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Near Infrared Reflectance Imaging Spectroscopy to Map Paint Binders In Situ on Illuminated Manuscripts**

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Dedicated to Ross Merrill

In recent years, visible and near infrared (NIR) reflectance imaging spectroscopy, i.e., the collection of contiguous calibrated spectral images to provide the reflectance spectra for each pixel of the scene, has been applied to the study of old master paintings. Its application to the study of light-sensitive works of art, such as illuminated manuscripts, has been limited to partial pigment identification using visible electronic transitions. Here we show the potential of NIR imaging spectroscopy in the 1000 to 2500 nm (10000–4000 cm^{-1}) spectral region to map and identify paint binders by utilizing vibrational features associated with methylenic, CH and amide functional groups. This is demonstrated by using a novel hyperspectral NIR imaging spectrometer (1000–2500 nm, 4.4 nm resolution) to map the use of a fat-containing paint binder (likely egg yolk) for certain compositional elements of a 15th century manuscript leaf. The use of a fat-containing binder for manuscript illumination is surprising in itself since egg white and gum Arabic (protein and polysaccharides) are historically considered to be the binders preferred by illuminators. This study offers the opportunity to map paint binders in situ on works of art, at a macroscopic scale, for the first time.

While analytical techniques using micro-samples (mg) taken from art objects can provide the most accurate identification of artists' materials, there is a preference for in situ methods. Among them, site-specific tools such as X-ray fluorescence (XRF), Raman spectroscopy and fiber optics reflectance spectroscopy (FORS) can identify pigments. Production of material maps on the macroscopic scale (entire artwork) has been limited to date, while mapping on the microscopic scale has progressed rapidly and has proven to be useful. Techniques that have been used include scanning electron microscope–energy dispersive spectroscopy (SEM-EDS), mid-IR (FT-IR), Raman, XRF, and luminescence spectroscopy using traditional as well as synchrotron sources.[1–4]

Given the 2-D nature of many works of art, the spatial information derived from macroscopic maps can provide important clues about an artist's working methods and help guide conservation choices. Hence, there is interest in the development of macroscopic mapping methods, which utilize existing analytical in situ methods such as XRF[5] and X-ray diffraction,[6] reflectance and luminescence spectroscopy.[7–9] These methods not only provide the identification and mapping of artist's materials, but also other information such as compositional changes and layering of paint.[5,10] Unlike XRF mapping, which provides elemental information and is thus limited to being used to infer inorganic pigments, X-ray diffraction and reflectance imaging spectroscopy provide information on the molecular structure of the pigment. Reflectance spectroscopy offers the capability to map also organic materials, such as dyes,[7] and recently a plasticizer in a PVC object.[11]

To date most studies using reflectance imaging spectroscopy have relied on electronic transitions in the visible range alone for pigment identification and have been only partially successful. Improved results have been obtained by extending into the NIR range (750–1700 nm) in order to collect vibrational band overtones and combinations associated with hydroxy inorganic pigments.[7] Extending the spectral range to 2500 nm to collect vibrational features associated with carbonate functional groups would be a further improvement.

While progress has been made on mapping artists' inorganic materials, the mapping of organic materials—paint binders in particular—has succeeded only on the microscopic scale utilizing mid-IR microscopes (650 to ca. 4000 cm^{-1}).[2] While remote-sensing hyperspectral imaging cameras operating in the mid-IR exist, such instruments require exotic infrared focal planes and cooling to temper-

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atures below 60 K, making their cost usually well out of the reach of the conservation field. Moreover the light levels required are likely to be unsuitable for many artworks.[12]

Recent in situ studies using non-imaging NIR spectrometers have shown that vibrational overtone bands from paint binders (drying oils, animal glues, whole egg versus egg white tempera) at wavenumbers $>4000\ \text{cm}^{-1}$ can be used to separate and identify these materials,[13] even in the presence of lead white, which often hinders binder identification in the mid-IR. The vibrational features in the NIR are associated with C−H, O−H and N−H functionalities.[14] Proteic media are characterized by features associated with amide and carbonyl groups,[13] whereas oils and fats by methylene, methyl and ethenyl functional groups.[14,15] While vibrational features are weaker in strength than their corresponding features in the mid-IR, working in the NIR relieves the stress on the technical requirements of the imaging spectrometer and light levels on the artwork.

Here we report on the use of a novel hyperspectral NIR imaging spectrometer (1000–2500 nm, 4000–10 000 cm^{-1}) having higher spectral resolution, light sensitivity, and spatial coverage than other instruments[11] making it possible to identify and map CH, methylenic and amide groups associated with organic binders in paint layers only tens of μm thick, at the low light levels required for the analysis of works of art on paper and parchment. This instrument, and an experimental procedure previously developed for paintings,[7] were used for the study of an early 15th century illuminated manuscript leaf on parchment painted by Lorenzo Monaco and representing a *Praying Prophet* within a decorated initial E on a gilded background (Figure 1 a). Illuminated manuscripts are rarely if ever sampled due to the small dimensions of the illuminations and their fragility, emphasizing the need for in situ methods.

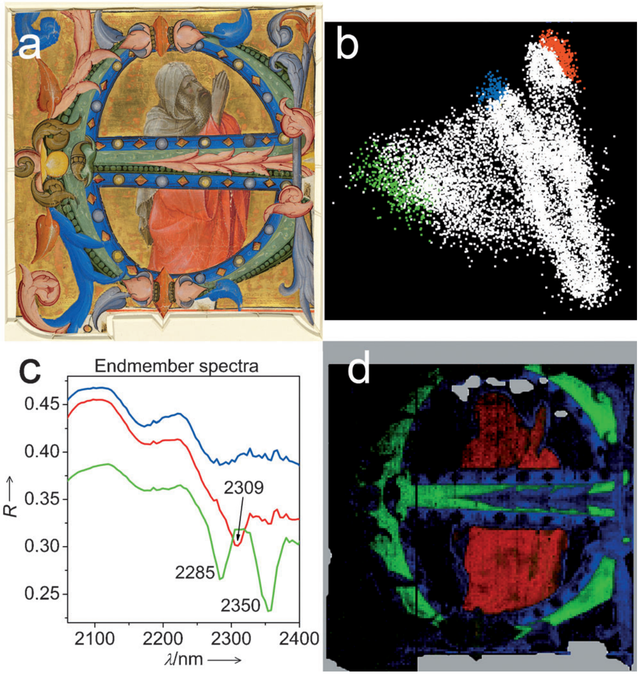

Figure 1. NIR image cube analysis of Lorenzo Monaco's *Praying Prophet* (1410/1413, 13.1 × 12.9 cm, Rosenwald Collection). a) Color image, courtesy National Gallery of Art, Washington. b) Projection map of 10-D clustering obtained from processing the reflectance image cube (79 bands, 2060 to 2400 nm). The green, blue and red points define the clusters used to generate the three endmember spectra in (c). R = reflectance. The spectral angle mapper algorithm is used to determine the locations to which the endmembers map. The resulting RGB image (d) shows the pixels whose spectra deviate from the endmembers less than the tolerance angles of R: 0.037, G: 0.064, B: 0.040 rad. Brightness varies inversely with deviation. Note that the matboard and areas of specular reflection (gilded background) were masked during image processing (gray pixels). The incomplete mapping on the left side is due to the limited specificity of the spectral features, combined with a fall-off of illumination intensity and limitations in the flat-fielding.

Initial analysis of the *Praying Prophet* by FORS identified azurite at various sites in green areas by the presence of hydroxy and carbonate bands at 1495, 2285, and 2350 nm. Narrow absorption bands at 2309 and 2350 nm were observed also in FORS spectra of several sites and their presence did not match any particular color. The presence of these vibrational bands makes this miniature a good test candidate for the NIR imaging spectroscopy. In order to collect spectral images under suitable light levels,[12] the miniature was illuminated from 1650 to 2500 nm using filtered lamps and imaged with the NIR hyperspectral camera. A thermal imaging camera established that the heating of the miniature was less than 1.4 K during the data collection. The calibrated image cube was analyzed using a minimum noise fraction transform (similar to principal components analysis, PCA) to determine the data dimensionality, and then convex geometry methods were used to find the spectrally pure pixels for clustering. The goal of the analysis was to find the basis set of spectral components ("endmembers") that describe the image cube.[7] We focused on the 2060–2400 nm range (79 spectral bands), which contains the unassigned vibrational features seen in the FORS spectra. The analysis yielded four well-separated spectral endmembers (Figure 1 b,c). Two of them have narrow absorption bands: one at 2285 and 2350 nm, characteristic of azurite (green cluster and spectrum), and the other at 2309 and 2350 nm, which do not match any pigment in our database (red cluster and spectrum). The other two endmembers have weaker spectral features; the first has broad bands at about 2176 and 2285 nm (blue cluster and spectrum), and is similar to the exposed parchment, and the other one has a uniformly low reflectance (bottom cluster, no spectrum shown). A spectral angle mapper algorithm was used to determine the locations to which these endmembers map, i.e., to identify and map pixels in the image cube whose reflectance spectra match those of the endmembers within a specified angle tolerance. Similar results are obtained by using a tuned matched filter to produce the maps from the endmembers. The result of this analysis is shown in Figure 1 d, and does not include the fourth endmember, which maps to all low-signal areas. The endmember with the broad vibrational features maps to most of the painted areas in the initial (blue map). The endmember corresponding to azurite maps to both dark and light green areas (green map), suggesting that the green consists of azurite mixed with a yellow pigment. Finally, the endmember with bands at 2309 and 2350 nm maps to the figure of the Prophet (red map): red robe, white headscarf, and flesh tones.

Since this endmember does not map to a specific pigment or to the bare parchment, we hypothesize its association with a paint binder. The 2309 nm and weak band at 2350 nm occur in a region associated with fatty acids of whole-egg tempera and drying oils.[13] Fats and oils have strong features in the 2240–2470 nm range, associated to combinations of C–H stretching (symmetric and asymmetric) and bending modes of methylene and methyl functional groups.[13–15] The presence of egg tempera rather than oil is historically more likely based on a comparison with early 15th century panel painting techniques in Florence. However, the identification of *any* paint binder containing fatty acids on an illuminated manuscript leaf is unexpected since traditional sources list egg white and gum Arabic as the binders most widely used by illuminators.[16,17] These consist mainly of proteins/glycoproteins and mono-/polysaccharides, and therefore are spectrally similar to parchment, whose main component, collagen, is also a glycoprotein.

To verify that, regardless of the presence and possible interference of the pigments, we could use NIR imaging spectroscopy to identify the NIR absorption features of egg yolk and distinguish it from egg white or gum Arabic on parchment, we prepared paintouts of varying thickness with a comprehensive set of pigments bound in these binders (Figure 2 A). In all cases the vibrational features from the parchment are observed, which are associated with the carbonyl and amide groups (2042 nm, 2175 nm).[13,18] Egg white, being mostly proteic, is indistinguishable from parchment, and gum Arabic is also similar to the parchment, but a broad absorption is seen at 2100 nm which is associated with polysaccharides.[18] Only where egg yolk was present were the two narrow absorption features at 2306 and 2350 nm observed in the FORS spectra (Figure 2 A) and also in the NIR image cube.[19]

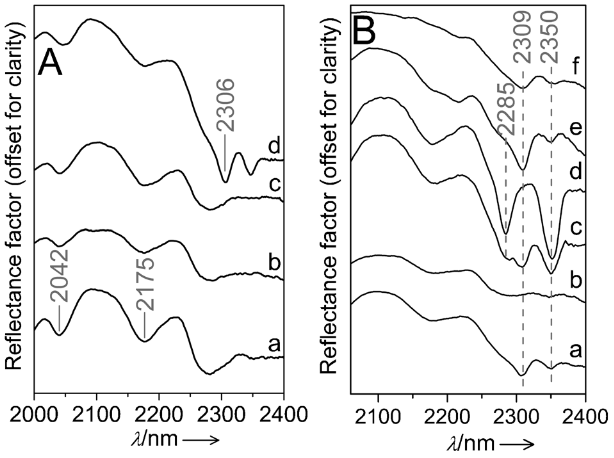

Figure 2. A) FORS spectra of a) bare parchment, and vermilion paint on parchment in various binders: b) gum Arabic, c) egg white, d) egg yolk. B) FORS spectra from illuminations in a choir book illuminated by Lorenzo Monaco and his collaborators: organic dye at site within (a) and outside (b) an illuminated initial, azurite at sites within (c) and outside (d) the initial; FORS spectra from red sites in e) a panel painting by Lorenzo Monaco (*Madonna and Child*, 1413) and f) a panel painting by Carlo Crivelli (*Madonna and Child Enthroned with Donor*, 1470). Both paintings are from the Samuel Kress Collection at the National Gallery of Art, Washington DC.

To assure ourselves that 2309 and 2350 nm features are not from a prior conservation treatment, such as consolidation, we acquired FORS spectra on a second manuscript leaf at the National Gallery of Art and on a total of 17 illuminated initials in the two original volumes to which the Gallery's two manuscript leaves originally belonged (currently in Florence, Italy). The results confirmed our findings (Figure 2 B): the absorption doublet was identified on all the pages, at sites in the figurative areas of the initials, but not at sites in the letters or the foliate decorations surrounding them.

In all the analyzed manuscripts' leaves, the spectra in which the C–H stretching bands were identified showed also a second, less intense, absorption doublet at 1729 and 1760–1763 nm, which can be assigned to the first overtones of the asymmetric and symmetric stretching of $-CH_2$, and which is also characteristic of egg yolk.[13]

The spectral map of the manuscript leaf, together with the results obtained on the model paintouts, show that a fat-containing binder, likely to be egg yolk, was used compositionally selectively to paint only the Prophet, while the decorated initial was painted using either egg white or gum. The finding of egg yolk tempera on a manuscript leaf is unexpected, but not implausible. References to the use of egg yolk or mixed binders for manuscript illumination, while scarce, can be found in traditional sources such as the early 15th century "Libro dei Colori".[17] Additionally, Lorenzo Monaco was also a painter of panels and frescos, and therefore accustomed to painting with egg tempera. FORS spectra of several sites in a panel painting by Lorenzo Monaco, entitled *Madonna and Child* (1413), were found to have absorption features at 2309 and 2350 nm as well (Figure 2 B). To confirm that the NIR vibration observed on this panel painting can be associated with egg tempera, FORS examination was performed on a panel painting by Carlo Crivelli entitled *Madonna and Child Enthroned with Donor* (1470), painted using an egg tempera binder as shown by FT-IR and GC/MS analysis of samples from selected sites. FORS spectra from these same sites also showed the vibrational bands at 2309 and 2350 nm (Figure 2 B).

Future work will focus on surveying a larger number of miniatures to help clarify whether the use of egg yolk in manuscript illumination is restricted to the circle of Lorenzo Monaco, and whether further evidence exists regarding its compositionally selective use. A preliminary FORS survey of several dozens of other 14th and 15th century Italian manuscript leaves has revealed no evidence for the use of egg tempera except in other miniatures painted by Lorenzo Monaco and his collaborators and followers.

This study shows that imaging spectroscopy in the NIR can be used effectively in situ, in conditions appropriate to the analysis of light-sensitive works of art, to map and separate paint binders in layers only tens of μm thick. The challenge remains to refine the technique not only to separate, but to accurately identify, a larger range of historic and modern paint binders such as drying oil, wax, acrylic and alkyd. The ability to map and identify a broader variety of media in situ is of critical importance to the preservation of historic and artistic works.

Experimental Section

The custom NIR hyperspectral line scanner (Surface Optics, CA) provides 342 spectral images each having 640 × 640 pixels. The camera consists of a scan mirror, imaging lens, transmission grating spectrometer (Specim Corp, Finland, model N25E), a relay lens, and a cryo-cooled 640 × 512 20 μm pixels InSb array operated at 60 K (Santa Barbara Focalplane, CA, SBF178). An order-sorting filter placed at the intermediate focus, and a cold filter in the Dewar, limit the spectral bandpass of the system to 1000 to 2500 nm. The spatial sampling at the artwork is 0.32 mm. The pixel-to-pixel non-uniformity correction is obtained using the shadowed regions of the image for the offset, and the beige matboard for gain determination. Two Spectralon (Labsphere, NH) standards (2 % and 99 % diffuse reflectors) are used to calibrate the image cubes to reflectance factor. Diffuse illumination is provided by two 150 W tungsten halogen lamps placed 0.5 m away. Longwave pass filters (Andover Corp, NH, 1.65ILP-50) limit the transmission of radiation to 1650–2500 nm, with an average spectral radiance of 16 $\mathrm{mW\,sr^{-1}\,m^{-2}\,nm}$.[7] A microbolometer thermal imaging camera (DRS Technologies, TX) is used to monitor the temperature change of a 2 % reflective Spectralon standard during the scan. Image processing is carried out using ENVI 4.4 (ITT Visual Information Solutions, CO) and Adobe Photoshop CS3. The cubes are cropped spectrally to cover the range of interest (2050–2400 nm, 79 bands), 2 × aggregated, and processed using the ENVI hourglass procedure[20] retaining only the first 10 eigenimages. A fiber optic spectroradiometer (ASD Inc, CO, FS3) is used to obtain FORS spectra (350–2500 nm). FT-IR was performed on a Thermo Nicolet Nexus 670 spectrometer fitted with a Continuum microscope. Two hundred fifty six scans were collected at 4 $\mathrm{cm^{-1}}$ resolution. Gas chromatography/mass spectrometry (GC/MS) was performed on samples that had been hydrolyzed (6 N HCl, 105 °C, 24 h, vacuum) and silylated (MTBSTFA/TBDMCS in pyridine, 105 °C, 5 h). A Varian CP3800 gas chromatograph and a Saturn 2200 mass spectrometer were used for the analyses. Ratios of amino acids and fatty acids observed in the chromatograms were used to determine the binding media. Norleucine was used as an internal standard.

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