

Search Strategies for IR Spectra - Searching ATR Spectra Against Transmission Data

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Attenuated Total Reflectance (ATR) spectroscopy is used in many facilities for analyzing various materials. A spectrum collected using this technique can differ from a spectrum collected using a transmission technique, particularly in the relative intensities of the bands. Most commercially available databases and proprietary databases have been collected using transmission techniques. This difference in technique, if not accounted for, can present difficulties when trying to search commercial or proprietary databases.

The pathlength for an ATR experiment varies directly with the wavelength of light used. The pathlength for a transmission experiment is constant throughout the experiment. The result, when comparing spectra from these two techniques, is that the ATR spectrum will have weaker peaks in the high wavenumber (shorter pathlength) regions and stronger peaks in the low wavenumber (longer pathlength) regions. Thus, the spectroscopist must have a means of reconciling these variations in effective pathlengths. This can be accomplished in two ways. One method is to limit the range of a full spectrum search. By limiting the range to a narrow region (about 100 - 500 wavenumbers), you can minimize the effect of the differences in relative intensities. However, with a severely limited range you may eliminate much of the information content of the spectrum which the search algorithm uses to discriminate between results.

A second method is to correct the absorbance of the ATR spectrum to account for the differences in the pathlength. If you have Bio-Rad's KnowItAll® software, this is an easy procedure. Just select the ATR correction from the process menu and click on done. If you do not have Bio-Rad's software, then you will likely have this option available within your instrument's software. However, you may need to know the refractive index of both the crystal used and the unknown material. You will also need to know the angle of incidence of the infrared light. (Note: These parameters are only required for quantitative

measurements; they are not necessary for qualitative measurements such as spectral searching where the intensities are normalized.)

An Example

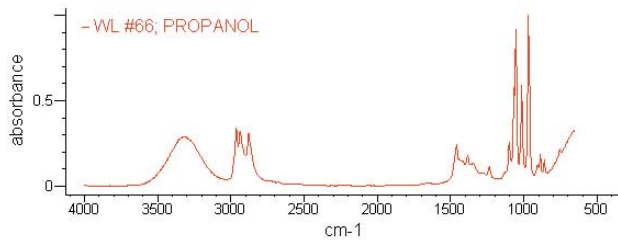
To illustrate the utility of Bio-Rad's easy ATR correction outlined above, some comparisons were made between identical samples in the Sadtler Solvents (Unblended) Database (designation LL) and our Sadtler Solvents by ATR Database (designation WL). Two crystals were used in the collection of the ATR of solvents database and an example from each is presented below. Table 1 summarizes the database search information and Figures 1 and 2 show the actual spectra. The hit indices are based on the Euclidean distance spectral matching algorithm.

For these two samples, the hit indices for ATR corrected spectra relative to databases of transmission type spectra are much better than for the ATR spectra that have not been corrected (HQIs of 636 and 582 versus HQIs of 805 and 898 for the ATR corrected spectra).

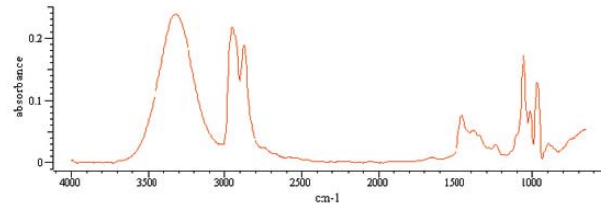
Conclusions

The ATR correction improves the quality of hits found by the search algorithms. The correction results in loss of all quantitative information, but the quantitative information is not used with the search algorithm.

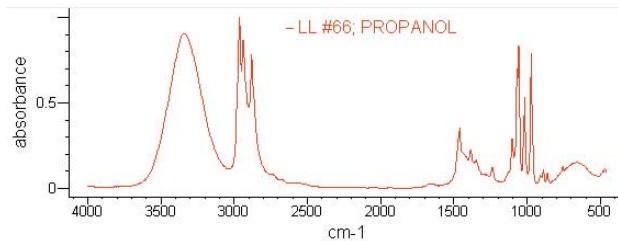
**Uncorrected ATR Spectrum
PROPANOL**



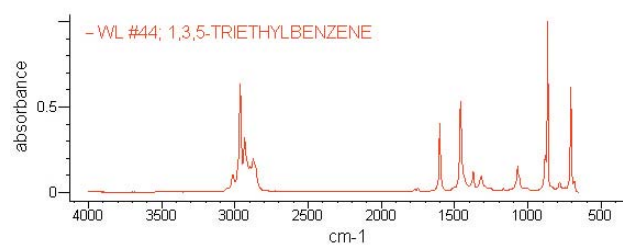
**ATR Corrected Spectrum
PROPANOL**



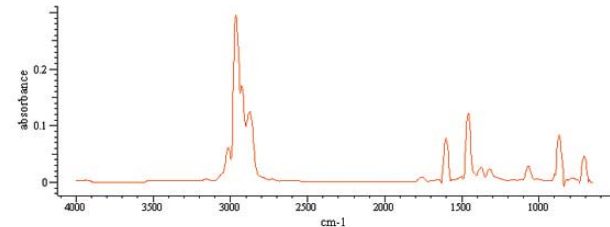
**Spectrum collected as transmission
LL66 PROPANOL**



**Uncorrected ATR Spectrum
1, 3, 5-TRIETHYLBENZENE**



**ATR Corrected Spectrum
1, 3, 5-TRIETHYLBENZENE**



**Spectrum collected as transmission
LL44 1, 3, 5-TRIETHYLBENZENE**

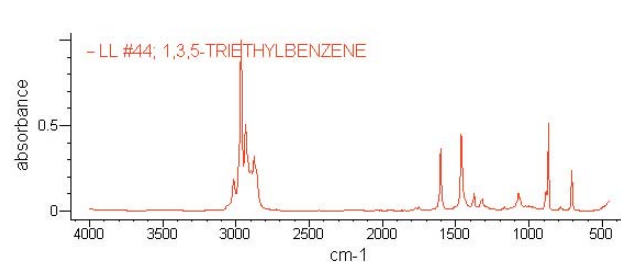


Figure 1. Spectra of propanol. Top: ATR spectrum, Middle: ATR corrected spectrum, Bottom: Database spectrum collected as transmission.

Figure 2. Spectra of 1,3,5 triethylbenzene. Top: ATR spectrum, Middle: ATR corrected spectrum, Bottom: Database spectrum collected as transmission.

"Unknown" ATR Spectrum	ATR Crystal	Hit Quality Index (HQI 999 = exact match)	
		uncorrected spectrum	ATR corrected spectrum
1, 3, 5-Triethylbenzene propanol	Ge	636	805
	ZnSe	582	898

Table 1. Result for uncorrected ATR and ATR corrected spectrum against a non-ATR database.



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