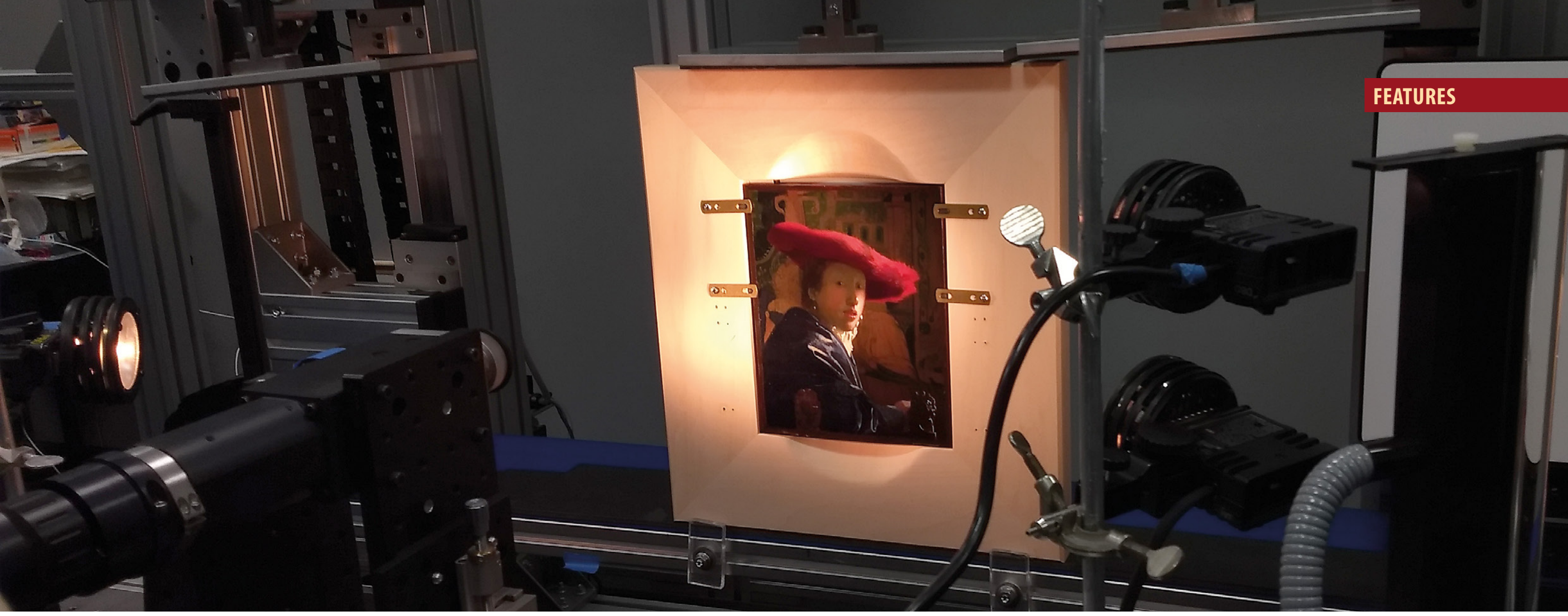


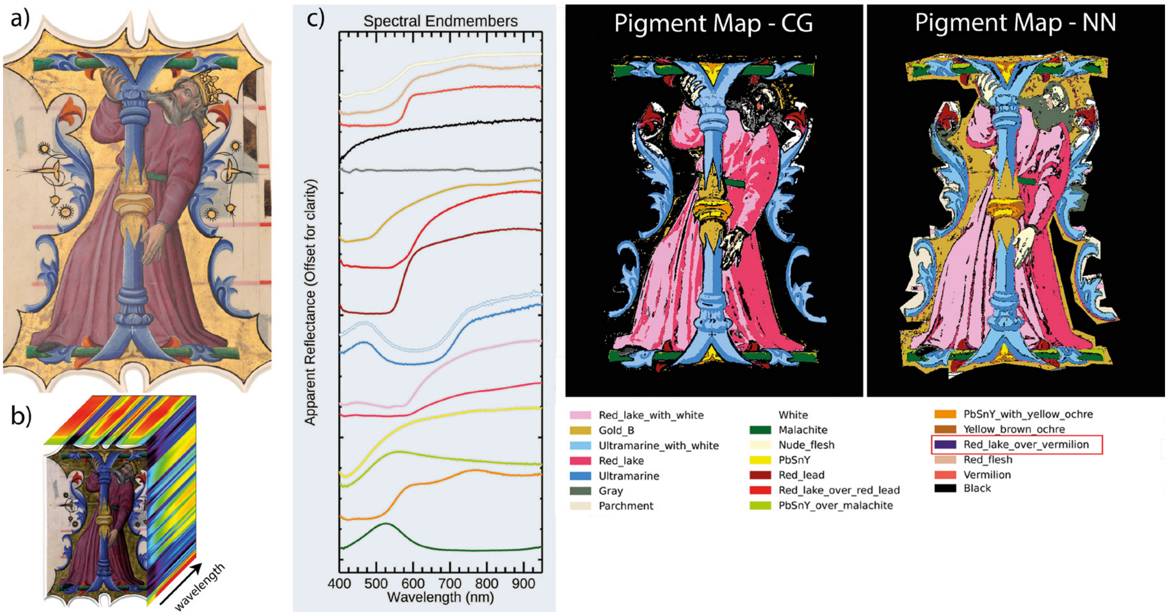
UTILIZING CHEMICAL IMAGING FOR PAINTINGS: MAPPING ARTISTS' MATERIALS AND UNDERSTANDING ARTISTIC TECHNIQUES

John K. Delaney and Kathryn A. Dooley – DOI: https://doi.org/10.1051/epn/2025408
Scientific Research Department, National Gallery of Art, Sixth St and Constitution Ave NW, Washington, D.C. 20565, United States.

Reflectance and X-ray fluorescence imaging spectroscopies are increasingly essential tools in cultural heritage, aiding in the preservation of paintings and addressing significant art historical questions. In this focus paper, we introduce these techniques and provide three examples involving a 15th century Spanish work on parchment, an Italian Renaissance painting, and a Dutch Golden Age painting.

Imaging spectroscopy has become an essential tool for identifying and mapping materials in objects where physical sampling is not possible. This technique can utilize various imaging modalities, including reflected light, emitted light such as fluorescence, or even Raman scattering. A significant example of this is the use of reflectance imaging spectroscopy to search for and map hydrated minerals—such as clays, hydrated silica, and sulfates—on the surface of Mars with the Compact Reconnaissance Imaging Spectrometer (CRISM). The CRISM instrument, which orbited Mars until 2023, employed solar light reflected off the Martian surface to create mineral maps. The presence of hydrated minerals suggests that liquid water existed on Mars in the past. Consequently, maps indicating the locations of such minerals are invaluable for selecting sample collection sites in the quest for evidence of past life on Mars.

Sampling a fine art painting to identify the artist's materials, such as the pigments and organic binding media in the paint layers, is significantly less challenging than sampling rock outcroppings on Mars. However, this sampling is limited to existing paint cracks and areas of damage, where only a small fragment about 200 micrometers in size or less can be taken. Sampling in pristine areas of a painting is not permitted. To help address this limitation, scientists are now using techniques like reflectance imaging spectroscopy and X-ray fluorescence imaging spectroscopy. These methods allow them to explore pristine areas of paintings and gather information about the pigments present on the surface as well as those ●●●



▸ **FIG 1:** Painted illumination from a 15th century Spanish choir book titled *Initial I with David*, 1430s, attributed to the Master of the Cypresses. (a) color image, (b) 3-D reflectance image cube, (c) reflectance spectra obtained using a convex geometry algorithm and associated pigment map (CG) and pigment map using Neural Network (NN).

● ● ● beneath it, sometimes revealing previously abandoned compositions.

Many artists' pigments are derived from minerals, which is why the imaging instruments used to study artworks resemble those employed for remote sensing of the Earth, Moon, and Mars. The spectral range of the reflectance imaging spectroscopy instruments we use extends from deep blue (400 nm) through the visible (400 to 750 nm) and into the near and shortwave infrared (NIR and SWIR, 750 to 2500 nm), with a spectral sampling of a few nanometers. Within this spectral range, various electronic and vibrational transitions occur, which are diagnostic for many inorganic and organic pigments used by artists, as well as for organic paint binders that contain lipids and/or proteins.

Imaging spectroscopy produces a three-dimensional data cube, which consists of a stack of images. Each image is captured within a narrow spectral band, typically just a few nanometers wide for reflectance measurements. The third dimension of this cube contains the spectral information that can be used to identify various artists' materials.

There are several types of instruments available for collecting this 3-D data. These include single-pixel scanners, line-scanning spectrometers, and imaging spectrometers equipped with 2-D detector arrays, such as imaging Fourier transform spectrometers. The volume of 3-D data generated can be substantial, ranging from a fraction of a gigabyte to several hundred gigabytes.

Analyzing these complex data sets has become a significant area of research, leading to the development of novel algorithms designed to condense the data into a manageable number of spectra that describe the scene. These algorithms identify the materials present based on spectral features and provide maps showing the distribution of these materials across the imaged area. The analysis tools used in this process draw from various fields, including physics, chemistry, signal theory, and even artificial intelligence.

Mapping pigments across a 15th century Spanish illumination of King David

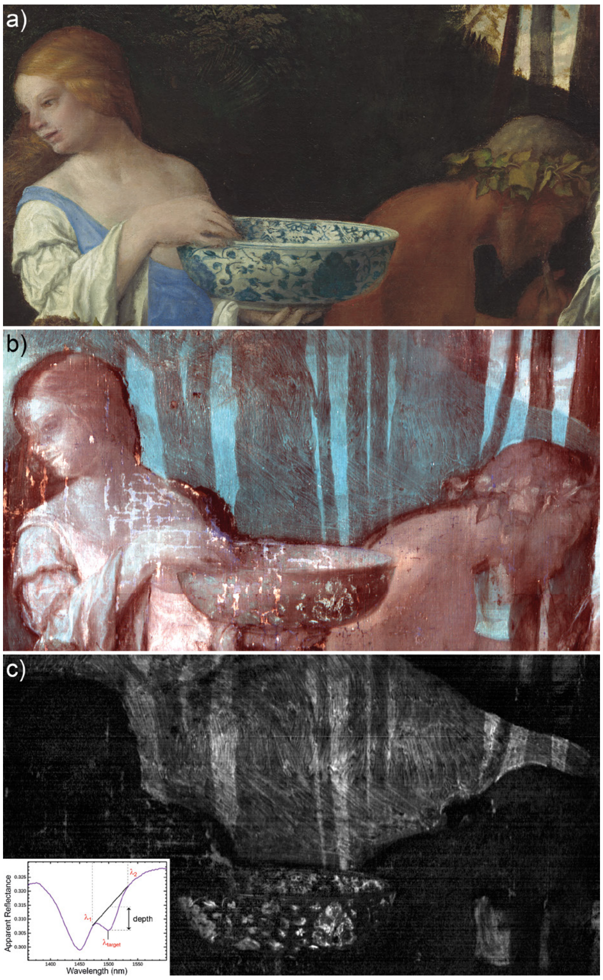
The colorful miniature paintings or illuminations in Medieval religious books from Europe are often too pristine for sampling. Here, the combined use of reflectance and X-ray fluorescence imaging spectroscopies has allowed the identification and mapping of pigments used. An example of the reflectance imaging results from such a study applied to a painted illumination from a 15th-century Spanish choir book titled *Initial I with David*, 1430s, attributed to the Master of the Cypresses, is shown in Figure 1. The artist painted this illumination of King David holding the initial I with a wide range of colors.

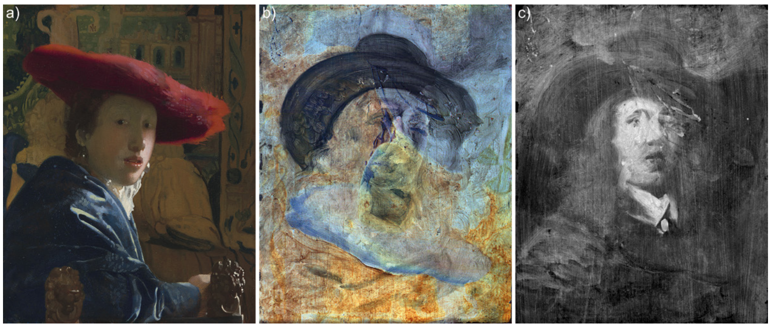
Reflectance imaging spectroscopy was utilized to identify and map the pigments employed by the artist. Analyzing the 3-D reflectance image cube (see Figure 1b) with multivariate analysis based on convex geometry revealed 15 different paints composed of one or more pigments. Most of these pigments could be identified from their reflectance spectral features alone (refer to Figure 1c). The pigment map labeled Pigment Map-CG indicates that the artist used a red lake pigment—derived from a soluble dye obtained from insects and precipitated onto a substrate like chalk to create an insoluble pigment—for King David's robe. The blue in the letter "I" and the surrounding leaves utilized ultramarine, an expensive pigment derived from processing lapis lazuli ore. The green horizontal bars in the letter "I" were painted with malachite, complemented by highlights of lead tin yellow. The orange and red leaves were created using red lead and red lake pigments. The multivariate convex geometry-based algorithm employed to analyze the reflectance image cube is semi-automated, often requiring several hours to run. This has prompted researchers to explore machine learning tools, including neural networks, to significantly reduce analysis time to just minutes, particularly when examining a large set of related paintings. Results from a recently developed neural network trained on other works by the same artist show that this method yields very similar outcomes and performs better in mapping flesh tones as well as the gold background (see Figure 1c, Pigment Map-NN).

Revealing Giovanni Bellini's hidden trees in the *Feast of the Gods*

Often, the visual surface of an artwork hides a longer history of revisions and reworkings that reside below the surface and cannot be seen by eye. Reflectance imaging spectroscopy can be a valuable tool in such cases, since most artists' pigments absorb less and scatter less photons in the NIR and SWIR spectral regions compared to the visible region, and therefore can allow us to collect subsurface information. Such is the case with the Renaissance masterpiece *Feast of the Gods*, which was originally painted by Giovanni Bellini in 1514. The patron who commissioned the painting also requested • • •

▾ FIG 2: (a) Color detail from *Feast of the Gods*, Giovanni Bellini and Titian, 1514/1529. (b) False-color infrared reflectance detail (B:1875 nm, G:2050 nm, R:2375 nm) revealing the location of original Bellini trees beneath the surface. (c) A map of the blue pigment azurite obtained using a characteristic absorption feature near 1500 nm in the reflectance spectra (see inset). Azurite is present in brushy paint strokes in the hillside associated with the intermediate landscape, as well as the blue design in the nymph's bowl.





▲ FIG 3: (a) Johannes Vermeer's painting *Girl with the Red Hat*, c.1669. (b) Infrared false-color image (rotated 180 degrees) showing some of the underpaint of an earlier painting of a man in a black hat obtained from reflectance imaging spectroscopy. (c) The optimized lead map (rotated 180 degrees) showing the use of mainly lead white in the painting of a man in a black hat obtained using X-ray fluorescence imaging spectroscopy.

● ● ● two reworkings of the background behind the gods, including the final mountainous landscape we see today, completed by Titian in 1529. Reflectance imaging spectroscopy helps to visualize and identify pigments in the original Bellini wooded landscape, consisting of many trees, as well as the intermediate landscape depicting a hillside. A detail of a satyr and nymph holding a bowl is shown in Figure 2a. The false-color infrared reflectance image in Figure 2b reveals the location of original Bellini trees beneath the surface as well as brushy paint strokes associated with the intermediate hillside. Figure 2c shows a map of the blue pigment azurite. Azurite was originally identified in the first paint layer applied over Bellini's trees in a paint sample, known as a cross-section, from the background landscape. Here, the azurite map shows the pigment is distributed throughout the brushy paint strokes associated with the intermediate landscape, as well as the blue design in the nymph's bowl.

Learning more about the painting of a man in a black hat beneath Johannes Vermeer's painting *Girl with the Red Hat*

Given the wide range of materials used by artists, it is not surprising that scientists also make use of spectral modalities such as X-ray fluorescence to help identify the pigments present. While reflectance spectroscopy provides molecular information, X-ray fluorescence provides information about the chemical elements (*i.e.*, lead, iron, copper, cadmium, tin, *etc.*). While element information does not always allow a unique assignment of a pigment, when combined with results from reflectance spectroscopy, an identification can often be made. For example, pigments made from semiconductors have simple reflectance spectra from which only the energy of the electronic transition can be determined, which is not sufficient to identify the specific pigment, but when combined with the elements present, it is possible. X-ray fluorescence uses X-ray energy to excite inner core electrons, and the emitted X-ray radiation gives spectra that allow the elements present to be identified. The development of high-sensitivity X-ray spectrometers allows scientists to make maps of the elements present in paintings. The combination of reflectance imaging spectroscopy and X-ray fluorescence imaging spectroscopy has not only allowed us to make better pigment maps, but it has also allowed us to obtain clearer images of an unfinished painting as described below.

Underneath Johannes Vermeer's painting *Girl with the Red Hat* (Figure 3a) is an unfinished portrait of a man in a black hat. The identity of the man is unknown as well as if Vermeer painted him or if the portrait is the work of another artist. The combination of infrared reflectance and X-ray fluorescence imaging spectroscopies has given us new, detailed images of the painting of the man. The false-color infrared image shows a brushy application of black paint that denotes the man's hat, facial features, and paint strokes in his garment (Figure 3b). The mathematical processing of high and low energy lead maps obtained from X-ray fluorescence imaging spectroscopy results in a clearer image of the man's face, his shirt collar, the sleeve of his garment, and even his wavy long hair. These images offer art historians the opportunity for further scholarship regarding the identity of the sitter as well as the artist who painted him. ■

About the Authors

John K. Delaney is a senior imaging scientist and currently serves as the acting head of the Scientific Research Department at the National Gallery of Art. He also oversees the Chemical Imaging Laboratory. His research focuses on developing new imaging-based spectroscopic methods for studying paintings.

Kathryn A. Dooley is an imaging scientist in the Chemical Imaging Lab of the Scientific Research Department at the National Gallery of Art. She is interested in spectroscopic techniques that allow for the identification of many materials without requiring a sample and that also enable mapping their distributions across the surface of an artwork.

References

[1] J. Mustard, S. Murchie, S. Pelkey, *et al. Nature* **454**, 305 (2008). https://doi.org/10.1038/nature07097

[2] C. Costanza, J. K. Delaney, and M. Picollo, *Accounts of Chemical Research* **49 (10)**, 2070 (2016). https://doi.org/10.1021/acs.accounts.6b00048

[3] F. Gabrieli, K. A. Dooley, M. Facini, and J. K. Delaney, *Sci. Adv.* **5(8)**, (2019). https://doi.org/10.1126/sciadv.aaw7794

[4] K. A. Dooley, B. H. Berrie, J. K. Delaney, "Appendix Two: Technical reexamination of the *Feast of the Gods*," in David Alan Brown, *Giovanni Bellini: The Last Works*, Skira Editore, Milan (2019).

[5] R. Radpour, T. Kleynhans, M. Facini, F. Pozzi, M. Westerby, and J. K. Delaney, *Applied Sciences* **14(16)**, 6857 (2024). https://doi.org/10.3390/app14166857

[6] K. A. Dooley, J. K. Delaney, E. M. Gifford, D. Anchin, L. D. Glinsman, A. Libby and M. E. Wieseman, "The Man Beneath Vermeer's *Girl with the Red Hat*: Improved Visualization Using Chemical Imaging," in *Closer to Vermeer: New Research on the Painter and His Art*, Rijksmuseum, Amsterdam / Hannibal Books, Veurne (2025).