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Microplastic chemical analysis using IR+Raman to detect particles in the under ten micron range.

Microplastics have recently gained tremendous exposure in recent years, both in scientific circles, but also with the broader public through media coverage, on such things as microplastics in bottled water and seafood. Currently a large gap exists in the scientific literature in the <10micron range. Raman microscopy, a complementary spectroscopy tool to FTIR, can assist in this regard, with spatial resolution down to ~1 µm being typically possible using IR+Raman.

IR+Raman microscopy can assist with spatial resolution down to ~1 µm being possible

Introduction

In this application note, we will focus on the analysis of microplastics in such things as bottled water and seafood. Thus far, analytical scientists working on these challenges have turned to traditional chemical analysis techniques, such as FTIR microscopy and Raman microscopy. Both techniques have advantages and disadvantages. FTIR has rich spectral profile that that is easily identifiable and is relatively easy to use, but does suffer from fundamental spatial resolution limit that sees most FTIR microscopy/imaging reports with spatial resolution no better than 10-20 microns. Furthermore, traditional FTIR or even newer QCL IR based microscopy systems also suffer from dispersive scatter artefacts, where, as the particle size of interest approaches the wavelengths of IR light used to measure them (~3-12 microns), the obtained spectra become very dependent on sample shape and size and thus become difficult to impossible to make confident spectral library matching possible. Currently a large gap exists in the scientific literature in this <-10 micron range. Raman microscopy, a complementary spectroscopy tool to FTIR, can assist in this regard, with spatial resolution down to ~1µm being typically possible. However, Raman microscopy does suffer from two key limitations, 1. Potential for fluorescence contamination of the signal and 2. Relatively weak signal necessitating longer scan times.

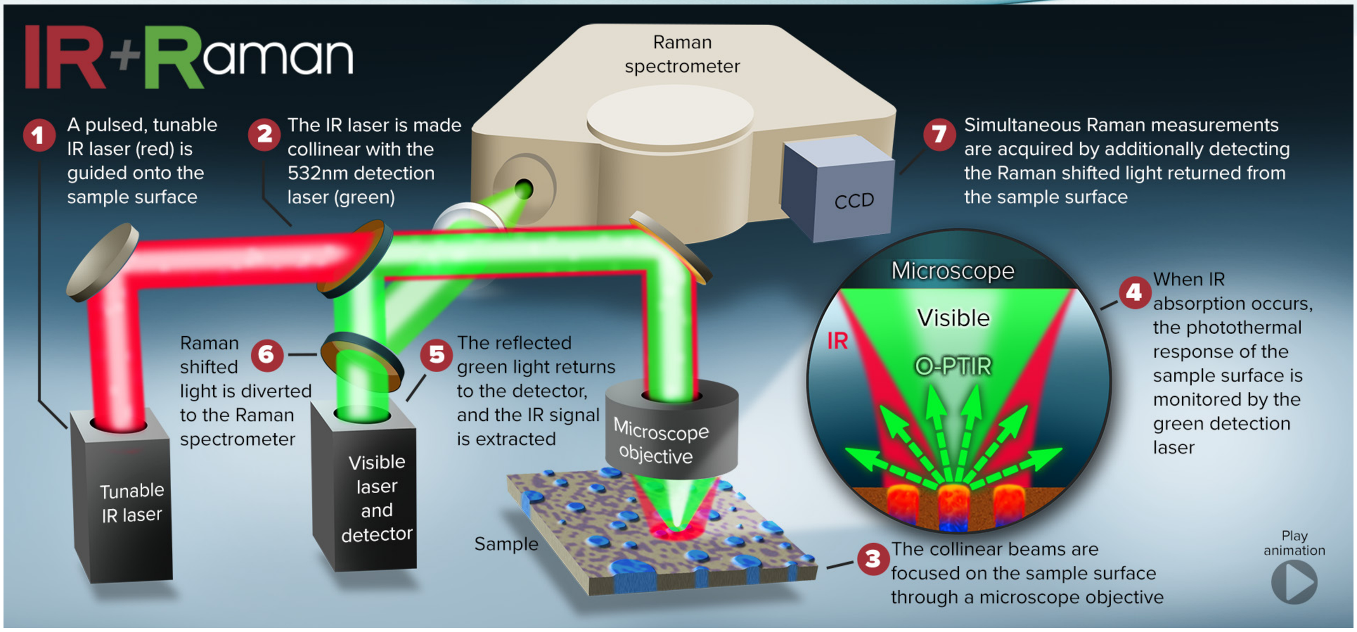

Figure 1: Schematic representation of the beam paths for the generation of simultaneous IR and Raman spectra.

In this application note, we will focus on the identification of various microplastics from a filter water sample containing unknown materials using the mIRage+R microscope, which simultaneously captures IR and Raman spectra from the same spot on a sample, with the same submicron resolution. Here we will focus on sub ~10 µm particles, a weakness for traditional IR techniques.

The principal behind the mIRage, Optical Photothermal IR (O-PTIR) spectroscopy enables, for the first time, submicron IR characterization of thin multilayer films via a non-contact reflection mode IR technique, while also significantly simplifying sample preparation and improving time-to-data. Furthermore, the IR probe laser generates Raman scattering, which when collected, allows for the simultaneous acquisition of both IR and Raman spectra, as shown in figure 1.

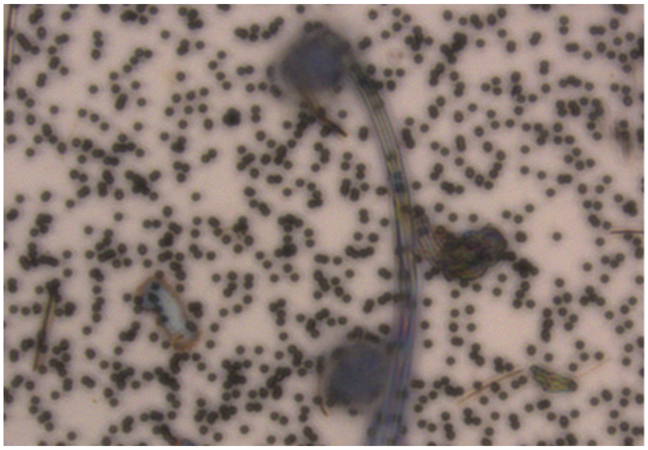

Figure 2: 40x Optical image of various sub 10 µm features on filter paper surface. Markers indicate position for simultaneous IR and Raman spectra.

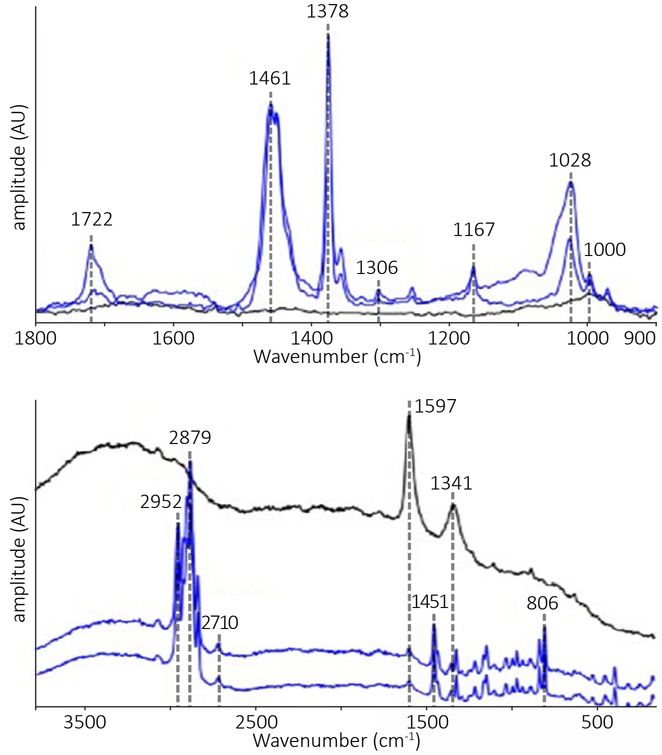

Figure 3: Top- IR spectra collected from film 1.
Bottom- Simultaneously collected Raman spectra.

(O-PTIR) Optical Photothermal IR spectroscopy

O-PTIR overcomes the IR diffraction limit by combining a mid-IR pulsed tunable laser with a visible probe beam. When the IR laser is tuned to a wavelength that excites a molecular vibration in the sample, absorption occurs, thereby creating photothermal effects. The visible probe laser, focused to ~0.5 µm spot size, measures the photothermal response via the scattered light, as shown in figure 1. The IR laser can be swept through the entire fingerprint region in one second or less to obtain an IR spectrum.

Minimizing sample preparation

Since it is a non-contact technique, O-PTIR provides IR measurements on a variety of sample types. This leads to dramatically easier sample preparation, improved ease of use and faster turnaround times. Conventional transmission mid-IR spectroscopy typically cannot be used to measure microplastics on filter paper, because the light cannot transmit.

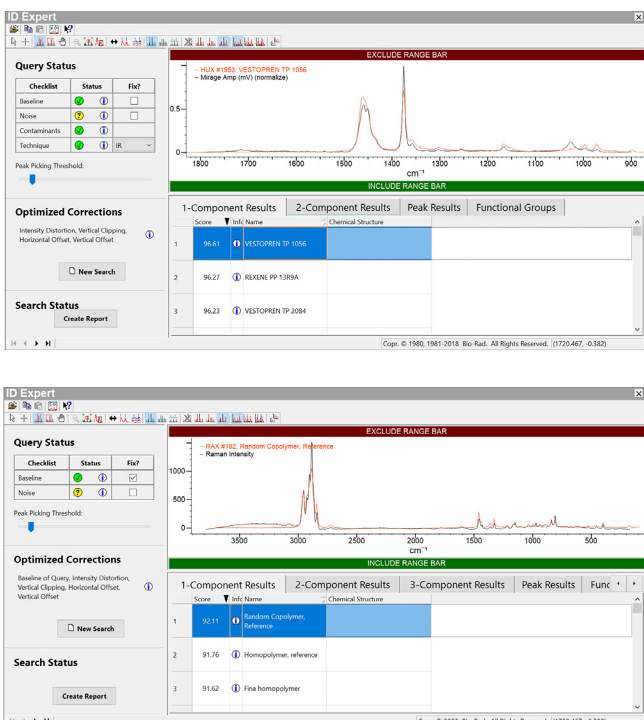

Figure 4: KnowItAll spectra database results for the main polymer layers in film 1. Top: Blue spectra identified as PE, Bottom: Red spectra identified as PP.

Simultaneous IR and Raman line array measurements

In this first example we can see the power of the simultaneously acquired IR and Raman analysis, with each technique being used to uniquely identify various components.

Representative IR and Raman spectra from each color-coded point in figure 2 are shown figure 3. The data spacing between points in the line array was 500 nm.

Due to the fact the O-PTIR spectra correlate excellently with traditional FTIR spectra, they can be easily searched using existing spectral databases. In this case, each of the spectra was searched against the KnowItAll spectral database from Wiley as seen in figure 4. The searches for the IR spectra clearly identify two main polymer layers, polyethylene and polypropylene, along with the embedding epoxy (not shown).

From the combinational analysis of both IR and Raman we can tell that the layer represented by the red spectrum is composed of polypropylene loaded with carbon black.

Single wavelength imaging for visualizing chemical distribution

When producing layered films, chemical distribution within the products is an essential part of product integrity. mIRage uniquely enables high resolution single wavelength imaging to highlight the chemical distribution of specific components in any sample as seen in figure 5. Once the O-PTIR spectra are collected

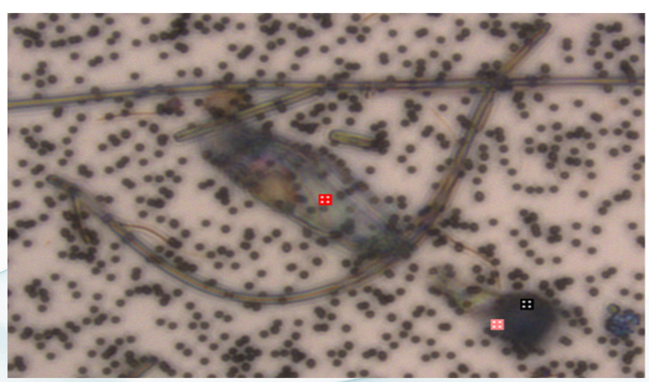

Figure 5: 40 x optical image of film two embedded in epoxy. Markers represent an 11 µm line array with 250 nm spacing.

on the film, images can be acquired at unique absorption bands to each layer, highlighting the layer boundaries and interfaces.

As we can see from the line array data, there is a region with a width of roughly 2 µm that shows a significantly different spectrum from surrounding regions. Red spectra show significantly increased C-H stretching with an additional peak at 1462 cm^{-1}. Single wavelength imaging allows us to visualize the clear thickness and distributions of various layers as shown in figure 8.

As we can see from the images that mIRage IR microscope can provide single wavelength images with unparalleled spatial resolution while operating in a reflective non-contact regime.

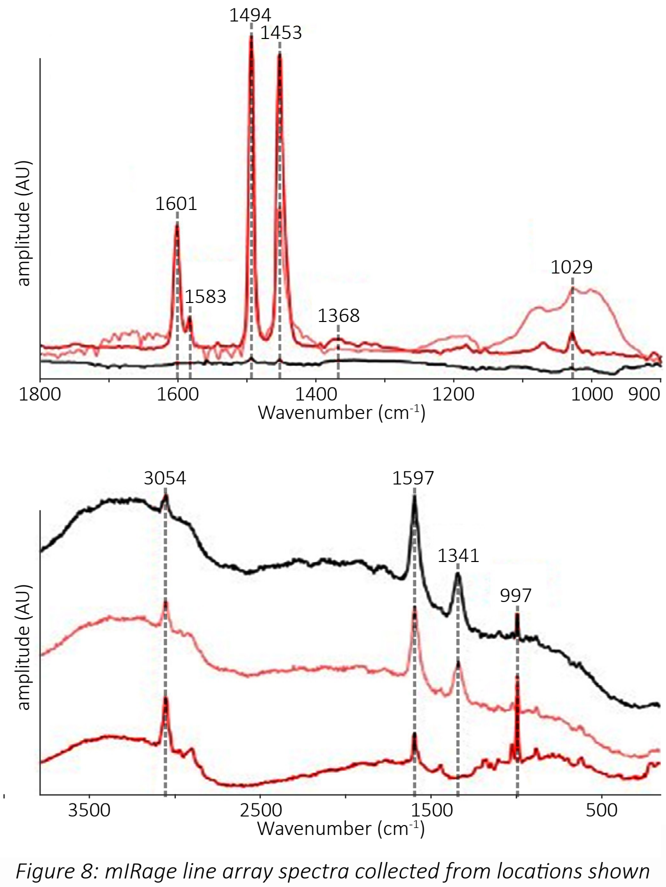

Figure 8: mIRage line array spectra collected from locations shown in figure 7. Data has been normalized to 1642 cm^{-1}

Summary

The mIRage+R microscope has been used to analyze various multilayer films by collecting both IR and Raman spectra simultaneously. The spectra that are collected show excellent correlation to traditional FTIR spectra and are searchable in existing databases. From these results and searches we can understand the entire composition of these films, when one technique alone may not be enough to obtain a complete understanding. Additionally, single wavelength imaging with O-PTIR allows for the complete visualization of the components within the sample with submicron resolution. Overall, O-PTIR provides reliable and reproducible sub-micron IR spectroscopy for the first time, making it a promising technique to solve many analytical and production challenges.

Acknowledgments

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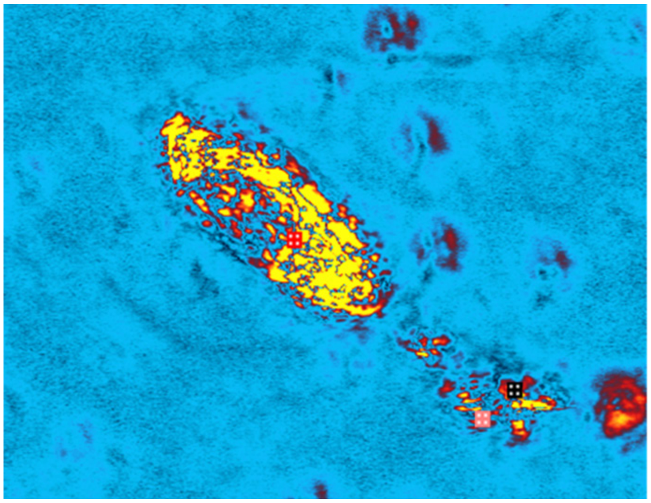

Figure 9: Top – mIRage image collected at 1642 cm^{-1} that visualizes the distribution of the nylon layers. Bottom – mIRage image collected at 1462 cm^{-1}.

Watch the realted webinar: Bioplastic laminate characterization IR+Raman spectroscopy

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