Analysis of artists' pigments by far-infrared microspectroscopy

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Introduction

The chemical identity of materials used in art pieces is of key importance to their authentication and preservation. By comparing the materials used relative to the time period in which the art was purportedly generated, conservators can quickly distinguish authentic pieces from well-made copies. Furthermore, identification of the materials used can also guide conservators on the proper cleaning and preservation techniques to slow the natural degradation processes of those art pieces. In many cases, it's also important to identify previously applied preservation materials.

Fourier transform infrared (FTIR) spectroscopy is a well-established technique to analyze and identify artists' materials.[1-10] Measurements are typically performed in the mid-IR spectral region (4000-400 cm^{-1}). The KBr optics commonly used in FTIR spectrometers impose a low frequency cutoff at about 400 cm^{-1}. Mercury-cadmium-telluride (MCT) detectors employed in FTIR microscopes further restrict the low frequency cutoff to the 700-500 cm^{-1} range. These low frequency cutoffs limit the effectiveness of mid-IR in identifying many inorganic pigments found in artwork, which often have characteristic absorption bands in the far-IR region (600-10 cm^{-1}). Raman spectroscopy, another primary vibrational spectroscopy technique for the molecular identification of cultural heritage materials, has a standard spectral range well below 400 cm^{-1}. However, fluorescence arising from both pigments and binding media is an often-encountered problem in the analysis of artistic pigments using Raman spectroscopy.[11]

The utility of far-IR spectroscopic characterization of pigment materials has been demonstrated for macro samples.[12-15] The far-IR microspectroscopy analysis of pigments, however, has been an unexploited field due to such challenges as the low radiance of thermal sources, relatively low responsivity of room temperature detectors, and reduction of throughput by aperture masks. Recent advances in optical materials and design have overcome many of these challenges and opened the far-IR region for the microspectroscopic application in pigment characterization. In this application note, we demonstrate the microspectroscopic analysis of a number of pigments using the Thermo Scientific™ Nicolet™ iS50 FTIR Spectrometer and the Czitek™ SurveyIR™ Microspectroscopy Accessory (Figure 1).

Figure 1: Nicolet iS50 FTIR spectrometer with the SurveyIR microspectroscopy accessory in the sample compartment.

Experimental

Measurements were done in attenuated total reflectance (ATR) mode using the SurveyIR diamond ATR attachment, or by reflectance with the samples on a low-E glass microscope slides. Spectra were collected using 256 scans at 8 cm^{-1} spectral resolution. Mid-IR spectra were measured using a Ge on KBr beamsplitter and DLaTGS detector with a KBr window allowing collection from 4000 to 400 cm^{-1}. Far-IR spectra in the range of 1800-50 cm^{-1} were collected using a solid substrate beamsplitter and a DLaTGS detector with a polyethylene window. Polyethylene is commonly used as a window material in the far-IR, but its strong absorbances around 1460 cm^{-1} and 770 cm^{-1} do not allow measurements in these specific regions. Changing the beamsplitter between measurements was easily accomplished with the automatic beamsplitter exchanger (ABX) on the Nicolet iS50 spectrometer. The unique ABX design allows automated switching between measurement modes with no loss of purge. No modifications of the SurveyIR accessory were necessary to allow it to measure spectra in both mid- and far-IR regions.

Results and Discussion

To demonstrate the utility of the far-IR method and performance, mid- and far-IR spectra of a coated paperboard were collected. The coating on the paperboard contained calcium carbonate ($CaCO_3$), kaolinite ($Al_2O_3 \bullet 2SiO_2 \bullet 2H_2O$), and a polyester binder. The coating spectra were collected in two modes using the SurveyIR diamond ATR microspectroscopy attachment. First, a spectrum was collected using a conventional KBr substrate beamsplitter and KBr window DLaTGS detector. This spectrum is displayed in Figure 2B in the 1850-400 cm^{-1} region. The optical configuration of the FTIR was then changed to the far-IR mode. The IR spectrum using this configuration was measured from 1850-50 cm^{-1} and is displayed in Figure 2C. The overall spectral quality and signal-to-noise ratios are quite satisfactory. Numerous absorption bands originating from calcium carbonate and kaolinite are observed below 400 cm^{-1} outside of the range of MCT detector and KBr window cut-offs. While these inorganic materials also exhibit features in the mid-IR, extending the range into the far-IR region provides more spectral details that can be beneficial in identifying materials or components in mixtures.
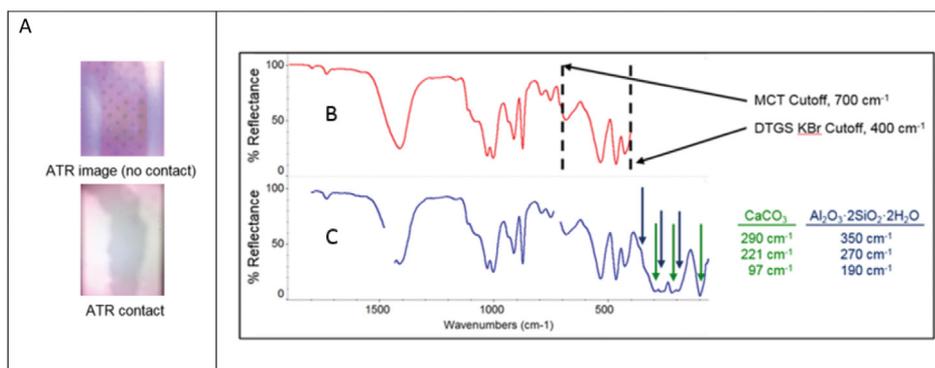

Figure 2: Measurement of coated paperboard by ATR. (A) Image of sample area through diamond ATR crystal before and after contact, allowing the user to verify the sample area being measured. (B) Mid-IR spectra with characteristic low end cut-offs of MCT and DLaTGS detectors indicated by dashed lines. (C) Spectral features seen in the far-IR spectrum indicative of calcium carbonate and kaolinite seen below the KBr and MCT low wavenumber cut-offs. Spectral regions around 1460 and 770 cm^{-1} are blanked due to the strong absorbance of polyethylene detector window at these locations.

The mid-IR and far-IR spectra of a modern paint are shown in Figure 3, as another comparison. These spectra were recorded using the SurveyIR diamond ATR microspectroscopy attachment. The observed mid-IR spectrum is consistent with polymers of ethyl acrylate and methyl methacrylate,[16-18] typical for a modern polymer-based paint binder. However, the far-IR spectrum allows the identification of the inorganic pigment, zinc oxide, or "zinc white" since it contains a characteristic absorbance peak at 380 cm^{-1}. Clearly, measurement of the mid-IR spectrum alone would not allow for a positive identification of zinc white.
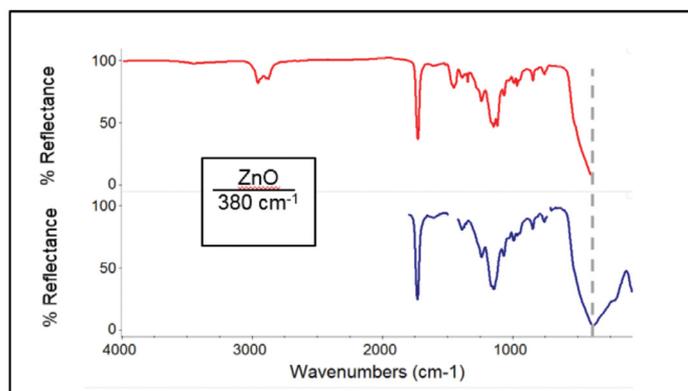

Figure 3: White paint containing zinc oxide. Top: Mid-IR spectrum showing only shoulder of zinc oxide absorption at 380 cm^{-1} (dashed line). Bottom: Far-IR spectrum clearly showing zinc oxide's absorption peak at 380 cm^{-1}.

Far-IR microspectroscopy was also employed in the analysis of pigments from a furniture piece in the collections of the Philadelphia Museum of Art (PMA). The piece, a wardrobe shown in Figure 4, was purportedly fabricated in China in the 18th century during the Qing dynasty. To help plan the conservation treatments, the decorative surfaces were analyzed to determine whether they are consistent with the 18th century in China or are later additions. A cross-section from a sample taken from an interior portion of the wardrobe is also shown in Figure 4.
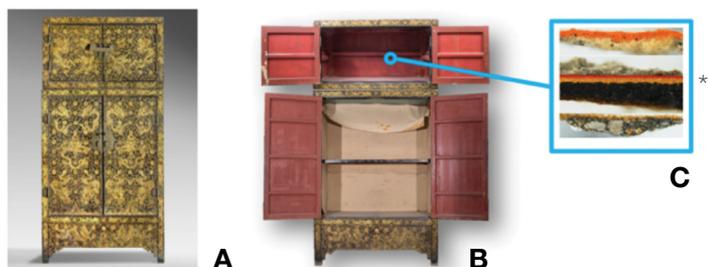

Figure 4. Qing dynasty lacquer clothes wardrobe and inset shows a cross-section from the interior used for analysis. (A) Exterior, (B) interior, and (C) cross-section analyzed from the compound wardrobe. The asterisk represents the original decorative surface. The layers above this point are later additions. *Accession number: 1940-7-2, Philadelphia Museum of Art; Artist/maker unknown Qing Dynasty (1644–1911); Lacquered wood with painted and gilt decoration; brass fittings. Purchased with the Bloomfield Moore Fund, 1940.*

Far-IR microanalysis was performed on the red and yellow layers of the cross-section. The images obtained from the red pigment particles are shown in Figure 5, Section A. Spectra of the red layer obtained by diamond ATR microscopy and a vermilion reference are shown in Figure 5, sections B and C, respectively. The vermilion reference was from the Forbes pigment collection at Harvard University.[19] The two spectra exhibit a high degree of similarity and confirm a positive identification. Vermilion is produced from the mineral cinnabar, HgS, mercury (II) sulfide. The observed bands are consistent with those from trigonal α-mercuric sulfide (cinnabar mineral) and are attributed to the lattice vibrations of the crystal.[20] Vermilion was a common red pigment used in the production of Chinese lacquerware[21] and its presence provides critical evidence of the wardrobe's authenticity. The captured images of the yellow particles (A), the far-IR spectra of the yellow lacquer layer pigment (B), and orpiment reference (As_2S_3) (C) are shown in Figure 6. Both spectra were recorded in the external reflectance mode from samples flattened onto low-E glass substrates. An aperture mask corresponding to 250 microns at the sample was used to target the pigment extracted from the yellow layer. The reference orpiment pigment was also from the Forbes collection. Orpiment is a mineral produced geothermally and was used as a yellow pigment from antiquity into the early 20th century. Prominent absorption bands are indicated in the figure. The absorption bands between the yellow pigment and the orpiment reference spectrum match well and agree with previous reports.[22-23] The results unequivocally indicate that the yellow pigment is orpiment. In the cases of both pigments, the lack of features in the mid-IR regions underscores the importance of far-IR measurements.
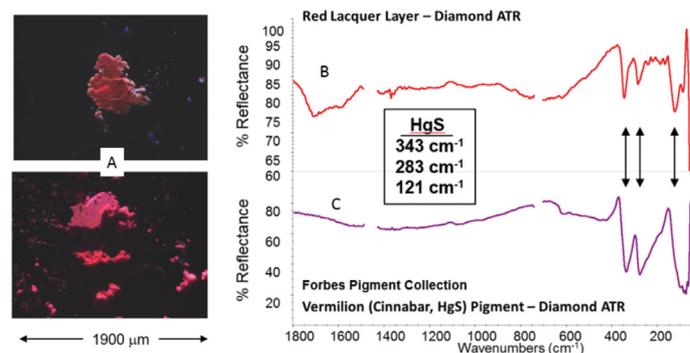

Figure 5: Far-IR ATR spectra: (A) images of red pigment extracted from wardrobe sample, (B) far-IR ATR spectrum of wardrobe sample and (C) vermillion reference.
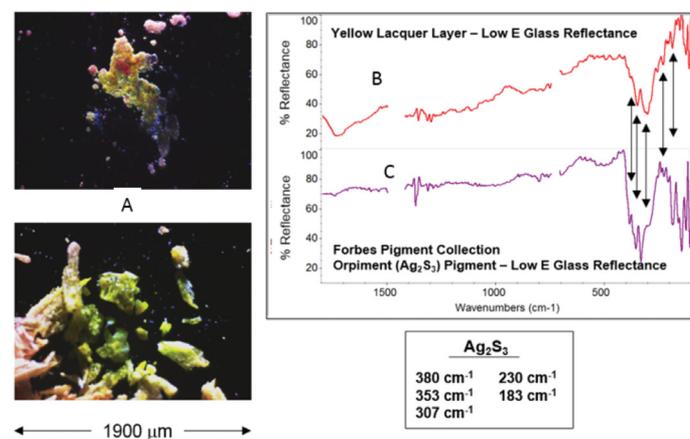

Figure 6: Far-IR ATR spectra: (A) images of yellow pigment extracted from the wardrobe sample, (B) far-IR reflectance spectrum of yellow wardrobe sample and (C) orpiment reference.

Conclusions

Mid-IR FTIR spectroscopy is an effective analytical tool for artworks, and the combination with microscopy is particularly beneficial as minimal sample is required for analysis. However, many materials, particularly pigments containing inorganic components, cannot be fully characterized with FTIR microscopes configured only for mid-IR operation. The analyses of zinc white and two layers of an antique artifact demonstrate the benefits of combining far-IR spectroscopy with microspectroscopy accessories, which allow for more insightful characterization of pigment materials. The chemical information gleaned from the interpretation of these spectra can be used to establish authenticity through dating of artworks, characterize previous conservation attempts, and plan new conservation campaigns.

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