

Principles of ATR

An attenuated total reflection accessory operates by measuring the changes that occur in a totally internally reflected infrared beam when the beam comes into contact with a sample (indicated in Figure 1). An infrared beam is directed onto an optically dense crystal with a high refractive index at a certain angle. This internal reflectance creates an evanescent wave that extends beyond the surface of the crystal into the sample held in contact with the crystal. It can be easier to think of this evanescent wave as a bubble of infrared that sits on the surface of the crystal. This evanescent wave protrudes only a few microns ($0.5\ \mu\text{m}$ - $5\ \mu\text{m}$) beyond the crystal surface and into the sample. Consequently, there must be good contact between the sample and the crystal surface. In regions of the infrared spectrum where the sample absorbs energy, the evanescent wave will be attenuated or altered. The attenuated energy from each evanescent wave is passed back to the IR beam, which then exits the opposite end of the crystal and is passed to the detector in the IR spectrometer. The system then generates an infrared spectrum.

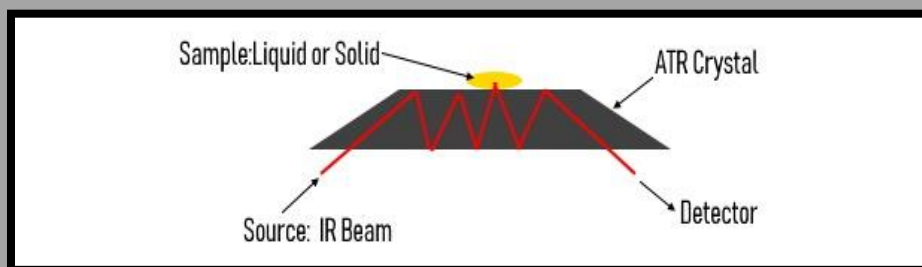


Figure 1

ATR Requirements:

1. The sample must be in direct contact with the ATR crystal, because the evanescent wave or bubble only extends beyond the crystal $0.5\ \mu\text{m}$ - $5\ \mu\text{m}$.
2. The refractive index of the crystal must be significantly greater than that of the sample or else internal reflectance will not occur – the light will be transmitted rather than internally reflected in the crystal. Typically, ATR crystals have refractive index values between 2.4 and 4.0 at $2000\ \text{cm}^{-1}$. It is safe to assume that the majority of organic solids and liquids have much lower refractive indices. For inorganic work, recent studies have introduced ATR. Some studies require the use of various crystal (Ge, ZnSe, and Diamond) to capture the best results.