



**FT-IR Spectrometers**

# **ATR Accessories and Modules**

**Tips for ATR Sampling**

269-277600 Revision A

June 2012

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# Tips for ATR Sampling

Attenuated Total Reflection (ATR) is a sampling technique for infrared spectroscopy that requires little or no sample preparation. We offer a variety of Thermo Scientific ATR modules and accessories that fit various Thermo Scientific Fourier Transform InfraRed (FT-IR) spectrometers. This document explains the ATR technique and its implementation for FT-IR/ATR sampling.

## Contents

- [Understanding FT-IR/ATR Sampling](#)
- [Samples Compatible with ATR](#)
- [Typical ATR Spectra](#)
- [Optimizing ATR Data Collection and Analysis](#)

## Understanding FT-IR/ATR Sampling

Your success with FT-IR/ATR sampling will be somewhat dependent upon your knowledge and understanding of the technique. ATR measures the response when a reflected infrared beam comes in contact with a sample, producing a “transmission-like” spectrum. These characteristics are critical:

- The technique works only for samples that have an index of refraction that is below the refractive index of the ATR crystal.
- The infrared beam interacts only with the surface of the sample so this is the only area measured.

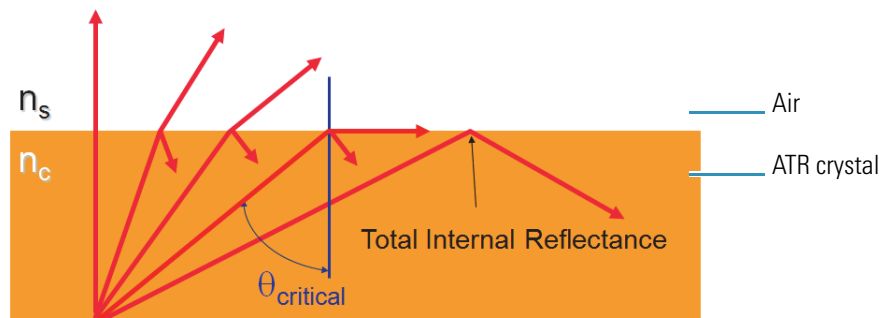
**Note** ATR can be useful for analyzing a uniform sample or the coating on a material such as a pharmaceutical tablet. If the surface composition does not represent the composition throughout the material, ATR may not be an appropriate for that sample, or the sample may need to be altered to obtain the desired information (see “[Samples Compatible with ATR](#)” for more information).

## How the ATR Technique Works

When light transitions between two materials that have different refractive indices, part of the light beam is refracted at the boundary surface and part is reflected. If the transition is from a higher refractive index material to a lower one, the incidence angle, or internal angle, is smaller than the transmitted, or external angle.

When the internal angle reaches a critical level, the external angle is 90 degrees and the propagation of light is parallel to the boundary surface. This is the critical angle ( $\theta_{\text{critical}}$ ) called out in the illustration below.

**Figure 1.** Critical angle



Where:

$n_c$  = Refractive index of crystal

$n_s$  = Refractive index of sample (or air)

If the internal angle is somewhat greater than the critical angle, all of the light reflects internally off the boundary surface. This is the “Total Internal Reflectance” beam called out in the illustration above. A common use of this phenomenon is a critically cut diamond (it maximizes the sparkle).

Similarly, if we direct the infrared beam from an FT-IR spectrometer into an ATR crystal at an angle that is sufficiently greater than the critical angle (this is the “angle of incidence” for the crystal), all of the light reflects internally off the surface of the crystal.

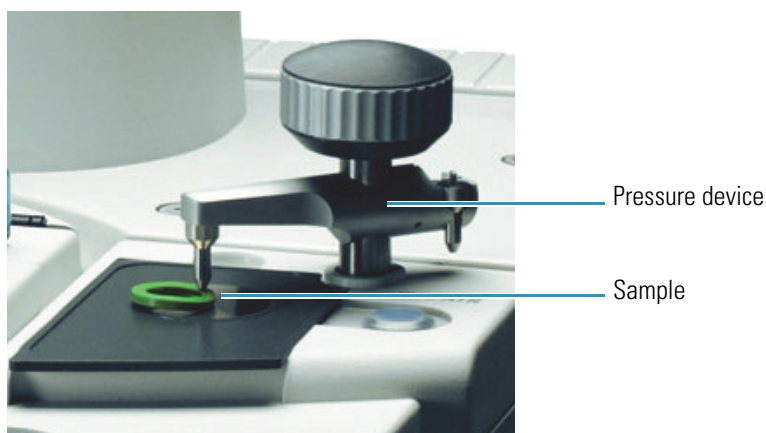
At each reflection point off the crystal surface, the light produces a small amount of radiation, called an “evanescent wave.”

**Figure 2.** Evanescent wave



If a material in contact with the crystal surface has a refractive index that is lower than that of the crystal, energy from the evanescent wave can be absorbed by the sample while penetrating only a short distance (1 to 4 micrometers) into the material. The energy that is not absorbed by the sample (that is, the attenuated energy) continues through the crystal to the infrared detector. When measuring a solid by ATR, a pressure device is needed to press the sample material firmly against the crystal.

**Figure 3.** iS50 ATR module ready for sample measurement

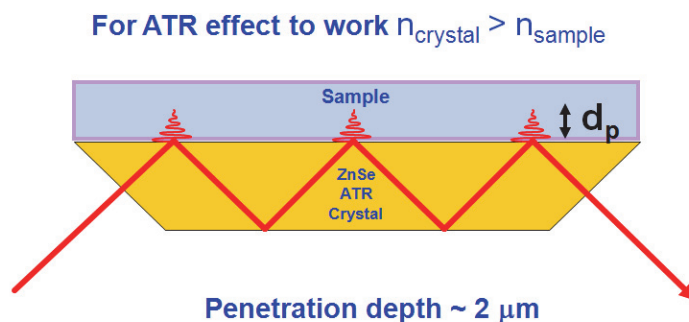


### What is the pathlength of the ATR measurement?

In general, the intensities of the bands in an infrared spectrum are determined by the distance the infrared beam travels through the sample (that is, the sample pathlength) as well as the composition of the sample. For an FT-IR/ATR measurement the pathlength is determined by the depth of penetration of the sample. This is equivalent to the sample thickness in a transmission experiment.

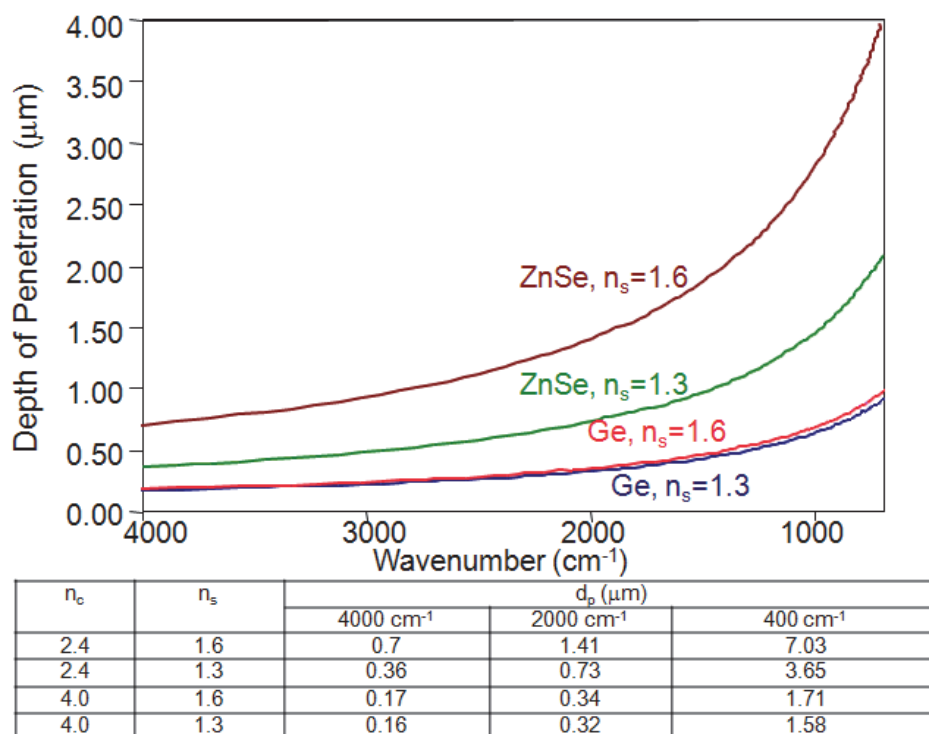
Based on the refractive index of a zinc selenide (ZnSe) crystal, the average penetration depth for an ATR module or accessory that produces one reflection is 2.0 micrometers at  $1000\text{ cm}^{-1}$  for a sample with a refractive index of 1.5. If the ATR crystal allows multiple reflections, as in the illustration below, the pathlength is equal to the penetration depth multiplied by the number of reflections.

**Figure 4.** Average depth of penetration for a ZnSe crystal with multiple reflection points



Depth of penetration is controlled by many factors and is wavelength dependent (longer wavelength waves penetrate deeper than shorter ones do). The graph below illustrates the relationship between wavelength and depth of penetration and their dependence on the refractive indices of the crystal ( $n_c$ ) and sample ( $n_s$ ).

**Figure 5.** Effects of wavelength and refractive index ( $n$ ) on depth of penetration ( $d_p$ )<sup>1</sup> for zinc selenide (ZnSe) and germanium (Ge) crystal types



## Samples Compatible with ATR

The ATR technique can be used to analyze any sample that allows good contact with the surface of the crystal and has an index of refraction that is less than that of the crystal (most organic materials range between 1.3 and 1.7).

**Note** If the sample and crystal have exactly (or nearly) the same index of refraction, the infrared light will not be internally reflected and the resulting spectrum will show little or no sample information.

ATR is an excellent technique for measuring the composition of bulk solids or the surface properties of a layered solid. Because the effective pathlength is short, ATR works well for analyzing strongly absorbing or thick samples which often produce large, unreadable peaks when measured by infrared transmission. Below is a list of examples.

<sup>1</sup> Angle of incidence is 45°;  $n_s$  = sample refractive index;  $n_c$  = crystal refractive index

**Table 1.** Samples compatible with the ATR technique

Sample	Type	Examples
Solids	Dark solids	Films, fabrics, papers, polymer sheets, glass substrates, rubbers
	Coated solids	Adhesives
	Organic solids	Paraffins, organometallics
	Inorganic solids	Paint chips, talc, geologic samples
	Fillers	Talc, clays, flame retardants, plasticizers
	Thick solids	Car bumpers, epoxy resins, expanded or extruded foams
Liquids	Aqueous solutions	Inks, dyes, surfactants, detergents, soaps
	Nonaqueous solutions	Lubricants, light oils, some solvents
	Solutions that cure	Glues, epoxies, paints
	Gels and pastes	Heavy oils, greases, polyols
	Biological materials	Tissue samples
Powders <sup>a</sup>	High molecular weight organic materials	Drugs, pigments
	Ground scraping	Scraping from automobile bodies, computer casings, sheet material

<sup>a</sup> Use a powder press, if available, to achieve even distribution and contact. The particles should be less than 25 micrometers in diameter. If the particles are too big, grind them with a mortar and pestle or an electric grinder.

#### NOTICE

- Make sure your sample material will not react with the ATR crystal. Each crystal material has unique characteristics. Refer to the documentation that came with your ATR module or accessory for details.
- Do not use the pressure device on your ATR module to crush a sample.

## Typical ATR Spectra

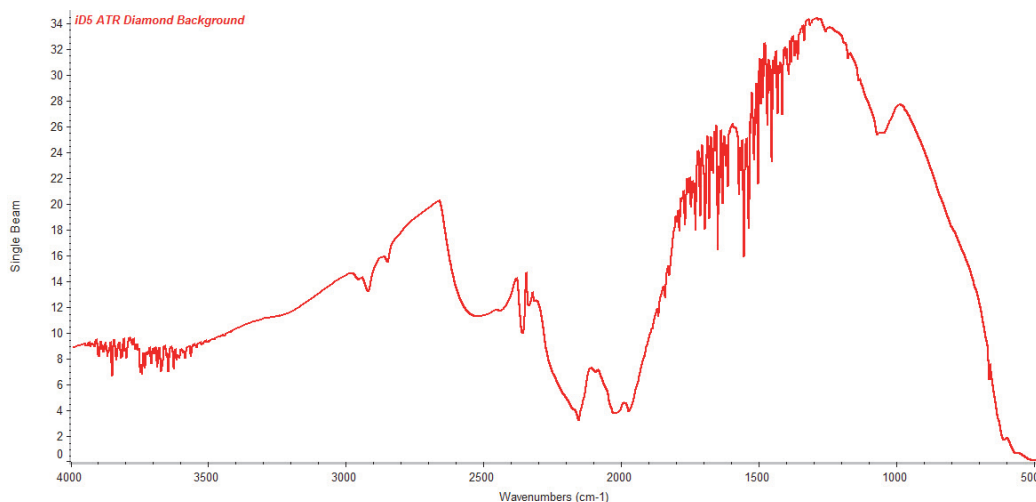
This section gives examples of sample and background spectra collected using an ATR accessory.

### Typical ATR Background Spectra

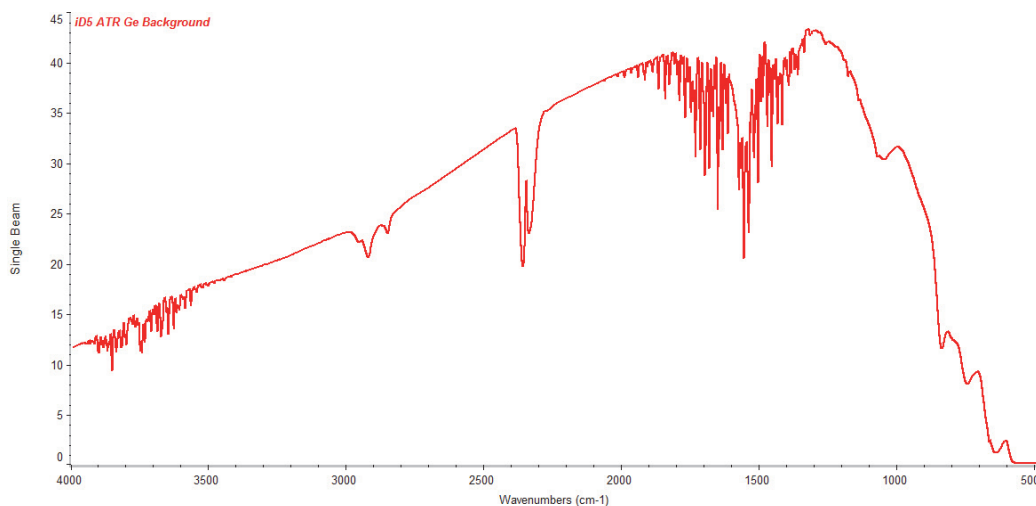
A background is a reference spectrum that accounts for the unique optics of the sampling module, the instrument and any installed sampling module or accessory. Each sample spectrum is ratioed against a background so that the final spectrum is free of these features.

The background spectrum is collected through the ATR beam path but without a sample in place. The overall shape of the background spectrum is dependant upon the spectrometer used to collect the data and the type of crystal in the ATR accessory or module. A typical ATR background spectrum should resemble the following.

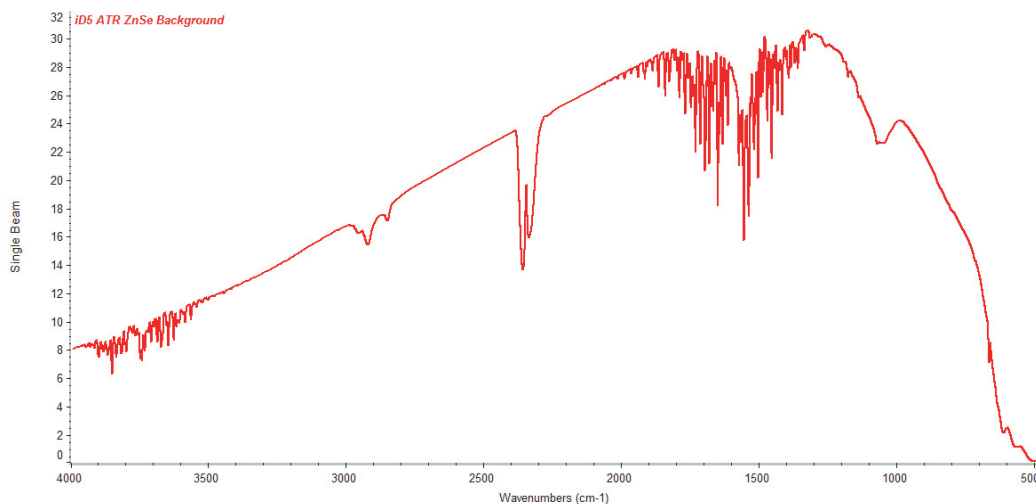
**Figure 6.** Typical ATR background spectrum collected using a diamond crystal



**Figure 7.** Typical ATR background spectrum collected using a germanium (Ge) crystal

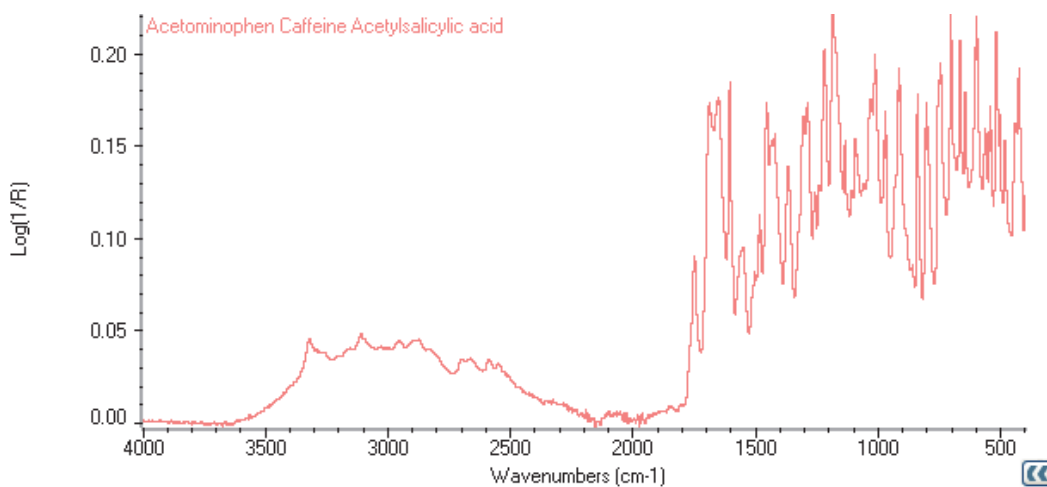




**Figure 8.** Typical ATR background spectrum collected using a zinc selenide (ZnSe) crystal

## Typical ATR Sample Spectrum

The sample spectrum shows the change in infrared energy (the background energy has been removed). The illustration and text below highlight the primary characteristics of an ATR spectrum.

**Figure 9.** Typical ATR sample spectrum

- **Spectral baseline.** In ATR sampling, baselines can slope up or down in the long wavelength (low wavenumber) region of the spectrum as shown in the example above.
- **Spectral range.** The region below the transmission range of the ATR crystal and the spectral range for the spectrometer provides no additional information about the sample and should be ignored.
- **Relative band intensities.** If you measure a sample that is thicker than 2 micrometers, the intensities of the peaks in the short wavelength (high wavenumber) region (i.e., from 4000 to about 2000  $\text{cm}^{-1}$ ) will be smaller than in a transmission spectrum of the same sample.

## Optimizing ATR Data Collection and Analysis

### Optimizing the Background Data

- ❖ **To optimize the background data**
  - Remove any sample and clean the crystal thoroughly before you collect a background spectrum.
  - Make sure the pressure device is not in contact with the crystal during the background measurement.
  - Except for the use of a pressure device, measure the background under exactly the same conditions as the sample.
  - Collect a background spectrum before each sample or every two hours if the samples are similar and the same instrument settings are used.

### Optimizing the Sample Data

To save time and avoid frustration, follow these proven techniques for ATR sampling:

- Clean the crystal thoroughly before use and between every sample (including solids and films) so you don't cross contaminate. Refer to the documentation that came with your ATR accessory for instructions and recommended solvents.
  - If noise or spurious peaks appear in the sample spectrum or you notice a change in the spectral baseline or absorptions due to water or carbon dioxide, collect a new background spectrum and then remeasure the sample.
- 
- ❖ **To optimize the spectrum of a solid**
    - Place the sample in the center of the crystal directly under the pressure point. For best results, the sample should cover the crystal completely.
    - Engage the pressure device fully (that is, continue turning the pressure control knob until it "clicks") to ensure good contact with the ATR crystal. Since the infrared beam migrates only a short distance from the crystal surface, if the sample isn't pressed firmly against the crystal, the sample information will not appear in the infrared spectrum.
    - If the sample peaks are small (this happens occasionally with samples that are extremely rigid or if the sample surface is very rough), reposition the sample and collect the spectrum again.
    - If you see extra peaks in the spectrum, clean the crystal (even if it looks clean) and then collect the sample spectrum again. Refer to the documentation that came with your ATR module or accessory for cleaning instructions and recommended solvents.

**Note** If the spectrum has no sample peaks, check that the sample material absorbs energy in the infrared spectral region and the index of refraction is well below that of the crystal.

❖ **To optimize the spectrum of a powder**

- Use a powder press and pressure device to ensure firm, even contact with the ATR crystal. Air gaps will reduce the size of the sample peaks and cause inconsistent results.
- Sprinkle a thick (1 to 3 millimeter) layer on the crystal, making sure the powder covers the crystal completely. Gently cover the sample with the powder press if available.

❖ **To optimize the spectrum of a liquid, paste or gel**

- Use a dropper or syringe to place a thin film of sample over the crystal. For best results the sample should cover the crystal completely.

If the sample is viscous, use a spatula to spread the sample over the surface of the crystal.

If the sample material is volatile, use a cover to prevent evaporation.

- If you see extra peaks in the sample spectrum, clean the crystal thoroughly and collect the spectrum again. Residual material from the previous sample may have been left on the crystal. Refer to the documentation that came with your ATR module or accessory for cleaning instructions and recommended solvents.

## Optimizing Quantitative ATR Experiments

❖ **To optimize your quantitative experiments**

- Position all samples and standards as precisely as possible on the ATR crystal.
- Use the same conditions to measure the background, samples and standards.
- Collect background spectra frequently.
- For solids, make sure the samples are of equal thickness and use the same pressure setting for all samples and standards.
- Make sure the sample covers the crystal completely. This is true for solids, liquids and powders.
- For solids, use a reference band to account for slight changes in pressure between samples. The reference band must be close to the band of interest.
- For liquids, use a reference band to account for differences between the sample and background measurement which are due to small scratches or chips on the crystal surface.

- If possible, use an ATR module or accessory that has a single-bounce optical design. The single-bounce design produces absorbance values that are well within the linear absorbance range of the spectrometer. The linear response permits more complete and accurate spectral processing and allows quantitative measurements of multicomponent mixtures.

### Optimizing an ATR Spectral Search

#### ❖ To search an ATR sample spectrum against a library of reference spectra

- Perform these corrections, if required, before you run the search:
  - **Correct or minimize any severely sloped, curved or offset baseline regions** in the sample spectrum so the baseline is as flat as possible. If you can't improve the baseline by collecting a new background and then recollecting the sample spectrum, use **Process > Automatic Baseline Correct** in OMNIC software to correct the baseline.
  - **Blank any totally absorbing bands** in the sample spectrum (or omit these regions from the search). Any band that is less than 1% Reflectance is considered totally absorbing and should be deleted or omitted. Use **Process > Blank** in OMNIC software to delete the data points in a specified spectral region, or use **Library Setup > Search Regions** to select specific regions to be searched.
- Display only the spectral region you want to search (omit the region beyond the end of the ATR detector's sensitivity range). Make sure the displayed region is within the spectral range of the reference library you plan to search.

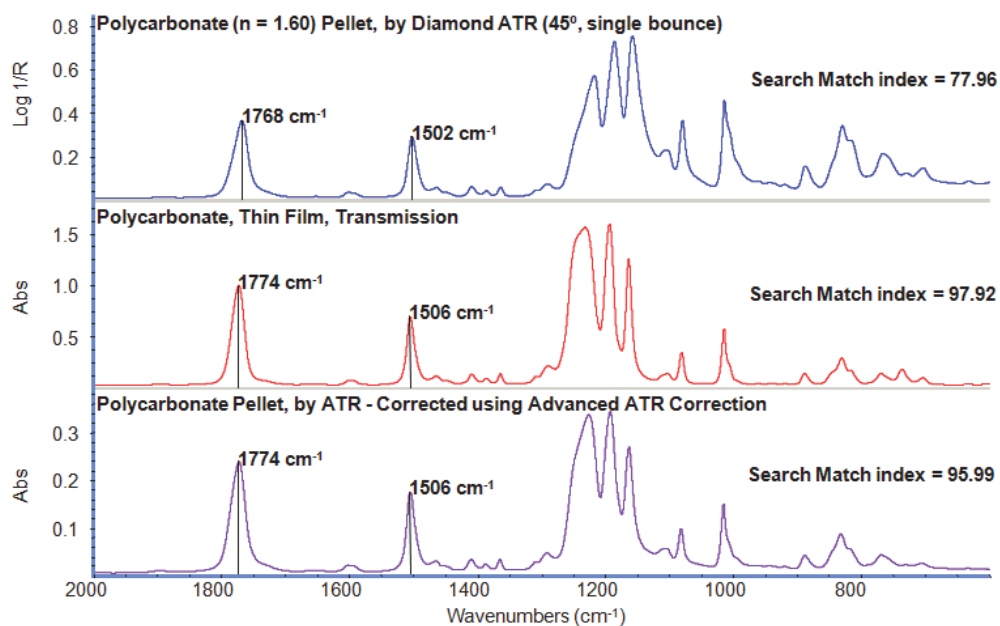
#### ❖ To improve search results using a transmission reference library

- Use **Process > Advanced ATR Correction** in OMNIC software to correct wavelength-dependent absorption anomalies (for example, reduced intensity values and peak shifting in the low wavenumber region of the sample spectrum).
- Use OMNIC's Correlation search algorithm, or another derivative algorithm, to perform the search. The derivative algorithms emphasize peak positions rather than peak intensities.

## About the Advanced ATR Correction Tool

Here is an example of the search results from a polycarbonate ATR spectrum with and without the Advanced ATR correction, and a polycarbonate transmission spectrum for comparison:

**Figure 10.** Advanced ATR Correction result\*

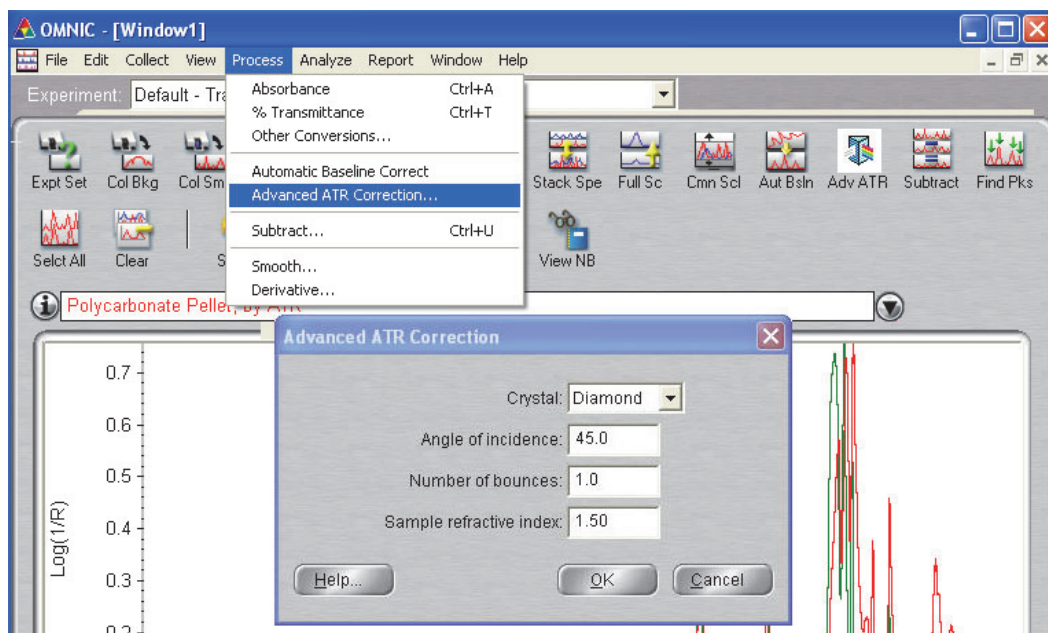


\* The low wavenumber region ( $2000\text{ cm}^{-1}$  to  $600\text{ cm}^{-1}$ ) has been expanded to show the effects of Advanced ATR Correction on peak intensity and peak position relative to the transmission data.

**Note** To reproduce the Advanced ATR Correction result in OMNIC, open the files **advatrcor.spa** and **advatrrref.spa**. Then select the spectrum titled **Polycarbonate Pellet by ATR** (advatrcor.SPA), choose **Process > Advanced ATR Correction** and then choose **OK**. Choose **View > Stack Spectra** to display the three spectra in separate panes.

Most of the information needed for Advanced ATR Correction (refer to the illustration below) is known, for example, crystal type, angle of incidence, and number of interactions with the sample. This information is included in the user documentation or specifications that came with your ATR module or accessory.

**Figure 11.** Advanced ATR Correction settings



To estimate the refractive index of an unknown sample, consider that most organic materials have refractive index values in the range between 1.3 and 1.7. Using an average refractive index of 1.5 for organic unknowns will yield a correction that is close to ideal.

# Index

## A

- Advanced ATR Correction
  - typical result 11
  - typical settings 12
- angle of incidence
  - for ATR technique 2
- ATR module
  - compatible samples 4
  - no sample peaks 9
  - sampling tips 1
- ATR reference library 10
- ATR sampling technique
  - Advanced ATR Correction settings 12
  - and quantitative analysis 9
  - angle of incidence 2
  - background collection frequency 8
  - background spectrum, described 6
  - correcting ATR spectra for use with transmission library 11
  - critical angle 2
  - depth of penetrations 3
  - evanescent wave 2
  - explained 1
  - no sample peaks 9
  - optimizing background data 8
  - optimizing sample data 8
  - optimizing spectrum of liquid, paste, gel 9
  - optimizing spectrum of powder 9
  - optimizing spectrum of solid 8
  - relative band intensities, described 7
  - sample index of refraction 1
  - sample pathlength 3
  - sample pathlength described 2
  - spectral baseline, described 7
  - spectral range, described 7
  - using a powder press 9

## B

- background spectrum
  - ATR, described 6

- collection frequency for ATR 8
- optimizing for ATR 8
- typical ATR diamond 6
- typical ATR Ge 6
- typical ATR ZnSe 7
- band intensities
  - typical ATR 7
- band, reference
  - for quantitative ATR experiments 9
- bands, spectral
  - typical ATR 7
- baseline
  - typical ATR 7

## C

- correcting
  - ATR spectra for use with transmission library 11
- critical angle
  - for ATR technique 2
- crystal
  - diamond ATR, typical background 6
  - germanium ATR, typical background 6
  - zinc selenide ATR, typical background 7

## D

- depth of penetration
  - and number of ATR reflections 3
  - and wavelength 4
  - for ATR technique 3
- diamond
  - typical ATR background spectrum 6

## E

- evanescent wave, described 2
- external angle
  - for ATR technique 2

## G

- gel, spectrum of
  - optimizing for ATR 9
- germanium
  - typical ATR background spectrum 6

## I

- incidence angle
  - for ATR technique 2
- index, refractive
  - estimating 12
  - for ATR samples 1
- internal angle
  - for ATR technique 2

## L

- liquid, spectrum of
  - optimizing for ATR 9
- liquids
  - compatible with ATR technique 5

## N

- number of ATR reflections
  - and depth of penetration 3

## P

- paste, spectrum of
  - optimizing for ATR 9
- pathlength
  - sample for ATR 2
  - sample for ATR technique 3
- penetration depth
  - for ATR technique 3
- powder press
  - used for ATR sampling 9
- powder, spectrum of
  - optimizing for ATR 9
- powders
  - compatible with ATR technique 5
- press, powder
  - for ATR sampling 9

## Q

- quantitative ATR experiments
  - optimizing 9

## R

- range, spectral
  - typical ATR 7
- reference band
  - used for quantitative ATR experiments 9
- reference library
  - ATR 10
  - transmission used for ATR search 10
- refractive index
  - estimating 12
  - for ATR samples 1

## S

- sample pathlength
  - for ATR technique 2
- sample spectrum
  - optimizing for ATR 8
  - typical ATR 7
- samples
  - ATR module, compatible 4
- sampling technique
  - ATR 1
- sampling tips
  - ATR 1
- search
  - ATR sample with ATR reference library 10
  - ATR sample with transmission reference library 10
- single-bounce ATR design
  - and quantitative analysis 10
- solid, spectrum of
  - optimizing for ATR 8
- solids
  - compatible with ATR technique 5
- spectral baseline
  - typical ATR 7
- spectral range
  - typical ATR 7
- spectral search
  - ATR sample with ATR reference library 10
  - ATR sample with transmission reference library 10
- spectrum
  - ATR background, described 6
- spectrum, background
  - optimizing for ATR 8
- spectrum, liquid, paste or gel sample
  - optimizing for ATR 9
- spectrum, powder sample
  - optimizing for ATR 9
- spectrum, sample
  - optimizing for ATR 8



spectrum, solid sample  
optimizing for ATR 8

## T

transmission reference library  
using for ATR search 10

## W

wave  
evanescent 2  
wavelength  
and depth of penetration 4

## Z

zinc selenide  
typical ATR background spectrum 7

