Application note

Solid-State Materials: Analysis Through UV-Visible Spectroscopic Techniques

UV-Visible techniques are used to observe how a substance behaves when irradiated with light in the UV and visible range of the electromagnetic spectrum. Possible interactions include transmission of light through the material, reflection off the surface of the sample, and absorption of the light by the material. Absorption measurements are by far the most common method for analyzing UV-Visible data as this value can be linearly correlated to the concentration of a given analyte through Beer's law (eqn. 1), where A is the absorbance of the sample, c is the concentration, l is the pathlength by which the light passes through, and ε is the extinction coefficient unique to the analyte measured. Often, UV-Visible absorption methods are used to analyze solution-phase samples, however, solid-state samples can also be readily measured using a variety of UV-Visible techniques.

$$A = cl\varepsilon$$

Equation 1.

The same principles which govern solution-phase samples also apply to solid-state substances, however there are a few major differences between the two sample types which must be considered when working with solid samples. Herein, we aim to discuss a few of the different possible analyses which can be performed on solid samples as well as the inherent considerations that must be accounted for when analyzing these materials.

First, unlike in solutions, reflections are often not negligible in solid-phase samples, and thus different methods of analysis are required. The reflection spectrum can contain valuable information about a given solid, including the color of a non-transmissive material or the usable reflective range for a mirror or coating. As such, reflection measurements of solids are not uncommon.

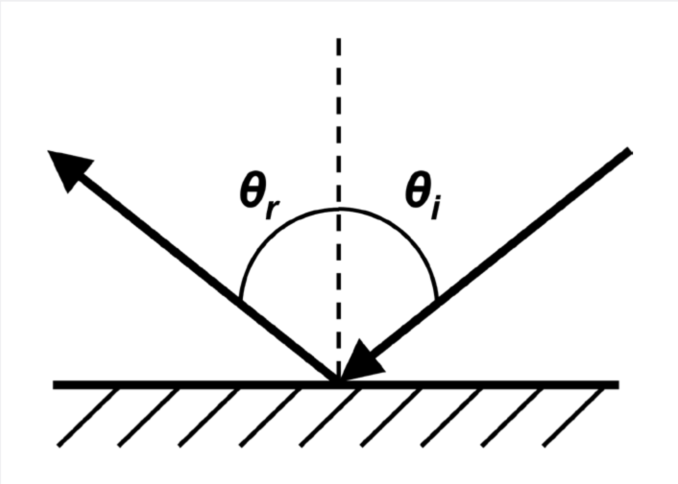

Figure 1. Diagram depicting angle of reflectance (θ_r) and angle of incidence (θ_i).

Reflections in spectroscopy can be defined as the redirection of light by a material at an angle (θ_r) equivalent to the angle of incidence (θ_i) as shown in Figure 1. There are two different forms of reflections possible when light interacts with the surface of a material: specular and diffuse. Specular reflections (Figure 2a) are mirror-like in nature.[1,2] These reflections involve the uniform reflection of light off the sample surface. Substances with more uniform surfaces are likely to be specular reflectors.

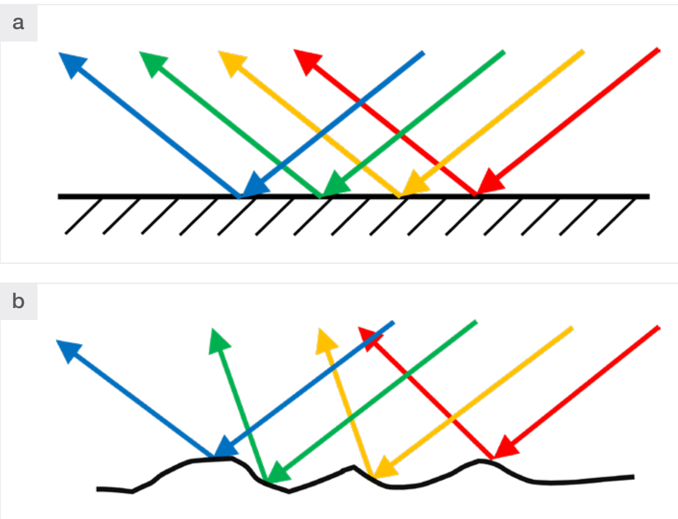

Figure 2. Example of (a) specular reflections off an ideal, uniform surface and (b) diffuse reflections off an irregular, nonuniform surface.

As an example, privacy screens (films for smart devices) can specularly reflect light. This film functions such that when viewed directly, light can be transmitted through the screen and can be seen, however when viewed from an angle, the screen appears black and light is either absorbed or reflected, protecting the user's privacy.[3,4] This material will inherently have an angle-dependent response to incidient light—a response which is important to monitor for QA/QC purposes. For these systems, it is important to measure the full reflection spectrum, as well as transmission spectrum, as a function of the angle of incidence. Figure 3 includes the specular reflectance spectra for a commercially available privacy screen. As would be expected, the recorded reflectance is higher for samples when the angle of incidence is wider compared to near-normal specular reflectance.

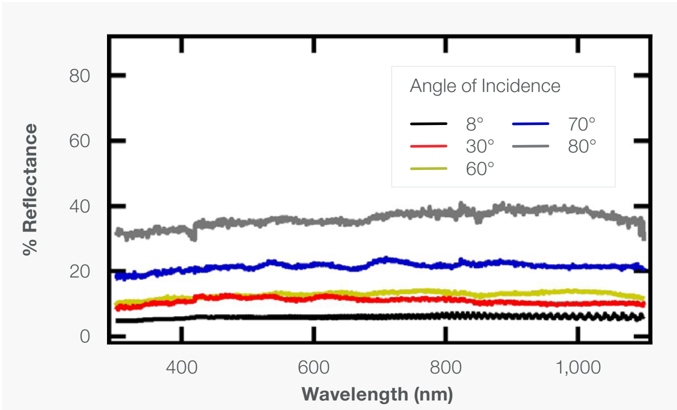

Figure 3. Specular Reflectance spectra of a privacy screen collected at different angles of incidence. Spectra were collected using the Thermo Scientific™ Evolution™ Pro UV-Visible spectrophotometer equipped with the VeeMAX variable angle specular reflectance accessory (30˚ – 80˚ angles of incidence) and 8˚ specular reflectance accessory.

Diffuse reflections are more irregular and typically arise from non-uniform or "rough" surfaces of a solid material (Figure 2b).[1,2] These reflections are often present with powdered samples or with opaque film samples, and are akin to scattering events in solutions where light is scattered in non-uniform directions. As with scattering events, the irregular direction of the light can cause this signal to be directed away from the instrument detector, resulting in a falsely low reflectance signal. These abnormalities can be corrected for if using the appropriate accessory (e.g., an integrating sphere).

Nanoparticles and nanomaterials are often analyzed in the solid phase, including as films or powders, using UV-Visible spectroscopy. Reflections of these substances, particularly powders, are typically diffuse as the surfaces of the film or particles are often irregular. As an example, Figure 4 includes the reflection spectra of TiO_2 nanoparticles of varying crystal structure. For semiconductors like TiO_2, changes in the reflection or absorption spectrum observed for samples of differing crystal structure can have implications for the electronic structure of a given material. Thus, UV-Visible analysis can be a helpful tool for materials characterization.[5-7]

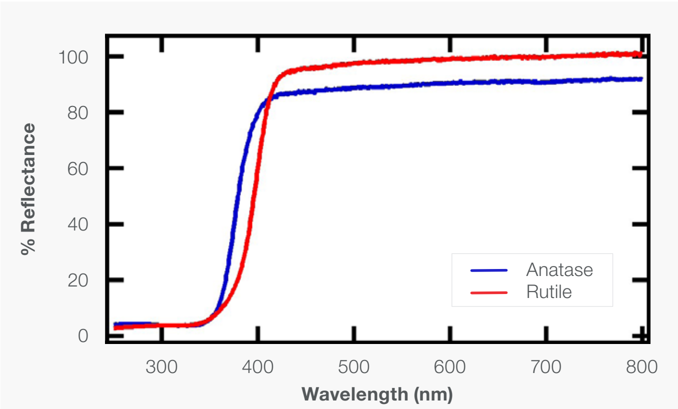

Figure 4. Reflectance spectra of anatase (blue) and rutile (red) TiO_2 collected using the ISA-220 and Thermo Scientific™ Evolution™ One Plus UV-Visible spectrophotometer.

In addition to films and powders, solid samples can also be made with different, non-uniform shapes. For example, some materials, like lenses for eyeglasses, have curved instead of flat surfaces. Due to refraction, these curved materials cause incident light to be transmitted in a non-collimate manner. Similar to diffuse reflections, the converging or diverging beam may not be able to reach the detector, requiring the use of an integrating sphere to properly direct the light to the detector. As an example, Figure 5 includes the reflectance and transmittance spectra of a blue light reduction eyeglass lens, acquired using an integrating sphere (ISA-220). Here, the ISA-220 is able to direct the light uniformly toward the detector, preventing the loss of light that does not transmit through the sample as a collimated beam.

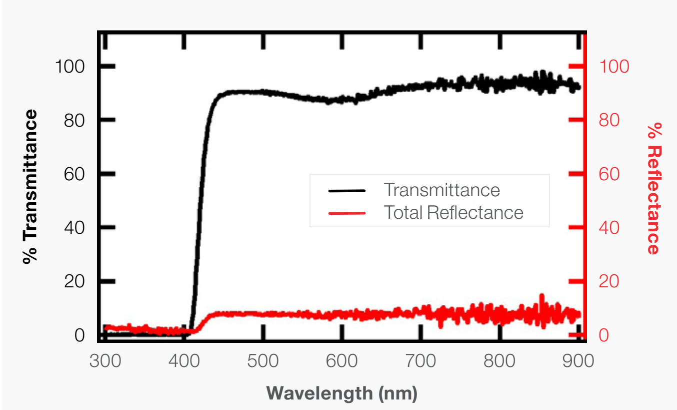

Figure 5. Transmittance (black) and Reflectance (red) spectra for a blue light reduction lens collected using the ISA-220 and Thermo Scientific™ Evolution™ One Plus UV-Visible spectrophotometer.

In addition to more prevalent contributions from reflections, the loss of degrees of freedom in the solid phase as compared to solutions can influence measurements in ways not observed for the latter sample type. Unlike in solutions where Brownian motion allows for the movement and mixing of compounds, leading to a homogeneous sample, solids can be fairly heterogeneous in nature. Under these circumstances, the amount of an analyte of interest present in a given sample can be highly spatially dependent, leading to differences in an observed spectrum from spot to spot. Furthermore, the rigidity of the material prevents the rotation of compounds within the solid matrix, leading to orientation-dependent effects on the collected UV-Visible spectrum not observed in solution-phase systems.

Tips and Tricks for Measuring Solid-State Materials with UV-Visible Techniques

As described previously, there are many different considerations which must be accounted for when studying solid-state materials. Below is a list of common tips and tricks that can help when studying solid substances.

- Unlike with solution-phase measurements, solid state materials can be highly heterogeneous. If repeat measurements are to be taken at different times or on different days, ensure the same spot is sampled to avoid errors due to spatial differences in the material's composition.
  - If there is concern about sample heterogeneity, it can be helpful to run the same sample in triplicate to determine an average spectrum. For films, choose different sampling regions on the same film. For powders, sample separate portions, allowing for mixing in between each replicate collection.

- For film measurements, the substrate is highly important in establishing the material's background for transmission measurements. Be sure to use a substrate which does not absorb greatly in the spectral region of interest for the sample. If the substrate absorbs too much, additional information cannot be obtained concerning the transmission of the sample alone.
  - If the spectrum of the substrate is unknown, take a blank measurement against air, with no sample or substrate in the light path. Then take a measurement of the substrate to determine the transmission spectrum of the material. After accounting for the air blank, the substrate spectrum can be subtracted from the transmission spectrum of the sample deposited on the substrate at a later time to correct for the transmission loss from the substrate.
- Ensure the film is facing the incident light beam. If the sample is facing the "wrong" direction, the light which interacts with the film may be attenuated by the substrate. For transmission measurements, the resulting spectrum will exhibit a lower %T than is expected in the regions where the substrate absorbs. In reflection measurements, attenuation by the substrate can also contribute to a loss of observed reflectance.
- If the thickness of the film is on the order of the wavelength of light used in the measurement (190 nm – 1100 nm for the Evolution Instruments), an interference pattern can be introduced in the spectrum as discussed previously. This pattern can be used to determine the thickness of the film; however, it can also obscure the true transmittance or reflectance spectrum of the material. Absorptive bands can dampen the effect of the interference, but complete removal of this interference pattern is difficult.
- For film samples, the deposited material is unable to rotate or "tumble" as it could in solution. This degree of freedom afforded to solution phase systems allows for the formation of an isotropic distribution of compounds present. As such, any light polarization dependencies will be averaged out as the molecules rotate in solution. In solids, polarization dependencies may be observed as the rigidity of a given molecule's orientation prevents averaging the observed impact of light polarization. Therefore, when working with a new material it can be helpful to measure the reflectance or transmittance in at least two different orientations to see if there is a polarization- or orientation-dependent effect present. This is particularly important for films which are highly ordered or crystalline in nature.

Conclusions

Though more complicated than solution-phase measurements, UV-Visible analysis of solid samples can provide valuable information about the behavior of a material. Herein, the use of UV-Visible transmission and reflection techniques was used to demonstrate effective analysis of powder, film and curved solid samples. To aid in these analyses, a variety of accessories compatible with the Evolution spectrophotometers can be used to measure powder or diffuse reflecting materials (ISA-220 and Praying Mantis) as well as determine the specular reflectance at multiple angles of incidence (VeeMAX variable angle specular reflectance accessory), including near-normal incidence (8° specular reflectance accessory).

References

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