Chemical Analysis of Microscopic Fluorescent Materials by Dispersive 1064 Raman System

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APPLICATION NOTE

Raman measurement on microscopic inclusions in fluorescent materials requires the ability to measure in small volumes, excellent throughput for superior SNR, and long wavelength excitation such as 1064 nm for fluorescence reduction. Carotenoids and keratin can be measured in epoxy and fossil amber by BaySpec's dispersive 1064 confocal Raman microscope.

Introduction

Inclusions, small particles less than 1 mm in diameter embedded in other materials are of interest in a number of different areas. In some manufactured products the inclusions can result in cosmetic, structural or chemical resistance defects in otherwise ideal materials. Non-destructive identification methods such as Raman spectroscopy of the contaminant composition can lead to the identification of the contamination source. In heterogeneous manufactured materials, especially pharmaceutical tablets or structured materials like multilayer polymer films, the measurement of the structures and their chemical identity helps the manufacturer understand quality. In the police and military, chemical identification of small particles, often embedded in other materials play an important role in characterization of evidence. Just as exciting is investigating archaeological materials and human-derived historical artifacts to learn more about our world and our role in it. In paleology, evidence is mostly physical and chemical. Wholly entrapped inclusions are a time-capsule from our past. In art conservation, structural and chemical information provides clues to the artists, intents and processes used in the painting. Chemical analysis provides clues. In addition, it provides insight into conservation efforts and forgeries. This article demonstrates a few examples on fast identification of microscopic fluorescent samples using Raman spectroscopy, which are unattainable previously.

Method

Chemical imaging of microscopic object requires an instrument that can precisely locate an object. Measuring the object without the matrix requires projecting light into and especially collecting light from only the region of the inclusion. Raman spectroscopy works well for this application as it is straightforward to focus the light on and collected from the region of interest deep within the material. The challenge for Raman spectroscopy is that it is susceptible to fluorescence. Working with 1064 nm wavelength lasers avoids fluorescence, by avoiding exciting the electronic transitions. Traditionally, due to grating and detector limitations, 1064 nm Raman is often obtained by FT-Raman system, which is very slow because each spectrum is composed by constantly moving interferometers. Therefore, mapping using FT-Raman system is almost impossible. With recent advances in gratings, and InGaAs detectors, today, using an automated stage, volume mapping, depth profiling and surface profiling can be accomplished easily. For instance, 1064 nm Raman microscope in dispersive configuration with f2 high-throughput Raman spectrometer is able to create a chemical image using Raman spectra in a short period of time. Dispersive Raman instruments provide this advantage. [1] The BaySpec Nomadic Raman microscope can create a Raman map of tens of thousands of spectra in as fast as an hour. Furthermore, such dispersive configuration allows great flexibility of the system, such as a high-magnification video probe being added to the system to image the area of interest and take the Raman measurement quickly on samples that do not fit under a microscope.

Discussion

Feathers can occasionally be found embedded in fossil amber. The feathers can hold clues about the color about the prehistoric animals. Carotenoids provide shades of red, orange and yellow in modern bird plumage. The individual parts of the feather are approximately 10 microns in diameter. Carotenoids were demonstrated to be measurable in modern feathers under fossil amber. The technique was successfully applied to fossil feathers by using BaySpec's Nomadic 1064 nm Raman microscope. [2]

Raman imaging of paintings provides two challenges, the size of the object can be much larger than the microscope stage and the pigments are frequently fluorescent at shorter wavelengths like 532, 785 and 830 nm. In terms of the regions that need to be analyzed can be spatially separated. Additionally, microscopic areas and vertical profiles can be measured. In Figure 2, a vertical profile of a painting is shown.[3] The versatility of the video probe in being able to make measurements of areas and depth is unmatched.

Raman imaging using 1064 nm excitation provides a unique ability to measure inclusions and profiles as chemical maps. The measurements are rapid and informative.

References

1. R. McCreery, *Modern Raman Spectroscopy: Has the sleeping giant finally awoken?* Pittcon, May 2009.
2. D.B. Thomas, P.C. Nascimbene, C.J. Dove, D.A. Grimaldi, H.F. James, *Sci. Rep.* **4**, 5226 (2014).
3. Domagoj Mudronja, personal communication.

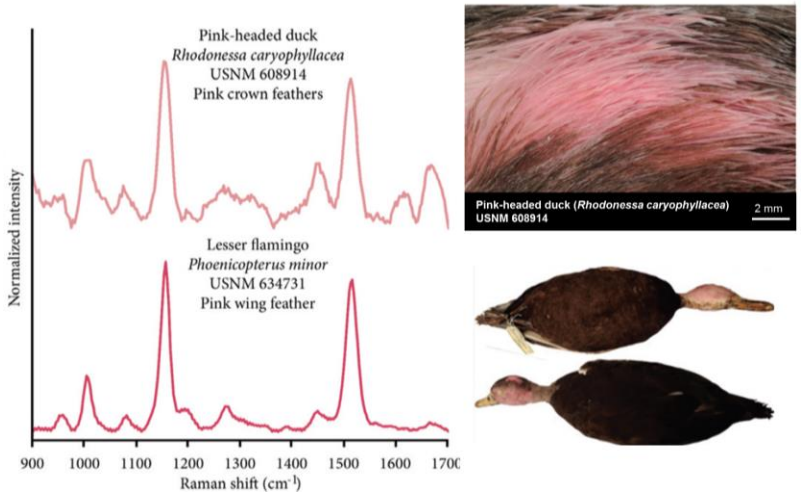

Figure 1. 1064 nm Laser Raman spectra of feathers from an extinct pink-headed duck and from a flamingo wing. Courtesy of Dr. Daniel Thomas, Smithsonian Institution. Refer to reference [2] for Raman spectra of feathers in fossil amber. Raman Data were taken by BaySpec's Nomadic 1064 nm Raman microscope.

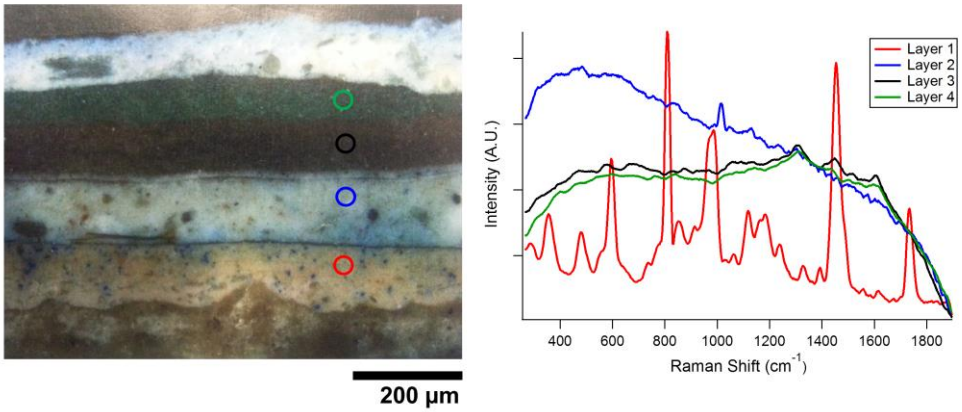

Figure 2. Painting cross-section and spectra of the different layers using a video microprobe attached to a BaySpec's 1064 nm Raman spectrometer.