APPLICATION NOTE

ATTENUATED TOTAL REFLECTANCE ABSORPTION SPECTROSCOPY

METHOD USED

ABSORPTION SPECTROSCOPY

Absorption spectroscopy is a powerful technique used to identify and quantify a wide range of analytes since the absorption bands directly correlate to electronic or vibrational energy level transitions. Most molecular vibrations tend to have very low transition energies between 0.05 and 0.5eV, corresponding to wavelengths from 2.5 μm to 25 μm. While low energy, these vibrational transitions are incredibly narrow, providing a high degree of selectivity for material identification. On the other hand, electronic transitions are at much larger energies, typically >1.5eV, requiring visible or ultraviolet excitation. Unlike IR absorption bands, UV/Vis absorption is far less discrete, making it less selective but more sensitive. For these reasons, the general rule of thumb is to use UV/Vis absorption for quantification and IR absorption for identification.

Absorption spectra are traditionally measured by passing a collimated broadband light source through a 1 cm path length sample and comparing the transmitted spectra to a “blank” reference scan. This simple optical geometry works exceptionally well for IR and UV/Vis absorption as long as the sample is relatively transparent, i.e. weekly absorbing. It is relatively easy to control the UV/Vis optical density through serial dilution when working in a laboratory setting, but this is often not an option when working in the field or on a production floor. Serial dilutions are far more challenging in the IR due to the large absorption cross-section of water. For opaque and semi-opaque solids, diffuse reflectance is a viable option for measuring absorbance in the UV/Vis; however, direct IR reflectance measurements are virtually impossible due to the optical challenges associated with the region.

FUNDAMENTALS OF ATR

To understand the advantages and disadvantages of ATR (Attenuated Total Reflectance) it is necessary to look beyond the simple ray optics description of how light reflects off an interface. When most people are introduced to the concept of total internal reflection, it is usually presented as the limit at which Snell's law breaks down, and light can no longer refract into a new medium. Total internal reflection occurs when light traveling in a high index material is incident at an angle greater than or equal to the critical angle (Θc), which can be determined using the following equation:

$$\Theta_c = \sin^{-1}\left(\frac{n_2}{n_1}\right)$$

Where n1 is the index of the first material, and n2 is the index of the second material. Typically omitted from introductory explanations of this subject is that as the light is "turned around" at the interface, a small portion of the electromagnetic wave crosses the barrier into the second material (see figure 1). The resultant an evanescent wave which can penetrate as much as 2 µm into the second material. Therefore, in an ATR probe, the incident light is coupled into a high index material (typically a crystal) at a steep enough angle to induce total internal reflection when in contact with most common samples.

The reflected light is then coupled to a spectrometer to measure the attenuation due to the sample and extract the absorption spectrum. While figure 1 shows only a single reflection, in reality ATR probes are typically designed with multiple reflections to increase efficiency. IR ATR probes generally are made from very high index materials such as ZnSe (n = 2.4), which allows for total internal reflection at 450, making it easy to design ATR probes with ten or more reflections. UV/Vis ATR probes are often limited in the number of reflections since they require lower index optically transparent materials such as sapphire (n=1.77) or cubic zirconia (n = 2.16), which need larger incident angles (~60o). Even though the reduced number of reflections reduces the magnitude of the evanescent field, it is not an issue since the total light intensity in the UV/Vis can be scaled easily. Furthermore, most analytes of interest are far more absorbent in the UV/Vis than the IR.

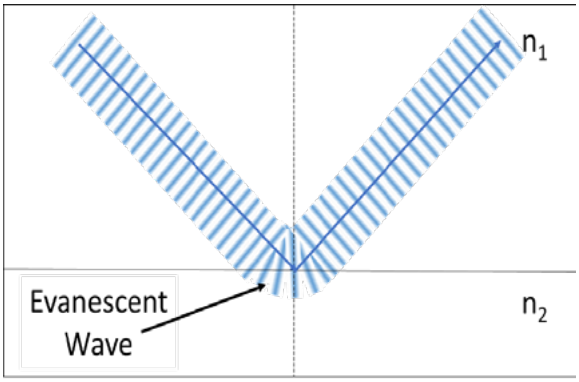

FIGURE 1: Schematic representation of total internal reflection showing the evanescent wave present in the lower index material (n2 < n1), superimposed with the traditional ray optics representation.

INSTRUMENTATION

Figure 2 shows an example of a typical ATR experimental set-up for measuring an extremely high optical density solution. This set-up utilizes an AvaLight-HAL-S-Mini, a compact, stabilized halogen light source (360 nm to 2,500 nm) with adjustable focusing of the fiber connection. The light source connects to the input fiber of Avantes' new AvaPRB-ATR fiber-coupled ATR probe, immersed in a high optical density viscous fluid. After the light passes through the ATR crystal at the distal end of the probe, the light is coupled to an AvaSpec-ULS2048CL-EVO from Avantes to measure the UV/Vis absorption spectra. The optical performance afforded by the AvaPRB-ATR allows for the use of a relatively low cost, uncooled spectrometer model for most UV/Vis ATR applications. In the case of a solid sample the probe tip would be pressed firmly against the sample, but the overall set-up would remain the same.

FIGURE 2: Three common viologen redox forms R, R' = alkyl or aryl group

While the experimental set-up shown in figure 2 is for a laboratory setting, it is essential to note that this probe can also be utilized in high-temperature and high-pressure industrial processing. The AvaPRB-ATR is designed to operate at temperatures ranging from -30°C to 280°C and pressures up to 1200 psi. In addition, the 316 stainless steel probe shaft and Kalrez® seal provide computability for most common process chemicals and biological. The AvaPRB-ATR fiber-coupled ATR probe comes in two main varieties depending on the exact needs of your application. The AvaPRB-ATR-Z includes a cubic zirconium crystal tip that can measure from 380 to 2200 nm and is compatible with samples up to a 1.9 index of refraction. For applications requiring deep UV absorbance, the AvaPRB-ATR-S uses a sapphire crystal that can collect spectra down to 250 nm but is limited to samples with an index of refraction of 1.5 or less. Both probes utilize a single-crystal optical design increasing the stability and providing a flatter baseline with a more linear response than other probes on the market, which require complex internal optical elements.

SUMMARY

FINAL THOUGHTS

Even though ATR has been used in IR for over 50 years, surprisingly few spectroscopists are aware that it can be used for UV/Vis absorption, too. By offering a fiber couple ATR probe designed for use in the UV/Vis and NIR spectral region, Avantes is making it easier than ever for chemists and engineers to measure incredibly optically dense media such as inks, dyes, coal, and sludge in and outside of the lab. While this application note focused mainly on ATR products, it should be pointed out that Avantes also offers modular and OEM absorption systems.

For more information about the full range of laboratory and OEM spectrometer options available from Avantes, including our light sources, probes, and sample accessories, please feel free to visit the website at **www.avantesusa.com** or give us a call at **+1 (303)-410-8668** where our knowledgeable applications specialists are standing by to help.

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CONTACT

WE'RE HAPPY TO HELP

Curious how spectroscopy can help you reveal answers by measuring all kind of materials, in-line, at your production facility, in a lab or even in the field? Please visit our website or contact one of our technical experts, we're happy to help you.

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