

Advanced ATR Correction Algorithm

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Key Words

- ATR and Search
- Convert ATR to Transmission Spectrum
- Frequency Shift
- Search Quality

Introduction

Attenuated total reflection (ATR) is now the most common sampling technique in FT-IR spectroscopy. The profusion of ATR accessories on the market today attests to the utility of the technique. Each accessory is designed to achieve optimum performance with a particular sample type. Diamond ATR devices, such as the Thermo Scientific Smart Orbit accessory, are highly suitable for hard or corrosive samples, whereas a germanium accessory is preferred for highly absorbing materials. The development of these accessories has greatly simplified sampling for FT-IR spectroscopy. However, ATR does present some challenges. An infrared spectrum of a sample obtained using an ATR accessory is not identical to the spectrum obtained by transmission. The ATR technique introduces relative shifts in band intensity and absolute shifts in frequency. The relative intensity shift is well-known and is readily corrected. The shift in frequency, which can result in a displacement of the peak maximum by several wavenumbers, is at once more serious and yet less often accounted for. As most commercially available spectral libraries and published peak tables contain and refer to transmission spectra, differences between ATR and transmission spectra can lead to poor spectral search results and ambiguous interpretation. This technical note explains the reasons for these differences and demonstrates a technique for their correction.



Figure 1: Smart Orbit diamond ATR accessory

Comparison of ATR to Transmission Spectra

The transmission sampling technique dominated the first decades of infrared spectroscopy. The optical arrangement required for transmission sampling is very simple and introduces few artifacts into the spectra. Consequently, most published peak tables are derived from transmission spectra. Furthermore, most commercial libraries contain transmission spectra. Spectrometer validation tests are usually performed using transmission samples because the band positions of standard materials are well known in the transmission sampling mode.

The optics involved in ATR are quite different from those used in the transmission experiment. As a result, the infrared spectrum of a sample obtained by ATR exhibits some significant differences when compared to its transmission counterpart. Some of these differences are desirable and have been used to considerable advantage. An example of an advantage of ATR is that it is sensitive to the surface of the sample. As a result, the technique has found utility in the characterization of coatings and the identification of surface contaminants. Less desirable characteristics of ATR are its distortion of the relative intensities of bands and the introduction of a shift to lower frequencies.

The shift of peak positions to lower frequencies is particularly problematic. When a spectrometer is validated by comparison of a peak position in the transmission spectrum of a standard material to its accepted value, peak shifts due to ATR characteristics may be difficult to rationalize. Searching an ATR spectrum against a transmission database is also compromised by peak shifts.

The distortion of relative peak intensities in an ATR spectrum is well known. In the transmission experiment, the pathlength is defined by the thickness of the sample and is therefore constant across the spectrum. However, in the ATR experiment, the depth to which the sample is penetrated by the infrared beam is a function of wavelength, as presented in Equation 1 where d_p , λ , θ , n_1 , and n_2 are the penetration depth, wavelength, incident angle,

$$d_p = \frac{\lambda}{2\pi n_1 \sqrt{\sin^2 \theta - (n_2/n_1)^2}} \quad (1)$$

ATR crystal refractive index, and sample refractive index, respectively. The relative intensity of bands in an ATR spectrum increases with wavelength. If n_2/n_1 is constant or a smooth function over the frequency range of observations, the penetration depth increases linearly with wavelength. Most spectroscopic software packages include an ATR correction function that simply applies a linear ramp to the ATR spectrum in order to approximate the relative band intensities that would be found in a transmission experiment. However, because the refractive index of the sample, n_2 , changes sharply around absorption bands, the wavelength dependence of d_p is further modified according to $(\sin^2 \theta - (n_2/n_1)^2)^{-1/2}$.

The second characteristic feature is the shift of absorption bands to lower frequency. ATR intensity is given by Equation 2 when the sample thickness is greater than the penetration depth.

$$A = -\log_{10}(\text{ART}) = (\log_{10} e) \frac{n_2}{n_1} \frac{E_0^2}{\cos \theta} \frac{d_p}{2} \alpha \quad (2)$$

Where E_0 and α are the electric fields of the evanescent wave at the boundary and the absorption coefficient per unit thickness of the sample, respectively. As Equation 2 indicates, the ATR spectrum is influenced by the refractive index of the sample. Also, according to Equation 1, penetration depth, d_p , depends on n_2 . Thus, instead of α , $n_2 d_p \alpha$ determines the absorption band positions. Because of the anomalous dispersion of the refractive index, $n_2 d_p \alpha$ always introduces a band shift to lower frequency and this shift becomes particularly noticeable for strong bands. In other words, the presence of absorptions in the infrared spectrum represents a change in the refractive index of the sample across the band and results in the shift to lower frequency.

As stated previously, most spectroscopic software packages only correct for the relative band intensity described by Equation 1. This is done by simply applying a ramp function to the uncorrected ATR spectrum.

The advanced ATR correction algorithm introduced in OMNIC™ 6.2 software for Thermo Scientific Nicolet™ FT-IR spectrometers corrects for:

- The relative band intensity distortion caused by the dependence of d_p on wavelength.
- The shift of bands to lower wavenumber caused by dispersion of the refractive index.
- The deviation from Beer's Law caused by non-polarization effects.

In order to apply the advanced ATR correction, four inputs are required:

- The refractive index of the sample.
- The refractive index of the ATR crystal (or internal reflection element (IRE)).
- The angle of incidence.
- The number of bounces.

With these four inputs, the software automatically calculates the corrected ATR spectrum. The ATR spectrum itself is used to calculate the optical properties of the sample that lead to frequency shifts predicted by Equation 2.

Of the four parameters, three are determined by the accessory itself. The IRE refractive index is determined by the material of the crystal, and the angle and number of bounces by the design of the accessory. The index of refraction of the material depends, of course, upon the material. However, most organic materials have an index around 1.5; use of this value generally provides excellent performance of the correction. Some materials, such as high carbon black rubbers, have higher indices, but even there 1.5 provides a good starting point.

Demonstration of the ATR Correction Algorithm – Polycarbonate

In order to test the effectiveness of the advanced ATR correction software, the algorithm was applied to a challenging spectrum. The anomalous dispersion of refractive index that leads to the shifting of bands to lower wavenumber is seen most prominently in the intense bands of the spectra of materials of relatively high refractive index obtained on crystals of low refractive index, such as diamond, ZnSe and KRS-5. A sample that demonstrates the problem nicely is polycarbonate.

The spectra of polycarbonate as run by transmission and ATR are presented in Figure 2, together with the corrected ATR spectrum. The distortion of relative peak intensities in the ATR spectrum, as predicted by Equation 1, is evident in the middle spectrum. This distortion is largely eliminated by the advanced ATR correction.

The strong ester bands in the fingerprint region of the ATR spectrum show a marked shift to lower frequencies. The expanded ATR spectrum is shown in Figure 3, together with the transmission spectrum and the advanced correction spectrum for comparison.

The transmission spectrum of polycarbonate shows bands at 1232 cm^{-1} , 1194 cm^{-1} , and 1164 cm^{-1} . In the diamond ATR spectrum, these bands are shifted by 14.1 cm^{-1} , 7.7 cm^{-1} , and 5.8 cm^{-1} toward lower frequency. These large frequency shifts and peak intensity changes will degrade the performance of any computer search routine. The advanced ATR correction algorithm has corrected all of the differences in peak positions, relative intensity ratios, and even overall spectral patterns in this region, as shown in Figure 3. After advanced ATR correction the band shifts to lower frequency are reduced to 1.1 cm^{-1} , 0.3 cm^{-1} , and 0.1 cm^{-1} . The new band positions and intensities after advanced ATR correction greatly improves the spectral search for the polycarbonate sample run by ATR as seen in Table 1.

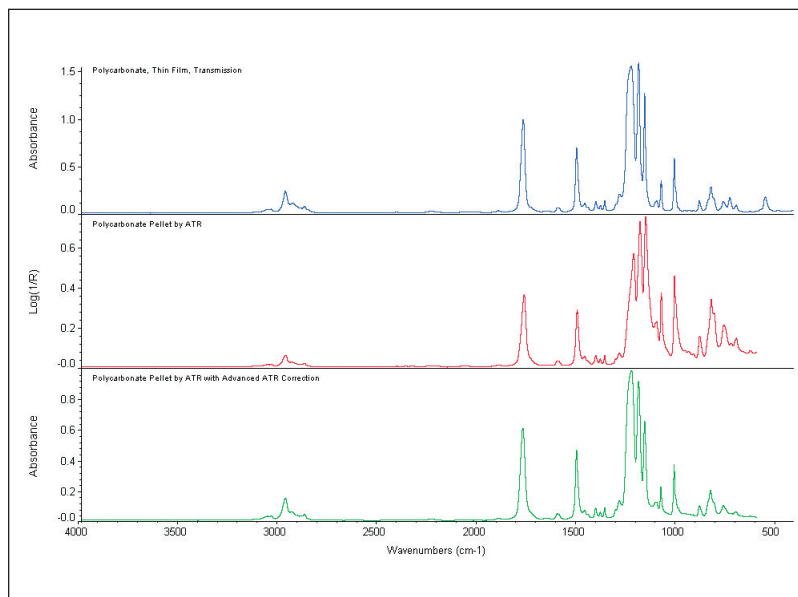


Figure 2: Polycarbonate FT-IR spectra run by transmission (upper), by ATR (center), and by ATR with advanced ATR correction (lower)

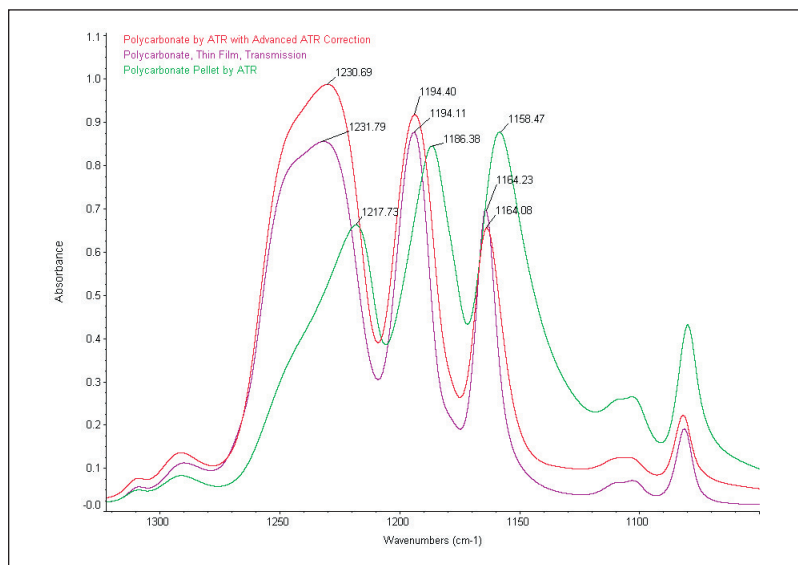


Figure 3: Expanded fingerprint spectral region for polycarbonate by ATR with ATR correction (upper), by transmission (middle) and by ATR (lower)

HIT #	TRANSMISSION	ATR	ATR CORR	ADV ATR CORR
1 Result	Polycarbonate	Polycarbonate	Polycarbonate	Polycarbonate
Match	99.39	67.01	68.85	98.53
2 Result	Polycarbonate	Polycarbonate	Polycarbonate	Polycarbonate
Match	97.94	67.01	68.85	97.03
3 Result	Polycarbonate	Polycarbonate	Polycarbonate	Polycarbonate
Match	97.92	60.12	61.63	97.03

Table 1: Comparison of spectral search results of polycarbonate run by transmission, by ATR, by ATR with basic ATR correction, and by ATR with advanced ATR correction

The column labeled 'ATR CORR' contains the results from a standard ATR correction algorithm that corrects for relative peak intensity only. As anticipated from theory, such an algorithm does nothing to correct for frequency shift and therefore has little impact on the search quality.

The column labeled 'ADV ATR CORR' contains the results from the Advanced ATR correction algorithm. Because the correction accounts for intensity and location shifts, the search results compare more favorably to the transmission match values.

Commercial libraries based on ATR spectra are available and have been proposed as a solution to the poor match of an ATR spectrum against a transmission library. The problem with this approach is that the distortions caused by the ATR technique are unique to the optical properties of the ATR device. Therefore, ATR libraries are of most utility when the spectra they contain are obtained on the same accessory used to collect the unknown spectrum to be identified. As the Advanced ATR correction algorithm corrects for the distortions caused by any ATR accessory, its application is more universal than a specific ATR library.

Conclusions

The ATR technique is highly popular and yet introduces some distortions into spectra. Such distortions create problems when comparing spectra obtained by ATR and transmission. The Advanced ATR correction algorithm corrects for band intensity distortion, peak shifts, and non-polarization effects. Corrected spectra are highly comparable to their transmission equivalents.

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