Getting the Best Results from NIR Measurements

Optimal results with NIR spectrometers depends on a good signal-to-noise ratio and less on high spectral resolution.

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In Chemistry, Agriculture and Geology near infrared measurements (700-2500 nm) are usually made in transmission and reflection and are used to probe the molecular structure and composition of materials. Near infrared is preferred over mid-infrared when measurements need to be made at a distance or with little or no sample preparation. The challenge is that the resulting spectra are difficult to interpret manually. Interpretation is frequently performed with the aid of multivariate analysis. This type of interpretation makes the choice of instrument characteristics less obvious but the physical and chemical fundamentals do not change.

The choices are dominated by the fundamentals of physics. The ability to project light, its interaction with the sample, the spatial or temporal modulation of light and its interaction with a optical-electrical transducer or "detector". The simplest part of the system is a broadband (white) light source, which is usually a tungsten or tungsten-halogen lamp. The light source is chosen to be bright enough to provide sufficient signal at the detector during the measurement time. The detector choices are made by the instrument designer to work optimally in a particular spectral range for that instrument.

The sample absorbs, reflects and transmits light. The amount of light absorbed at each wavelength relative to source intensity is usually the quantity of interest as it directly relates to the molecular structure and composition of the material. The energy of the photons absorbed is related to vibrational transitions from the ground state to excited states as shown in Figure 1. The energy of the transition is affected by bond strength and intermolecular interactions. This pattern of energy transitions allows pattern recognition for identity and quantitative analysis.

There are three fundamental sources of noise in measurements that limit both identification and quantitative analysis. These are: 1) instrumentation noise 2) presentation noise (reproducibility in sample
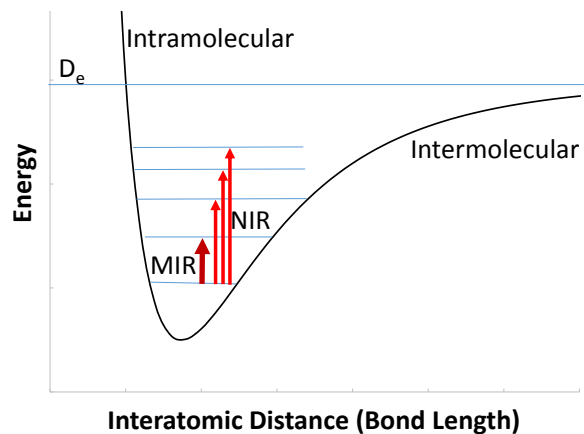
Figure 1. *Vibrational energy diagrams provide insight into energies of vibrational transitions and their sensitivity to the local environment. De indicates the dissociation energy of the molecule. Vibrational energies near De are strongly affected by intermolecular forces.*

presentation) and 3) inherent sample variability. Understanding the role of each provides the information needed to select the proper instrumentation. [1, 2]

Instrumentation noise is present in all instruments. Specification sheets for instrument divide these types of specifications among photometric errors, dynamic range, and stability. The first two are generally well described in graduate-level Analytical Chemistry texts. [2] The third and fourth are part of the art of optical design. Instruments with good wavelength stability over a wide range of environmental conditions frequently provide robust calibrations. Instrument wavelength stability should be $1/10^{th}$ or better of the instrument resolution at the central wavelength. At this level of stability, instrument resolution needs to be no better than the Nyquist sampling frequency for any given band, although band shape information is lost. Recommendations from various textbooks on spectroscopic analysis are that five resolution elements across a band are desirable when band shape is important. [2] The narrowest absorption band for liquids and solids measured in the NIR are water in talc and asbestos crystals. The band at 1392 nm is 1.2 nm at full-width half-maximum (FWHM). More typically, NIR bands are more than 40 nm FWHM. Polystyrene,

as shown in Figure 2, is used as a wavelength calibration standard because of its sharp, well-spaced bands. [3, 4] The isolated polystyrene band near 1160 nm is 30 nm FWHM. The breadth of the bands is related to the influence of the external environment from both steric and dielectric effects. Most substances are have greater disorder than the materials mentioned above. Resolution is frequently less important than stability, linearity and photometric noise to instrument performance.

Presentation noise is frequently a limiting source of noise in the near-infrared. For liquids, cell path lengths should be controlled to 0.1% if possible and temperature controlled to 1 °C or better. Solutions containing water may need to be controlled to 0.1 °C to avoid shifting of the water bands. Temperature is important for solids too. Thermal effects, especially drying and phase transformation, can lead to calibration bias. With solids, particle size control and homogeneity provide the greatest challenges. Experimental designs can, and should, be used to evaluate and accommodate particle size variations, thermal effects and effective path length.

Inherent variation in many samples, especially those from manufacturing processes and natural origin is often significant. Impurities and manufacturing variability can frequently be detected either through physical or chemical effects on the spectra. Laboratory-generated samples may lack this type of variability especially since analytical instruments and high purity reagents are used as a reference.

Purchasing an instrument that is appropriate to the problem needs is a straightforward process. Evaluation of the specifications with respect to expected variations (noise) leads to an optimal balance of budget and instrumentation performance. Resolution requirements need to be balanced with other instrument characteristics for the application. Pursuing high resolution solely could be a waste of money and effort.
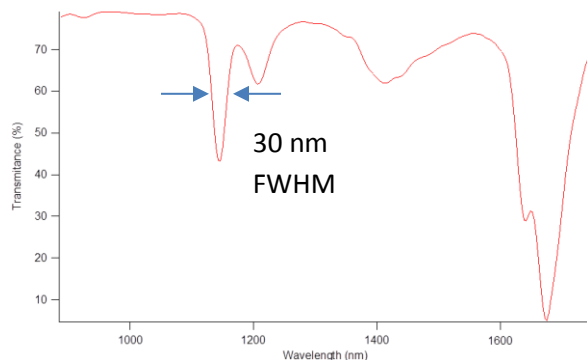
Figure 2. An NIR transmission spectrum of a polystyrene film. The narrow feature at 1160 nm is approximately 30 nm FWHM.

References

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