

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

■ Introduction

Museums house 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, such as 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.

Fourier Transform Infrared (FT-IR) spectroscopy 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 compact-microscope from Redwave Technologies coupled with Shimadzu's compact IRSpirit FTIR spectrophotometer provides a perfect solution for microanalysis of artist's materials. Since sample size or area of these samples are often larger than 60 μm (the smallest measurable size of the system), the standard detector used for measurement and the need for cryogenic cooling is eliminated.

This also provides a portable solution allowing microanalyses in situations where samples cannot be removed from the location of the artwork. The microscope software also employs digital imaging software to observe, document, analyze, and store images.

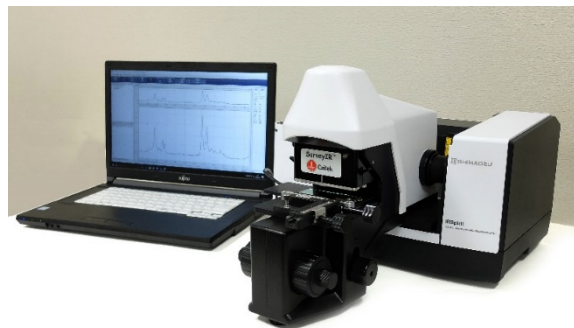


Figure 1: IRSpirit FTIR spectrometer with the SurveyIR microscope mounted in the sample compartment

■ Results and Discussion

The identity of pigments in paintings can be used to determine authenticity. Figure 2. shows two small paint chips taken from different works of art which, upon initial subjective observation, appear to be very close in color and largely indistinguishable.



Figure 2: (Left) Acrylic Prussian blue hue; (Right) Oil based Prussian blue

The image in Figure 2 (left) of Prussian blue hue, an acrylic paint, was not developed until the late 1940's^[3]. On the right (Figure 2) 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 paints appear similar to the naked eye; however, the IR spectra in Figure 3 demonstrate that their chemical compositions are very different.

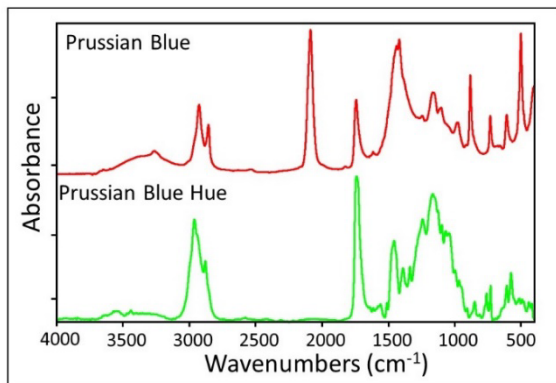


Figure 3: IR spectra of oil-based Prussian blue (Top, Red) and acrylic Prussian blue hue (Bottom, Green).

The most notable difference between the two paint chip spectra displayed in Figure 3 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 1000-1300 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.

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.

The specimen was flattened and placed onto an IR transparent Potassium Bromide (KBr) window for analysis. The image in Figure 4 was recorded with oblique illumination, one of SurveyIR's unique features.

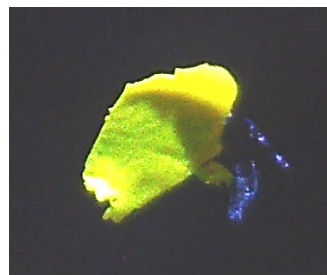


Figure 4: A paint sample imaged with oblique illumination and viewed through the diamond ATR.

Three components were identified within the artwork sample in Figure 5 (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. It is normally used 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 require special environmental conditions, in contrast to other natural pigments such as red lake.

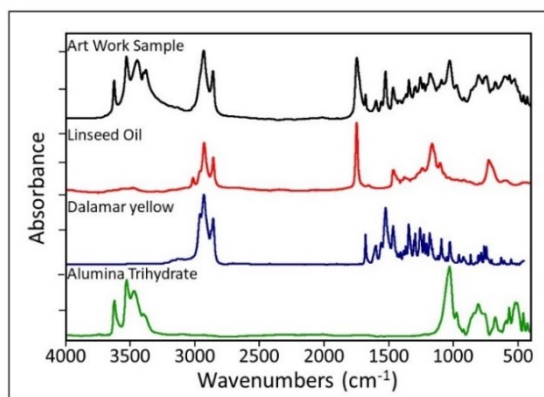


Figure 5: IR spectra of the artwork sample (top, black) and its complementary components.

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. Shimadzu IRSpirit FTIR spectrophotometer coupled with the SurveyIR microscope accessory can facilitate identification at the location of the work.

■ Acknowledgement

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■ References

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