which green pigments were preferred by French illuminators during the medieval and Renaissance period – but also to gain information on each of the analysed manuscripts. Sample data obtained on two individual manuscripts will be presented first, followed by the overall results of the survey.

Fitzwilliam Museum MS 92

Eight folios were analysed on FM MS 92, produced in central France at the turn of the sixteenth century.[21] Results obtained on fol. 27r are reported here, as they well represent those obtained on the entire manuscript.

The vast majority of the green pigments analysed were identified as malachite,[17] as shown by spectra A and B in Fig. 2b. Blue-green areas, on the other hand, were painted using an azurite mixture, as shown by absorption bands at 1491, 2285 and 2352 nm (6707, 4376 and 4252 cm^{-1}), characteristic of azurite[22] (Fig. 2b, spectrum C).

It is noteworthy that the malachite spectra obtained from green areas within the larger miniatures on each folio (spectrum B) all differ from those acquired on the borders (spectrum A) for the presence of different absorption bands in the range 2200–2350 nm (4255–4545 cm^{-1}). Bands in this range are due, both for azurite and for malachite, to overtones and combinations of stretching and bending modes of O–H groups and carbonate ions (CO_3^{2-}), and their position varies with composition.[7,23] This could be an indication that the miniatures and the borders were painted either at different times, or by two different artists/workshops each using their own supply of malachite. Trace-element analysis by total-reflection XRF or the identification of the crystallographic structure by X-ray diffraction (XRD) may help better specify the nature and possibly trace the provenance of these two types of malachite.

Future work will be aimed at establishing the entire range of pigments used on this manuscript, with a focus on similarities

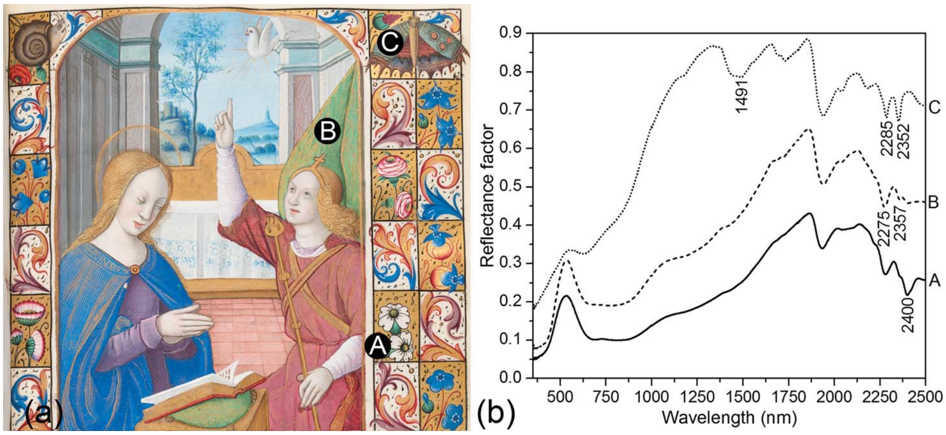

Fig. 2 FM MS 92, Book of Hours, Loire region (Angers?), c. 1490–1510 (a) detail from fol. 27r, indicating areas of analysis © Fitwilliam Museum, Cambridge; (b) corresponding FORS spectra.

and differences between the large miniatures and the borders, in the hope of clarifying questions of authorship and relative dating of its decorations.

Fitzwilliam Museum MS 62

Eleven folios were analysed on FM MS 62, the so-called *Hours of Isabella Stuart*, a profusely illuminated Book of Hours produced in Northern France circa 1431.[24] A group of artists, collectively identified as the 'Rohan Masters', have been identified as the authors of its complex decorative programme, which comprises 24 large miniatures and over 500 marginal illustrations, in addition to a full-page illumination depicting the Virgin and Child (Fig. 3b), very 'painterly' in appearance and unique within the manuscript.

The vast majority of the green pigments analysed have been identified as malachite, as shown by spectra B and C in Fig. 3c, corresponding to the green pavement in the marginal illustration on fol. 28r (Fig. 3a) and to the bright green area in the lower left corner of the full page illumination on fol. 141v (Fig. 3b). There appear to be only two exceptions to this use of malachite, of greens which appear to have been obtained with organic colourants:

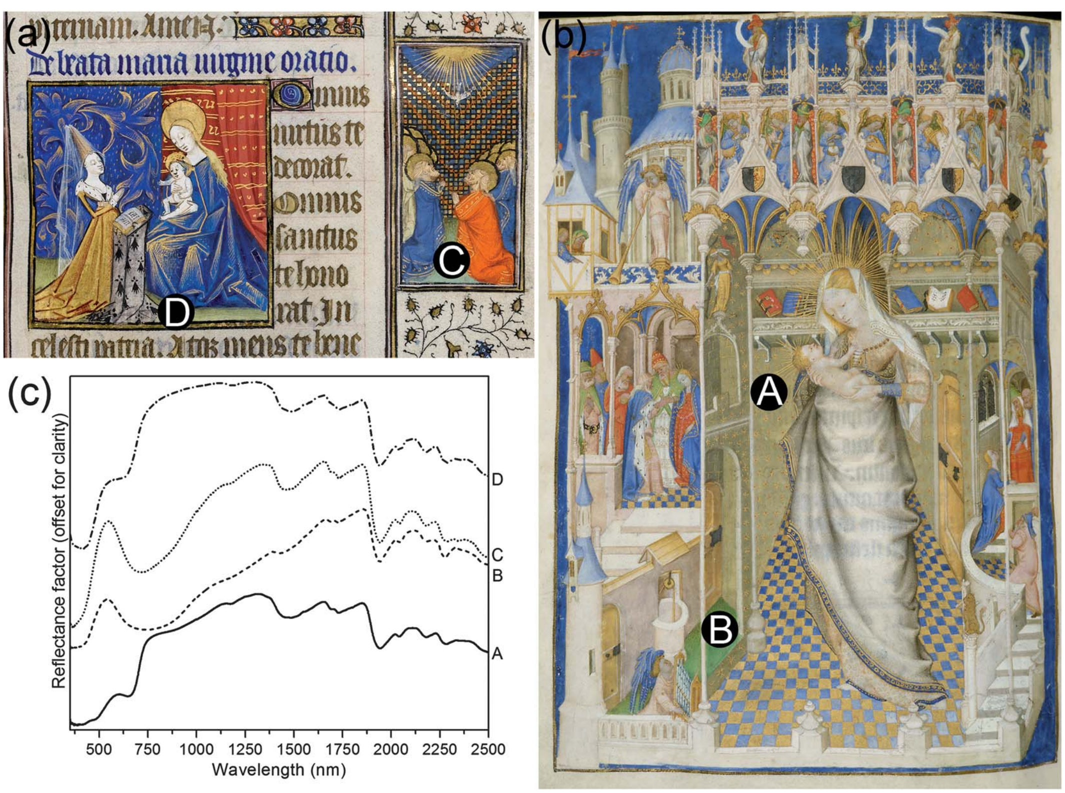

Fig. 3 FM MS 62, the Hours of Isabella Stuart, Northern France (Angers?), c. 1431 (a) detail from fol. 28r, indicating areas of analysis © Fitwilliam Museum, Cambridge; (b) detail from fol. 141v, indicating areas of analysis; (c) corresponding FORS spectra.

- the green pavement in the central miniature on fol. 28r (Fig. 3c, spectrum D), which is considered on stylistic grounds to have been added to the manuscript at a later time, possibly when the manuscript changed owner. Incidentally, the blue robe of the Virgin and the background in this miniature are the only instances identified within the manuscript where azurite was used as the blue pigment instead of ultramarine. Such a marked difference in the use of both green and blue pigments supports the different date of the individual miniature compared to the rest of the manuscript;

- the 'muddy' green-coloured architectural background of fol. 141v (Fig. 3c, spectrum A). This observation contributes to raising the question of whether a more skilled artist, perhaps also active as a panel painter, illuminated just this one page, which appears different from all the others not only in scale and in the use of perspective, but also from the point of view of painting technique, including the use of a unique shade of green and of a different material to obtain it.

The green colourant(s) used in these two areas were likely obtained with mixtures of yellow pigments with indigo, as suggested by the overall shape of the spectrum and the rapid rise in reflectance between 700 and 750 nm.[25] The nature of the yellow component of the two mixtures will be further investigated by XRF and Raman spectroscopy.

Survey of green pigments

Fig. 4 summarises the green pigments and mixtures identified on the French manuscripts analysed.

Verdigris was clearly the green pigment of choice in France during the 13th and 14th century, and continued to be used at later times. It is also the only green pigment identified on the 13th century Silesian manuscript. The increasing availability of a wider range of green pigments from c. 1400 onwards appears clear from the timeline: malachite seems to have been used widely by French illuminators, beginning in the 15th and throughout the 16th century. This matches the observation that malachite is only sparsely mentioned in earlier technical literature, as well as the fact that it has been most often identified in European easel paintings of this same period.[26]

A thorough comparison of our results with literature data is beyond the scope of this work; however this 'turnover' c. 1400 between the use of verdigris and malachite in French illumination has also been evidenced by previous studies, such as the early work by Françoise Flieder.[19,27]

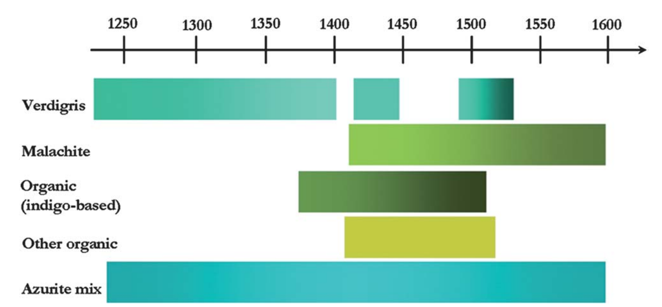

Fig. 4 Timeline summarising the green pigments and mixtures identified on the French manuscripts analysed. See text for a detailed discussion.

Indigo mixtures and other organic greens were identified on several manuscripts, both French and Italian, dating from the late 14th century onwards. Finally, azurite mixtures were identified on French manuscripts throughout the time range considered, but mainly to obtain blue-green/turquoise hues. Only on four manuscripts produced in France during the second half of the 15th century did we find azurite mixtures used to obtain a 'real' green colour. Azurite mixtures appear instead to have been the preferred way to obtain bright green hues for late 14th and early 15th century Florentine illuminators, as shown by the results obtained on Florentine cuttings and manuscripts analysed during this and previous studies.[6,28] In some of the Florentine material, the presence of peaks related to tin in the XRF spectra suggests that the yellow component in these mixtures is lead–tin yellow.

The identification of verdigris on the two Persian manuscripts included in this survey seems to suggest a preference for this pigment over malachite on the part of 16th century Eastern European illuminators, contrary to what happened in Western Europe. This is only an indication, based on a very small sample; only by analysing a larger number of similar manuscripts can this hypothesis be confirmed. A range of green organic colourants and indigo-based mixtures was also identified on the Persian manuscripts; the identification of arsenic by XRF indicates that orpiment was probably the yellow component in such mixtures.

Conclusions

With its ability to identify pigments on manuscripts non-invasively, FORS provides us with a powerful tool further to categorise artworks following stylistic analyses by art historians. Its greatest advantage for the kind of research described in this study is the possibility to acquire large amounts of data *in situ* in short amounts of time while provoking no damage to the analysed objects, and still obtain meaningful, albeit not fully comprehensive, results. This preliminary survey of the use of green pigments in French illumination between the 13th and the 16th century has established what appears to be a trend in the use of verdigris until c. 1400, followed by a preference for malachite. The survey also yielded interesting comparisons with contemporary manuscripts of different geographic origin. Much work still needs to be done: a more complete characterisation of mixtures and organic glazes is needed, as well as a more in-depth investigation of historic recipes and further comparisons with analytical results previously published by other authors. As more and more technical analyses are performed *in situ* on manuscripts, no doubt more trends will emerge in the use of different pigments by different artists or workshops, and in different periods of time and geographic areas.

Acknowledgements

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