What is the effect of stray light on ATR spectra?

In ATR spectroscopy, light internally reflects from the sampling surface of the ATR element. The portion of the sampling surface illuminated by the incoming light can be referred to as the hot-spot. The layer above the hot-spot within which the evanescent wave has a significant intensity can be considered the sampling volume. Only the parts of sample physically positioned within this sampling volume participate in the light absorption process, the rest of the sample is a nonparticipating bystander. If the sample completely fills the sampling volume, then there is no stray light in the measurement process. If, however, areas of the sampling volume contain no sample, there is stray light in the process where stray light is the portion of light involved in the measurement process that does not completely interact with sample. The phrase complete interaction does not imply that the light has to be completely absorbed, but that it only needs to be provided with a completely filled sampling volume.

So what is the damage to the measuring process if there is some stray light in a measurement? Let's look first into a transmission measurement with some stray light present. Imagine that the sample is a film of thickness d placed into the beam and that there is a hole within the portion of the sample illuminated by the beam. If the cross section of the beam is S and cross section of the hole is S_h than the transmittance measured is:

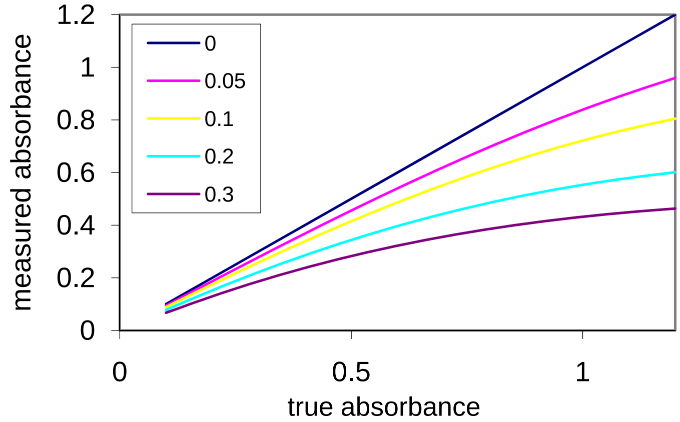
$$T(S_h) = (1-\frac{S_h}{S})10^{-\alpha d} + \frac{S_h}{S} \qquad (1)$$

Absorbance is defined as a negative logarithm of transmittance. The relationship, in the case of no stray light, yields a quantity proportional to absorption coefficient.

The graph in Figure 1 shows the relationship between the true absorbance and measured absorbance as a function of the amount of stray light present in the experiment. As expected, stray light introduces non-linearity.

In the case of an ATR measurement, stray light is identified as the light that was detected by the spectrometer detector but did not interact with the sample. This occurs when the sample in contact with the ATR crystal is not fully covering the spot illuminated by the sampling radiation seen by detector. The obvious case of this happening is when the sample itself is smaller than the hot spot. The less obvious case if that of a sufficiently large sample pressed against

Figure 1. The stray light effect on absorbance



the ATR crystal but with non-uniform contact over the area of hot spot. A familiar illustration of this second case is one of the powdered samples pressed against the crystal. Only the portions of the grains within the active sampling volume are participating in the measurement. The voids between the grains do not contribute to the measurement and hence the light that incompletely interacted with the sample is identified as stray light. Once stray light is present in the measurement, the same non-linearity shown above for the case of transmission follows.

If a sample is imbedded in an absorbing matrix, the problems caused by stray light are no longer of the quantitative type only. The absorbance bands due to the matrix interfere with the spectra of pure sample and must be subtracted. The subtraction may suffer from non-linearities described above, thus impeding the ability to cleanly subtract the matrix contribution, leaving spurious matrix bands in the spectrum of the sample.

Harrick Scientific Products, Inc. | 141 Tompkins Ave, 2nd Floor | P.O. Box 277 | Pleasantville, NY 10570
P: 914-747-7202 | F: 914-747-7209 | www.harricksci.com | email: info@harricksci.com