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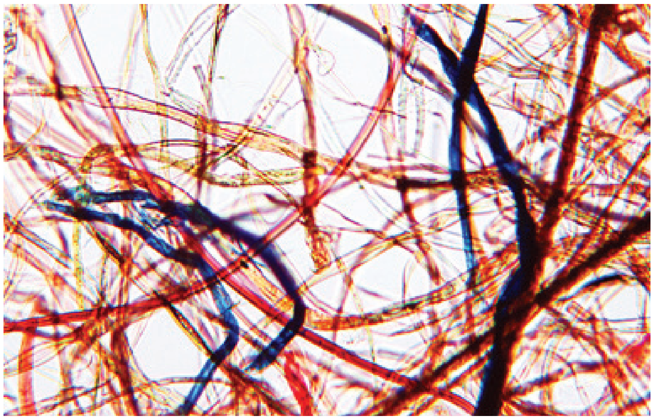
Submicron, simultaneous and non-contact IR+Raman spectroscopy for direct fiber characterization

In this Application Note, we will focus on the analysis of those fibers ranging from 800 nm to 22 microns as well as fibers with surface treatments, using the mIRage+R, IR+Raman microscope, based on the newly pioneered Optical-Photothermal Infrared (O-PTIR) spectroscopy. All fibers have been analyzed directly without applying additional modification or sampling accessories. The resulting O-PTIR spectra resembles the transmission-like IR spectra in non-contact (far-field) mode. Spatially resolved (micron) spectra reveal the distribution of the surface treatment on the micron-sized fibers without dispersive/scattering artifacts. Finally, we further extend the application of mIRage into the analysis of a single nanofiber of 800 nm to complete the possibility of analyzing the full-sized range of fibers for forensics, textiles, filtration, medical scaffolds, art conservation, microplastics, and intellectual property protection.



This detection mechanism offers significant advantages:

- Sub-micron IR spatial resolution, providing ~20x improvement over traditional FTIR/QCL Microscopy
- Non-contact, reflection (far-field) mode measurements, generating FTIR transmission-like spectral quality
- O-PTIR is insensitive to fluorescence allowing the analysis of colored specimens
- Upgradability to include submicron simultaneous IR+Raman, providing for IR and Raman spectra from the same spot and the same time with the same spatial resolution

Introduction

Fiber identification and characterization often relies on collecting infrared spectra using an FTIR microscope and then comparing the spectra with commercial or custom IR databases. The dimension of a fibrous filament can be greatly varied, from sub-micron to many tens of microns diameter, which covers approximately the wavelength of the infrared light used to measure the

Figure 1: The mIRage O-PTIR instrument, Photothermal Spectroscopy Corp., Santa Barbara, CA

fibers. At this regime, infrared light could be scattered and dispersed leading to baseline offsets and tilts, rendering the use of reflection mode FTIR on fibers impossible.[1, 2] Potential solutions may include flattening of the fiber with roller knives[3] or by a diamond compression cell or by using a micro ATR accessory. In doing so, the fibers can be damaged and/or the molecular orientation modified, which if these are trace samples, could compromise its accurate characterization. Forensic applications are particularly vulnerable due to limited availability of the evidence. These limitations are equally applicable to newly emerging QCL IR microscopic technologies as well. To date, these issues have placed restrictions on how effectively IR microscopy has been used for fiber analysis.

The aforementioned issues are essentially eliminated with the advent of Optical Photothermal Infrared (O-PTIR), which operates by exciting the sample with IR light from a widely tunable and pulsed QCL to induce a localized modulated photothermal effect. A 532 nm probe laser is co-localized with the IR light for detecting the effect and defines the spatial resolution rather than the long IR wavelengths. This effectively breaks the diffraction limit suffered by traditional FTIR/QCL microscopy.

Experimental

An eight factor multi-fabric test sample was obtained from Kimble. A short strip of the fabric was cut from the bundle and placed directly into the sample chamber of mIRage+R Infrared and Raman Microscope, pictured in Figure 1, with a piece of adhesive tape without additional sample preparation.

Results

The O-PTIR spectral collection of the eight-factor multi-fiber standard testing material has been easily achieved to yield conventional IR spectra, all collected in reflection mode. The individual fiber diameters of this test material, range from 8-22 microns. Using these spectra, shown in Figure 2, we can readily identify each of the layers using commercial IR databases, such as Wiley's (formally BioRad) KnowItAll®.

The simultaneous IR+Raman feature of the mIRage turns identification of unknowns into a highly definitive process. When both the O-PTIR and Raman data are searched against a commercially available infrared and Raman database, the result list only contains one probable result, which is the acetylated derivative of cellulose, as shown in Figure 3. The use of simultaneous submicron IR+Raman data from the same spot, at the same time with the same resolution can be considered to be complementary and confirmatory.

The true value of the mIRage lies in its ability to provide spatially resolved conventional IR spectra well below the diffraction limit of infrared wavelengths and that no sample preparation was necessary to achieve the same regardless of the diameter of the fiber. As shown in Figure 4, the mIRage spectra are spatially resolved to provide the relative concentration profile along the length of the fiber. Spectrum A represents the nearly pure IR

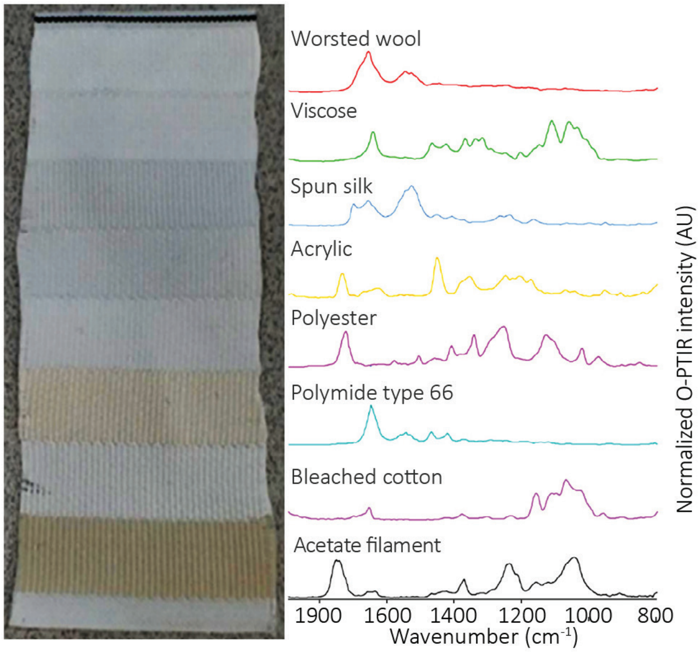
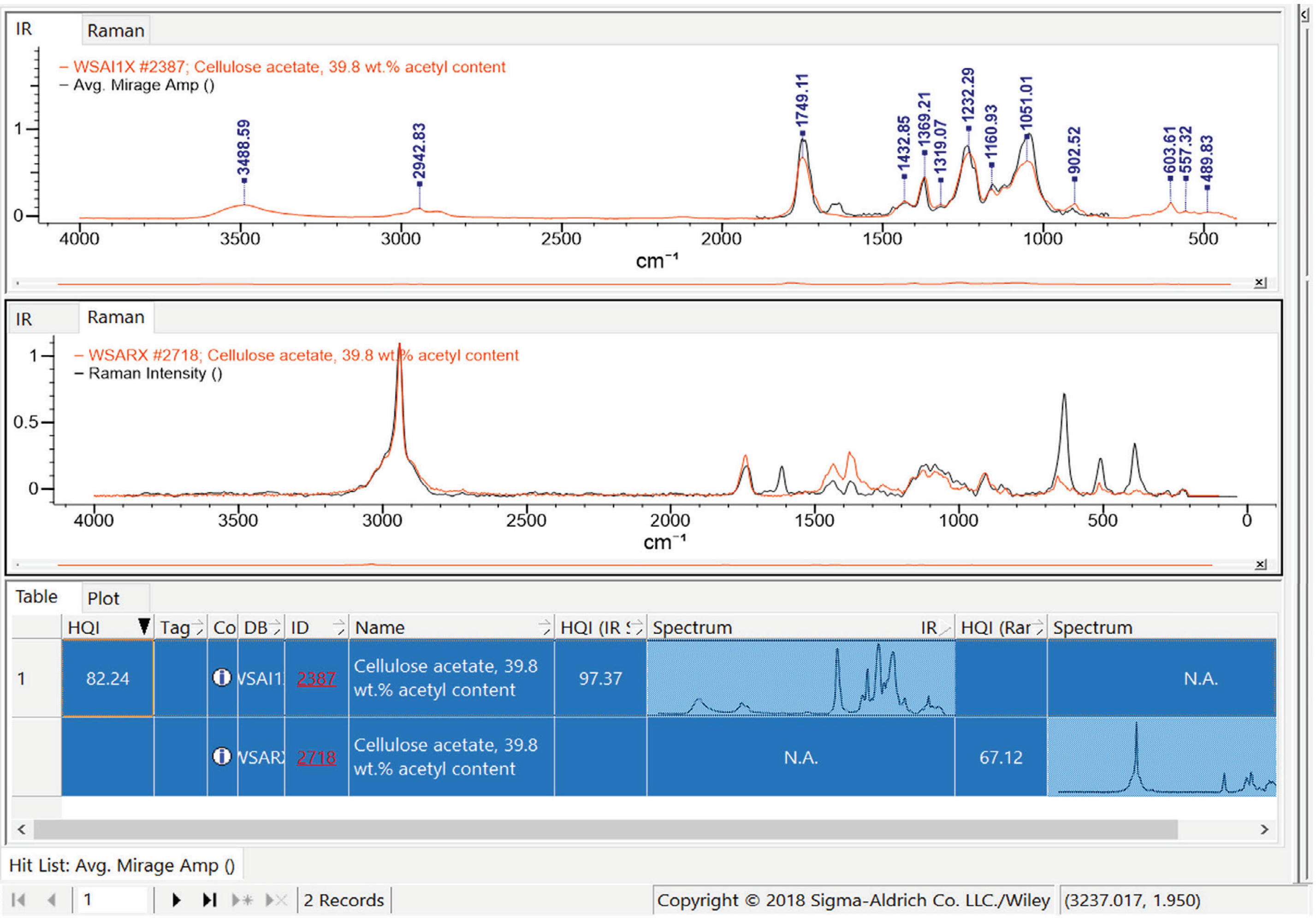


Figure 2: O-PTIR spectra of single fibers in each of the eight layers of fabrics within the standard multi-fabric sample



	HQI	Tag	Co	DB	ID	Name	HQI (IR	Spectrum IR	HQI (Rar	Spectrum
1	82.24		ⓘ	VSAI1	2387	Cellulose acetate, 39.8 wt.% acetyl content	97.37			N.A.
			ⓘ	VSAR	2718	Cellulose acetate, 39.8 wt.% acetyl content		N.A.	67.12	

Hit List: Avg. Mirage Amp ()

1 2 Records Copyright © 2018 Sigma-Aldrich Co. LLC./Wiley (3237.017, 1.950)

Figure 3: Bio-Rad KnowItAll simultaneous search list of both the IR and Raman spectra, reflecting cellulose acetate as the only probable search result

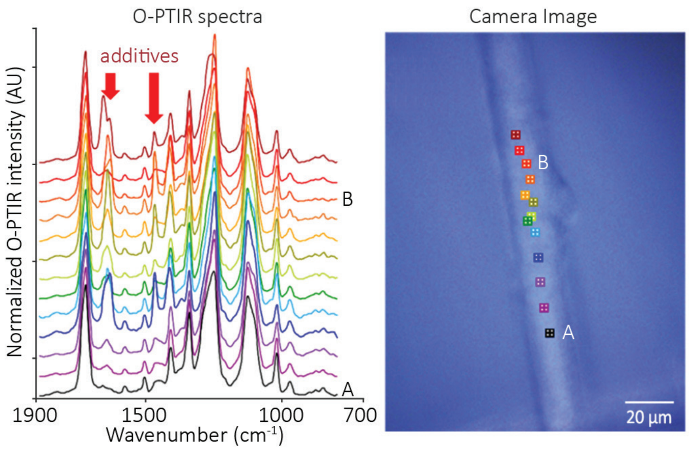


Figure 4: O-PTIR spectra collected along the length of a free-standing fiber in a piece of polyester fabric

spectrum from the polyester fiber while Spectrum B contains a high concentration of the additive. Here, the primary amide absorption at 1650 cm^{-1} and the CH2 scissoring band at 1456 cm^{-1} are both increasing along the fiber length. These absorptions are consistent with primary alkylamides additives that are present usually in less than 1% w/w for processing of polyester as it is being dry spun.[4] The mIRage can even collect high quality spectra on nanofibers with diameter similar to the spatial resolution of the mIRage nstrument. Without flattening physically, the mIRage can still collect IR absorption spectra of such fibers in free air that show no dispersive artifacts without making physical contact, as shown in Figure 5, and no chance for cross-contamination which are a risk with an micro ATR. Here, the stearic acid additives from polypropylene nanofiber can be clearly seen along with the polypropylene base material. The 1705 cm^{-1} and 1650 cm^{-1} correspond to the dimer and the dissociated carboxylic acids. This material is known for controlling the diameter of the nanofiber as it is being electrospun.[5]

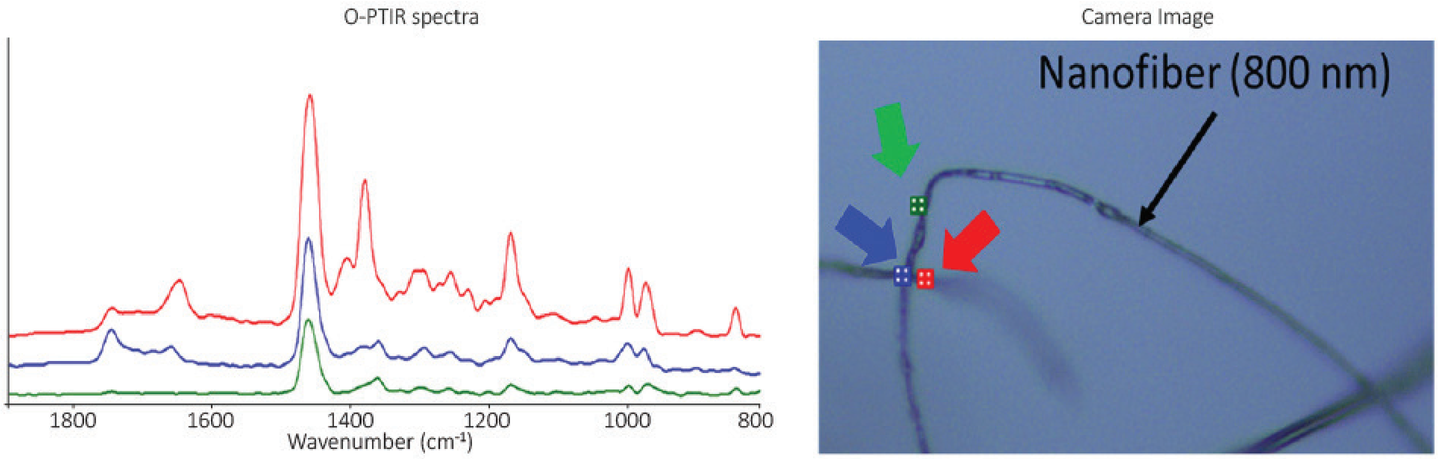


Figure 5: O-PTIR spectra of PP-based nanofibers with 800 nm diameter

Conclusion

Using the mIRage+R Infrared and Raman Microscope, both the O-PTIR and Raman spectra can be collected in one click on a single fiber. Transmission FTIR-like spectra of fibers 8-22 µm and 800 nm in diameter have been observed consistently, where the band shapes show no dispersion artefact to allow for easy unambiguous spectral interpretation and matches in commercially available infrared and Raman databases. By searching for both channels of simultaneous IR and Raman data from the mIRage+R microscope, the combined thorough spectroscopic characterization will ensure the ultimate accuracy in identifying unknown fibers (and other materials).

References

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325 Chapala Street, Santa Barbara, CA 93101
(805) 845-6568 info@photothermal.com www.photothermal.com