2015

04, Illuminating the Medieval Manuscript: Pigment Analysis of a French Book of Hours

Kenna Miller
Portland State University

Illuminating the Medieval Manuscript: Pigment Analysis of a French Book of Hours

Kenna S. Miller

Through pigment identification using spectroscopic analytical techniques, one can gain insight into the history and origins of cultural heritage materials, such as historic manuscripts. This information also allows for more successful preventative care of the item. To identify the materials used in the production of a manuscript, a wide variety of analytical instrumentation have been developed. One of these methods, X-ray fluorescence spectroscopy, was used to examine the recently acquired Portland State French medieval Book of Hours, created around 1470 (Ill. VI). Filled with thick red and black gothic script, ornate illuminations, floral marginalia and Biblical miniature paintings, our research shows that the PSU Book of Hours is a prime example of which pigments were readily available during that time.

With the help of the Lasseter Clare Regional Laboratory for the Science of Cultural Heritage Conservation located at PSU, I analyzed many of the pigments that compose the multicolored decorations using a non-destructive spectroscopic method called X-ray fluorescence spectroscopy, or XRF. An XRF spectrometer emits x-rays, which are directed at and absorbed by the sample pigment to be identified. Once the excited atoms of the pigment relax, a specific wavelength, or energy, unique to each element, is given off.[1] These energies are then detected and counted by the instrument. The data is processed by specialized software, generating XRF spectra. Because a spectrum visually represents the quantity of each elementally unique energy emitted from a sample, the elemental composition of the pigment can be determined. In addition to XRF, a complimentary method that analyzes a pigment on a molecular, rather than elemental, level is infrared spectroscopy. This method relies on an emission of multiple wavelengths of infrared energy directed at the pigment sample. Depending on the types of molecules present, some of these wavelengths are absorbed, while others are transmitted.[2] This unique behavior of the molecular structures designates and identifies the sample pigment.

Like many of its contemporary book of hours, the Portland State medieval French Book of Hours contains an illuminated calendar before the main text. In this calendar, shown in Illustration VII, important feast dates are highlighted in a bright, saturated red color. Through XRF spectroscopy, high concentrations of mercury were found to be present in these sample areas, indicating the use of the pigment cinnabar or vermilion for the red color. While cinnabar is naturally occurring and sourced from a mine, vermilion is

---

[1] Douglas Skoog , F. James Holler, and Stanley Crouch. *Principles of Instrumental Analysis,* 6th ed. (Belmont, CA: Brooks/Cole Cengage Learning, 2007), 303-304

[2] Pavia, Donald L. *Introduction to Spectroscopy*, 4th ed. (Belmont, CA: Brooks/Cole Cengage Learning, 2009), 14-17

synthetically produced but molecularly identical.[3] With the knowledge that this pigment was used, a conservator can work to prevent blackening of the red color. Impurities present during production of the pigment are the catalyst to this common problem.[4] Because vermillion darkens more often when mixed with egg tempera binders, identifying the binder using infrared spectroscopy can aid further prevention of a medieval manuscript.

The remainder of the structured gothic text was written using black ink. A favored type of ink, commonly used on medieval manuscripts, was iron gall. Tannic and gallic acids were extracted from gall-nuts and combined with an iron salt solution, producing the black ink.[5] The faded, red appearance of the Portland State Book of Hours' black text further suggests that this type of ink is present. While it is difficult to confirm iron gall through XRF spectroscopy, analysis of the black dots within the marginalia shows the use of a different black pigment, most likely produced from burning animal bones or linseed oil.[6]

Along with the important dates, the bright red flowers and strawberry-like plants scattered throughout the ornate marginalia contained high concentrations of mercury, confirming the use of vermillion. Some areas of red paint also contained high concentrations of lead, indicating that white paint containing the pigment lead white was mixed with the vermillion paint (Ill. VIII). Lead white was also identified as the pigment used in the manuscript's delicate, white flowers and the skin of the painted figures. The dynamic red-orange filigree contained only lead, rather than a mix of lead and mercury, suggesting the presence of the pigment red lead. Lead white and red lead, although drastically different in color, are synthetically produced using the same material. To manufacture lead white, sheets or coils of lead were exposed to acetic acid and carbon dioxide, resulting in a white crust that was ground into a powder[7]. A product of the lead and acetic acid reaction was removed and roasted until the substance become bright orange in color, creating red lead pigment.[8]

Also found in the Portland State medieval French Book of Hours are high concentrations of copper in green and blue colored sample areas. These results suggest that the weaving vine work and filigree were likely painted with malachite, while the robes of the Virgin Mary were likely painted with. Both of these common medieval pigments contain copper.[9] Unlike the almost purple, rich Ultramarine blue pigment,

---

[3] Thompson, Daniel V. *The Materials and Techniques of Medieval Painting* (New York: Dover Publications, 1956), 102-104
[4] Thompson, *The Materials and Techniques of Medieval Painting*, 107-108
[5] Hamel, Christopher. *Scribes and Illuminators* (Toronto: University of Toronto Press, 1992), 32-33
[6] Thompson, *The Materials and Techniques of Medieval Painting*, 83-85
[7] Thompson, *The Materials and Techniques of Medieval Painting*, 90-92
[8] Thompson, *The Materials and Techniques of Medieval Painting*, 100-101
[9] Ricciardi, Paola, Anuradha Pallipurath, and Kristen Rose. "It's Not Easy Being Green: A Spectroscopic Study of Green Pigments Used in Illuminated Manuscripts." *Analytical Methods* 5, no. 16 (2013): 3820-3821

azurite is generally a more neutral blue with a lighter tone. When exposed to moisture in the air, the crystals of the pigment react and turn into malachite, which is green.[10] Even though this potential conservation issue is not yet affecting the illuminations of the Portland State Book of Hours, those areas of pigment can be monitored over time for change.

With each material that is identified, more conservation issues can be determined and monitored. X-ray fluorescence and infrared spectroscopy are invaluable analytical methods, although both benefit from other complimentary techniques for a more thorough investigation of an item. Using further non-destructive methods of analysis, the remainder of the pigments, binder, and other materials used within the Portland State University French Medieval Book of Hours can be identified, illuminating the history of an object and protecting it for the future.

Bibliography

Hamel, Christopher. *Scribes and Illuminators* (Toronto: University of Toronto Press, 1992)

Pavia, Donald L. *Introduction to Spectroscopy*, 4th ed. (Belmont, CA: Brooks/Cole Cengage Learning, 2009)

Ricciardi, Paola, Anuradha Pallipurath, and Kristen Rose. "It's Not Easy Being Green: A Spectroscopic Study of Green Pigments Used in Illuminated Manuscripts." Analytical Methods 5, no. 16 (2013): 3820-3821

Skoog, Douglas F., James Holler, and Stanley Crouch. *Principles of Instrumental Analysis*, 6th ed. (Belmont, CA: Brooks/Cole Cengage Learning, 2007)

Thompson, Daniel V. *The Materials and Techniques of Medieval Painting* (New York: Dover Publications, 1956)

[10] "Pigments through the Ages", Michael Douma, accessed April 11, 2015, http://www.webexhibits.org/pigments/indiv/overview/azurite.html