Referencing of NMR spectra, $\varXi$ scale (06/2011)

Several possibilities exist to reference your NMR spectra: Addition of an internal standard (for ^{1}H and ^{13}C usually TMS), use of an external standard (e.g. for ^{31}P or ^{19}F) with the aid of a capillary tube or, last but not least, by employing the so-called $\varXi$ (Xi) scale [$\varXi_X \equiv 100 \times (\nu_x / \nu_{TMS}^{obs})$], a procedure, which was suggested some years ago by IUPAC and which represents a very useful means of referencing, esp. if heteronuclear spectra are concerned.

In the following, we explain the principle of the $\varXi$ scale approach using the example of an fictitious sample containing ^{1}H and ^{19}F signals. Note, that the same three step approach can be transferred to any other NMR-active nucleus.

(1) First of all, a ^{1}H NMR spectrum needs to be recorded. You need to calibrate the signal of TMS to 0 ppm and then determine the absolute frequency [Hz] of the TMS signal (in our example, this will be done for a 400 MHz ^{1}H spectrum).

(2) The frequency value, called Θ*(TMS) or* ν_{TMS}^{obs}, read out for the TMS signal (e.g. 400130006.82 Hz for TMS in the ^{1}H spectrum of our virtual sample) now needs to be multiplied with a reference frequency value, the so-called $\varXi(^{19}F)$, for the heteronucleus in question. In case of ^{19}F, this value is 94.094011 (see table on next page). Finally, the result is divided by 100 MHz, to yield the frequency of the chemical shift of 0 ppm in ^{19}F.

[expressed as an equation: $\nu_F = \nu_{TMS}^{obs} \dfrac{\varXi_F}{100}$].

(3) This value (in our example 376.4983726 MHz) can be entered in the NMR software as the value for the reference frequency (in TopSpin, it is the parameter *SF*, accessible e.g. in the edp menu). Like this, you change the ^{19}F NMR spectrum to a corrected referencing, related to the TMS reference in the ^{1}H NMR spectrum.

The approach described above is the one favoured by IUPAC, it is highly recommended for use with heteronuclear spectra and easy to apply. On the next page, a table with $\varXi$ values for selected nuclei is provided, which was taken from the original IUPAC publication first published in 2001 in Pure and Applied Chemistry (*Pure Appl. Chem.* **2001**, *73*, 1795)

Tabelle 1: Die Spineigenschaften von Spin-$\frac{1}{2}$-Kernen.[a]

Isotop[b]	natürliche Häufigkeit x [%][c]	magnetisches Moment μ [μ_N][d]	gyromagnetisches Verhältnis γ [10^7 rad s^{-1} T^{-1}][d]	Frequenzverhältnis Ξ [%][e]	Referenzverbindung	Probe[f]	Lit. für Ξ	relative Rezeptivität[g] D^p	D^c
^{1}H	99.9885	4.837353570	26.7522128	100.000000[h]	Me$_4$Si	CDCl$_3$, φ = 1%	–	1.000	5.87×10^3
^{3}H[i]	–	5.159714367	28.5349779	106.663974	[^{3}H$_1$]Me$_4$Si	[i]	[10]	–	–
^{3}He	1.37×10^{-4}	−3.685154336	−20.3801587	76.179437	He	Gas	[11]	6.06×10^{-7}	3.56×10^{-3}
^{13}C	1.07	1.216613	6.728284	25.145020	Me$_4$Si	CDCl$_3$, φ = 1%	[12,13]	1.70×10^{-4}	1.00
^{15}N	0.368	−0.4904746	−2.71261804	10.136767	MeNO$_2$	in Substanz/CDCl$_3$[k]	[9]	3.84×10^{-6}	2.25×10^{-2}
^{19}F	100	4.553333	25.18148	94.094011	CCl$_3$F	[i]	[14]	0.834	4.90×10^3
^{29}Si	4.67	−0.96179	−5.3190	19.867187	Me$_4$Si	CDCl$_3$, φ = 1%	[15]	3.67×10^{-4}	2.16
^{31}P	100	1.95999	10.8394	40.480742	H$_3$PO$_4$	[i]	[16]	6.65×10^{-2}	3.91×10^2
^{57}Fe	2.119	0.1569636	0.8680624	3.237778	[Fe(CO)$_5$]	C$_6$D$_6$[i]	[9]	7.24×10^{-7}	4.25×10^{-3}
^{77}Se	7.63	0.92677577	5.1253857	19.071513	Me$_2$Se	in Substanz/C$_6$D$_6$[k]	[9]	5.37×10^{-4}	3.15
^{89}Y	100	−0.23801049	−1.3162791	4.900198	Y(NO$_3$)$_3$	H$_2$O/D$_2$O[m]	[9]	1.19×10^{-4}	0.700
^{103}Rh	100	−0.1531	−0.8468	3.186447[n,o]	[Rh(acac)$_3$][p]	CDCl$_3$, gesätt.	[18]	3.17×10^{-5}	0.186
(^{107}Ag)	51.839	−0.19689893	−1.0889181	4.047819	AgNO$_3$	D$_2$O, gesätt.	[9]	3.50×10^{-5}	0.205
^{109}Ag	48.161	−0.22636279	−1.2518634	4.653533	AgNO$_3$	D$_2$O, gesätt.	[9]	4.94×10^{-5}	0.290
(^{111}Cd)	12.80	−1.0303729	−5.6983131	21.215480	Me$_2$Cd	in Substanz[i]	[19]	1.24×10^{-3}	7.27
^{113}Cd[q]	12.22	−1.0778568	−5.9609155	22.193175	Me$_2$Cd	in Substanz[i]	[19]	1.35×10^{-3}	7.94
(^{115}Sn)	0.34	−1.5915	−8.8013	32.718749	Me$_4$Sn	in Substanz/C$_6$D$_6$[k]	[9]	1.21×10^{-4}	0.711
^{117}Sn	7.68	−1.73385	−9.58879	35.632259	Me$_4$Sn	in Substanz/C$_6$D$_6$[k]	[9]	3.54×10^{-3}	20.8
^{119}Sn	8.59	−1.81394	−10.0317	37.290632	Me$_4$Sn	in Substanz/C$_6$D$_6$[k]	[9]	4.53×10^{-3}	26.6
(^{123}Te)	0.89	−1.276431	−7.059098	26.169742	Me$_2$Te	in Substanz/C$_6$D$_6$[k]	[9]	1.64×10^{-4}	0.961
^{125}Te	7.07	−1.5389360	−8.5108404	31.549769	Me$_2$Te	in Substanz/C$_6$D$_6$[k]	[9]	2.28×10^{-3}	13.4
^{129}Xe	26.44	−1.347494	−7.452103	27.810186	XeOF$_4$	in Substanz[i]	[20,21]	5.72×10^{-3}	33.6
^{183}W	14.31	0.20400919	1.1282403	4.166387	Na$_2$WO$_4$	D$_2$O, 1 M	[11]	1.07×10^{-5}	6.31×10^{-2}
^{187}Os	1.96	0.1119804	0.6192895	2.282331	OsO$_4$	CCl$_4$, 0.98 M	[22]	2.43×10^{-7}	1.43×10^{-3}
^{195}Pt	33.832	1.0557	5.8385	21.496784[m]	[PtCl$_6$]$^{2-}$	D$_2$O, 1.2 M	[9]	3.51×10^{-3}	20.7
^{199}Hg	16.87	0.87621937	4.8457916	17.910822	Me$_2$Hg[i]	in Substanz	[11]	1.00×10^{-3}	5.89
(^{203}Tl)	29.524	2.80983305	15.5393338	57.123200[q]	Tl(NO$_3$)$_3$	[i]	[24]	5.79×10^{-2}	3.40×10^2
^{205}Tl	70.476	2.83747094	15.6921808	57.683838	Tl(NO$_3$)$_3$	[i]	[25]	0.142	8.36×10^2
^{207}Pb	22.1	1.00906	5.58046	20.920599	Me$_4$Pb	in Substanz/C$_6$D$_6$[k]	[9]	2.01×10^{-3}	11.8