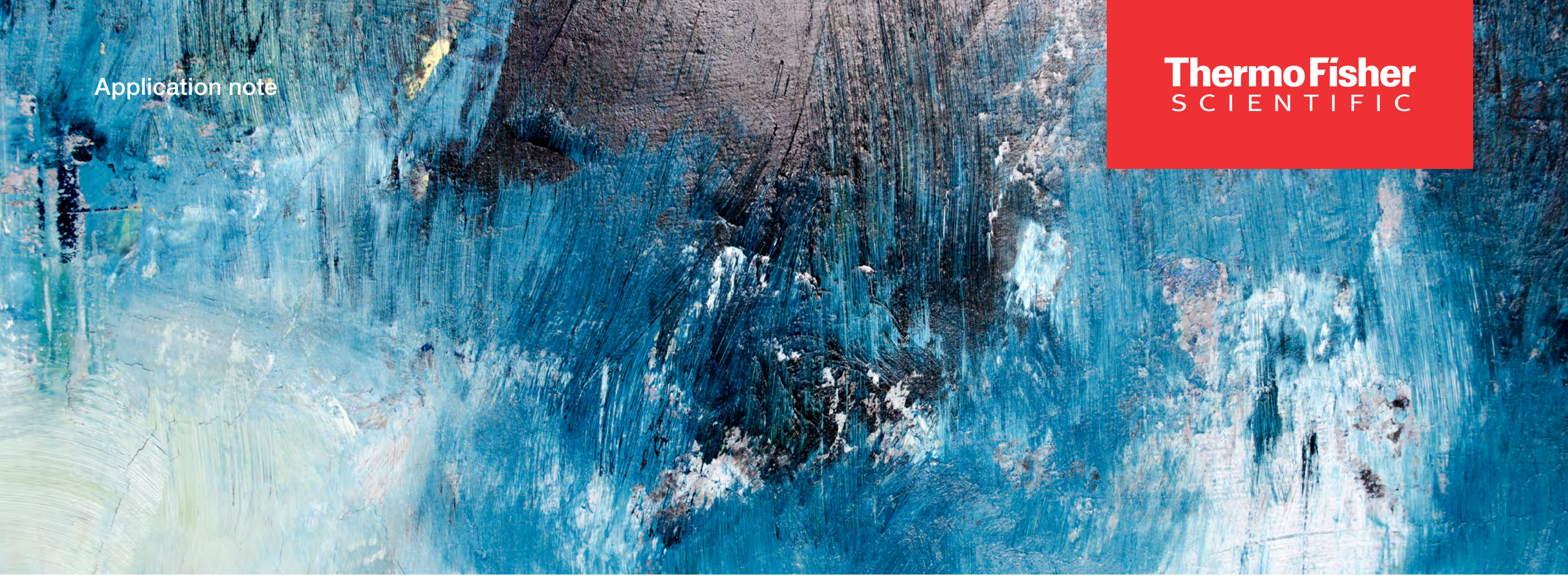
Application note



Non-contact and non-destructive analysis of artists' paints by reflectance FTIR

Introduction

Fourier-transform infrared spectroscopy (FTIR) is an established tool for the conservation and authentication of fine art paintings, but typically requires the removal of small sample sections for analysis. In contrast, FTIR reflectance spectroscopy offers a non-contact, non-destructive method of analysis. This study presents results from several samples in both the mid-infrared spectroscopy (mid-IR) and far-infrared spectroscopy (far-IR) regions, demonstrating the capability of reflectance mode measurements to provide insight into the components of artists' paints.

Authentication and conservation of fine art paintings require identifying paint components in as much detail as possible. Moreover, correct materials characterization can be essential in establishing the period of a piece's origin or determining the optimum restoration or conservation procedure. This is a demanding task as artists' paints are combinations of pigments, fillers, and binders that have spanned many materials over time. FTIR has proven to be an effective tool to characterize artists' paints. In the past, it typically required the removal of a small portion of the artwork for investigation by infrared (IR) microscopy. Analysis by IR microscopy can be carried out using several sampling techniques. The most common are transmission and attenuated total reflectance (ATR) modes. Spectral collection by transmission requires that the sample be thin enough to produce a good quality spectrum, which might involve cutting or compressing the sample to a thickness of about 5 to 30 microns. ATR on the other hand requires good contact between the ATR crystal and the sample. A third technique of microscopy, the reflectance mode, offers the benefit of non-contact analysis. However, positioning a sample under a microscope objective requires removing a section of the sample for analysis.

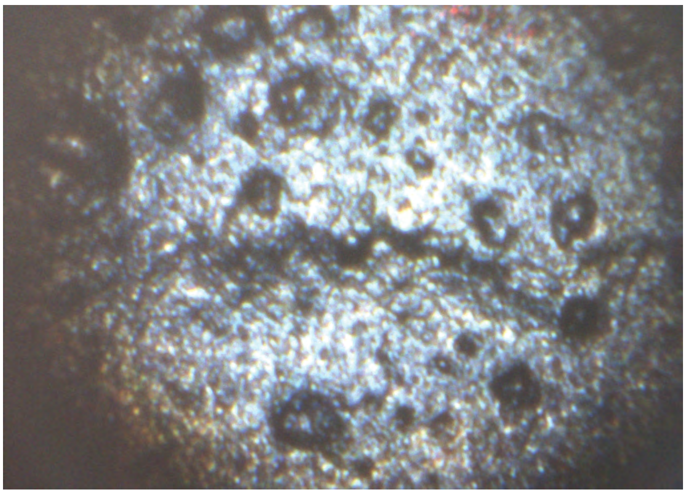


Figure 1. ConservatIR External Reflection Accessory video image of Prussian Blue oil paint.

The use of the Thermo Scientific™ ConservatIR™ FTIR External Reflection Accessory for reflectance analysis not only allows for no-contact analysis, but also eliminates the need to put the sample onto a microscope stage or in a standard sample compartment. In this application note, we illustrate the use of non-destructive, non-contact IR measurement using the ConservatIR FTIR External Reflection Accessory with a Thermo Scientific™ Nicolet™ iS50 FTIR Spectrometer to characterize various artists' paints.

Experimental

A variety of commercially available artist paints and an artist acrylic medium were each brushed on separate pieces of card stock and allowed to dry. The sampling aperture of the ConservatIR External Reflection Accessory is located at the end of an arm with a wide range of possible angles facilitating the measurement of samples outside of the spectrometer's sample compartment at different sample orientations.

Reflectance spectra were collected using the ConservatIR External Reflection Accessory mounted in a Thermo Scientific iS50 FTIR Spectrometer by positioning the sample 1 to 2 mm from the sampling aperture of the ConservatIR External Reflection Accessory. The final optimum sampling distance was determined by maximizing the IR signal and observing a sharp ConservatIR External Reflection Accessory video image in real time (Figure 1). ATR spectra were also collected to serve as a comparison to reflectance measurements. ATR spectra were measured with the built-in ATR of the iS50 FTIR Spectrometer using its pressure tower to provide good contact between the sample and the diamond ATR crystal. All mid-IR spectra were collected from 4,000 to 400 cm^{-1} at 4 cm^{-1} resolution using a KBr beamsplitter. A DTGS detector with a KBr window was used for mid-IR reflectance measurements. For mid-IR ATR measurements, the dedicated DTGS detector of the built-in ATR of the iS50 was used. Far-IR spectra were collected from 1800 to 100 cm^{-1} at 4 cm^{-1} resolution with a solid substrate beamsplitter. Reflectance far-IR spectra were collected with a deuterated triglycine sulfate (DTGS) detector with a polyethylene window. For far-IR ATR spectra, the iS50 FTIR Spectrometer's built-in ATR dedicated DTGS detector was used to collect spectra in the same range. All spectra were measured with Thermo Scientific™ OMNIC™ Software and Kramers-Kronig (KK) transformation and ATR corrections through OMNIC Software were applied where indicated.

Results and discussion

Examples of mid-IR paint analysis

Figure 2 demonstrates the effectiveness of FTIR reflectance spectroscopy applied to paint measurements in the mid-IR spectral region. The sample is an acrylic paint containing Pyrrole Red, a synthetic pigment developed in the 1980s.[1]

Many portions of the reflectance spectrum shown in Figure 2A display a derivative-like shape commonly seen in specular reflection measurements due to anomalous dispersion. The KK-transformed and baseline-corrected spectrum is shown in Figure 2B. Excellent agreement between the corrected reflectance spectrum and the spectrum of the same sample measured by ATR (Figure 2C), demonstrating the effectiveness of the KK transformation. Finally, the presence of an acrylic binder in this paint is confirmed by the comparison with the spectrum of an artist acrylic medium in Figure 2D, where the key peaks of the binder material are at approximately 1730, 1450, and 1180 cm^{-1} are clearly seen in the paint spectra.

Figure 3 shows another example of characterizing paint components using FTIR non-contact reflectance measurement. In this case, a sample of oil paint containing the pigment Prussian Blue was measured. Prussian Blue is a synthetic pigment that was first synthesized in 1704 and has been commercially available since 1724.[2] In Figure 3, spectrum A is the reflectance spectrum obtained from this sample using the ConservatIR External Reflection Accessory. The KK transformed spectrum (Figure 3B) displays a strong peak at approximately 2100 cm^{-1}, which is attributed to the $C \equiv N$ stretch of the cyano groups in iron hexacyanoferrate, the basis of Prussian Blue. The KK-transformed spectra (Figure 3B) is virtually identical to the sample's ATR spectrum (Figure 3C), further illustrating the usefulness of the KK transformation in producing a more conventional IR spectrum. Finally, the presence of alumina trihydrate, a filler that enhances the color in paints, is also confirmed in the sample by comparing the paint spectrum to a library spectrum of alumina trihydrate (Figure 3D), notably by the spectral similarities in the 3700–3200 cm^{-1} and 1000–500 cm^{-1} regions.

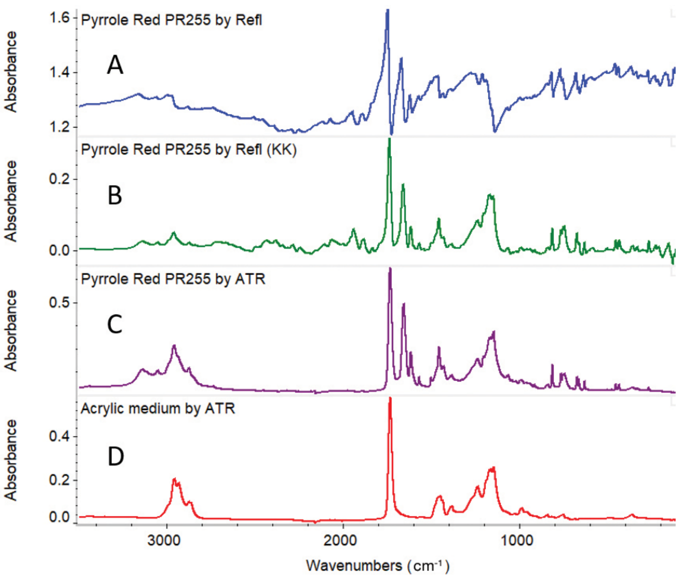


Figure 2. Pyrrole Red acrylic paint sample: (A) Reflectance spectrum (B) Reflectance spectrum after KK transformation and baseline correction, and (C) ATR spectrum. ATR spectrum of artist acrylic medium shown for comparison (D).

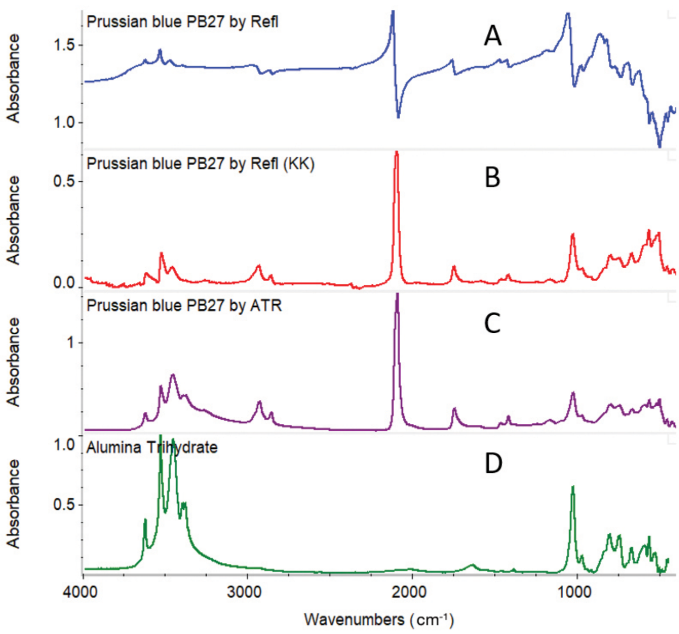


Figure 3. Prussian Blue oil paint sample: (A) Reflectance spectrum (B) Reflectance spectrum after KK transformation and baseline correction, (C) ATR spectrum after ATR correction. (D) Library spectrum of alumina trihydrate.

Benefits of combined mid-IR and far-IR range

The ConservatIR External Reflection Accessory contains all-reflectance optics, allowing measurements in both the far-IR and mid-IR ranges once the FTIR Spectrometer has been properly configured. The far-IR measurements can be particularly useful when paints contain inorganic pigments that typically have only weak or no mid-IR spectral signatures. Figure 4 illustrates a comparison of two acrylic paint samples: Zinc White and Titanium White, which appear to be almost identical in color. The fingerprint region of the mid-IR and the far-IR portions of the KK transformed spectra of these two paints are shown in Figures 4A and 4B. The mid-IR region of the two spectra are almost identical because both are dominated by spectral features of the acrylic binder (Figure 4C). However, the spectra in the far-IR region (800 to 100 cm^{-1}) can readily distinguish between these two pigment types.

FTIR multi-range reflectance analysis can be applied to readily differentiate traditional inorganic pigments from more recently developed in synthetic organic pigments of similar color. While inorganic pigments tend to yield spectral features only in the far-IR region, synthetic organic pigments often contain their strongest features in the mid-IR region. Figure 5 shows a comparison between two acrylic paints, cadmium yellow, and benzimidazolone yellow. Cadmium yellow pigment is cadmium sulfide (CdS) and has been commercially available since 1919.[3] On the other hand, benzimidazolone yellow is a synthetic organic pigment developed in the 1960s and introduced as artist pigment in the late 1970s.[1] The reflectance spectra obtained from these two paints after KK transformation are shown in Figure 5. The cadmium yellow paint in the mid-IR region is dominated only by features of the acrylic binder of the paint (peaks at 1740, 1470, and 1170 cm^{-1}). In contrast, the benzimidazolone yellow organic pigment has many strong features in the mid-IR, in addition to the same acrylic peaks observed in cadmium yellow. Further examination of the far-IR spectrum shows that cadmium yellow has a strong, broad absorption at 275 cm^{-1}. Thus, both spectral regions provide insight into the composition of the two paints.

The pigment spectrum of benzimidazolone was obtained by subtracting the spectrum of the artist acrylic medium sample from the reflectance spectrum of benzimidazolone yellow paint (Figure 6A), and the result is shown in Figure 6B. The resulting spectrum matches extremely well to the commercial library spectrum of that pigment in powder form (Figure 6C).

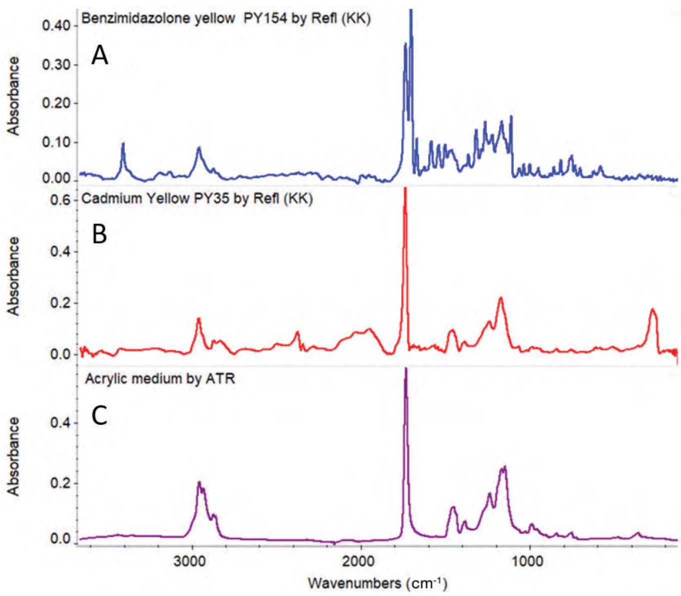


Figure 5. Reflectance spectrum of acrylic paint sample after KK transformation and baseline correction: (A) Benzimidazolone Yellow (B) Reflectance spectrum of Cadmium Yellow. ATR spectrum of acrylic medium (C) shown for comparison.

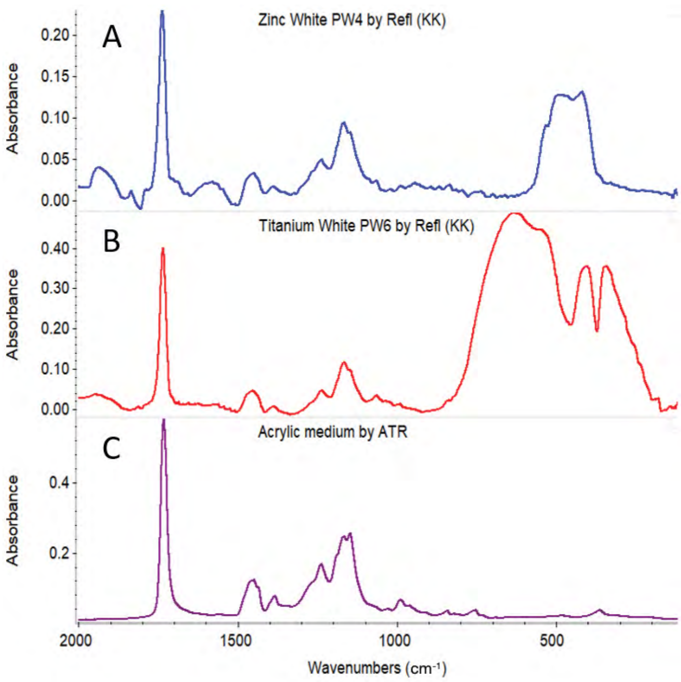


Figure 4. Reflectance spectrum of acrylic paint samples after KK transformation and baseline correction: (A) Zinc White and (B) Titanium White. ATR spectrum of acrylic medium (C) shown for comparison.

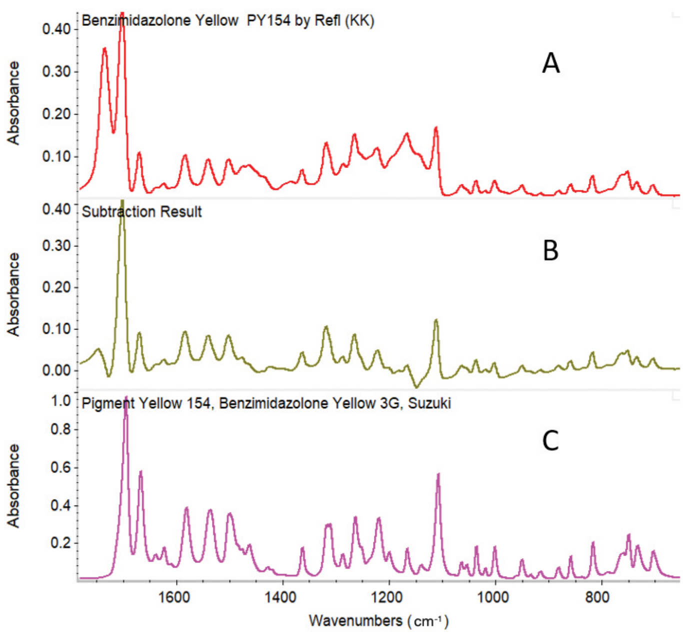


Figure 6. (A) Reflectance spectrum of benzimidazolone yellow acrylic paint sample after KK transformation and baseline correction (B) Result after spectral subtraction of the acrylic medium from corrected benzimidazolone yellow spectrum (C) Library spectrum of benzimidazolone yellow for comparison.

Conclusions

FTIR reflectance spectroscopy with the ConservatIR External Reflection Accessory provides a straightforward method to obtain component information in artists' paint in a non-contact manner, as demonstrated in this note, especially for those samples that would not readily fit on a microscope stage or even a conventional FTIR sampling compartment. An integral part of the measurements is the application of KK transformation to the raw reflectance spectra, which produce spectra more consistent with other FTIR methodologies, such as ATR. Finally, the use of all-reflective optics in the ConservatIR External Reflection Accessory allows facile measurements in spectral regions outside of the mid-IR range, which is particularly useful when analyzing inorganic pigments that contain spectral features only in the far-IR region. While the ConservatIR External Reflection Accessory was used with a Nicolet iS50 FTIR Spectrometer for the case studies described in this note, it can be utilized with any Thermo Scientific FTIR Spectrometer.

Thermo Scientific Nicolet iS50 FTIR Spectrometer with the ConservatIR External Reflection Accessory

References

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