

Any measurement involves some level of noise superimposed onto a "true" value of the quantity measured by the experiment. This noise comes from the factors that influence the value of the measured quantity but are not fully controlled by the experimenter. The spectroscopic measurement has yet another level of subtlety stemming from the fact that the quantity directly measured by the experiment is not the light intensity itself. The spectroscopic observable is a loss of intensity due to the interaction of light with the sample. In particular, we will examine factors influencing the S/N of an FTIR spectroscopic measurement.

In an FTIR spectrometer, the quantity measured is not the light intensity as a function of wavenumber (frequency, wavelength) but the Fourier transform of that quantity. This is a consequence of using Michelson interferometer and recording an interferogram. The detector converts light intensity into a voltage which is subsequently digitized. The electrical circuit employed by the detector should ideally read zero in absence of light, but, in reality, there will always be some level of random voltage presented to digitizing circuitry. One source of noise present in the circuit is the so called Johnson noise. This noise is of thermal origin and the RMS of the detector voltage due to this noise is proportional to the square root of the product of bandwidth, absolute temperature and resistance. This noise is thus independent of the signal on the detector.

Another source of noise is due to the digitization process. The digitization process has finite resolution and rounding off of the continuous value introduces error into the measurement process. The minimization of this type of noise is achieved by appropriate amplification of the detector signal so that the full dynamic range of the A/D converter can be utilized. Another source of noise is due to the triggering error in the measurement of a point of interferogram. The interferogram points are supposed to be measured at equally spaced intervals along the scanning mirror movement. To assure this, scanning mirror movement is tracked by the interferogram of a laser of a known wavelength. The interferogram of the tracking laser is a sine wave and positive zero crossings of the laser interferogram usually serve as triggers for reading of the IR signal. As with every other electrical signal, the laser interferogram contains some small level of random noise, hence the triggering includes small time fluctuations around the true triggering time. This time, the noise level is not independent of the signal measured. The noise due to triggering error at a point of interferogram is proportional to the product of the timing error and the slope of the interferogram in this point.

The collected interferogram consists of a "true" signal and a noise:

$$I_n = I_n^o + \delta_n \quad (1)$$

where I_n is the n^{th} measured interferogram point, I_n^o is the true value of the interferogram at the n^{th} point, and δ_n is the noise at that point. If N interferograms are co-added, the relative strength of the random portion of the noise is reduced by a factor $1/\sqrt{N}$. In computing the Fourier transform, one gets:

$$S(k_m) = \sum_n I_n e^{-ik_m x_n} = \sum_n I_n^o e^{-ik_m x_n} + \sum_n \delta_n e^{-ik_m x_n} = S^o(k_m) + \Delta(k_m) \quad (2)$$

Note that for random noise δ_n the value of $\Delta(k_m)$ is actually not a function of the wavenumber k . It is however useful to retain the nominal functional dependence to reflect the fact that the noise value is computed at a given wavenumber and will change from point to point. For an interferogram consisting of M points, the value of the noise can be estimated based on the randomness of δ_n . If the RMS of δ_n is d then the RMS of $\Delta(k_m)$ is:

$$D = d\sqrt{M} \quad (3)$$

The important consequence of the above result is that, everything else being the same, the larger the size of interferogram, *i.e.* the larger M , the worse S/N of the resulting single beam spectrum.

The transmission spectrum is calculated as the ratio of a sample spectrum to a background spectrum. Thus the noise from the single beam spectra propagates to the noise in the measured transmittance as follows:

$$T(k) = \frac{S_S^0(k) + \Delta_S(k)}{S_B^0(k) + \Delta_B(k)} = T^0(k) + \frac{\Delta_S(k) + \Delta_B(k)}{S_B^0(k)} + \dots = T^0(k) + \delta T(k) \quad (4)$$

Thus when the noise in the measurement of the interferogram is independent of the signal measured, the resulting uncertainty in the measured transmittance is independent of the transmittance.

The transmittance however is not the quantity of immediate interest in spectroscopy. Beer's "Law" states that the logarithm of transmittance is approximately proportional to the sample concentration. The negative logarithm of transmittance is called absorbance. Thus of interest is to find out how the noise acquired in collecting the interferogram is propagated into uncertainties in measured absorbance of the sample, since this uncertainty is directly proportional to the uncertainty in the estimate of the sample concentration that follows from it. Consequently:

$$A = -\log(T) = -\log(T^0(k)) \left(1 + \frac{\delta T(k)}{T^0(k)}\right) = A^0 + \frac{\delta T}{T^0} \quad (5)$$

from (5) it follows that:

$$\delta A = \frac{\delta T}{T} \quad (6)$$

Since by definition (5) we know that $T = 10^{-A}$, we finally obtain:

$$\delta A = \delta T \cdot 10^A \quad (7)$$

and since δT is independent of T, it is also independent of A. Absorbance thus represents the "signal" that has direct relevance to the analytic measurement and δA represents noise (or uncertainty) in that measurement. Hence the signal to noise is given by the ratio:

$$\frac{A}{\delta A} = \frac{1}{\delta T} A \cdot 10^{-A} = \frac{1}{\delta T} A e^{-\ln 10 \cdot A} \quad (8)$$

It is easy to see that the S/N ratio for a spectroscopic measurement as a function of absorbance reaches maximum for the value of absorbance of $A=1/\ln(10)=0.434$.

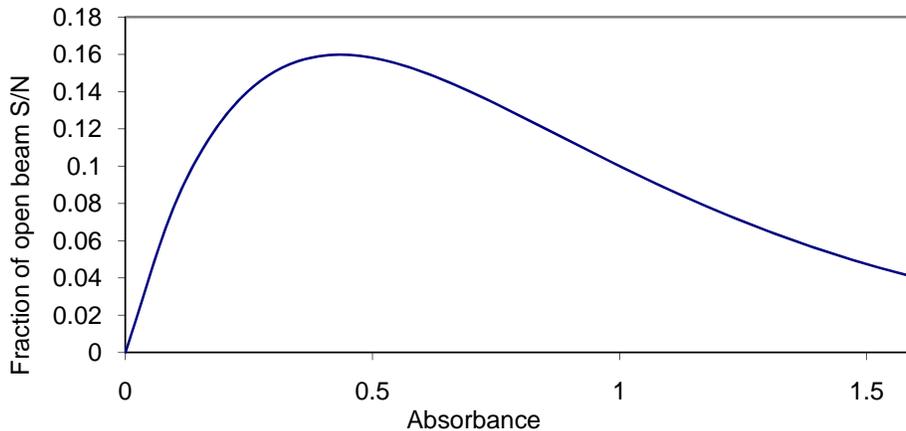


Figure 1. S/N as a function of absorbance.

Two things are obvious from the graph in Figure 1. First, at best only 16% of the spectrometers S/N at a particular wavelength ($1/\delta T$) is available for the S/N of the absorbance measurement. Second, to maximize S/N of the measurement one must be able to control the level of absorbance at a particular wavelength in order to tune in to the maximum. In a transmission experiment, the level of absorbance is easily adjusted by adjusting the pathlength. This is straightforward with liquids and gasses. With solids, the adjustment of pathlength can be more problematic. Similarly, in an ATR measurement, a number of reflections, angle of incidence and/or refractive index of IRE can all be utilized to tune the absorbance level to a desired value.