

Analysis of Noise — Part II

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In our previous column (1) we brought up the question of how various types of noise are related to the noise characteristics of the spectra we observe. In this installment and in the next few columns, we will derive the expressions for the various situations that arise, as described in the previous column. We begin with a fairly simple case — that of constant detector noise. This installment will also serve to lay out the general conditions and nomenclature that apply to these derivations. We will treat this first case in excruciating detail, so that the methods we will use are clear; then, for the cases we will deal with in the future, we will give an abbreviated form of the derivations, and anyone interested in following through themselves will see how to do it. Also, some of the results are so unexpected that, without our giving every step, they may not be believed.

Because the measurement of reflectance and transmittance are defined by essentially the same equation, we will couch our discussion in terms of a transmittance measurement. The important difference lay, as we discussed previously, in the nature of the error superimposed on the measurement. Therefore, we begin by noting that transmittance (T) is defined by the equation:

$$T = \frac{E_s - E_{0s}}{E_r - E_{0r}} \quad [1]$$

where E_s and E_r represent the signal due to the sample and reference readings, respectively; E_{0s} and E_{0r} are the “dark” or “blank” readings associated with E_s and E_r . ($E_r - E_{0r}$) of course, must be nonzero.

The measured value of T , caused by the error ΔT , is:

$$T + \Delta T = \frac{(E_s + \Delta E'_s) - (E_{0s} + \Delta E'_{0s})}{(E_r + \Delta E'_r) - (E_{0r} + \Delta E'_{0r})} \quad [2]$$

where the Δ terms represent the fluctuation in the reading caused by instantaneous random effect of noise. An important point to note here is that E_s , E_r , and T , for any given set of readings at a given wavelength, are constants. All variations in the readings caused by noise are associated with ΔE_s , ΔE_r , and ΔT . Rearranging Equation 2:

$$T + \Delta T = \frac{(E_s - E_{0s}) + (\Delta E'_s - \Delta E'_{0s})}{(E_r - E_{0r}) + (\Delta E'_r - \Delta E'_{0r})} \quad [3]$$

The difference between two random variables is itself a random variable. Therefore, we replace the terms $(\Delta E'_s - \Delta E'_{0s})$ and $(\Delta E'_r - \Delta E'_{0r})$ in Equation 3 with the equivalent, simpler terms ΔE_s and ΔE_r , respectively:

$$T + \Delta T = \frac{E_s - E_{0s} + \Delta E_s}{E_r - E_{0r} + \Delta E_r} \quad [4]$$

The presence of a nonzero dark reading, E_{0s} , will, of course, cause an error in the value of T computed; however, this is a systematic error and therefore is of no interest to us here; we are interested only in the behavior of random variables. Therefore we set E_{0s} and E_{0r} equal to zero and note; if T as described in equation 1 represents the “true” value of the transmittance, then the value we obtain for a given reading, including the instantaneous random effect of noise, is:

$$T + \Delta T = \frac{E_s + \Delta E_s}{E_r + \Delta E_r} \quad [5]$$

and we also find that on setting E_{0s} and E_{0r} equal to zero in equation 1, equation 1 becomes:

$$T = E_s / E_r \quad [6]$$

where ΔE_s and ΔE_r represent the instantaneous, random values of the change in the sample and reference readings caused by the noise. Because, as we noted above, T , E_s , and E_r are constant for any given reading, any change in the measured value because of noise is contained in the terms ΔE_r and ΔE_s . In statistical jargon this would be called “a point estimate of T from a single reading,” and ΔT is the corresponding instantaneous change in the computed value of the transmittance. Again, E_r must be nonzero.

We note here that ΔE_s and ΔE_r need not be equal; that will not affect the derivation. For the case we are considering in this column, however, we are assuming constant detector noise; therefore, when we pass to the statistical domain, we will consider σ_{E_s} to be equal to σ_{E_r} . That, of course, refers only to the expected values; because the noise is random, the instantaneous values will virtually never be the same.

On subtracting Equation 6 from Equation 5 we obtain the following:

$$T + \Delta T - T = \frac{E_r + \Delta E_r}{E_r + \Delta E_r} - \frac{E_r}{E_r} \quad [7]$$

$$\Delta T = \frac{E_r(E_r + \Delta E_r) - E_r(E_r + \Delta E_r)}{E_r(E_r + \Delta E_r)} \quad [8]$$

$$\Delta T = \frac{E_r E_r + E_r \Delta E_r - E_r E_r - E_r \Delta E_r}{E_r(E_r + \Delta E_r)} \quad [9]$$

$$\Delta T = \frac{E_r \Delta E_r - E_r \Delta E_r}{E_r(E_r + \Delta E_r)} \quad [10]$$

Equation 10 might look familiar. If you check an elementary calculus book, you'll find that it's about the second-to-last step in the derivation of the derivative of a ratio (about all you need to do is go to the limit as ΔE_s and $\Delta E_r \rightarrow$ zero). However, for our purposes we can stop here and consider Equation 10. We find that the total change in T — that is, ΔT — is the result of two contributions:

$$\Delta T = \frac{E_r \Delta E_r}{E_r(E_r + \Delta E_r)} - \frac{E_r \Delta E_r}{E_r(E_r + \Delta E_r)} \quad [11]$$

We note that, because by assumption E_r is nonzero, and ΔE_r is nonzero and independent of E_r , the first term of Equation 11 is nonzero. The value of the second term of Equation 11, however, will depend on the value of E_s — that is, on the transmittance of the sample.

To determine the standard deviation (SD) of T we need to consider what would happen if we take multiple sample and reference readings; then we can characterize the variability of T . Because E_r and E_s are fixed quantities, when we take multiple readings we note that we arrive at different values of $T + \Delta T$ because of the differences in the values of ΔE_r and ΔE_s on each reading, causing a change in ΔT . Therefore we need to compute the standard deviation of ΔT , which we do from the expression for ΔT in Equation 11:

$$SD(\Delta T) = SD\left(\frac{E_r \Delta E_r}{E_r(E_r + \Delta E_r)} - \frac{E_r \Delta E_r}{E_r(E_r + \Delta E_r)}\right) \quad [12]$$

or equivalently, we calculate the variance of ΔT , which is the square of the standard deviation:

$$Var(\Delta T) = Var\left(\frac{E_r \Delta E_r}{E_r(E_r + \Delta E_r)} - \frac{E_r \Delta E_r}{E_r(E_r + \Delta E_r)}\right) \quad [13]$$

The proof that the variance of the sum of two terms is equal to the sum of the variances of the individual terms is a standard derivation in Statistics, but because most chemists are not familiar with it, we present it in the appendix sidebar. Having proven that theorem, and noting that ΔE_s and ΔE_r are independent random vari-

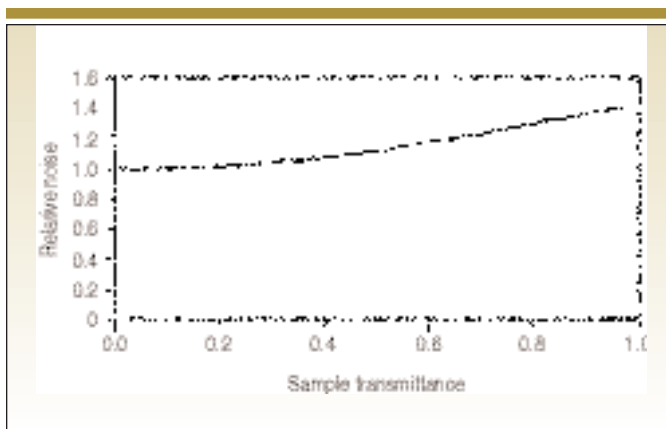


Figure 1. Noise level of a transmittance spectrum as a function of the sample transmittance.

ables, they are uncorrelated and we can apply that theorem to show that the variance of ΔT is:

$$Var(\Delta T) = Var\left(\frac{E_r \Delta E_r}{E_r(E_r + \Delta E_r)}\right) + Var\left(\frac{-E_r \Delta E_r}{E_r(E_r + \Delta E_r)}\right) \quad [14]$$

Because ΔE_r is small compared to E_r , the ΔE_r in the denominator terms will have little effect on the variance of T . In a case where this is not true, the derivation must be suitably modified to include this term. This is relatively straightforward: substitute the parenthesized terms into the equation for variance (for example, as we do in the appendix), hook up about a 100-hp motor or so, and “turn the crank” — as we will do in due course. It's mostly algebra, although a lot of it!

In our current development, however, we assume ΔE_r is small and therefore we replace $(E_r + \Delta E_r)$ with E_r :

$$Var(\Delta T) = Var\left(\frac{E_r \Delta E_r}{E_r^2}\right) + Var\left(\frac{-E_r \Delta E_r}{E_r^2}\right) \quad [15]$$

$$Var(\Delta T) = Var\left(\frac{\Delta E_r}{E_r}\right) + Var\left(\frac{-T \Delta E_r}{E_r}\right) \quad [16]$$

We have shown previously that if a represents a constant, $Var(aX) = a^2 Var(X)$ ((2), or see (3) chapter 11, p. 94). Hence Equation 16 becomes:

$$Var(\Delta T) = \left(\frac{1}{E_r}\right)^2 Var(\Delta E_r) + \left(\frac{-T}{E_r}\right)^2 Var(\Delta E_r) \quad [17]$$

Because we have assumed constant detector noise for this column, $Var(\Delta E_s) = Var(\Delta E_r) = Var(\Delta E)$

$$Var(\Delta T) = \frac{1 + T^2}{E_r^2} Var(\Delta E) \quad [18]$$

Finally, reconverting variance back to standard deviation by taking square roots on both sides of Equation 18:

APPENDIX: PROOF THAT THE VARIANCE OF A SUM EQUALS THE SUM OF THE VARIANCES

Let A and B be random variables. Then the variance of $(A + B)$ is by definition:

$$V(A + B) = \frac{\sum \left((A + B) - \overline{(A + B)} \right)^2}{n - 1} \quad [A1]$$

Because $\overline{(A + B)} = \bar{A} + \bar{B}$

we can separate the numerator terms and then expand the numerator:

$$V(A + B) = \frac{\sum \left(\begin{array}{l} A^2 + AB - A\bar{A} - A\bar{B} + AB + B^2 - \bar{A}B - B\bar{A} \\ -A\bar{A} - \bar{A}B + \bar{A}^2 + AB - A\bar{B} - B\bar{A} + \bar{A}^2 + \bar{B}^2 \end{array} \right)}{n - 1} \quad [A2]$$

We can now collect terms as follows:

$$V(A + B) = \frac{\sum (A^2 - 2A\bar{A} + \bar{A}^2)}{n - 1} + \frac{\sum (B^2 - 2B\bar{B} + \bar{B}^2)}{n - 1} + 2 \frac{\sum (A - \bar{A})(B - \bar{B})}{n - 1} \quad [A3]$$

Equation A3 can be checked by expanding the last term, collecting terms, and verifying that all the terms of Equation A2 are re-generated. The third term in Equation A3 is a quantity called the *covariance* between A and B . The covariance is a quantity related to the correlation coefficient. Because the differences from the mean are randomly positive and negative, the product of the two differences from their respective means is also randomly positive and negative, and tends to cancel when summed. Therefore, for independent random variables the covariance is zero, because the correlation coefficient is zero for uncorrelated variables. In fact, the mathematical definition of “uncorrelated” is that this sum-of-cross-products term is zero. Therefore, because A and B are random, uncorrelated variables:

$$V(A + B) = \frac{\sum (A - \bar{A})^2}{n - 1} + \frac{\sum (B - \bar{B})^2}{n - 1} \quad [A4]$$

The two terms of Equation A4 are, by definition, the variances of A and B .

$$Var(A+B) = Var(A) + Var(B) \quad [A5]$$

QED.

$$SD(\Delta T) = \sqrt{1 + T^2} \frac{SD(\Delta E)}{E_r} \quad [19]$$

We remind our readers here that ΔE , as we have been using it in this derivation, is the difference between $\Delta E'$ and $\Delta E'_0$ in Equation 4 and the expected value in the statistical nomenclature is therefore $2^{1/2}$ times as large as $\Delta E'$ (because it is the result of the difference between random variables with equal variance), a difference that should be noted when comparing results with the original definition of S/N in Equation 2.

We next note, and this is in accordance with expectations, that the noise of the transmission spectrum, $SD(\Delta T)$ depends on the noise-to-signal ratio of the readings, the inverse of S/N commonly used and presented as a spectrometer specification — at least, as long as the noise is small compared to the reference energy reading so that the approximation made in Equation 15 remains valid. Recall that E_r is the energy of the reference reading and $SD(\Delta E)$ is the noise of the readings from the detector; this ratio of $SD(\Delta E)/E_r$ is the (inverse of the) true signal-to-noise ratio; the noise observed on a transmission spectrum, while related to S/N , is in itself not the true signal-to-noise ratio.

Next we note further, and this is probably contrary to most spectroscopist's expectations, that the noise of the transmittance spectrum is not constant, but depends on the transmittance of the sample, being higher for highly transmitting samples than for dark samples. Because T can vary from 0 (zero) to 1 (unity), the noise level can vary by a factor of the square root of two, from a relative value of unity (when $T = 0$) to 1.414... (when $T = 1$). This behavior is shown in Figure 1.

The increase in noise with increasing signal might be considered counterintuitive, and therefore surprising, by some. Intuition tells us

that the S/N ratio might be expected to improve with increased signal regardless of its source, or that the noise level of the transmittance spectrum should at least remain constant, for constant detector noise. This misapprehension has worked its way into the modern literature:

“In most infrared measurements situations, the detector constitutes the limiting noise source. Because the resulting fluctuations have the same effect as a fixed uncertainty in the signal readout, they appear as a constant error in the transmittance.” (4)

Intuition tells us that if the transmittance is zero, then it should have no effect on the readings. In fact this is true, but it is also misleading. The transmittance being zero, or the sample energy being zero, does not mean that the *variability* of the reading is zero. The explanation of the actual behavior comes from a careful perusal of the intermediate equations developed in the course of arriving at Equation 19, specifically Equation 14. From the first term in that equation we see that the irreducible minimum noise is contributed by the reference signal level (E_r) multiplied by the *variation* of the sample signal (ΔE_s), independently of the *value* of the sample signal. Increasing sample signal then serves to add additional noise to the total, through its contribution, in the second term of Equation 14, which comes from the sample signal through its being multiplied by the *reference* noise.

Conventional developments of the subject contain flaws that are usually hidden and subtle. In Ewing's book, for example (5), the development includes the step (see page 43, the section between Equations 3-6 and 3-7) of noting that, because the reference energy is essentially set equal to unity, $\log(E_r)$ (or P_0 , the equivalent in Ewing's terminology) is set equal to zero. However, this is done *before* the separation of P_0 from ΔP_0 , creating the implicit, but erroneous, result that ΔP_0 is zero as well. In our nomenclature, this causes the second term of Equation 14 to vanish, and as a conse-

quence the erroneous result obtained is that ΔT is independent of T . This, of course, appears to confirm intuition and, because it is based on mathematics, appears to be beyond question. Other treatments (6) simply don't question the origin of the noise in T and assume *a priori* that it is constant, and work from there.

The more sophisticated treatment of Ingle and Crouch (7) comes very close but also misses the mark; for some unexplained reason, they insert the condition: "... it is assumed there is no uncertainty in measuring E_{rt} and E_{0t} ...". Now in fact this could happen (or at least there could be no *variation* in ΔE_p); for example, if one reference spectrum was used in conjunction with multiple sample spectra using an FTIR spectrometer. However, that would not be a true indication of the total error of the measurement because the effect of the noise in the reference reading would have been removed from the calculated SD, whereas the true total error of the reading would in fact include that source of error, even though part of it was constant. It is to their credit that these authors explicitly state their assumption that they ignore the variability of E_r rather than hiding it. Furthermore, they allude to the fact that *something* is going on when they state "... the approximation is good to within a factor of $2^{1/2}$." Nevertheless, they failed to follow through and derive the exact solution to the problem.

The bottom line to all this is that in one way or another, previous treatments of this subject have invariably failed to consider the effect of the noise of the reference reading, and therefore arrived at an erroneous conclusion.

Whew! I think that's enough for one column. I need a rest. And so does the typesetter! We will continue the derivation in our next column.

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