Expanded Spectral Range Germanium ATR Crystal

Experimental data show the crystal dimensions of an ATR-FTIR sampling accessory influences the usable spectral range. An expanded range germanium crystal is introduced for the measurement of high refractive index samples.

Attenuated total reflection (ATR) for FTIR sampling requires that the beam angle of incidence (AOI) is greater than the critical angle, which is defined as $\sin^{-1}(n_2/n_1)$ where $n_2$ and $n_1$ are the refractive index of the sample and ATR crystal, respectively. For high refractive index materials a germanium crystal is often necessary to reduce the critical angle to below 45°, the most common AOI for single reflection ATRs. Violating the critical angle rule prohibits total internal reflection in the crystal, results in a baseline shift, and often produces derivative shaped bands (Figure 1).

Experimental Conditions
PIKE Technologies’ GladiATR single reflection ATR (Figure 2) equipped with a Ge crystal was used to collect an infrared spectrum of malachite green oxalate. The energy throughput for this accessory is generally greater than 30% at 1000 cm$^{-1}$. This enhancement is achieved by treating the Ge surface with an anti-reflective coating. Data collection time was 1 min, and the resolution was 4 cm$^{-1}$. A spectrum of the sample was also collected with PIKE Technologies’ single reflection MIRacle ATR equipped with a Ge crystal using the same instrument and collection parameters.

Results
The spectral cut-off of a Ge ATR crystal decreases as the distance the beam travels within the crystal increases. The MIRacle single reflection ATR has a small sampling surface, 1.8 mm diameter, yet the beam travel distance inside the crystal is approximately 18 mm because the crystal is dome-shaped and serves as a refractive optic. Alternatively, the GladiATR single reflection ATR uses all reflective optics and a circular prism-shaped crystal with a sampling surface of 2 mm diameter and 45° side angles. The beam travel distance through the GladiATR crystal is 2.5 mm. Figure 3 compares...
the spectral range of the GladiATR compared to the MIRacle accessory with a Ge ATR crystal.

![Figure 3. Energy throughput of the GladiATR and MIRacle accessory with a Ge ATR crystal.](image)

Malachite green oxalate, a material dye, serves as an ideal sample for ATR sampling on a Ge crystal because of its high refractive index. The sample spectrum shows the effect of crystal dimensions (Figure 4). MIRacle offers a spectral range of 4000 – 575 cm\(^{-1}\), whereas the GladiATR's useable spectral data is 4000 – 420 cm\(^{-1}\), providing additional spectral information across the low vibrational frequencies. Types of high refractive materials that would benefit from sampling on an expanded range Ge ATR crystal include inorganic materials such as oxides, aluminas, titania, and minerals.

![Figure 4. Comparing the expanded spectral range of the GladiATR using a Ge ATR crystal (in red) at the low vibrational frequencies to the range of the MIRacle Ge ATR (in blue); sample is malachite green oxalate.](image)

**Conclusions**

The GladiATR's compact-size Ge ATR crystal in combination with all reflective optics offers an expanded spectral region, from 4000 to 420 cm\(^{-1}\), which is beneficial when testing high refractive index materials.

**References**