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Application News

AIRsight™ Infrared/Raman Microscope

Analysis of Pigment Degradation Using AIRsight Infrared/Raman Microscope

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User Benefits

- Using an AIRsight microscope enables the measurement of infrared and Raman spectra in the same location without moving the sample being measured.
- That makes it ideal for measuring pigments that contain both organic and inorganic matter using a combination of infrared and Raman spectroscopy.
- Because micro sample quantities can be measured, AIRsight microscopes are especially useful for measuring precious samples with historical value.

■ Introduction

Pigments have been used for all sorts of purposes since before the common era. Though inorganic pigments created from natural minerals are commonly used in paintings and murals in historical buildings, organic synthetic pigments are widely used today due to their availability in large quantities at lower prices. Identifying both ancient and modern pigments requires measuring both organic and inorganic substances, which can be accomplished by using a combination of infrared and Raman measurements and then interpolating between those results.

The AIRsight infrared/Raman microscope is a new type of microscope that includes a Raman unit built into an infrared microscope. A photograph of the system is shown in Fig. 1. The AIRsight microscope enables the acquisition of both infrared and Raman spectra from the same spot with a single instrument, rather than the two instruments required previously and without having to move the sample. Furthermore, the ability to control both infrared and Raman measurements using the same AIMsolution software makes it extremely easy to operate.

In the example described below, the AIRsight microscope is used to measure the infrared and Raman spectra from pigments used in ancient China and analyze their UV degradation.

Fig. 1 External Appearance of AIRsight™ Microscope

■ Measuring Vermilion Pigment

Due to the preciousness of pigments used in historically valuable paintings and murals, such works must be analyzed with very small sample quantities. Because the AIRsight is able to measure both infrared and Raman spectra from the same small spot without moving the sample, samples do not need to be sampled multiple times, which means samples can be measured with very small sample quantities.

The two measured samples are shown in Fig. 2. The vermilion pigment applied to the wood substrates is the same as used in ancient China. Measurement conditions are listed in Table 1.

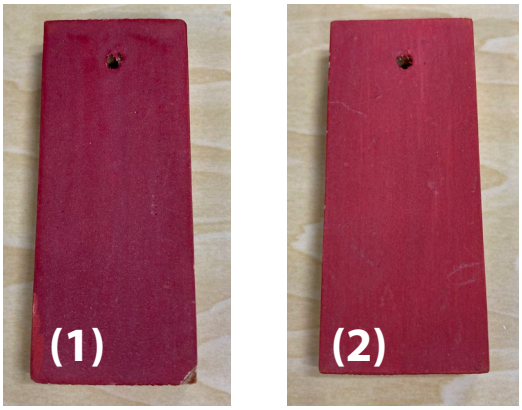

Fig. 2 External Appearance of Vermilion Pigment

Table 1 Measurement Conditions

Instruments:	IRTracer™-100, AIRsight
Infrared Spectrophotometry	
Resolution:	8 cm^{-1}
Accumulation:	100
Apodization Function:	SqrTriangle
Detector:	T2SL
Raman Spectrophotometry	
Accumulation:	100
Exposure Time:	1.0 sec
Objective Lens:	50x
Excitation Wavelength:	785 nm
Detector:	CCD

A microscope image of sample (1) is shown in Fig. 3.

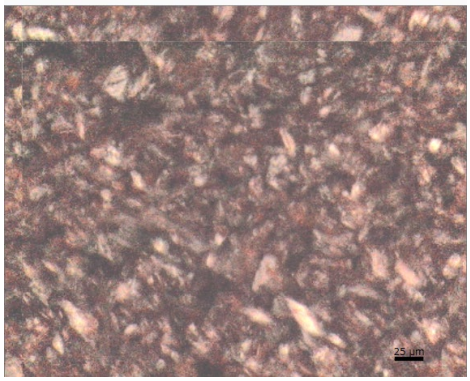

Fig. 3 Microscope Image of Sample (1)

The surface of sample (1) appears non-uniform in Fig. 3, so infrared and Raman spectra were measured at multiple locations, but no differences were confirmed in the spectra from different locations. Accordingly, typical infrared and Raman spectra are shown in Fig. 4.

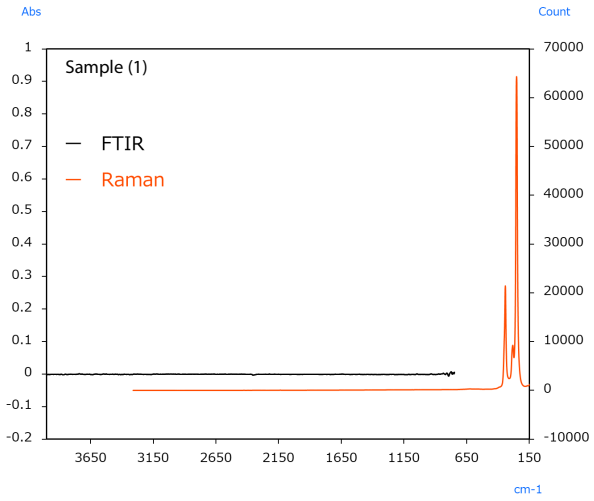

Fig. 4 Infrared and Raman Spectra of Sample (1)

Raman measurement results indicated peaks from HgS near the 370 to 185 cm^{-1} region. Cinnabar is a pigment that contains HgS and is known to have been used in ancient China.[1] The fact that no peaks were detected in infrared measurements performed by the microscope ATR method indicates a low probability of the sample containing organic matter. Consequently, we can infer that the only principal component is HgS.

Next, the microscope image for sample (2) is shown in Fig. 5.

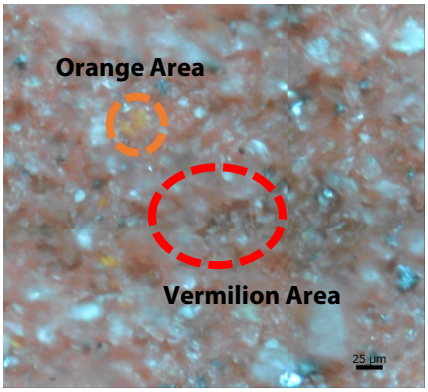

Fig. 5 Microscope Image of Sample (2)

The fact that the surface of sample (2) appears non-uniform in Fig. 5 indicates that the color also differs in different locations.

In this case, infrared and Raman spectra were measured from vermilion and orange areas in Fig. 5. The resulting spectra are shown in Fig. 6 and 7.

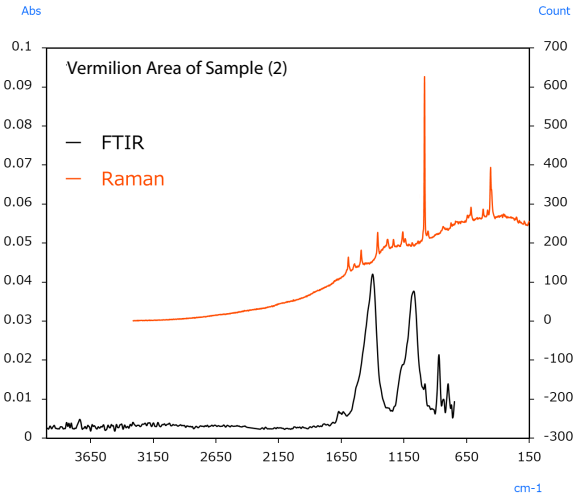

Fig. 6 Infrared and Raman Spectra of Sample (2) (Vermilion Area)

Raman measurement results from the vermilion area indicated a sharp peak from $BaSO_4$ at 990 cm^{-1}. The infrared measurement results indicated peaks from $CaCO_3$ near 1,400 cm^{-1}. The results also indicated peaks from $BaSO_4$ near 1,050 cm^{-1}. The $BaSO_4$ and $CaCO_3$ detected in these measurements were added to increase the pigment quantity or change its optical properties.[2]

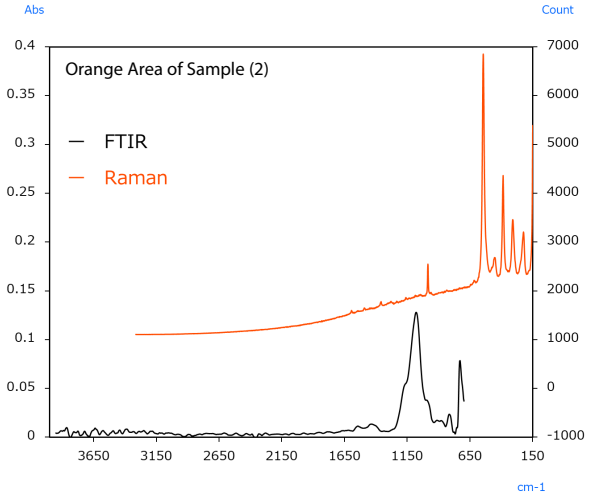

Fig. 7 Infrared and Raman Spectra of Sample (2) (Orange Area)

Raman measurement results from the orange area indicated peaks from Pb_3O_4 near 620 to 150 cm^{-1}. Similar to HgS, Pb_3O_4 was also used as a vermilion pigment in ancient China. The FTIR results also indicated the same $BaSO_4$ peaks for the extender pigment as in the vermilion area.

Using Raman spectrophotometry also enabled qualitative analysis of trace inorganic compounds, which were difficult to detect with FTIR.

■ Pigment Changes Due to UV Rays

The two types of samples shown in Fig. 2 were exposed to sunlight for two years and then the changes in the pigment caused by UV rays were evaluated. Sample appearance after exposure is shown in Fig. 8, with corresponding measurement results shown in Figs. 9 to 11.

Fig. 8 Appearance of Vermilion Pigment after Exposure Test

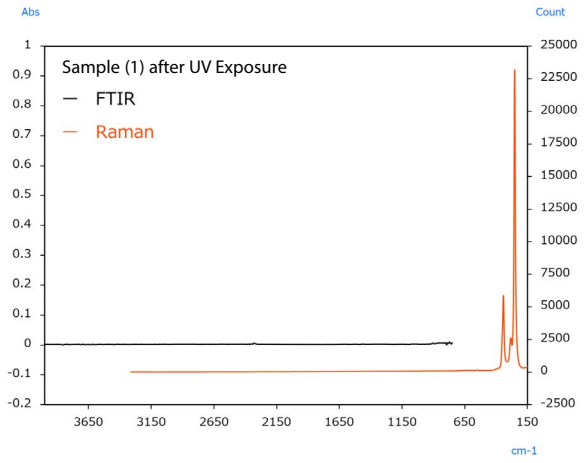

Fig. 9 Infrared and Raman Spectra of Sample (1) after UV Exposure

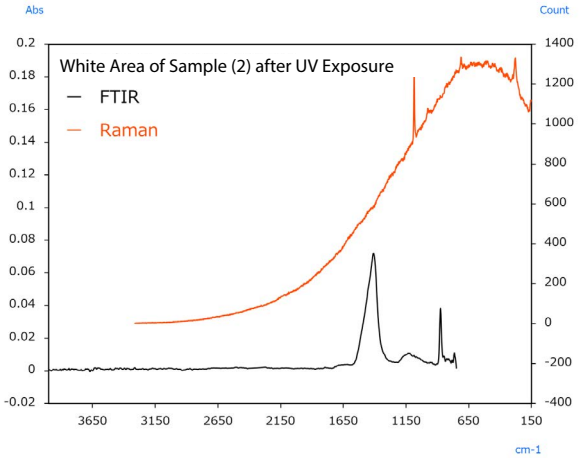

Fig. 10 Infrared and Raman Spectra of Sample (2) after UV Exposure (White Area)

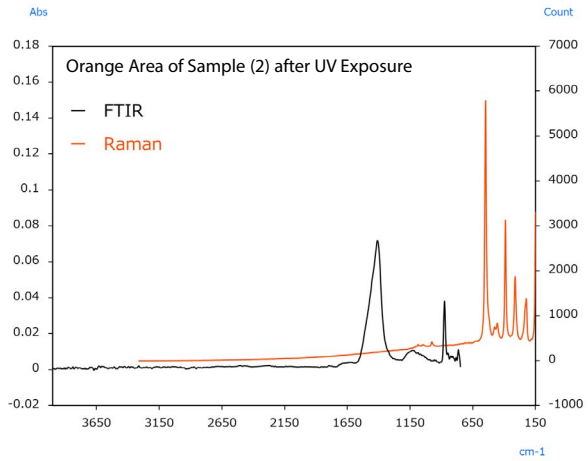

Fig. 11 Infrared and Raman Spectra of Sample (2) after UV Exposure (Orange Area)

The color of sample (1) faded somewhat after UV exposure, but the Raman spectrum remained the same as before exposure and indicated the presence of HgS on the surface even after exposure. There was no change in the infrared spectrum after exposure either, which indicated there was no difference in the constituent components.

The vermilion color in sample (2) mostly faded after UV exposure, which accentuated the white and orange areas. The wood substrate was also exposed in some places. From the white area, peaks for $CaCO_3$ appeared in the Raman spectrum at 1,080 cm^{-1} and in the infrared spectrum at 1,400 cm^{-1}. From the orange area, Pb_3O_4 peaks were indicated in the Raman spectrum near 620 to 150 cm^{-1}. The $BaSO_4$ peak measured from the orange area before exposure did not appear, presumably due to UV degradation.

The pigment used in sample (2) was more prone to fading than the pigment in sample (1), which suggests that it contained more pigment extender material. Even for samples with identical vermilion pigment, the results showed that the degree of fading and changes in component composition caused by UV degradation varied depending on the component composition.

■ Conclusion

This Application News article described measuring vermilion pigment using an AIRsight infrared/Raman microscope. By using the AIRsight microscope, both infrared and Raman spectra can be obtained from the same location with only one sample. Because measurements can be obtained from micro sample quantities, AIRsight microscopes are especially useful for measuring precious samples with historical value.

Reference Documentation

1) Eiichi Tsuruta: Lecture on Artist Paints (Lecture II)—History of Pigments, Journal of the Japan Society of Colour Material, 75 (2022) 189

2) Fukuji Suzuki, Maneo Tanaka: Lecture on Pigments (Lecture II)—Inorganic Pigments-I, Journal of the Japan Society of Colour Material, 55 (1982) 413

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