Application of Visible and Infrared Imaging Spectroscopy To The Study of Paintings

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Imaging spectroscopy, the collection of hundreds of contiguous narrow-band images, offers an improvement over site-specific fiber optic reflectance measurements by combining both spatial and spectral information. We have focused on developing portable high sensitivity hyperspectral cameras capable to operate at low light levels, which is necessary for the examination of paintings, drawings, illuminated manuscripts. The cameras operate from the visible (380 to 750 nm) and Near-infrared (750 to 2500 nm) and have both high spectral (2.4 to 4 nm) sampling and high spatial sampling (0.2 to 0.1 mm per pixel at the artwork). The cameras utilize transmission-grating spectrometers and state-of-the-art infrared detectors, such as InGaAs and InSb arrays. Use of a whiskbroom-scanning mirror allows for a portable system as it eliminates the need to translate the camera across the painted surface.

In this talk, we present findings on the use of visible and infrared reflectance imaging spectroscopy to identify and map artist materials in situ as well as improve the visualization of preparatory sketches and paint changes. Visible and Near-infrared reflectance imaging spectroscopy has been shown to be a useful tool to map and identify various artists' pigments [1]. This approach has utilized both electronic transitions (color) and vibrational overtones from hydroxyl (-OH) and carbonate groups (-CO3). Utilizing analysis methods developed for remote sensing we have been able to identify and map the pigments used in Picasso's "Harlequin Musician" (1924) as well those in early Italian Renaissance Paintings such as Cosimo Tura's 'The Annunciation with Saint Francis and Saint Louis of Toulouse' (c. 1475; Figure 1).

Recently we have been investigating the potential of this method to map and identify non-pigment artist materials such as paint binders and textile fibers in situ. Identification and mapping of these organic materials is done using the higher harmonics of the vibrational features found in the mid-IR which are routinely used to identity these materials in situ. These chemical signatures include overtone and combination vibrational features associated with amide bonds, -CH2 -OH, and -CO3 groups. The instrument's performance is being verified using test panels and paintings in the National Gallery's collection whose composition is known by GC-MS and FTIR analysis. To date we have demonstrated (i) mapped regions of the use of egg yolk binder in illuminated manuscript attributed to Lorenzo Monaco "Praying Prophet" and (ii) selective use of animal skin glue and egg yolk in Cosimo Tura's 'The Annunciation with Saint Francis and Saint Louis of Toulouse' (c. 1475.) [2].

Traditional infrared reflectography (IRR) allows conservators to visualize preparatory underdrawing and compositional paint changes. The technique employs near infrared cameras in single broad spectral band, typically from 800 to ~1400 nm. Research by several groups has resulted in improved visualization, achieved by using low noise detectors, interference filters to isolate the spectral region of maximum content. While significant progress has been made, there remains an interest in extending IRR to works of art on paper, and on paintings to determine the type of drawing materials used in preparatory sketches (e.g. dry versus liquid), and for separating out features in complex over-painted compositions.

The NIR hyperspectral cameras have provided increased visibility and better understanding of preparatory sketches and compositional paint changes over the prior monochromatic and even multi-spectral methods. The narrow spectral sampling can provide increased visibility and improved separation of painted compositions, such as being painted one on another in Picasso's "The Tragedy" (1903). Using the hyperspectral NIR cameras, in several blue period paintings by Picasso improved visualization of the prior portraits that have been painted over has been achieved. These have included Picasso's "Old Woman Ironing" at the Guggenheim, the "Le Gourmet" (1901) at the National Gallery of Art and "The Blue Room" (1901) at The Phillips Collection, DC. The ability to obtain reflectance spectra not only allows for distinguishing among artist materials that only appear as 'varying gray levels' in broadband IRR images, but also provides a basis for determining requirements of imaging systems. This has closed the loop in system design, by establishing the spectral radiance differences associated with various combinations of grounds, drawing materials, and paints.

The knowledge gleaned from these instruments about pigments, such as where they are found and information related to the initial drawings and compositional paint changes have the potential for art historians to better understand, and conservators better preserve, important works of art.

References:

[1] Delaney et al, Applied Spectroscopy **64** (2010), p. 584.
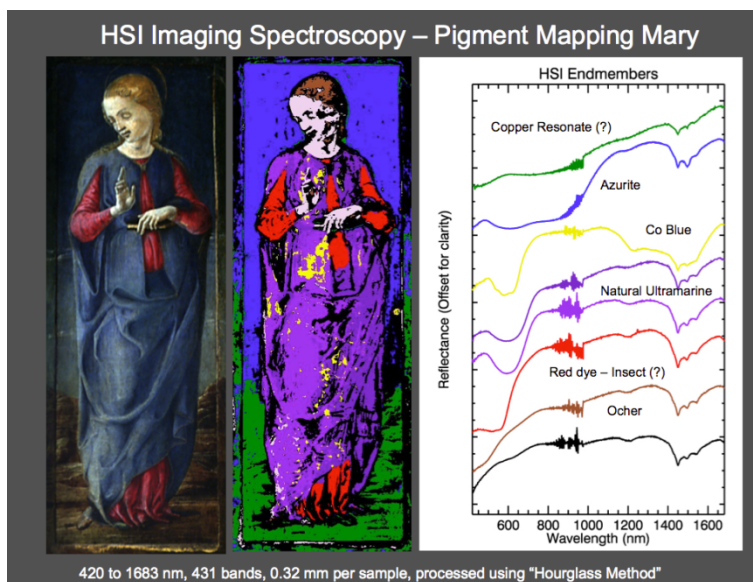[2] Dooley et al, Analyst, **138** (2013), p. 4838.

Figure 1. Reflectance Imaging Spectroscopy used to map the pigments in panel containing the painting of Mary from Cosimo Tura's 'The Annunciation with Saint Francis and Saint Louis of Toulouse' (c. 1475), National Gallery of Art, DC.