Temperature Calibrations (~ ±0.5 °C)

Adapted from H.Günther, NMR Spectroscopy, 2nd edition, page 66
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A.L. Van Geet, ***Anal. Chem.*** **40**, 2227 (1968); **42**, 679 (1970)
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I. Low temperature calibration

Temperature range: 175 to 330 K (-98 to +57 °C)
Sample: aerated, pure methanol (neat, i.e. no solvent and not degassed)
A trace amount of HCl (< 0.03 % v/v) can be used to collapse methanol multiplets without changing the equations, if desired.
The calibrations are based on the hydrogen bonding strength of the methanol hydroxyl group as a function of temperature.
Anything besides temperature that influences the hydrogen bonding (e.g. water), will add an additional source of error.
Since oxygen is paramagnetic, its presence decreases the relaxation time constant (T_1) of the sample. There is no need in this experiment to degas to achieve longer T_1's.
The sample should be free of temperature gradients (high enough gas flow) and the solution temperature should be at equilibrium.

Measurement:

1. Insert sample into magnet, as usual, with or without spinning, as desired
2. Turn off the "sweep" button light on the BSMS keyboard, if it is lighted
3. Read a normal ^{1}H parameter set appropriate for the probe in use (rpar)
4. ns 1, ds 0, rga, zg, ft, apk
5. Measure the difference in Hz between the two peaks, the absolute value is $\Delta\nu$

Analysis:

Use the following equation with the appropriate values of A and B for the magnetic field you are using to calculate the actual temperature (K) of the sample (T_c):

$$T_{calibrated}\ (K) = 403.0 - A*\Delta\nu - B*(\Delta\nu)^2$$

B_o (MHz)	A	B
200	0.147	5.96×10^{-4}
300	0.098	2.65×10^{-4}
400	0.074	1.49×10^{-4}
500	0.059	9.53×10^{-5}
600	0.049	6.62×10^{-5}

Note: If you prefer to use pure deuterated methanol, ***instead***, the equation is slightly different and the uncertainty of the calibration increases to an error margin of ±0.7 °C. Please refer to page 66 of H. Günther's book cited at the top of this page for more details.

II. High temperature calibration

Temperature range: 310 to 410 K (+37 to +137 °C)
Sample: aerated, pure ethylene glycol (neat: no solvent and not degassed)

"Freshly opened bottles of glycol with a nominal water content of 0.06 % were used." quoted from Kaplan et al, ***Anal Chem* 47:** 1703 (1975).

The calibrations are based on the hydrogen bonding strength of the hydroxyl group as a function of temperature.

Since oxygen is paramagnetic, its presence decreases the relaxation time constant (T_1) of the sample. There is no need to degas to achieve longer T_1's.

The sample should be free of temperature gradients (high enough gas flow) and the solution temperature should be at equilibrium.

Measurement:

1. Insert sample into magnet, as usual, with or without spinning, as desired
2. Turn off the "sweep" button light on the BSMS keyboard, if it is lighted
3. Read a normal ^{1}H parameter set appropriate for the probe in use (rpar)
4. ns 1, ds 0, rga, zg, ft, apk
5. Measure the difference in Hz between the two peaks, the absolute value is $\Delta\nu$

Analysis:

Use the following equation with the appropriate values of A and B for the magnetic field you are using to calculate the actual temperature (K) of the sample (T_c):

$$T_{calibrated}\ (K) = 466.0 - C*\Delta\nu$$

B_o (MHz)	C
200	0.508
300	0.339
400	0.254
500	0.203
600	0.169