

Infrared Reflection Spectrometries

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Spectral analysis of irreplaceable works of art presents important technical challenges due to the need for minimally invasive or non-invasive methods. The artworks should, as much as possible, remain intact. For mid-infrared spectrometric analyses, reflection methods, that is, specular reflection, attenuated total reflection, and diffuse reflection, present attractive options. Still, each of the three spectrometric techniques presents its own issues with respect to sensitivity and spectral anomalies. The gold standard for infrared spectra is regarded as transmission spectrometry, which requires invasive sampling of the original item to be analyzed. Transmission spectra, if collected carefully, have no band distortions or band shifts, if the instrument is operating correctly. The reflection methods, have distinctly different characteristics, for which the theoretical aspects are quite well understood. To understand the differences, the optical constants, refractive index and the absorption index, must be considered. The different reflection methods are affected in different ways by the optical constants. A theoretical discussion of optical constants is beyond the scope of this presentation, and only a brief introduction will be given.

Attenuated Total Reflection (ATR) spectrometry has become the most popular general sampling technique for infrared spectra due to the lower sample preparation requirements compared to other techniques. The drawback, particularly with samples that cannot be damaged, is that the sample must be in intimate contact with the ATR internal reflection element (or IRE, sometimes erroneously called a "crystal"). Intimate contact can be an issue, as the infrared radiation only extends a few micrometers beyond the surface of the IRE, and often some pressure must be exerted to record a good spectrum, which could damage the sample. While ATR spectra are straightforward to collect, there are anomalies associated with the spectra. The "depth of penetration" of the infrared radiation into the sample is a function of wavenumber and refractive index of the sample. The refractive index is generally around 1.5 for most organic compounds, but that is true only where there is no absorption. Inside an absorption band, the refractive index can vary greatly, and the band intensities, shapes, and even positions can be distorted. There are algorithmic corrections that may be applied to the spectra, but care must be taken to assure no additional anomalies are introduced.

Specular reflection spectrometry overcomes at least some of the issues of ATR spectrometry because it is a non-contact technique. Distinction has to be drawn between bulk samples, where the sample thickness is greater than or equal to the incident wavelength, and thin samples, where the sample is thinner than the wavelength. Thin samples need a reflective surface upon which the sample sits, or the radiation will not readily be reflected back to the spectrometer. Bulk samples are more directly measured, but the refractive indices and the absorption indices of the sample affect the spectrum. For most organic molecule samples, the refractive index dominates the reflection spectrum, and as such, the resulting reflectance spectrum appears as a refractive index spectrum. (Reflectance is the intensity of the reflected radiation ratioed by the incident radiation.) The refractive index across absorption bands

varies with wavelength, and the spectral features are similar to first derivatives of the spectral bands. Judicious application of a Kramers-Kronig (KK) transform can yield the true refractive index spectrum and the absorption index spectrum. The absorption index spectrum is related to the absorption spectrum. An issue that can arise with reflection spectra of bulk samples is in the measurement of some pigments. If pigments contain minerals, which are largely composed of oxyanions, the absorption index can be very high. If the absorption index is sufficiently high, no radiation can be propagated into the sample, and the reflectance is largely or completely reflected. This reflectance radiation is known as "residual rays" or, more frequently, as *Reststrahlen* bands.

Diffuse Reflection (DR) spectrometry is a suitable technique in some cases. In the mid-infrared region, the sample must be diluted into a solid solution to produce a good spectrum. Typically, this is done in a salt such as KBr. This requires that the sample be extracted and pulverized to a small particle size and mixed carefully with the ground salt. Fortunately, an alternative sampling technique can be used to scrape the surface of the sample very lightly with a small piece of silicon carbide paper. An advantage of DR spectrometry is that the analyte produces better spectra when its concentration is very low. As such, minimal damage to the original sample may result. The raw spectrum is measured in reflectance. It is common practice to convert the reflectance spectrum to absorbance; however, the spectrum may represent a true absorption spectrum better if converted to Kubelka-Munk units.

There are several other issues that can be examined; that is, what else may be used to enhance the results without the introduction of anomalies? It is not always apparent that infrared spectra, or any optical spectra, may not correctly represent band intensities and shapes. Beers Law fails at high absorbances in such a way that band intensities and even shapes may be distorted. It is not uncommon to measure samples that are too concentrated or thick, and sometimes there is no alternative. The definition of high absorbance is subject to a number of factors, but most prominently, the apodization function or line shape function of the spectrometer determines the limit at which Beers Law fails. A simple rule of thumb is to keep the strongest absorbances below 1 absorbance unit (AU). Why is adherence to Beers Law important? If spectral subtraction is needed to resolve components of a mixture spectrum, then if the reference spectrum and the sample spectrum have different non-linear absorbances, the difference spectrum will have anomalies. The same criterion applies to spectral searching; poor search results will occur if the spectra do not obey Beers Law. Other standard computer operations, such as baseline correction, may distort spectra and actually shift band centers. Even spectrometer calibration is important to assure instrumental errors do not introduce anomalies into spectra.