The Doty NMR S/N Applet – For Any Probe, Any Nuclide, Any Sample, …

Allows you to easily and anonymously compare the S/N of your probe to Doty Probes

A lot of useful expressions have been derived and published for calculating the S/N of an NMR probe, but generally they are either very difficult to apply or of limited validity. In our experience, the most generally valid expression predicting the S/N may also be the most difficult to use – until now. The Doty S/N applet makes it easy to estimate the S/N that can be expected from any NMR probe for any conditions with minimal and easy-to-determine input information.

The Doty S/N applet basically just needs to know the rf power P required to achieve a $\pi/2$ pulse τ_{90} of some known length for any nuclide in your probe at any polarizing field B_0. It then calculates the S/N of your probe for any sample, nuclide, temperature, linewidth, B_0, etc. – for a single acquisition following a 90^0 pulse at thermal equilibrium.

Comparing Your Probe to a Doty Probe. To compare the S/N of your probe to a Doty probe, select the Doty probe of interest from the list for which data are shown, and appropriate default parameters will appear. (Perhaps at some point in the future we'll include data for some competitor's probes. Perhaps they'll provide you the needed data so you can make the comparison.)

Calculating Expected S/N for Your Conditions. One begins by entering B_0, the nuclide, τ_{90}, P, sample volume V_S, and pulse power P at which the probe design has been characterized. It is not necessary to know this information for the B_0, nuclide, sample, or temperature of interest if the probe circuit design is basically similar over a range of fields. The applet knows how to scale the calibration information to different fields, nuclides, sample volumes, and temperatures, assuming the circuit design is similar for the different cases. For example, this means if you have calibration data for an E-Free, T3, or Bmax probe at 500 MHz, you can get excellent S/N predictions for a probe of similar design at any other field.

Of course, there are some limitations on the accuracy of the prediction, particularly if it is for a radically different frequency or temperature than that for which the reference $\pi/2$ and P were obtained, but even then the prediction should be quite useful, subject to a few more limitations mentioned shortly. (And yes, the applet appears to be asking for some of the same information twice, but only what is needed to calculate performance at a field different from that for which calibration data are known.)

After entering the pulse width numbers needed for calibration, the following inputs are needed to calculate the expected S/N following a single $\pi/2$ pulse for the conditions of interest.

Sample [HMB, glycine, H_2O, …other]
nuclide abbreviation (e.g., 103Rh)
B_0, polarizing field [T]
τ_{90}, $\pi/2$ pulse length [μs]

(Note: Here, you may enter any number you wish for τ_{90}. The purpose here is simply so the applet can calculate the power required the $\pi/2$ pulse used. At this point, it has no effect on the calculated S/N. The circuit efficiency has already been determined from the probe calibration data and any needed scaling.)

V_S, active sample volume [mL]
T_S, sample temperature [K]
T_R, mean temperature of coils and capacitors [K]
mm, sample molecular mass
ρ, sample density [g/mL]
ne, number of equivalent sites in the spectral line of interest
a, nuclide abundance, %
X, sample concentration, %
FWHM, expected experimental linewidth, [Hz]
NF, system noise figure, dB

number of scans, n
Cross polarization (Y, N)

The largest uncertainty in the predicted S/N often comes from uncertainty in the linewidth, and the next largest source of error is likely to be V_S. The nuclide abundance a is the % abundance of the nuclide of interest at the site of interest. (If the sample is not labeled, then the appropriate number here is the natural abundance, which appears as the default.) The sample concentration X is the molar % of the molecule of interest in the solvent (or matrix).

There may be other factors that need to be taken into account, as optimum experiments often don't use 90^0 pulses with delay between scans of more than $4T_1$ to permit full relaxation, but those are normally minor corrections and are not addressed in this applet.

The $\pi/2$ pulse width is always somewhat dependent on sample volume because of B_1 field inhomogeneity and possibly sample loading, but there is not a good way to account for that in a simple program. So if the active sample volume (or its conductivity) for which one wishes to find the S/N is significantly different from the volume that was used in characterizing the probe's τ_{90} and P to start with, some adjustment in the initial inputs may be needed. For example, if the input τ_{90} was with a sample that extended well beyond the homogeneous field and the new V_S is for a small sample that is confined just to the center of the coil, and in both cases the sample losses are small compared to other losses (as is often the case), a reasonable correction would be to assume the τ_{90} is 20% smaller for the same P in the center of the coil.

The calculation takes into account the normal frequency and temperature dependences of Q_L subject to the assumption that sample losses are small compared to circuit losses, as is usually the case with small samples. The program doesn't know or care what the Q actually is, just how it changes from the reference calibration conditions to the new conditions, so that ratio is shown. If for some reason you know it is not right (for example, because the new sample losses are very different) you may wish to make an appropriate correction in the predicted S/N.

There will increasingly be more use of novel methods for increasing the polarization compared to thermal – especially Dynamic Nuclear Polarization, paramagnetic hydrogen, hyperpolarized Xenon, and probably others. For now, these effects are left for the user to add. In all cases, all of the basic NMR factors included in this calculator are still completely relevant and establish the starting point for S/N calculations. The theory behind the calculator is presented in the following section, but you don't need to worry about these details to use the calculator.

EPR S/N. The NMR S/N calculator should also (in principle) work for pulsed EPR by entering e- for the nuclide abbreviation. Some limitations in EPR would be actually knowing a $\pi/2$ pulse length, linewidth, effective NF, and P, partly because the microwave power incident on the EPR cavity is often much less than that leaving the source, and the effective NF must take into account the effects of the circulator, to mention but a few of the complicating factors.

NMR S/N Theory. The classic derivations give the NMR S/N from a single 90^0 pulse (at thermal equilibrium) with an optimum filter [$1/(\pi\Delta\nu) = T_2^*$, the effective transverse relaxation time] and quadrature reception as:

$$S/N = 1000 \left[\frac{\hbar^2 \sqrt{2\pi\mu_0}}{12 k_B^{3/2}} \right] \left[\frac{n_S \gamma I_x (I_x+1) \sqrt{T_2^*}}{T_S \sqrt{T_R + T_P}} \right] (\eta_E \, \eta_F \, Q_L V_S)^{1/2} \omega^{3/2} \qquad (1)$$

where $\hbar$ is Plank's constant divided by 2π, μ_0 is the permeability of free space, k_B is Boltzmann's constant, n_s is the number of spins at resonance per Liter in the spectral line, γ is the magnetogyric ratio, I_x is the spin quantum number, T_2^* is calculated from the actual linewidth (not just the spin-spin relaxation time), T_S is the sample temperature, T_R is the temperature of the circuit resistance (coil and capacitors), T_P is the effective preamp noise temperature, η_E is the rf efficiency (fraction of power dissipated in the coil and sample), η_F is the magnetic filling factor (classic definition), Q_L is the loaded and matched circuit quality factor, V_S is the

sample volume [mL], and ω is the Larmour precession frequency, γB_0 [1-6].   The factor of 1000 is required when everything is SI except as noted above.

Equation (1) ignores radiation damping, but that is never a problem when single-pulse S/N is not very high.   Equation (1) also requires some modification when the linewidth is greater than the probe resonance width, that is, when $\Delta v > \omega/2\pi Q_L$, but those conditions are rare. The changes in T_1 and T_2 as the temperature is reduced usually means the optimum temperature (particularly when signal averaging is required) is not simply the lowest that can be obtained. Equation 1 does not take into account the effect of T_1 on multiple acquisitions. Equation (1) also does not explicitly include the effect of the cable between the probe circuit and the preamp. It should appear as an additional additive term along with T_R and T_P, that can usually easily be made small compared to T_R, except in cryoprobes.

Review of the probe development literature reveals that many prior efforts have not paid sufficient attention to maximizing η_F, η_E, T_2^*, and V_S, and to minimizing T_R. Part of the reason is that prior to the advent of modern full-wave EM software (available only since circa 2005, give or take), it has been very difficult to accurately determine η_F, magnetic filling factor,

$$\eta_f = \frac{\int_s B_1^2 dV}{2\mu_0 U}$$

(2)

where U is the total peak magnetic energy of the sample coil at resonance, B_1 is the transverse component of the magnetic field, and the integration in the numerator is over the sample space. Also, prior to the availability of good circuit simulation tools (since ~1990), it was not easy to determine η_E, rf circuit efficiency, in complex circuits, and many old-school probe designers have been slow to take advantage of modern software. One can find published examples of cases where either (and maybe even both) of these factors is an order of magnitude below what is possible in a more optimized design. Some solids probe design efforts have also not paid sufficient attention to coil effects on B_0 inhomogeneity, and hence T_2^*.

Because of the general difficulty in calculating η_F, an alternative starting point often works better. When the wavelength is large compared to the sample dimensions (the usually case in NMR), it can be shown that the mean B_1 [T] is given by the following, which also serves to define β, a dimensionless magnetic effectiveness determined solely by the coil geometry.

$$B_1 = 0.0001\beta \sqrt{\frac{2\eta_E P Q_L}{f_M V_C}} \qquad \text{(mixed units)}$$

(3)

where the frequency f_M here is in MHz and the coil volume V_C is in mL. The magnetic filling factor η_F of the sample coil can be shown to be given (exactly for uniform B_1, where β can be defined) by the following [6]:

$$\eta_F = \frac{\beta^2}{20} \frac{V_S}{V_C}$$

(4)

Combining the two above equations gives the product $\eta_E \eta_F Q_L$ needed in eq. (1):

$$\eta_E \eta_F Q_L = \frac{2.5E6 f_M V_S B_1^2}{P} = \frac{5\omega V_S B_1^2}{4\pi P}$$

(5)

B_1 is readily determined from the NMR measurement by the following:

$$B_1 = \frac{\pi}{2\gamma\tau_{90}}$$

(6)

The last two terms of equation (1) can now be re-cast into a form that is often more convenient,

$$(\eta_E \eta_F Q_L V_S)^{1/2} \omega^{3/2} = \left(\frac{5\pi}{P}\right)^{1/2} \frac{V_S \omega^2}{4\gamma\tau_{90}}$$

(7)

and the following expression for single-pulse S/N can then be written:

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$$S/N = 1000 \left[\frac{\hbar^2 \pi \sqrt{10\mu_0}}{48 k_B^{3/2}} \right] \left[\frac{n_S \, I_x (I_x + 1) V_S \omega^2 \sqrt{T_2^*}}{\tau_{90} T_S \sqrt{P(T_R + T_P)}} \right] \tag{8}$$

Of course, equations 1 and 8 give identical results, and in either case a correction factor of 0.7 is required for linear polarization. In both cases, T_2^* is calculated from $1/\pi\Delta\nu$, where $\Delta\nu$ is the FWHM linewidth. Equation (8) is often preferred initially; but after the product $\eta_E\eta_F Q_L$ is determined from equation (5), equation (1) is generally more convenient for predicting performance for other nuclides or conditions, as it does not require knowledge of the experimental P and τ_{90}.

The product $\eta_E\eta_F Q_L$ is not a constant for a given probe and circuit, but it is generally sufficiently predictable to permit very good extrapolations. The second term in it is quite constant over a very wide range of frequencies, and the first term is usually fairly constant for a given circuit, though often increasing a little at the upper end of the normal tuning range. In NMR probes will small samples, the losses that determine Q_L are usually mostly in the coils and leads. Their inductance is constant, so their Q's would increase as $f^{1/2}$ and as roughly $T_R^{-0.8}$ over the temperature range from 80-500 K. However, the capacitor losses (which typically account for 25% of the losses) have inverse dependence on frequency and usually no temperature dependence. Likewise, the solder junction losses, which are often ~10% of the total, are constant with temperature. A reasonable estimate then of the $\eta_E\eta_F Q_L$ product at the frequency, temperature, and sample volume of interest then would be

$$(\eta_E\eta_F Q_L)_2 = (\eta_E\eta_F Q_L)_0 \left(\frac{V_{S2}}{V_{S0}} \right) \left(\frac{f_2}{f_0} \right)^{0.4} \left(\frac{T_{R0}}{T_{R2}} \right)^{0.5} \tag{9}$$

where the "0" subscripts denote the values at the reference conditions (from eq. 5), and the "..2" subscripts denote the values at the new conditions of interest.

Published papers usually do not report many of the parameters needed in eq. (1), but if the mean $\pi/2$ pulse length τ_{90} for V_S is reported at a given power P, the sensitivity of the probe can be determined quite accurately for a wide range of conditions – often subject primarily to some uncertainty in n_s, T_2^*, V_S, and T_R.

To access the S/N calulator: https://dotynmr.com/snr/

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