What is a good rule of thumb for pathlength in ATR?

The expressions for effective thickness are quite complex. For a detailed description, see N.J. Harrick's *Internal Reflection Spectroscopy*, Harrick Scientific Products, Inc., Ossining, NY 1987 (p 43). Using the Harrick Scientific's CristalCalc™ software we can, however, quickly obtain the following relationships:

$$d_{e\parallel} = 0.550\lambda$$

and

$$d_{e\perp} = 0.550\lambda$$

Where $d_{e\perp}$ is the effective thickness for perpendicular (s) polarization, $d_{e\parallel}$ is the effective thickness for parallel (p) polarization, and λ is the wavelength in microns.

To obtain these two relationships, the following inputs were made to CristalCalc™: ZnSe, with a refractive index of 2.42, was chosen as the ATR material, 1.5 was chosen as the refractive index of the sample, 45° was chosen as the angle of incidence, and 10,000cm-1 (1 micron) was chosen as the wavelength. To obtain d_e, the effective thickness for unpolarized light

$$d_e = \frac{d_{e\perp} + d_{e\perp}}{2} = 0.412\lambda$$

which shows a single relationship between the effective thickness and wavelength. A more general form is

$$d_e = 0.412N\lambda$$

where *N* is the number of internal reflections interacting with the sample. Hence, if there are 8 internal reflections, and the wavelength is 10 microns:

$$d_e = 33 \text{ microns}$$