HARRICK Scientific Products
Solutions in Optical Spectroscopy

How is ATR used for depth profiling?

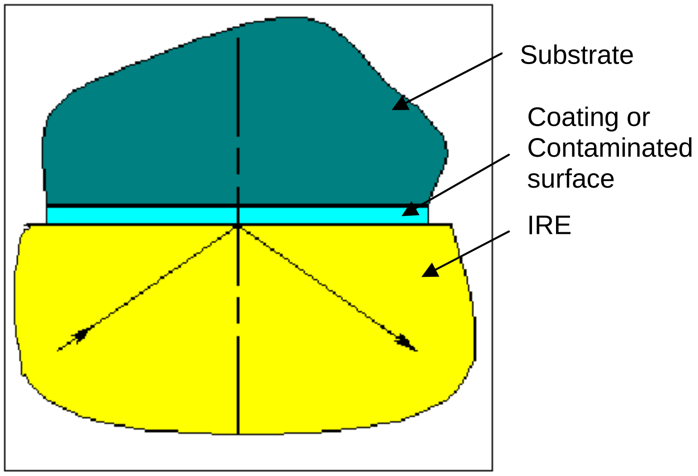
The defining feature of ATR spectroscopy is the presence of an evanescent wave. The evanescent wave is a special type of electromagnetic radiation:

- It is present only in the regime of supercritical internal reflection
- It propagates parallel to the interface
- It is confined to a narrow region outside the sampling surface of the internal reflection element (IRE)
- Its intensity decreases exponentially with the distance from the sampling surface of IRE
- Its penetration depth outside IRE is on the order of wavelength
- The penetration depth d_p as a function of experimental parameters is:

$$d_p = \frac{\lambda}{2\pi\sqrt{n_o^2 \sin^2\theta - n_s^2}}$$

The penetration depth is controllable through experimental parameters by either changing the refractive index of IRE (n_o) or changing the angle of incidence (Θ). The ability to change the penetration depth enables depth profiling, *i.e.* the ability to distinguish the composition of surface from that of the bulk. Typical samples for which depth profiling is useful include:

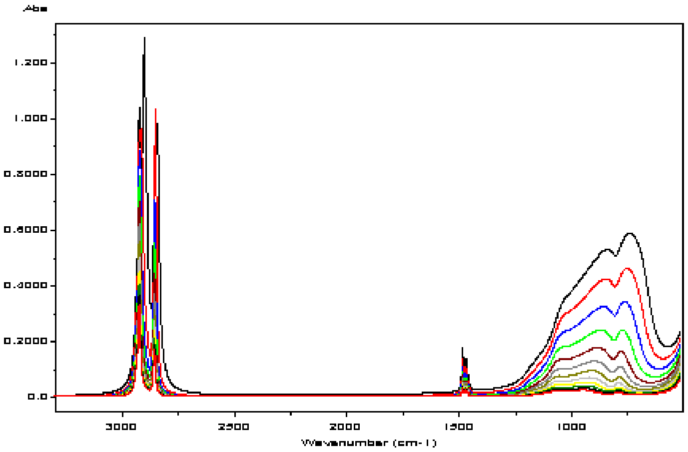
- Polymers with chemically modified surfaces
- Samples with very thin coatings (thicknesses on the order of the infrared wavelength)
- Contaminated surfaces



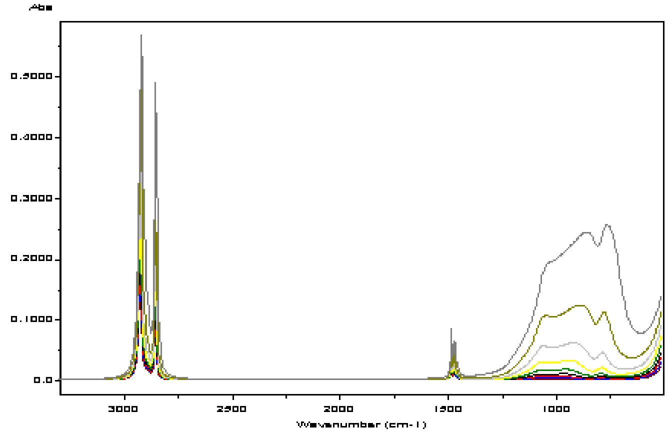
The information that can be extracted from depth profiling includes:

- The chemical composition of surface layer
- The chemical composition of substrate
- The average thickness of surface layer

To demonstrate the effects of the changing the incident angle and the refractive index of the IRE on the spectra, infrared spectra were simulated using Harrick's SOS™ software. The sample chosen was a 2µm thick polyethylene coating on a glass substrate.

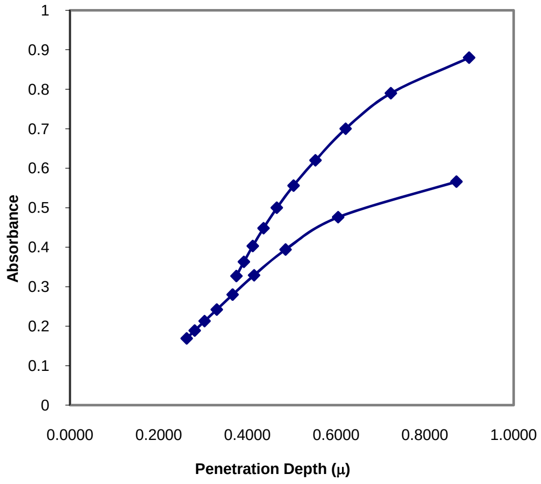


Spectra were simulated examining this sample with a ZnSe ATR element over a range of incident angles from 42° to 60° in 2° increments. The results are presented above.

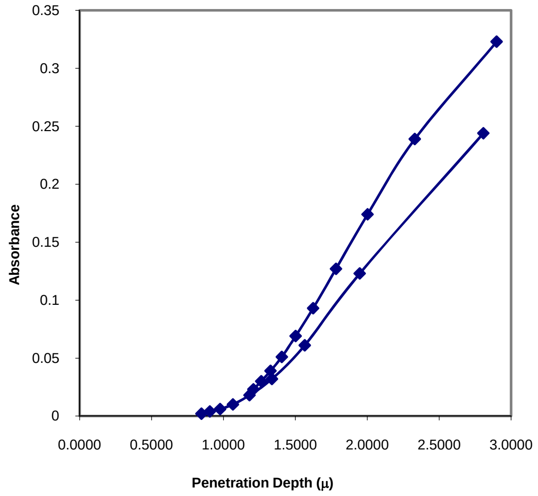


Spectra were also generated using a higher refractive index ATR crystal, Ge, over a range of incident angles from 24° to 40°, in 2° increments. This is shown in the figure above.

Now, let's examine the change in absorption with penetration depth for a distinctive band in each material.



The absorption of the polyethylene band at 2900 cm^{-1} as a function of the penetration depth is shown in the figure above, while the absorption of the glass band at 900 cm^{-1} as a function of the penetration depth is shown below. In both figures, the upper curve illustrated the absorption measurements using a ZnSe IRE and the lower curve shows the results using a Ge IRE.



For the polyethylene bands, the approximately linear relationship between absorbance and penetration depth continues to hold as the penetration depth tends to zero. This implies the presence of polyethylene at the very interface with IRE. For the glass bands, however, the absorbance drops to zero below a penetration depth of one micron, implying that glass is not present at the very surface of IRE. In ATR, the layers of sample closer to the IRE surface contribute much more strongly to the measured absorbance than do the layers further away from the surface.

The ability to vary the penetration depth (i.e. the mean penetration), by changing either the angle of incidence or the refractive index of the IRE, enables obtaining spectra with a contribution from a particular layer varying in proportion to the overall absorbance. Thus a number of spectra can be recorded at varying penetrations with an intention to extract the information on composition depth profile. However, ATR enables only a coarse depth profile.