TN21-01: Basics of ATR Spectroscopy

In this issue: Learn about the basic theory of attenuated total reflectance spectroscopy

The Quest™ is our routine sampling ATR accessory. It is suitable for a wide range of common sample types including liquids, pastes, powders, and solids.

- Interchangeable pucks allow easy switching between different crystals and sampling modes
- All-reflective optics and robust monolithic crystals give market leading performance
- Pressure tower for consistent pressure application on solid and powder samples. The built-in "click" feature indicates a full 40 lb load has been reached.

Introduction

ATR has become the dominant method for collecting an FTIR spectrum of solid materials. It requires little or no sample preparation and is effective at both qualitative and quantitative measurements.

Compared to the older method of preparing a KBr pellet for transmission spectroscopy, important differences emerge. An ATR spectrum is not directly comparable to a transmission spectrum, although software algorithms are available in most commercial spectrometers capable of converting an ATR spectrum into a transmission-like spectrum should the analyst wish to compare them.

This note outlines the basics of the ATR method, providing the analyst with the information they require to gain the most out of the technique.

How does ATR work?

The basic theory of ATR is straightforward. An IR beam is reflected off the surface of a crystal from the underside and interacts with a sample of lower refractive index placed onto the surface of the crystal. Recording the intensity of the light reflected before and after placing a sample on the crystal surface produces the characteristic infrared spectrum of your sample. The basic setup is shown in Figure 1.

In order to ensure that the beam of light is reflected rather than transmitted through the surface of the ATR crystal the angle of incidence must be above the critical angle. This varies depending on the crystal material chosen. The Specac Quest™ has a fixed angle of incidence of 45° which is above the critical angle for all ATR crystals.

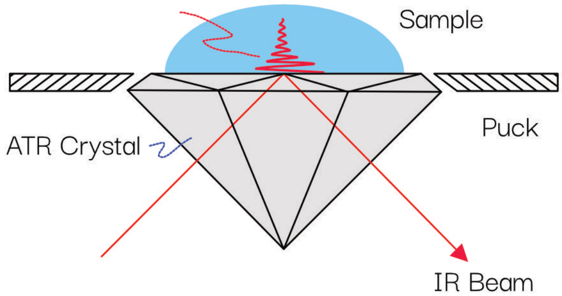


Figure 1: Graphical representation of a single bounce ATR

Penetration Depth

It is important to state that the IR beam does not exit the surface of the crystal at the crystal/sample interface. Instead, the electric component of the light propagates into the rarer sample medium. This is known as an evanescent wave, and its strength decreases exponentially as it propagates into the sample. As a result, the penetration depth of ATR spectroscopy is very short. The exact depth depends on several factors including the sample type and the wavelength of the light.

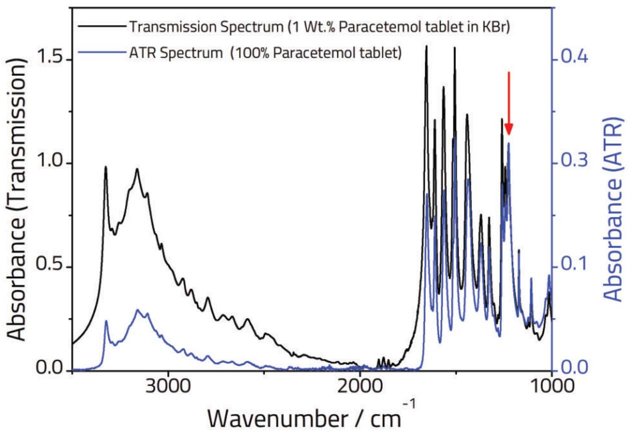


Figure 2: Comparison of an ATR and transmission spectra of paracetamol. The two spectra have been scaled such that the peak at 1230 cm^{-1} (indicated by the red arrow) is of equivalent scaling between transmission (left y-axis) and ATR (right y-axis).

Higher frequencies have a smaller penetration depth, so one difference between a transmission and ATR spectrum is that the relative peak intensities at higher wavenumbers are reduced relative to the lower frequency end of the spectrum as illustrated in Figure 2.

Learn more: Penetration depth is discussed in more detail in our Technical Note: TN21-02: ATR Penetration Depth

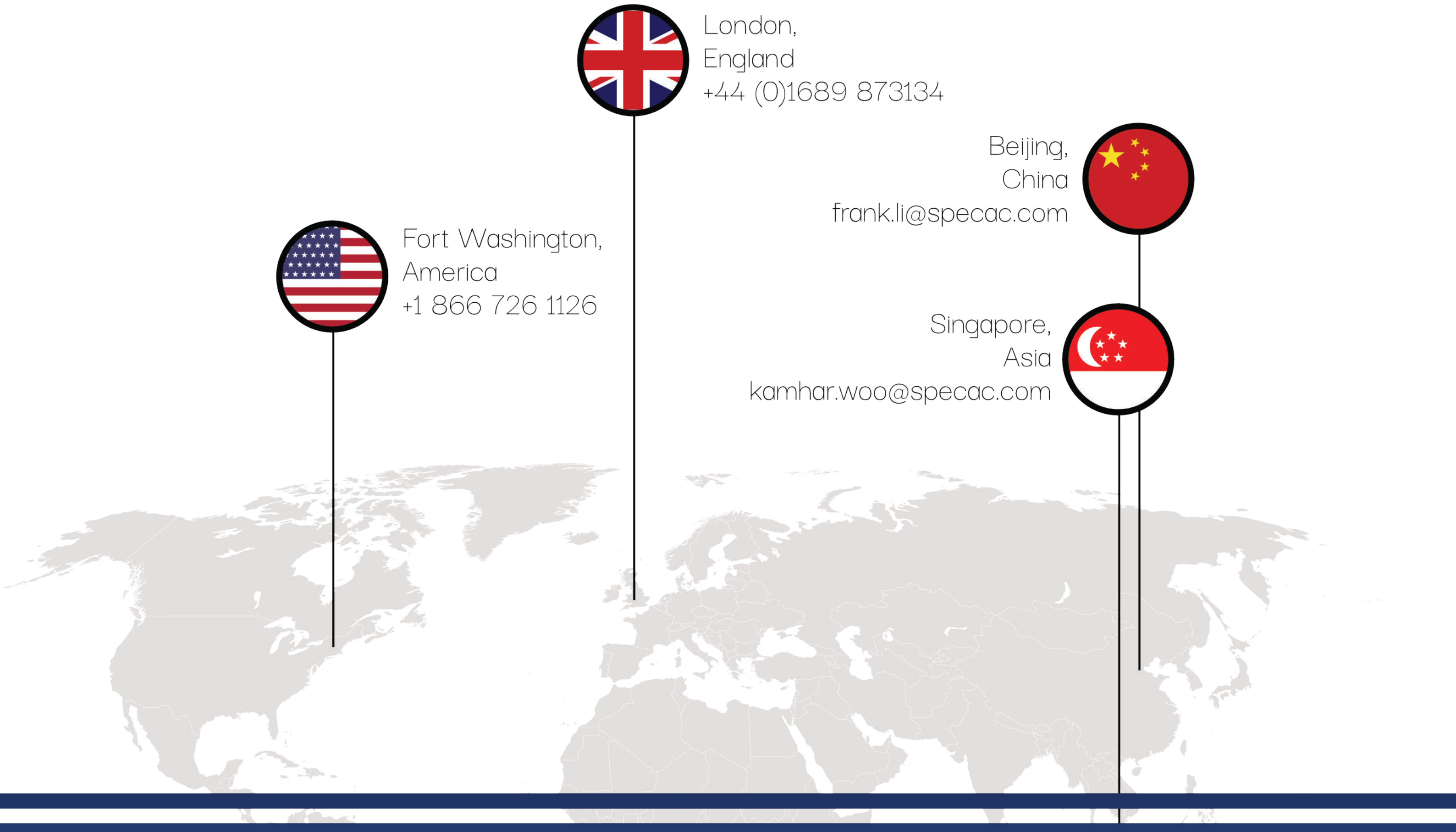
Crystal Choice

A range of materials are available to choose from for your ATR crystal. The best one to choose depends on your application. ZnSe is suitable for day-to-day applications, however care should be taken to avoid harder samples and point loads as these can cause the crystal to shatter. It is also critical to ensure the ZnSe is not exposed to acidic or strongly basic samples as these can cause the formation of toxic fumes.

Ge is suitable for materials with a high refractive index and for surface studies owing to its smaller penetration depth.

Diamond is the real workhorse of ATR spectroscopy. It is extremely hard wearing and is virtually indestructible. Other commercial ATR accessories often employ a laminated diamond, which can delaminate over repeated use. To prevent this the Quest™ and Golden Gate both use a monolithic diamond crystal ensuring your ATR can last for years. Two different options are available – a standard puck with anti-reflective coating to improve the signal-to-noise ratio in the mid-IR, and an uncoated extended range diamond that extends into the far-IR.

Learn more: A thorough examination of crystal choice is provided in "TN21-03: ATR Crystal Choice and Quest Puck Guide".



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