

Application News

No. A476

Spectrophotometric Analysis

Advanced ATR Correction to Convert ATR Spectra to Transmission Spectra

The ATR method is used not only for verification testing, it is a technique that is widely used for contaminant analysis. Comparing the spectrum acquired by the ATR technique with that obtained using transmission spectroscopy, the values indicated on the respective vertical and horizontal axes, in principle, are slightly different. Accordingly, an appropriate correction must be applied to the vertical and horizontal axes of the ATR spectrum when matching the ATR spectrum to a transmission spectrum or database to obtain more accurate results. Here, we introduce an advanced ATR correction processing feature which permits an ATR spectrum to approximate a transmission spectrum, along with an evaluation of the result.

■ Penetration Depth Dependency of Absorbance and Transmittance for ATR Spectrum¹⁾

When acquiring the infrared spectrum of a given sample, the sample's thickness and concentration must be optimized to prevent the occurrence of saturation when using the transmission method. On the other hand, when using the ATR method, an infrared spectrum of a sample depth measuring just a few μm from the sample surface can be acquired via close contact between the sample and prism, so optimization such as that with the transmission method is unnecessary. However, in the case of a spectrum acquired by the ATR method, the penetration depth of infrared light (dp) is not constant over the entire wavenumber range. Thus, when comparing spectra acquired using the ATR and transmission techniques, the lower the wavenumber region the greater will be the depth using the ATR method, resulting in peaks showing a trend of greater intensity. Shown below is the formula for calculating the theoretical penetration depth of infrared light using the ATR method.

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

Here, θ is the angle of incidence of infrared light, λ is the wavelength, and n_1 and n_2 are the refractive indices of the ATR prism and sample, respectively. Thus, it is clear from this expression that the penetration depth of infrared light (dp) is proportional to the wavelength (λ). However, the above expression holds true only if there is no peak in the infrared spectrum.

■ Peak Shift in ATR Spectrum¹⁾

When an infrared spectrum is acquired, typically, various peaks are obtained. If, indeed, a peak is obtained, its absorbance (A) is expressed by the following expression.

$$A = (\log_{10} e) \frac{n_2}{n_1} \frac{E_0^2}{\cos \theta} \frac{dp}{2} \alpha$$

Here, E_0 is the evanescent wave of the electric field, and α is the extinction coefficient corresponding to the sample thickness. It is clear from this expression that the penetration depth of the infrared light is different before and after the peak, and that a peak shift occurs in the lower wavenumber side when compared with spectra obtained by the transmission method.

■ Advanced ATR Correction

Shimadzu's Advanced ATR correction feature permits correction corresponding to changes in the ordinate / abscissa mentioned above. This process simultaneously corrects for:

1. Peak intensity changes due to wavelength dependence of infrared light penetration depth
2. Peak shift to lower wavenumbers caused by anomalous dispersion of the refractive index
3. Deviation from Lambert-Beer's law due to polarization characteristics

■ ATR Spectrum of Polycarbonate

Fig. 1 shows the infrared spectra of polycarbonate obtained using the ATR method and transmission method, respectively, and Table 1 shows the measurement conditions that were used. Here, the intensity of the transmission spectrum was corrected so that the absorbances would match in the vicinity of 1190 cm^{-1} to permit easier comparison with the ATR spectrum.

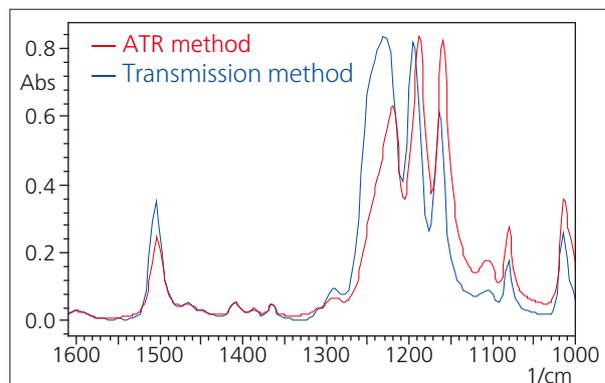


Fig. 1 ATR Spectrum and Transmission Spectrum of Polycarbonate

Table 1 Instrument and Analytical Conditions

Instruments	: IRTracer-100, DuraSampIR-II (ATR), MHP-1 (Transmission)
Resolution	: 4 cm^{-1}
Accumulation	: 45
Apodization	: Happ-Genzel
Detector	: DLATGS

It is clear from Fig. 1 that not only the peak intensities, but the peak positions as well are quite different using the two methods. Next, Fig. 2 shows an overlay of the ATR spectrum of Fig. 1 (red trace) in which ordinate correction of the penetration depth of the infrared light (ATR ordinate correction) has been applied, together with the transmission spectrum. It is obvious that the transmission spectrum cannot be approximated using ATR ordinate correction.

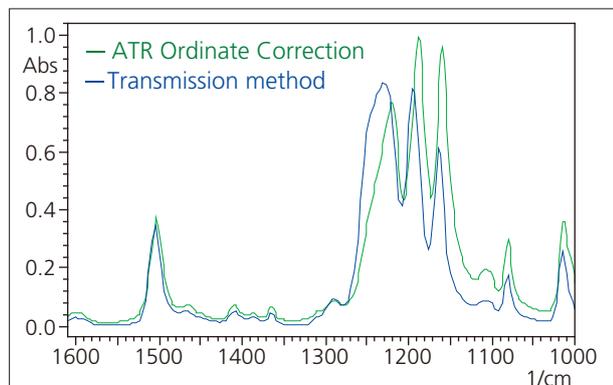


Fig. 2 Effect of ATR Ordinate Correction

Finally, Fig. 3 shows the overlaid ATR and transmission spectra, in which the Advanced ATR correction introduced here was applied to the ATR spectrum (red trace).

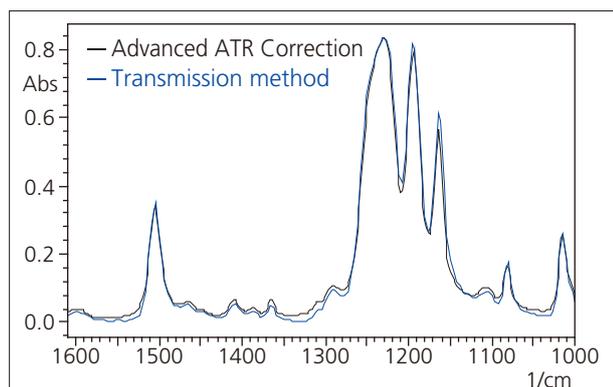


Fig. 3 Effect of Advanced ATR Correction

Comparing the spectrum processed using the Advanced ATR correction with the transmission spectrum, it is clear that extremely good approximation of peak intensities and peak shapes is obtained.

■ Influence on Search Result

We investigated the effect on the ATR spectrum hit rate during a search of a database created by the transmission method. Fig. 4 shows the search results obtained without correction of the acquired ATR spectrum, Fig. 5 shows the search results after ATR ordinate correction, and Fig. 6 shows the search results following advanced ATR correction. As can be seen from the results, the number of first place hits rose from 844 points, to 858 points and to 957 points, using no correction, ATR ordinate correction and Advanced ATR correction, respectively.

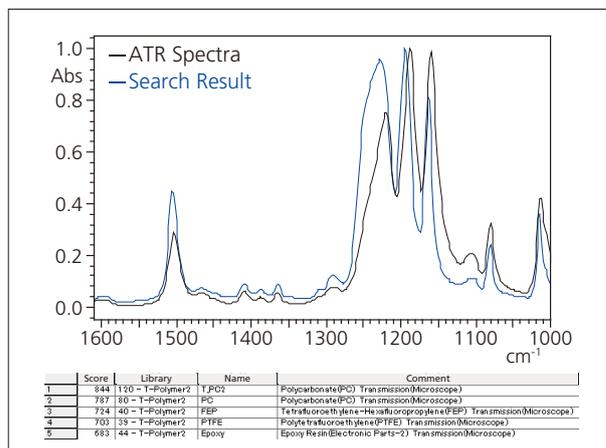


Fig. 4 Search Result Without Correction

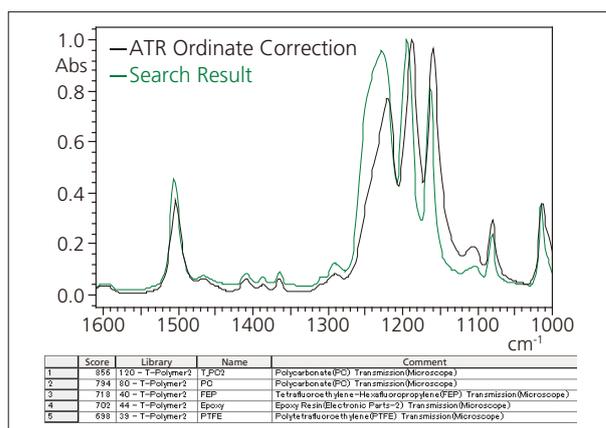


Fig. 5 Search Result after ATR Ordinate Correction

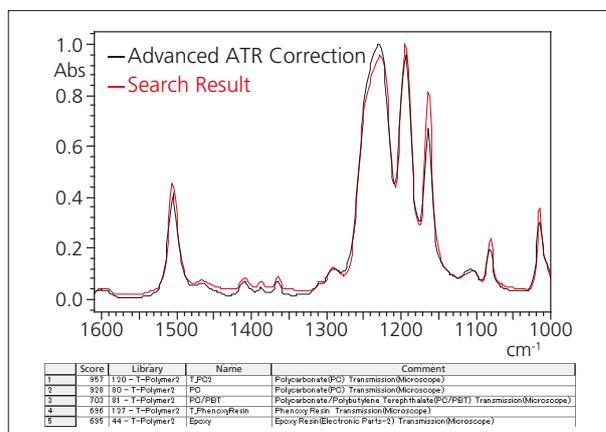


Fig. 6 Search Result after Advanced ATR Correction

■ Conclusion

Advanced ATR correction processing permits a spectrum obtained by the ATR method to approximate a spectrum obtained by the transmission method. This correction process makes it possible to obtain high-accuracy verification results even on the ATR spectrum hit rate during a search of a database created by the transmission method.

1) Materials Analysis by Infrared Spectroscopy Fundamentals and Application Koichi Nishikida, Reikichi Iwamoto, et al, Kodansha Ltd..