

Sigma, σ , versus Delta, δ , Chemical Shift Scales in NMR

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IUPAC has set new definitions and standards for NMR referencing.¹ See the following [link](#) for more information:

http://cic.chem.wisc.edu/nmr/Guides/other/Xi_chem_shift_scale.pdf.

Sigma, σ , and delta, δ , chemical shift scales:

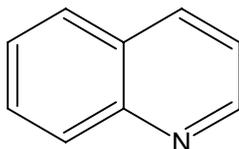
IUPAC has restated their recommendation that NMR researchers use the δ chemical shift scale.² Hopefully, this recommendation will be followed more closely in the future, since even minor redefinitions, such as the σ chemical shift scale (popular with theorists) can cause considerable confusion. The following is an illustrative example.

Witanowski, et al.,³ use the σ scale in their large tabulation of ^{15}N chemical shifts. The σ scale has the opposite sign from the more common δ scale (see the figure below). Most chemists are taught the δ scale convention: as a nucleus resonates to higher frequency, or is less shielded (more deshielded/downfield), it has a more positive chemical shift. The σ scale is just the opposite: a lower frequency, or more shielded (upfield), is a positive shift.

If σ versus δ scales were the only issue, using Witanowski, et al.'s tabular data would not be too confusing. We often have to deal, however, with secondary chemical shift standards. For ^{15}N , Witanowski, et al., use neat nitromethane as the primary reference,⁴ in accordance with the IUPAC.⁵ Ref. 1 provides data for a number of ^{15}N secondary references.⁶ In particular, a common reference for ^{15}N —especially in biochemical NMR—is liquid NH_3 .⁷

Witanowski, et al., give $\sigma = +380.23$ ppm for liquid NH_3 referenced to neat nitromethane.⁸ One must keep in mind that this is *not* a δ scale chemical shift: liquid NH_3 resonates to lower frequency, *shielded* from nitromethane (see figure below).

Confusion typically sets in when another chemical shift is looked up in Ref. 3. An example is the reference for **1**, given as $\sigma = 66.9$ ppm in acetone.⁹ Again, it is crucial to realize that this shift is a sigma shift, *shielded* from nitromethane. Compound **1** has a chemical shift in the δ scale that is *negative* ($\delta_1 = -66.9$ ppm) with respect to nitromethane, and *positive* with respect to liquid NH_3 ($\delta_1 = 380.23 - 66.9 = 313.33$ ppm). Graphical aids such as that shown below can help remove confusion when having to translate between scales and different reference standards.



1

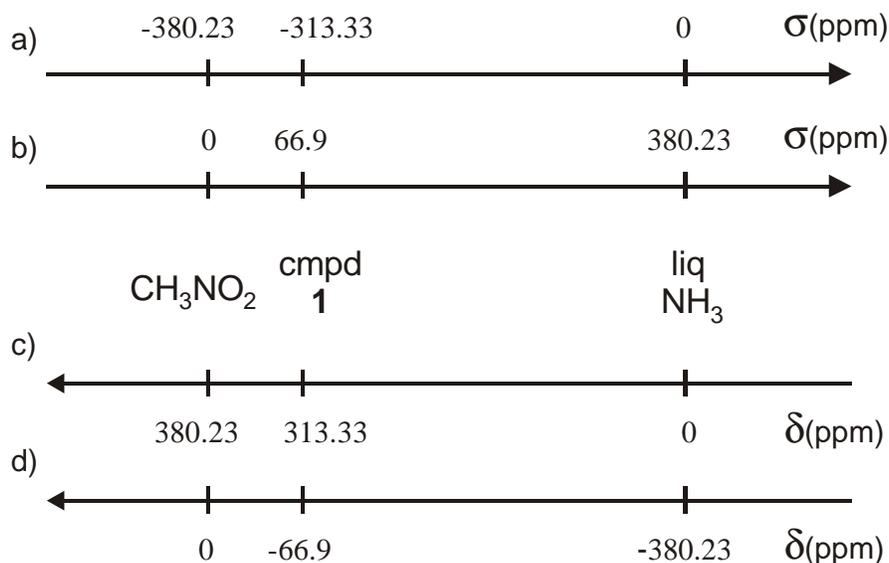


Figure 1. ^{15}N chemical shifts of nitromethane, liquid NH_3 , and compound **1**.

- σ -scale with liquid NH_3 as the reference;
- σ -scale with nitromethane as reference (as chosen by Witanowski, et al.);
- δ -scale with liquid NH_3 as reference (common scale for protein researchers);
- δ -scale with nitromethane as reference (recommended by IUPAC).

- R.K. Harris, E.D. Becker, S.M. Cabral de Menezes, R. Goodfellow, and P. Granger, "NMR Nomenclature. Nuclear Spin Properties and Conventions for Chemical Shifts (IUPAC Recommendations 2001)", *Pure and Applied Chemistry* 73, 1795-1818 (2001).
- Ref. 1, section 3, pgs. 1804ff.
- M. Witanowski, L. Stefaniak and G. A. Webb, "Nitrogen NMR Spectroscopy," *Annual Reports on NMR Spectroscopy*, vol. 18 (Academic Press, London, 1986). Pgs. 1-761.
- Ref. 3, pg. 27ff.
- Note that the *primary* chemical shift reference for chemical shift calculations—i.e., for IUPAC's "Unified Scale"—is ^1H of TMS, 1% in CDCl_3 . Thus, nitromethane is a *primary* reference only in terms of ^{15}N referencing outside of the unified scale. In the unified scale scheme, $\Xi_{^{15}\text{N}} = 10.136767$ is proper value relating the nitromethane unified scale secondary reference to the primary reference of ^1H in TMS.
- See Table 4 in Ref. 1, pg. 1813.
- For liquid NH_3 , $\Xi = 10.132912$, Table 4 in Ref. 1, pg. 1813.
- Ref. 3, pg. 29.
- Ref. 3, pg. 495.