Identify an Unknown Sample with ATR

Your FTIR spectrometer and OMNIC Paradigm software can help you determine what's in an unknown sample. This article demonstrates how to measure and analyze a sample using the Attenuated Total Reflection, or ATR, sampling technique. It is a common and "mess-free" technique for acquiring FTIR data from a sample material. This article includes a number of examples to help you build confidence in interpreting your analysis results.

You will learn how to:

- Prepare the ATR accessory
- Set up and run the analysis, and
- Evaluate and confirm the results

Follow these instructions to measure and analyze an unknown pure sample using the ATR sampling technique.

Prepare the ATR Accessory

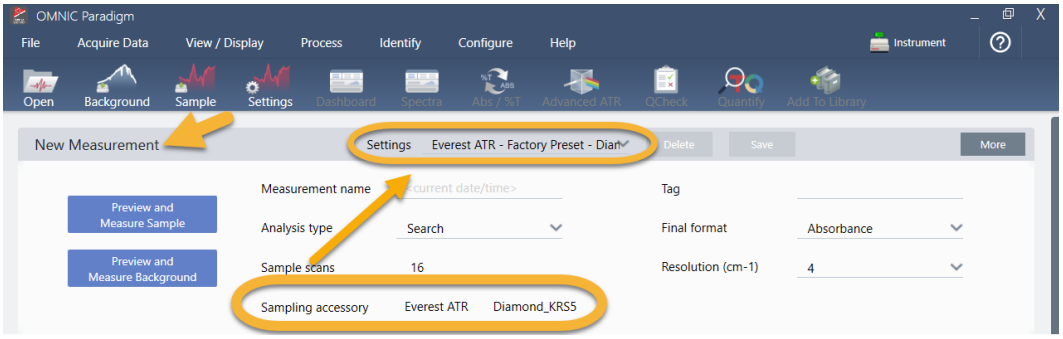
To begin, make sure your ATR accessory is inserted in the spectrometer sample compartment and that it has an appropriate crystal installed. Each crystal material provides some kind of sampling advantage such as a wider spectral range, a higher energy throughput, or more durability. The correct choice depends on what crystals are available, which one works best with your sample material, and which one produces the needed information. See the information that came with your ATR accessory for more information.

Here is the Thermo Scientific™ Everest ATR accessory with a diamond crystal installed in our Nicolet™ Summit FTIR spectrometer.

Make sure the crystal is clean so the spectrometer can take an accurate background measurement when it's ready. To clean the crystal, dab it with a soft cloth. If the crystal requires more rigorous cleaning, check the user guide that came with your ATR accessory. The guide should list appropriate cleaning solvents for each crystal type.

Set Up the Analysis

The next step is to set up the OMNIC Paradigm software. After you open the software, you see the dashboard in the main window. The important measurement settings are at the top.



First, make sure the Sampling Accessory readout shows the installed accessory. If it doesn't, reseat the accessory. Notice that the factory presets for that accessory appear under "Settings."

Then enter a measurement name, or you can leave the suggested name, which is the exact date and time of the measurement.

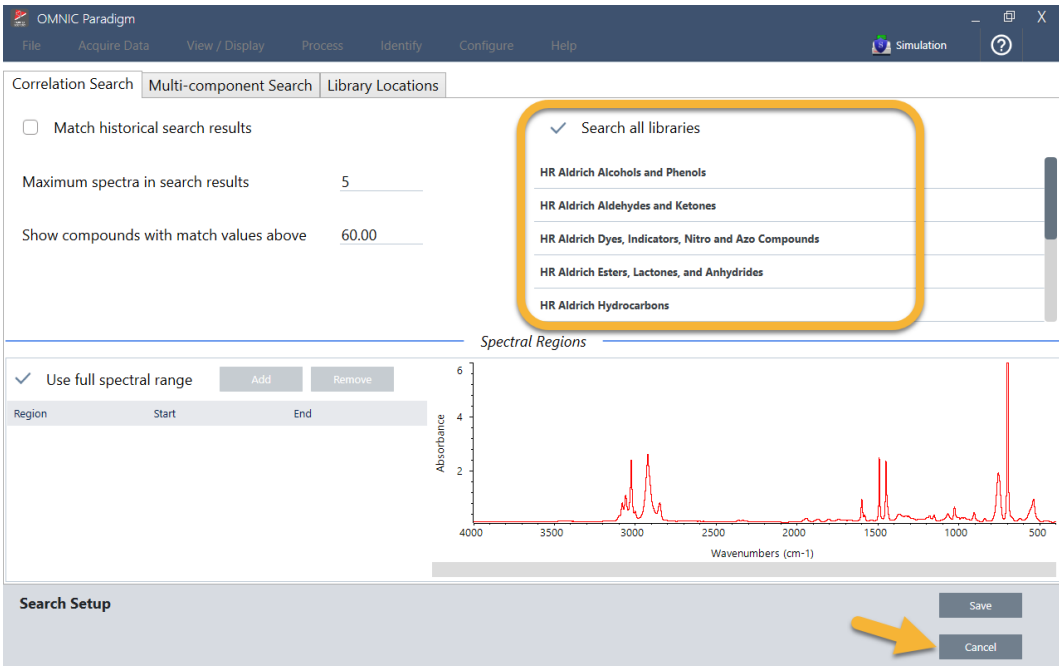
Next make sure the Analysis Type is set to Search. This performs a point-by-point comparison of the sample spectrum against FTIR library spectra. The quality of the output depends on the source and quality of the spectra in the selected libraries.

Finally, check the acquisition settings (sample scans, resolution and final format). The settings shown above are all good starting values for this analysis.

It's important to note that the quality of the sample data you acquire will affect the analysis results. For example, speeding up the analysis by measuring fewer scans, or decreasing the resolution could lead to a less certain analysis result.

Consider Your Spectral Libraries

All existing spectral libraries are selected automatically by default. Choose **Search Setup** in the Identify menu to view or change your library selections.



For this demonstration, we are using the free libraries provided with OMNIC Paradigm software.

Choose **Cancel** to close the Search Setup window.

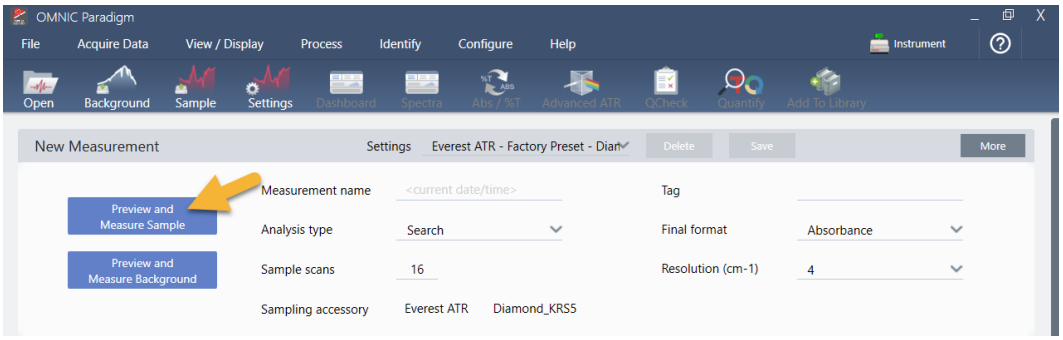
You can also use the Library Manager in the same menu to easily create a spectral library. Any libraries you create should be from pure materials that represent what you expect to find in your unknown samples.

The library spectra are normally the same quality or higher quality than the sample spectrum. It is also helpful if they are acquired using the same sampling technique (ATR in this case). If your library spectra were acquired using the transmission technique, OMNIC Paradigm software has a correction that can be applied to the sample spectrum to improve the results. You'll learn more about that later in this article.

There is no need to perform conversions such as final format, resolution or spectral range on the sample data before performing a search—the software does that for you.

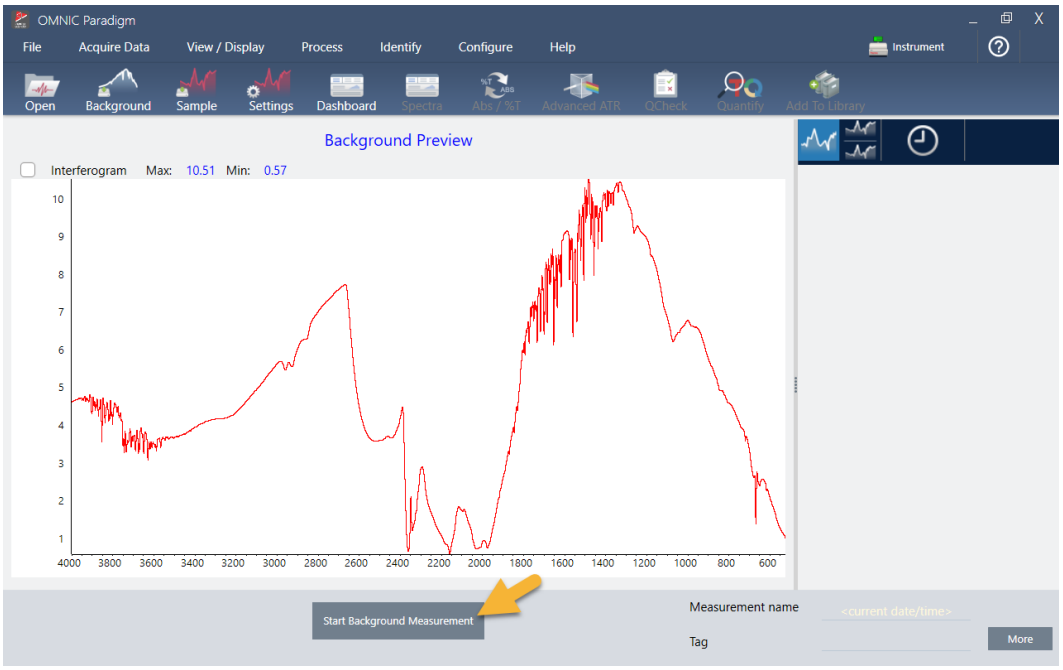
Measure and Analyze the Sample

To start the analysis, click **Preview and Measure Sample**.



The analysis starts with a background measurement. The only requirement for an ATR background is to make sure the crystal is clean. The background spectrum is used to eliminate any signals in the sample data that are due to the spectrometer, the ATR crystal, or the background environment.

The software shows a preview of the current background spectrum in the spectral pane. The background shape shown below is typical for a diamond crystal.

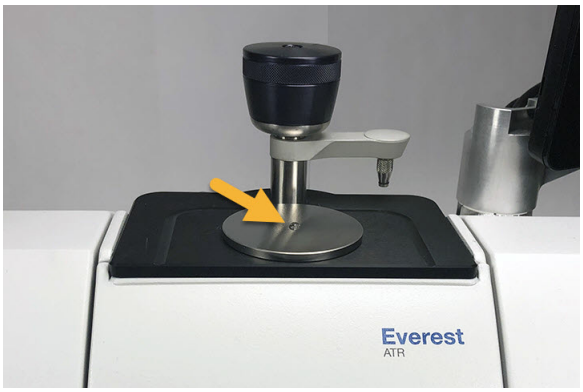


Click **Start Background Measurement**.

When the background measurement is completed, its image appears in the results panel and in the spectral pane.

If your sample is a liquid, raise the pressure tower and rotate it out of the way. Use a clean pipette to place a single drop on the crystal. Keep in mind that crystal types vary in size and some may require more sample. Use just enough sample to cover the crystal completely.

Figure 1. Measure a liquid with ATR

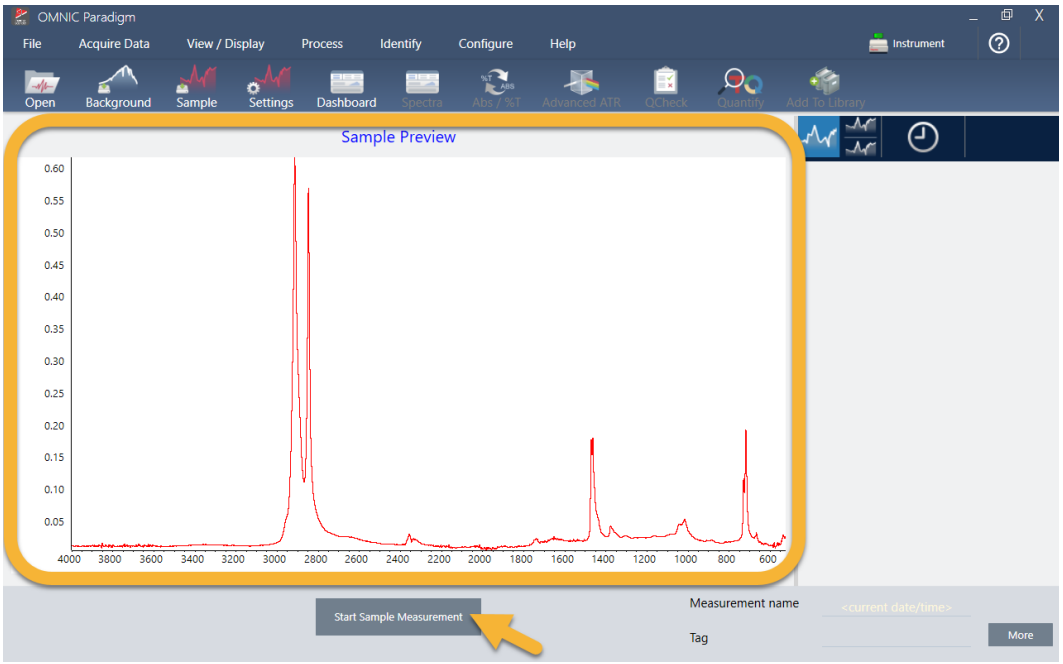


The pressure tower should not be used when analyzing a liquid sample

For a solid sample, rotate the knob on the pressure tower counterclockwise to raise the arm. Then place the sample on the crystal and rotate the knob clockwise to lower the arm. Continue to rotate the knob until clicks. For this demonstration, we are measuring a plastic bag.

Figure 2. Measure a solid with ATR

Once a sample is in place, click **Preview Sample** to preview the sample data in the spectral pane. If the peaks in the preview spectrum are very small, use a more concentrated liquid sample. If you are measuring a solid, reposition the sample on the ATR crystal and reapply pressure.



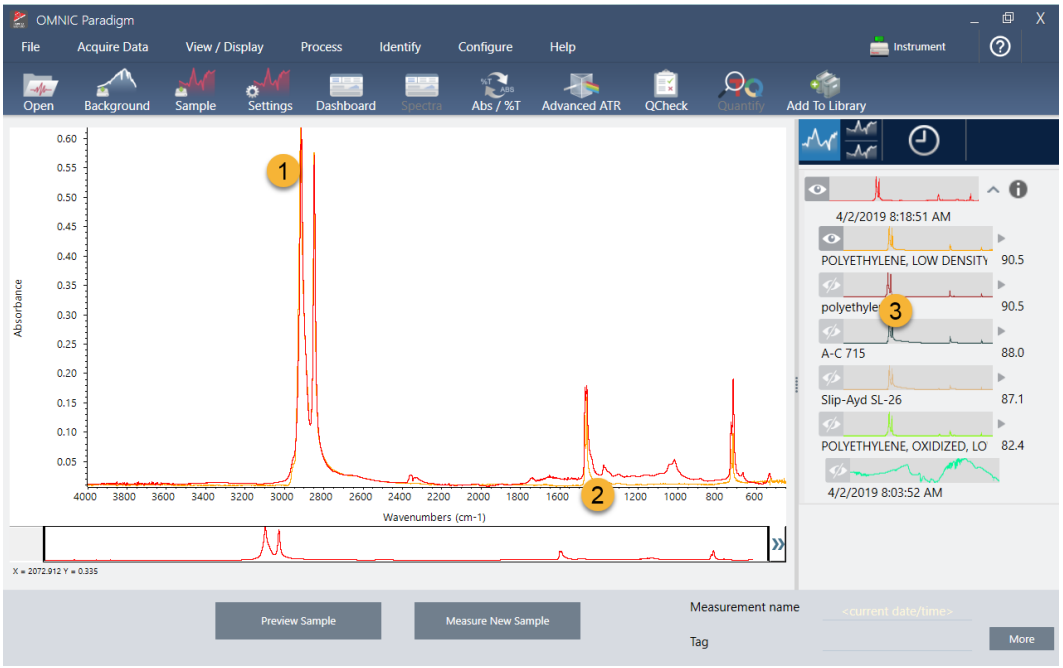
If the spectrum has no sample peaks, check that the sample material absorbs energy in the infrared region of the light spectrum. If you observe extra peaks in the spectrum, make sure the crystal is clean.

When you are ready to continue, choose **Start Sample Measurement** (see the previous image) and wait for the progress bar to complete. The software quickly compares the sample spectrum to the selected library spectra and shows you the results.

What's in My Sample?

The spectral pane shows the sample spectrum along with the best matched spectrum from the selected libraries. The two spectra are overlaid with the same Y-axis scale so you can compare the results visually. (If the spectra are very similar, as in this case, there are other views that will highlight the differences. We'll talk more about that later.) The results panel shows a list of the 5 best matched spectra, along with their match values.

Figure 3. Sample and top search result displayed together using the same Y-axis scale

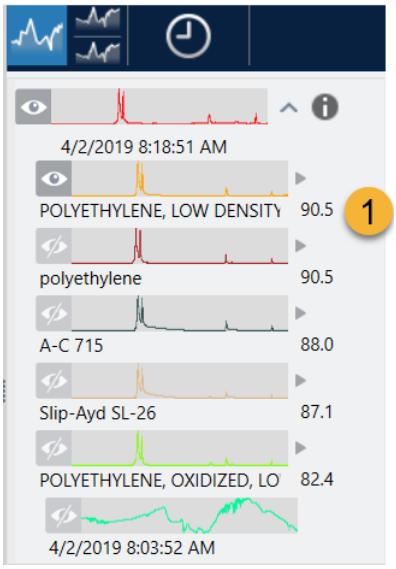


1. Sample spectrum (red)
2. Best match (yellow)
3. Results panel
4. Stack button

The match values tell you how well each library spectrum matches the unknown sample. The closer this value is to 100, the better the match.

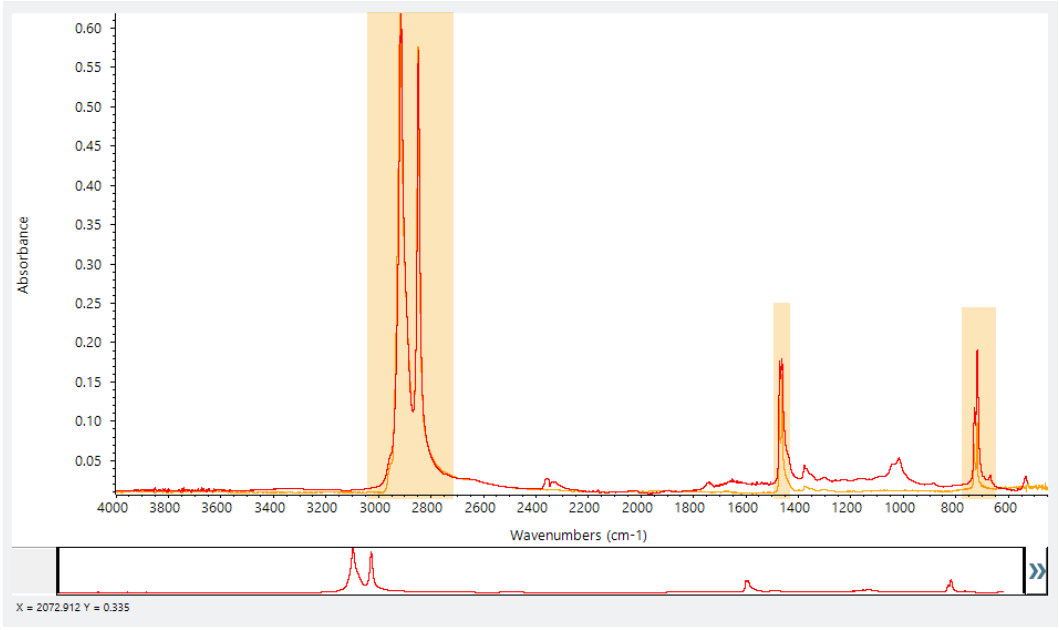
In this example, the top two matches (the same compound from two different libraries) have match values that are above 90, which indicates a good match. The match value for the next spectrum in the list is well below that.

Figure 4. Match values showing a clear best match



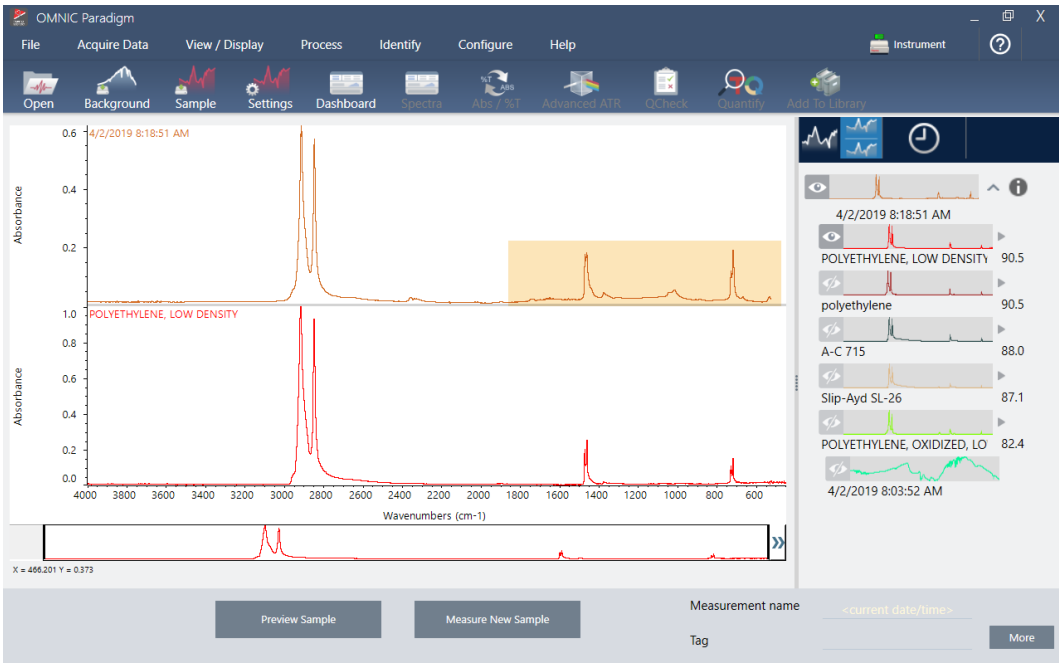
If we look at the overlaid spectra in the spectral pane, the positions of the main peaks line up along the X-axis, and they differ only in their peak heights.

Figure 5. Overlaid spectra showing a clear match



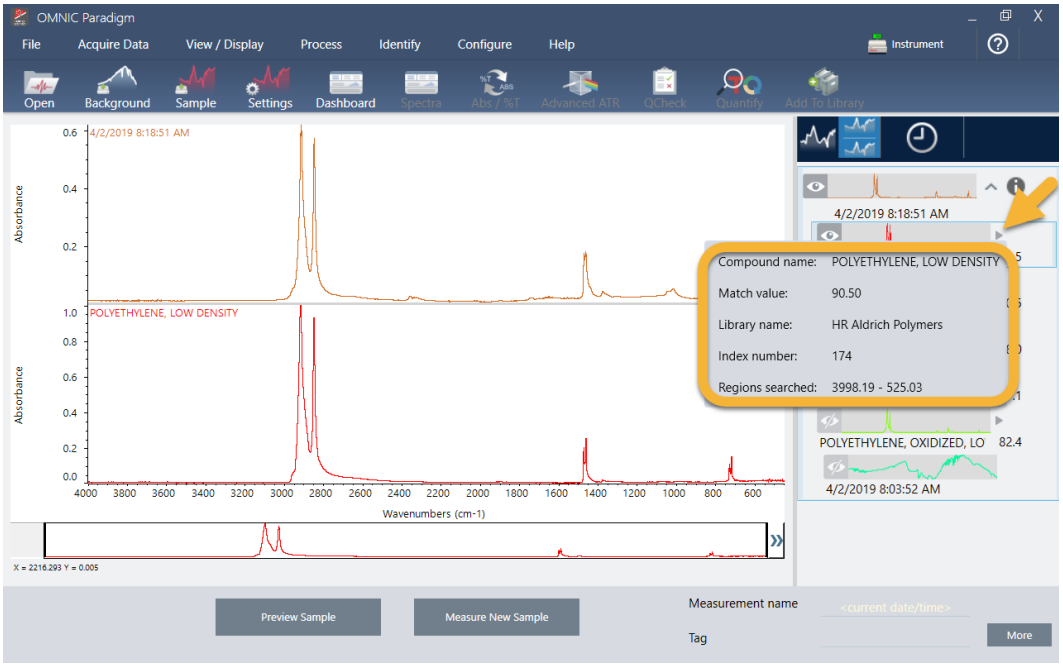
Click the Stack button to see the two spectra scaled to fill each Y-axis. Again, the spectra are well matched except for the raised baseline in the sample spectrum's low frequency region. As a result, we can conclude that the sample is polyethylene and the analysis is complete.

Figure 6. Stacked spectra showing a minor difference in the low frequency region



To get more information about a spectrum in the match list, including the library it came from and its ID number, click the spectrum's grey arrow in the results panel.

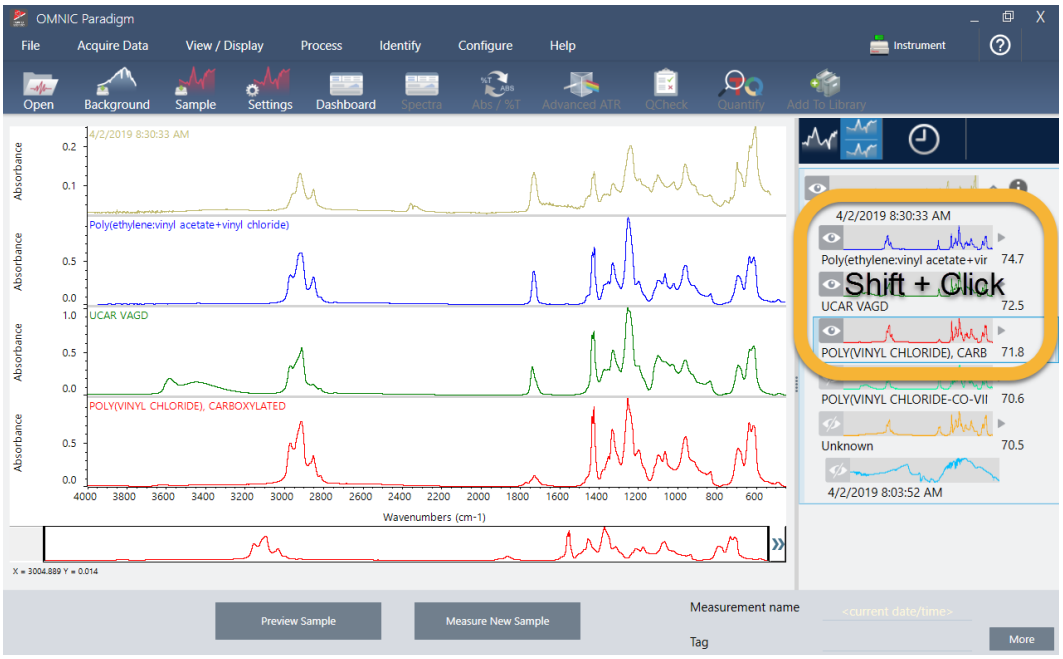
Figure 7. Information button for a library spectrum



What if there isn't a clear (single) match?

If the analysis results show several matches that all have similar match values, as in this example, Shift + click the three matches in the results panel to add all three spectra to the spectral pane.

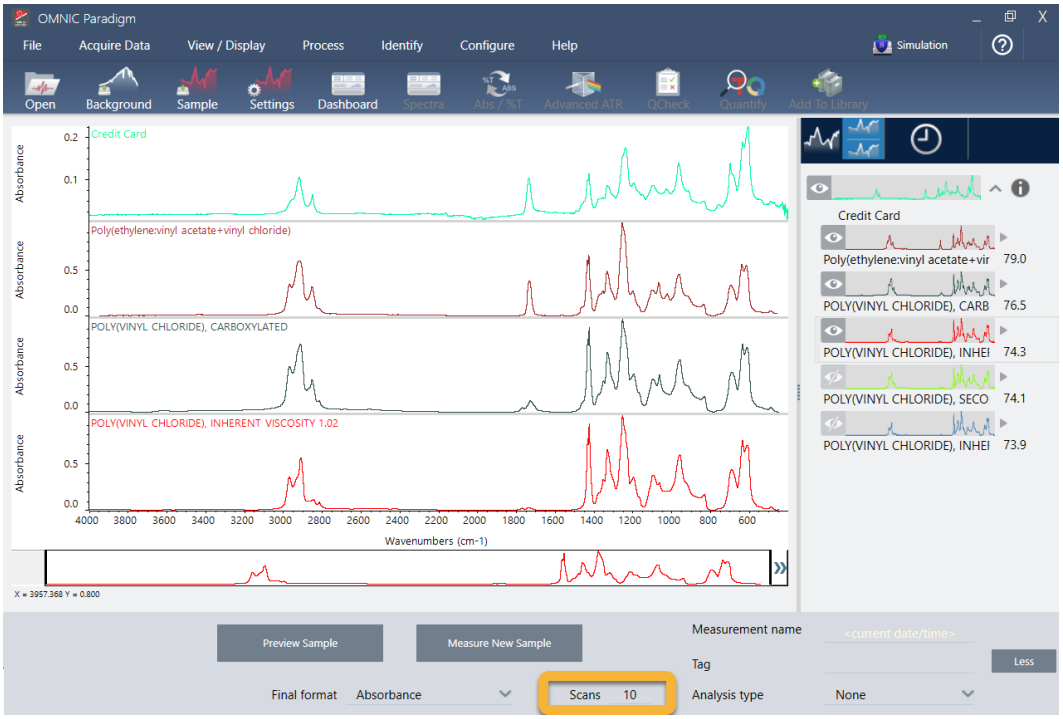
Figure 8. Stacked spectra showing several similar matches



How can I improve my analysis results?

If no clear match appears, there are a number of options to consider that may improve your results. (Some setting adjustments will require a new background measurement.)

Figure 9. Search results with changeable measurement settings displayed



For starters, you can return to the dashboard and adjust the Resolution setting for the unknown sample. For example, you can acquire the spectrum at a higher resolution by using a lower Resolution setting. If the sample peaks are sharper or more numerous, you may get a better analysis result.

You can also acquire more scans (see image above) to reduce spectral noise, which can also affect the results. Then restart the analysis by choosing **Identify** (menu) > **Correlation Search** or click the **Search** button on the toolbar.

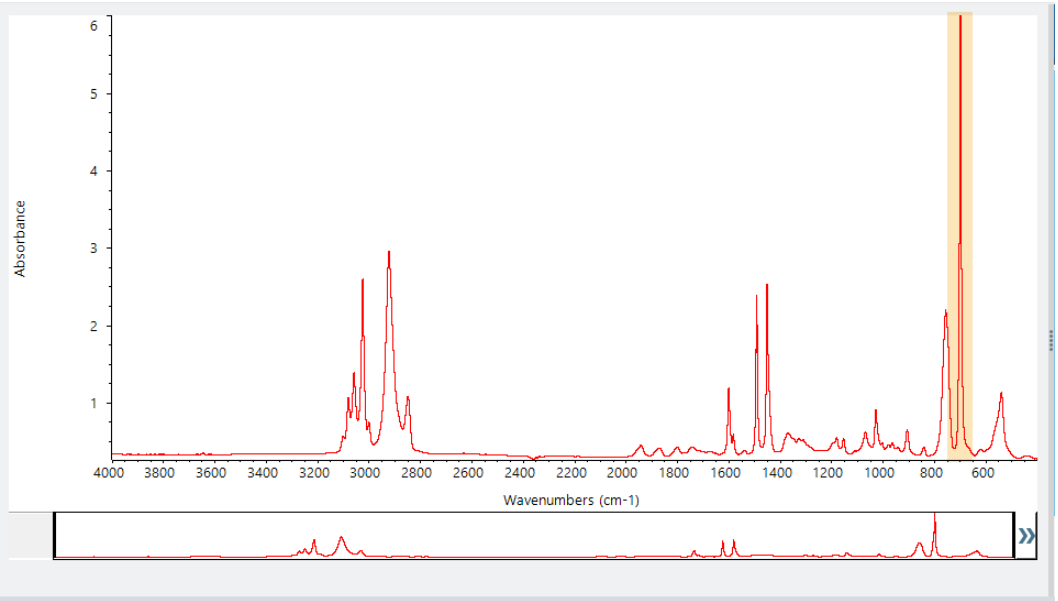
If the sample spectrum has a tilted or curved baseline, try applying Automatic Baseline Correction (Process menu) to your sample spectrum and then restart the analysis.

If you need to search against transmission spectra, try using the Advanced ATR Correction (Process menu) and then repeat the analysis. This correction adjusts an ATR spectrum so that it looks more like a transmission spectrum, which can improve the results.

How to Specify the Spectral Region for the Analysis

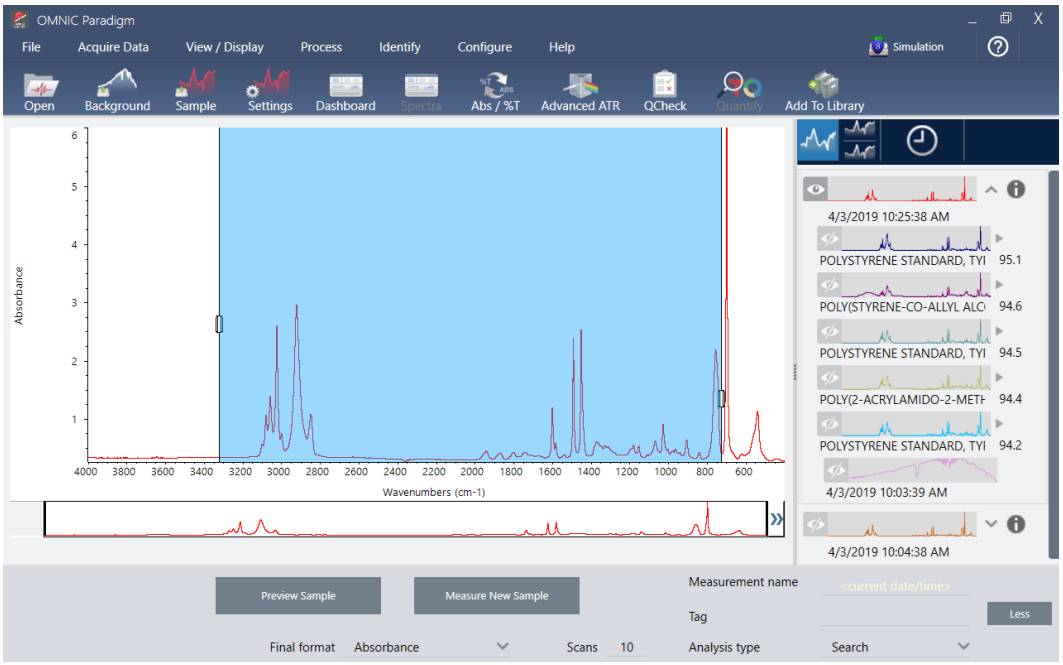
If your sample spectrum has a peak that is so large it is off the Y-axis scale, you may want to exclude that peak from your analysis. Here is an example:

Figure 10. Example of a totally absorbing peak



These “flat topped” peaks are referred to as “totally absorbing” and can contain excessive spectral noise, which affects the analysis results. To exclude a totally absorbing peak, right-click the sample spectrum and choose **Add Region**. Use the vertical bars to select a region that excludes the peak in question and then rerun the analysis.

Figure 11. Using Add Region to exclude a peak from the search



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