Using IR and Raman to solve real-world problems

A KnowItAll polymer case study

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Introduction

Wiley Science Solution's software package [KnowItAll](#) helps users identify, analyze and interpret spectra, whether they are IR, mass spectrometry, near-IR, NMR, Raman or UV-Vis. Powered by the world's biggest spectral library, it provides a user-friendly interface with which to investigate all kinds of materials.

In a new webinar series, IR interpretation expert Dr. Curtis Marcott from Light Light Solutions shows how the real-world problems of people working with polymers and polypeptides can be solved using KnowItAll. He presents three illustrative case studies: identification of the layers in a polymer laminate; the molecular-scale analysis of an innovative conductive knit fabric; and contamination on cross-sections of hair.

The key to all three is to get as much information as possible about the sample, including both IR and Raman spectra.

If you can get both an IR and a Raman spectrum of your sample, says Dr. Marcott in the webinar, that is ideal.

Why is this so advantageous? Firstly, the two techniques have different selection rules, and consequently they tend to emphasize different molecular vibrations. In some cases, specifically when the molecule has a center of symmetry, the two techniques can even be mutually exclusive: the motion producing the IR signal will not show up in the Raman spectra and vice versa. This makes them ideal complimentary techniques.

Secondly, Raman signals are influenced by the choice of excitation laser wavelength (λ). Raman signals scale according to $1/\lambda^4$, so, for example, the signal will be 16 times stronger if excited at 532 nm compared to 1064 nm. Having IR spectra collected at the same time can help to guide identification when this comes up – as we shall see later.

These days, no one should be put off by using both techniques in their work. With the development of spectral libraries such as Wiley's KnowItAll Spectral Library collections, they have become much easier to employ, also for the more occasional user.

So whether you are a full-time spectroscopist or not, the combination of IR, Raman and Wiley's KnowItAll software puts you in a great position to crack your chemical problem. As Dr. Marcott shows, this is also true for questions involving polymers and polypeptides that you might come across in industry.

In Dr. Marcott's first example, he is looking at a polymer laminate made of mixed materials. *"A lot of times you might get a competitor sample, and you want to identify what the layers are,"* he explains. *"It might come into your laboratory as an unknown."*

He has worked on this particular material for over twenty years, so he knows it well – but he wants to show, having obtained IR and Raman spectra from both layers and at the interface, how to use KnowItAll to exploit the combined techniques and identify the different layers.

His spectra are a beautiful example of how IR and Raman can complement each other. At one end, in the fingerprint region between 900 and 1800 cm⁻¹, the IR spectrum is full of peaks, including a strong carbonyl band around 1740 cm⁻¹, but it has hardly any signal in the rest of the spectrum. By contrast, the Raman is strong in the other end, showcasing the CH-stretching bands near 3000 cm⁻¹.
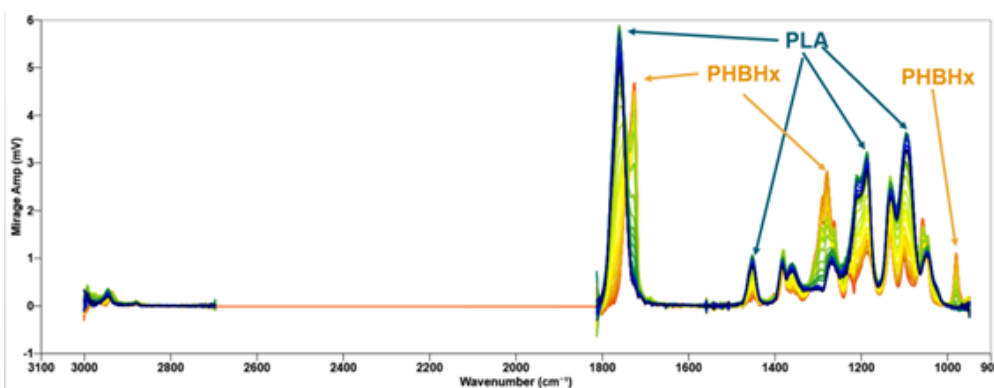

Figure 1: *Overlay of several closely spaced IR spectra spanning both layers of the polymer laminate. Note strong carbonyl signal at 1740 cm⁻¹.*
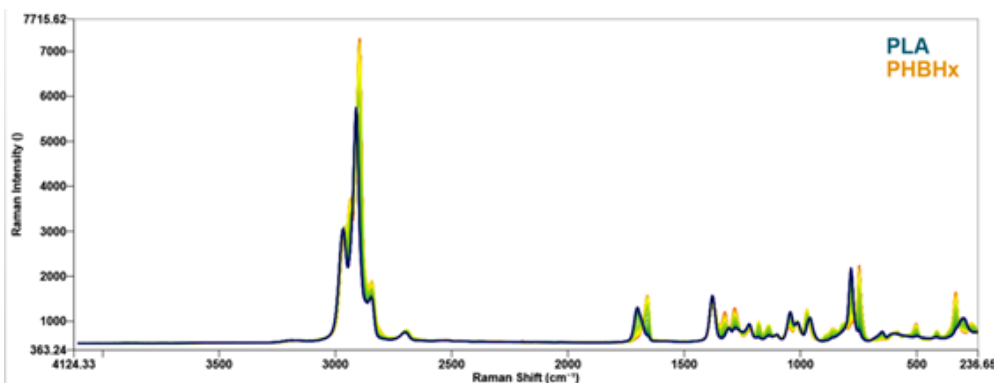

Figure 2: *Overlaid Raman spectra spanning both layers of the polymer laminate collected simultaneously and at the same locations as the IR spectra shown in Fig. 1. Note the strong CH-stretching peaks around 3000 cm⁻¹.*

"But there is something odd going on in the boundary region between the layers. There appears to be a possible tie layer, showing up in the IR carbonyl stretching band. As tie layers are often of interest in industry, this will be a crucial thing to pin down," says Dr. Marcott.
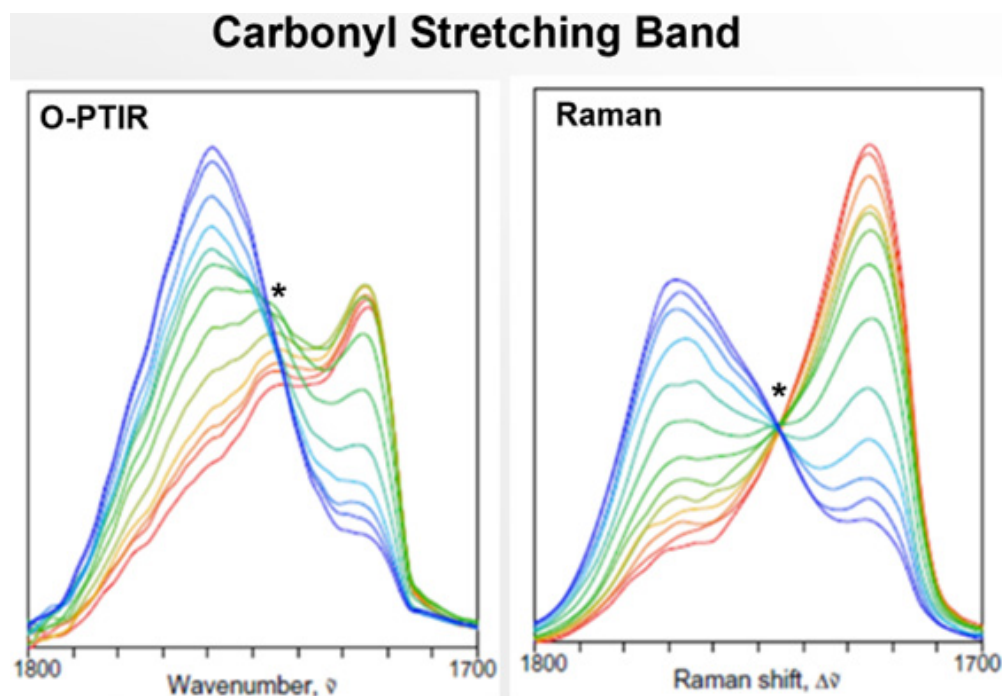
Figure 3: *Closely spaced IR and Raman zoomed in on the carbonyl stretching region. Asterisks denote the wavenumber where a new IR peak is appearing at the boundary.*

In the KnowItAll software, Dr. Marcott uses the SearchIt function to look at the first layer. *"Since we're going to be doing a dual search, we're going to be simultaneously searching the Raman spectrum and the IR spectrum,"* he says, adding both libraries to the search.

The software provides its best hits, handily represented in a scatterplot with IR hit scores on the x-axis and Raman hit scores on the y-axis. This function allows the user to quickly ascertain which material has the highest hit scores for both spectra.

However, a not entirely unexpected complication arises. The supposedly best hit is not quite right; there is some additional CH_2 in the suggested material compared to what Dr. Marcott knows is there. This, he believes, is due to a difference in excitation wavelength between the Raman spectrum he collected and the one in the library – that classic difficulty with Raman comparisons. *"The C-H stretch is not correct intensity-wise, so it picked something with more CH_2 because it matched better,"* he says.

His next step is to go back to the scatterplot and pick the hit that has a slightly lower Raman score but a higher IR score, because IR is not affected by excitation wavelength. *"Now we get a match,"* he says. KnowItAll has found the correct material: polylactic acid or PLA, which is a bioplastic. It just goes to show, he says, *"you have a better chance when you have two techniques."*

For the second layer, Dr. Marcott knows to be careful of the Raman C-H stretches and immediately goes to the next-best hit on the scatterplot, which gives him the correct material in one go. *"This is the exact compound,"* he says. It is a biocompostable plastic marketed as Nodax.

Polylactic acid (PLA)
• **Compostable** bioplastic
• Synthesized with monomers derived from **starch**

Poly(hydroxybutyrate-*co*-hydroxyhexanote) (PVBHx)
• **Marine** and **biodegradable** plastic, aka *Nodax*
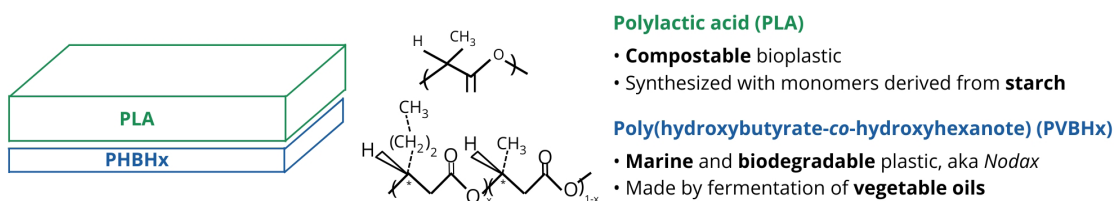• Made by fermentation of **vegetable oils**

Figure 4: *A diagram of the polymer laminate with the identified layers.*

This identifies the laminate as composite of PLA and Nodax. But to get to that possible tie layer in the middle, we need to look at the mixed spectrum right at the interface. For this, Dr. Marcott uses SearchIt's two-component search, looking just at the fingerprint region. It gets PLA straight away – but it misses Nodax entirely. Instead, it suggests another, very similar compound.

This, however, tells Dr. Marcott what he needs to know. It misses Nodax because the Nodax spectrum in the library is from a very crystalline sample. Crystallinity can dramatically affect the carbonyl peak, indicating that at the boundary, the Nodax in the laminate is less similar to the library sample than the main layer. This tells us that *"the boundary layer between the PLA and the Nodax is populated heavily with a more amorphous form of the Nodax,"* Dr. Marcott says.

Three searches in, each taking less than a minute to run, Dr. Marcott has managed to fully identify every layer in the laminate.

Although all the layers were correctly identified, the case clearly shows that KnowItAll should not be thought of as a black box. Understanding how excitation wavelength affects Raman signals and how crystallinity can shape an IR peak was critical for Dr. Marcott to get the right compounds. In other words, training one's interpretation skillset and knowledge of spectroscopy should be a priority for any KnowItAll user.

At the same time, both the software and the large library proved powerful tools, even for an IR expert such as Dr. Marcott. *"I used to think KnowItAll was a crutch [because] I'm good at spectral interpretation,"* he says. But the scale of the library, which contains more than 300,000 spectra, is hard to beat. *"No one can interpret 300,000 spectra."*

In the webinar, Dr. Marcott goes through two additional examples, one examining silver added to a polyethylene terephthalate (PET) knit fabric and one investigating contaminants on hair. These demonstrate the breadth of polymer and polypeptide questions that can be tackled using combined IR and Raman.

So, whether your goal is to familiarize yourself with the competition, understand what is happening at the molecular level of your new product, or investigate biological specimens, Wiley Science Solutions' KnowItAll software package can help you get the most out of your spectra and your sample.

Citations and Sources

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