Values of Gyromagnetic Ratios

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The gyromagnetic ratio of a particle is the constant that relates the Larmor precession frequency ω_L to the magnetic flux density B:

$$\omega_L = \gamma B$$

The Larmor frequency is often expressed as a frequency f_L, in MHz, instead of radians/sec:

$$f_L = \frac{\gamma}{2\pi} B$$

The γ of the sample material is the fundamental physical constant that underlies NMR magnetometry (see our article on NMR and EPR Technology). Therefore, if you want to know exactly how the measurements of our NMR magnetometers relate back to international metrological standards, you need to know what gyromagnetic ratio is built into our instruments, and where those values came from. Here's the story.

Ancient – but relevant – history

Metrolab's first NMR magnetometer, the Precision Teslameter PT2020, was based on a CERN design, dating from the mid-1970's, called the "NMR Magnetometer Type 9298." Section 2 of CERN's documentation, "Remarks on the NMR Techniques Used," quotes the following values:

Γ_p = 4257.608(12) Hz/G for protons in a cylindrical sample of H_2O
Γ_d = 653.569(2) Hz/G for deuterons in a cylindrical sample of D_2O

(The numbers in parentheses indicate the uncertainty in the last few digits.)

The references cited are:

- Cohen, E. Richard, and Taylor, Barry N. "The 1973 Least-Squares Adjustment of the Fundamental Constants," J. Phys. Chem. Ref. Data 2 (1973): 718.
- Fuller, Gladys H. "Nuclear Spins and Moments," J. Phys. Chem. Ref. Data 5 (1976): 885.

In a slightly different form, these same values still appear in Chapter 7 of the PT2025 User's Manual, "Theory of Operation":

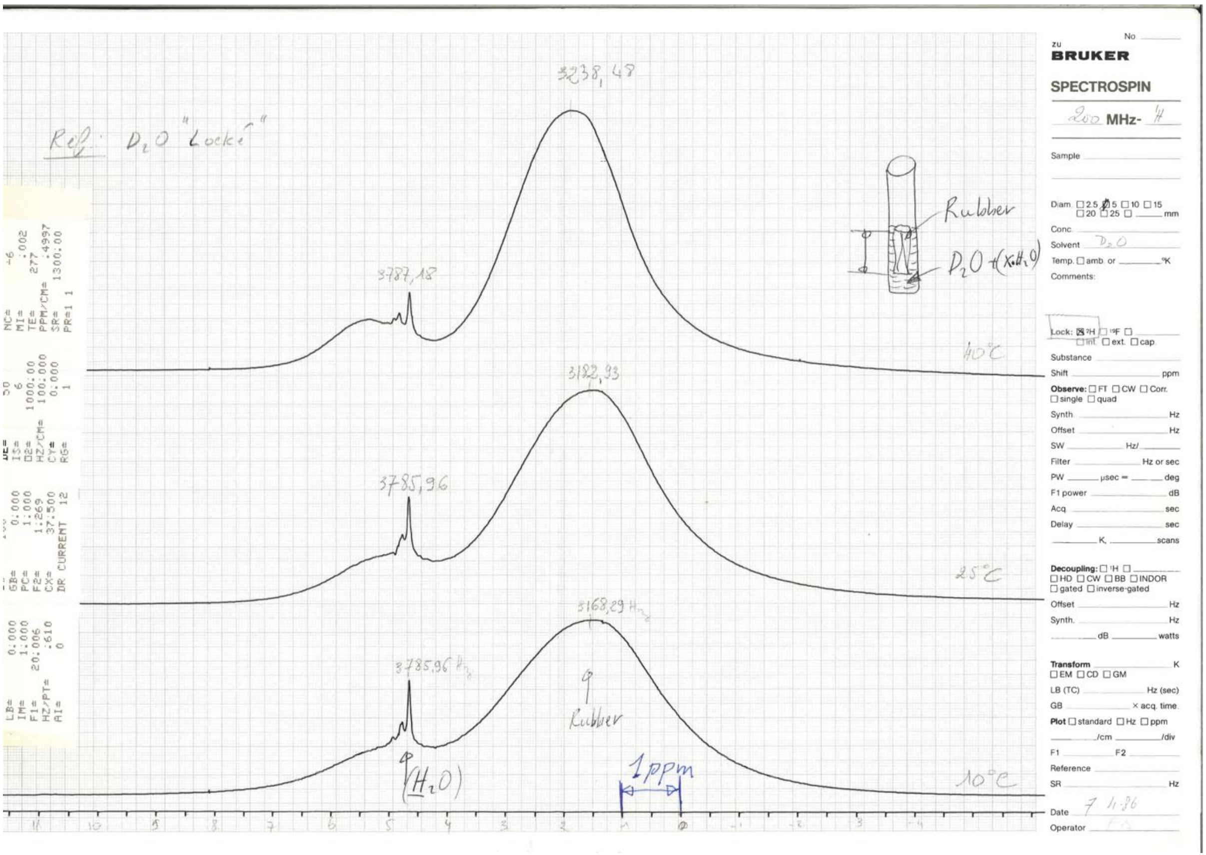
Gp, 1H = 42.57608(12) MHz/Tesla for protons
Gd, 2H = 6.53569(2) MHz/Tesla for deuterons

Physical constants are constantly re-measured, and since the 1980's, the Committee on Data for Science and Technology (CODATA) regularly reviews these measurements and publishes a recommended set of self-consistent values. These internationally accepted values are published by the standards institutes, for example the National Institute of Standards and Technology (NIST) in the USA.

Note that CODATA distinguishes between "proton gyromagnetic ratio" and "shielded proton gyromagnetic ratio." The former refers to free protons (e.g. a proton beam), whereas the second refers to protons in water, where the proton is partially shielded from external magnetic fields by the molecule's electron cloud.

From water to rubber

In 1986, when updating the PT2020 design, in what became the [Precision Teslameter PT2025](), Metrolab decided to use isoprene rubber, rather than water, as sample material. The 1986 CODATA values had just been published, but the shielding parameter of rubber is different from water, so the CODATA values are not directly applicable. To make the link, Metrolab relied on NMR spectroscopy measurements of a rubber sample that also contains water. Here is a copy of one of the original measurements:



The hand-drawn sketch explains what was in the spectrometer's sample tube: a piece of isoprene rubber (CH_2=C(CH_3)-CH=CH_2), bathed in heavy water (D_2O) and a trace of regular water (H_2O). The NMR resonance of the deuterium (D) nuclei serves as a reference, to lock the NMR spectrometer's RF generator. The spectrometer then accurately measures the NMR resonance spectrum of the Hydrogen (H) nuclei in both rubber and water.

The plots show that isoprene rubber has two relatively broad NMR resonance peaks, the large one on the right due to protons in the CH_2 and CH_3 groups, and a smaller one to the left due to protons in the CH groups (less abundant, therefore smaller peak). On top of the CH peak, we see the much sharper resonance of protons in water, allowing the rubber peak to be related back to the CODATA measurements for water.

Each tick on the horizontal axis corresponds to 100 Hz. We used a 200 MHz magnet (~4.7 T), so 2 ticks correspond to 200 Hz / 200 MHz = 1 ppm. We see that the main rubber peak is almost exactly 3 ppm off the water peak. At a given field, the Larmor frequency of rubber is higher than water, so the gyromagnetic ratio of rubber is lower.

The three traces, with measurements at 10°C, 25°C and 40°C, show that within the measurement precision, the water peak does not move, but that the rubber peak does.

According to these measurements, isoprene rubber's gyromagnetic ratio varies ±0.3 ppm over this temperature range. This is one of the reasons why Metrolab claims "only" 5 ppm absolute accuracy for its NMR instruments (more important reasons include the susceptibility and geometry of the sample and surrounding objects).

PT2025 proton probes

The PT2025 distinguishes between two probe types: Range 1 to 5 are proton probes (isoprene rubber), and Range 6 to 8 are deuterium probes (heavy water).

The gyromagnetic ratio for proton probes is based on the physical constants recommended by CODATA in 1986, as published in:

> Taylor, Barry N., and Cohen, E. Richard. "The 1986 CODATA Recommended Values of the Fundamental Physical Constants," J. Res. Natl. Inst. Stand. Technol. 92.2 (1987): 90.

The 1986 CODATA value for the gyromagnetic ratio of shielded protons is:

$\gamma'_p/2\pi = 42.576\,375(13)$ MHz/T

(Again, the numbers in parentheses indicate the uncertainty in the last few digits.)

The 3.0±0.3 ppm shift for isoprene rubber yields a theoretical value of:

$\gamma''_p/2\pi = 42.576\,247(26)$ MHz/T

Due to digitization, the effective value implemented in the PT2025 is:

$\gamma''_p(\text{eff})/2\pi = 42.576\,246$ MHz/T

PT2025 deuterium probes

For deuterium probes, the target gyromagnetic ratio built into the PT2025 remained the historical value that Metrolab inherited from the CERN:

$\gamma_d/2\pi = 6.535\,69(2)$ MHz/T

Due to digitization, the effective value implemented in the PT2025 is:

$\gamma''_d(\text{eff})/2\pi = 6.535\,691\,4$ MHz/T

We didn't realize it at the time, but a more accurate value of the gyromagnetic ratio for deuterium probes could also be computed from the CODATA 1986 values, as follows:

$\gamma_d/2\pi = \mu_d/h$, where

μ_d is the deuteron magnetic moment, and

h is Planck's constant.

$= 0.433\,073\,75\,(15) \times 10^{-26}$ J/T / $6.626\,0755\,(40) \times 10^{-34}$ J s

$= 6.535\,901\,(6)$ MHz/T

The shielding parameter for deuterons in heavy water is roughly the same as for protons in water, since the molecular structure is the same. This shielding correction was listed in 1986 CODATA as:

$\sigma_{H2O} = 25.689(15)$ ppm

Thus, according to the 1986 CODATA values, the gyromagnetic ratio of shielded deuterons in heavy water is:

$\gamma'_d/2\pi = 6.535\,733\,(6)$ MHz/T

Accordingly, the PT2025 measurements for deuterium probes are 6 ppm too high, which exceeds the specified absolute error of 5 ppm. This error was apparently known as far back as the year 2000, but was forgotten until the writing of this technical note. We offer our apologies for this error.

MFC3045

The Magnetic Field Camera MFC3045, released in 1998, returns the measured frequency directly, without the possibility of converting to Tesla. This instrument therefore does not incorporate the gyromagnetic ratio.

Section 1-1 of the MFC3045 User's Manual does, however, give the following value of the gyromagnetic ratio:

$\gamma = 42.576\ 255$ MHz/T

In addition, the WinMFCTool software includes the possibility of displaying results in MHz or Tesla. The value of the conversion factor is:

0.02348727032789000090 T/MHz

The software conversion corresponds to the gyromagnetic ratio cited in the manual. Unfortunately, it is no longer clear where this value came from: it does not correspond to 1986 CODATA, nor to the update suggested by the NIST in 1990, nor to 1998 CODATA, 2002 CODATA, 2006 CODATA, or 2010 CODATA. A mystery.

PT2026 probes

The situation is relatively simple for the Precision Teslameter PT2026: the gyromagnetic ratio is stored in each probe, as a 64-bit floating-point number. This practically eliminates digitization errors, and allows building probes with non-standard sample materials.

The latest published value (2014 CODATA) for the gyromagnetic ratio of the shielded proton is:

$\gamma'_p/2\pi = 42.576\ 385\ 07(53)$ MHz/T

Taking into account the 3.0±0.3 ppm shift for isoprene rubber, the value for **standard proton probes** is:

$\gamma''_p/2\pi = 42.576\ 257(13)$ MHz/T

Metrolab occasionally also uses **silicone rubber** (Polydimethylsiloxane, or PDMS, $(SiO(CH_3)_2)_n$), instead of isoprene rubber. One of its advantages is that this rubber only has CH_3 groups, and therefore a single NMR peak. NMR spectroscopy measurements show that this peak is approximately 5 ppm above that of water. Thus, using the 2014 CODATA values, the gyromagnetic ratio for silicone rubber is:

$\gamma''_p/2\pi = 42.576\ 172(13)$ MHz/T

Using the 2014 CODATA values, we can also recalculate the current values of **deuterium probes**:

$$\gamma_d/2\pi = \mu_d/h = 0.433\ 073\ 5040(36) \times 10^{-26}\ \text{J/T} / 6.626\ 070\ 040(81) \times 10^{-34}\ \text{J s}$$
$$= 6.535\ 902\ 90(13)\ \text{MHz/T}$$

The 2014 CODATA value for the shielding parameter is:

σ_{H2O} = 25.691(11) ppm

Thus, the gyromagnetic ratio of shielded deuterons in heavy water, based on 2014 CODATA, is:

$\gamma'_d/2\pi$ = 6.535 734 99(13) MHz/T

Finally, the PT2026 also includes the option of displaying the measurements in **units of MHz$_p$**. For this, Metrolab uses 2014 CODATA value of the gyromagnetic ratio for the shielded proton:

$\gamma'_p/2\pi$ = 42.576 385 07(53) MHz/T