

Analysis of Artists' Paints using FT-IR Microspectroscopy - Conservation and Authenticity Studies

Introduction

Museums house and display priceless works of art that draw visitors from around the world. Conservators are challenged to keep these works in pristine condition. The question lies in how to best care for these assets. Conservators must identify the materials in the piece of art before making the appropriate recommendations for display, care, restoration, or storage. In the business of art, forgeries are a significant concern. Recent high-profile cases of organized forgery enterprises highlight this concern [1,2]. Identification of materials on the work can date the piece and establish authenticity.

Identification of historical materials on works of art presents challenges, as the coatings on the piece are likely composed of numerous components. Also, artists' coating materials have historically evolved. Unlike today's modern, synthetic acrylic-based paints, older painting materials were comprised of ingredients found in nature. Many natural materials undergo degradation and the work can change in color over time. For example, Van Gogh frequently used an organic red pigment, red lake, which quickly fades when exposed to light. If you look at his famous painting "Roses," you will see that once pink roses have faded to white.

Fourier Transform Infrared Spectroscopy (FT-IR) provides a wealth of information regarding the molecular structure of materials, through the observation of the molecular vibration transitions in the spectrum. FT-IR is a non-destructive technique and in the case of microspectroscopy, very little sample is required to make an accurate identification.

FT-IR microspectroscopy is especially useful in the microanalysis of artists' materials. The quantity of sample required is very small and therefore, does not impact the integrity of the work. By its nature, FT-IR microspectroscopy greatly aids the analysis of complex, multi-component samples. Microscopical observation allows the targeting of select areas that can then be measured spectroscopically.

The SurveyIR from Czitek is a new, compact FT-IR microspectroscopy accessory that mounts to any commercially available FTIR instrument. Using the standard detector found in most instruments, the need for cryogenic

cooling is eliminated. SurveyIR is also compact and easy to install. With modern, small FT-IR instruments, the combination provides a portable solution allowing microanalyses in situations where samples cannot be removed from the location of the artwork. SurveyIR also employs digital imaging software to observe, document, analyze, and store images.

Results and Discussion

The identity of pigments in paintings can be used to determine authenticity. Fig. 1 shows two small paint chips taken from different works of art which, upon initial observation, appear to be very close in color and largely indistinguishable.



Figure 1: (Left) Acrylic Prussian blue hue; (Right) Oil based Prussian blue.

The image in Fig. 1 (left) of Prussian blue hue, an acrylic paint, was not developed until the late 1940's [3]. On the right (Fig. 1) is a paint sample containing the older inorganic pigment Prussian blue, first synthesized in 1704 and commercially available by 1724. In older paintings an oil binder was used [4] in contrast to today's synthetic polymers. Both of these paints appear similar to the naked eye; however, the IR spectra in Fig 2 demonstrate that their chemical composition is very different.

The most notable difference between the two paint chip spectra displayed in Fig. 2 is the band at 2083 cm^{-1} in the spectrum of Prussian blue (Red). The band at 2083 cm^{-1} is due to the $\text{C}\equiv\text{N}$ stretch of the cyano groups in iron hexacyanoferrate (Prussian blue). In Prussian blue hue (green), the main acrylic component dominates the spectrum from $1000\text{-}1300\text{ cm}^{-1}$. The actual pigment within the acrylic paint does not have as dominant features as the oil based paint due to the quantity of organic pigment present. Understanding the composition of these paint

samples permits collectors to investigate claims of legitimacy by confirming the materials coincide with the artists' time period.

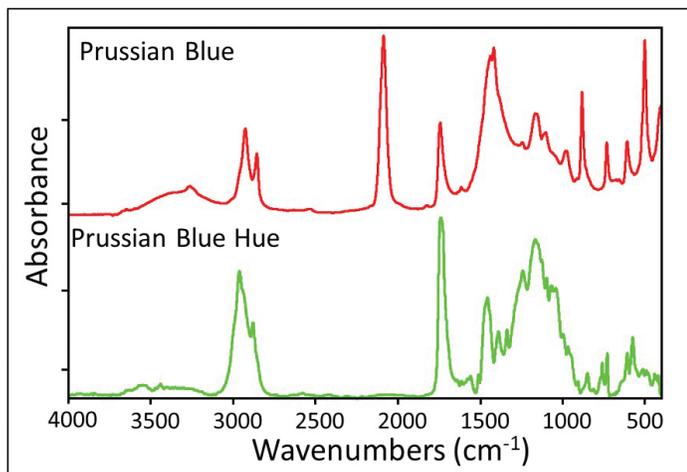


Figure 2: IR spectra of oil based Prussian blue (Top, Red) and acrylic Prussian blue hue (Bottom, Green).

While pigments can be used to investigate claims of authenticity in older works of art, identifying all the components can assist in their preservation. Commonly, older works of art contain materials that can be sensitive to environmental conditions [5]. The following example is a yellow paint sample removed from a historical painting.

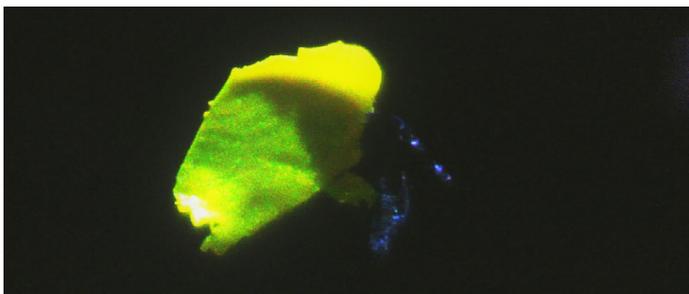


Figure 3: Yellow paint chip imaged with oblique illumination.

The specimen in Fig. 3 was flattened and placed onto an IR transparent Potassium Bromide (KBr) window for analysis.

Three components were identified within the art work sample in Fig. 4 (black). The main vehicle for the paint pigment is linseed oil (red), a very common oil used throughout the ages for oil based paints. The pigment Dalamar yellow (blue) was identified through a spectral library search after the linseed oil was spectrally compensated. The final component, alumina trihydrate, (green) was identified and serves as a filler and extender that helps bring out the brilliant yellow color. In this case, Dalamar yellow, a resilient azo dye complex, is known to be fairly stable and doesn't

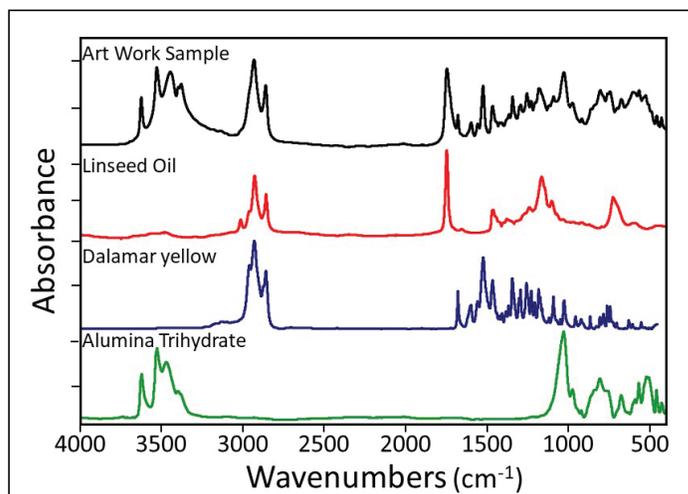


Figure 4: (Right) IR spectra of the art work sample (top, black) and its complimentary components.

require special environmental conditions, in contrast to other natural pigments such as red lake. This example demonstrates the power of FT-IR microspectroscopy in analyzing complex compositions. Three molecular constituents were identified from a microscopic paint chip, less than one (1) microgram of material.

Conclusion

There is a growing trend to understand the detailed chemical composition of works of art from the standpoint of conservation and authenticity. FT-IR microspectroscopy provides a powerful solution for conservators and forensic scientists to identify complex compositions of materials in artworks. In addition to reducing risk of damage from transport or theft, several international conventions exist that prevent artwork and antiquities from being relocated. The unique SurveyIR microscope accessory can facilitate identification at the location of the work.

References:

1. Gates, Anita, "Where Art Forgeries Meet Their Match," New York Times, 2 May, 2018.
2. Moynihan, Colin, "Knoedler Gallery Director's Lawyer Says Other Experts Were Duped by Fake Rothko," New York Times, 26 Jan., 2016.
3. Phaidon Press (2001). The 20th-Century art book (Reprinted. ed.). London: Phaidon Press. ISBN 0714835420
4. Douma, M., curator. (2008). History. In Pigments through the Ages. Retrieved 6 22, 2017, <http://www.webexhibits.org/pigments/indiv/history/prussblue.html>
5. Hoeve, Claire L. "A Study of the Discoloration Products Found in Lead White Paint Films." The Book and Paper Group Annual, vol. 4, 1986, <http://cool.conservation-us.org/coolaic/sg/bpg/annual/v04/pubinfo.html>