Application Note: 50745

Improving Search Results Using High Resolution Libraries

Key Words

- High Resolution Spectra
- Identifying Unknowns
- Library Search
- Spectral Match
- Spectral Subtraction

Introduction

Spectroscopists are often faced with the problem of identifying an unknown compound from a measured spectrum, defining what impurities are found in a sample, and verifying sample integrity. All of these applications can be solved by performing a spectral search.

In the past, spectral searching was done using deresolved or low resolution spectra. However, the availability of more affordable disk storage space and the introduction of faster computers combine to make searching higher resolution spectral libraries a much more viable and attractive option. The benefit of using the high resolution libraries, available from Thermo Fisher Scientific, is greatly improved spectral search results.

In addition to standard deresolved spectral data bases that contain spectra at 16 cm^{-1} resolution with data points every 8 cm^{-1} and 8-bit ordinate precision, Thermo also offers high resolution, 4 cm^{-1} spectral libraries with data points every 2 cm^{-1} and 16-bit ordinate precision. Searching with the high resolution, 4 cm^{-1} library vs. the standard deresolved, 16 cm^{-1} library results in improved spectral matches, enhanced spectral subtraction results, and overall better search results.

Improved Spectral Match

High resolution libraries will improve the spectral match between the unknown sample and the library sample spectra since these libraries contain more spectral information and are more similar to the sample being collected. Comparison of the number of data points collected for both high and low resolution libraries shows that there are four times more points collected for a 4 cm^{-1} resolution spectrum, resulting in four times the information found in a deresolved spectrum. The 4 cm^{-1} spectra found in the high resolution libraries are also more similar to the sample spectra typically collected at 4 cm^{-1} resolution. When the sample and library spectrum are collected at the same resolution, the number of points collected and the data spacing are identical, resulting in peak heights and band shapes that more closely resemble one another.

Figure 1 shows three different spectra of a polypropylene sample. The top spectrum is a 25 µm film produced with the Spectra-Tech Universal Film Maker™. The bottom two spectra were copied from the high resolution and deresolved Hummel Polymer spectral libraries respectively. From this plot we can see differences in the spectra over a wide range as well as a detailed look at the region from 1600 to 600 cm^{-1}. The effect of lower resolution on a spectrum is seen on the full range plot, but the loss of spectral information is more pronounced when comparing the two spectra over the narrow region shown.

A significant amount of information is lost in the lower resolution spectrum, and this loss of information is enhanced when the spectrum contains narrow bands or subtle spectral features. Since there are fewer data points collected in the lower resolution spectrum, more space exists between the points collected and more information is lost between data points. This loss of data results in lower intensity peaks that do not accurately represent the sample.

An example of the effect of resolution on a narrow band can be seen in the peak at 1380 cm^{-1} in Figure 1. The intensity of this peak drops from 0.5 absorbance units to 0.35 absorbance units in the deresolved spectrum. When spectral features are small, the information in a deresolved spectrum may be lost completely. Both peaks at 1435 and 1360 cm^{-1}, found on the shoulder of a stronger absorbing peak, are easily distinguished in the unknown sample spectrum and the high resolution library spectrum; however, this peak can not be seen in the 16 cm^{-1}, low resolution library spectrum.

Improved Spectral Subtraction Results

Library spectra are also commonly used to determine what impurities are present or if an additive is contained within a sample. Performing a spectral subtraction of the known component using the spectrum from a library may reveal the sample impurity. A high resolution library spectrum will enhance results obtained when performing this operation.

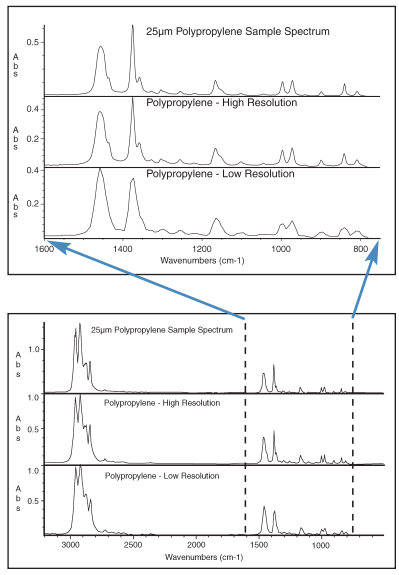

Figure 1

Figure 2 shows an example of the advantage of using the high resolution libraries for spectral subtraction. The top spectrum is a 4 cm^{-1} resolution

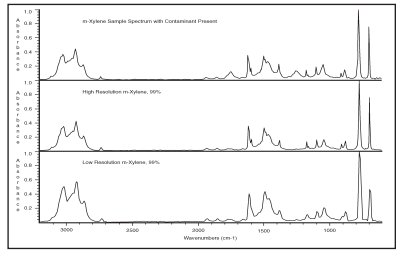

Figure 2

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spectrum of m-xylene with 1% ethyl acetate contaminant. The second and final spectra are pure m-xylene spectra from the high resolution and deresolved Aldrich Condensed Phase Supplement Libraries respectively. Two "extra" peaks are found in the sample spectrum, one at 1740 cm^{-1} and the other at 1245 cm^{-1}. A spectral subtraction can be performed to determine the identity of the impurity.

The interactive subtraction of the high resolution spectrum of m-xylene from the sample spectrum is shown in Figure 3. Figure 4 shows a search of the subtraction result with the high resolution Aldrich Condensed Phase library, which reveals the contaminant to be ethyl acetate. When a subtraction is performed with a low resolution library, the sample spectrum must be deresolved to match the resolution of the library spectrum. Deresolving the sample spectrum results in a loss of spectral information and produces spectral artifacts including negatively absorbing peaks in the subtraction result.

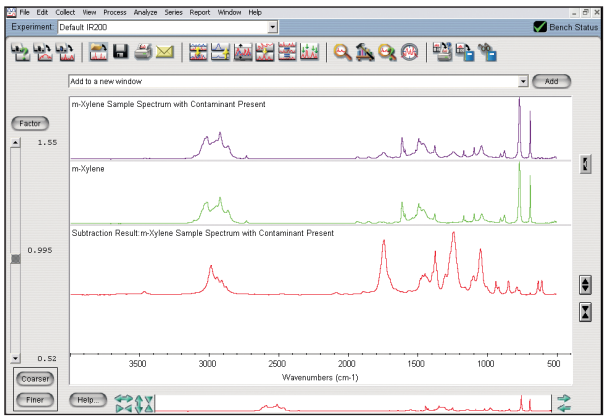

Figure 3

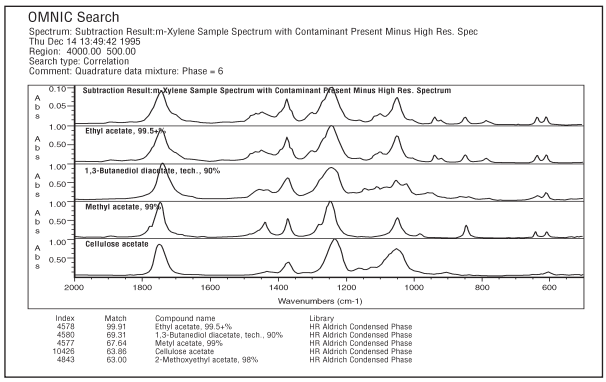

Figure 4

Improved Search Results

High resolution libraries not only improve the spectral match between the sample and library spectrum, they also improve search results. The higher resolution libraries contain spectra that are more similar to the spectra collected in your lab. Searching with high resolution libraries will not necessarily increase the match number obtained; however, the difference between the first and second match in the search list will increase.

The match number is a measure of how well your sample spectrum matches a spectrum from the chosen library. A match number of 100 indicates a perfect match. This number alone, however, does not confirm an acceptable spectral match. A better measure of the search results is obtained through comparison of the match number from the first, second, and possibly third spectrum selected as the best match for the sample spectrum. If there is a small difference between match numbers, the sample could be any one of the compounds chosen and search results are less definitive; by using high resolution libraries the difference between match numbers of the selected compounds increases.

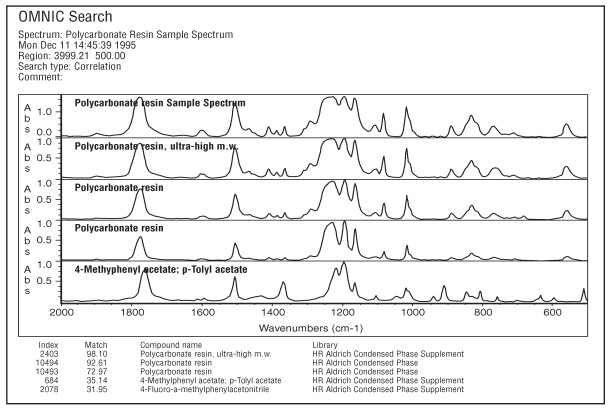

Figure 5a

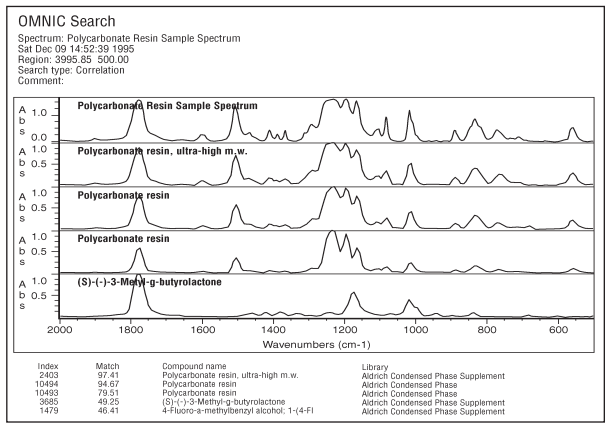

Figure 5b

The spectrum of a 15 µm film of polycarbonate resin was collected at 4 cm^{-1} resolution by transmission and then searched using the high and low resolution versions of the Aldrich Condensed Phase and Aldrich Condensed Phase Supplement Libraries. The results of the searches can be seen in Figures 5a and b. The match number using the high resolution library is slightly higher for this sample, but the advantage of using high resolution libraries is seen in the difference between the first, second, and third match numbers. The high resolution results have 6 units between the first two matches where the low resolution results have fewer than 3 units difference.

Conclusions

Several advantages exist for using high resolution libraries to spectrally search the sample spectrum. High resolution libraries contain spectra with more spectral information, enhance results obtained from a spectral subtraction, and produce improved search results. Whether using libraries to identify an unknown sample, to determine what impurities are contained in an otherwise known sample, or to verify the sample integrity, a 4 cm^{-1}, high resolution library will improve the results.

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