

Tiers G V D. Proton nuclear resonance spectroscopy. I. Reliable shielding values by "internal referencing" with tetramethylsilane. *J. Phys. Chem.* 62:1151-2, 1958.
[Central Research Department, Minnesota Mining and Manufacturing Co., St. Paul, MN]

This was the paper that introduced tetramethylsilane (TMS) as the standard proton NMR reference. Further, it demonstrated the advantages of the internal referencing technique over the accepted but largely nonconvertible external referencing methods used at that time. Finally, in it the TMS-based τ -scale of chemical shifts was proposed. [The SCI® indicates that this paper has been cited in over 515 publications.]

How TMS Put NMR in the Organic Chemistry Lab

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3M had just bought our first NMR, Varian 40 MHz, which I knew would be of tremendous value for structural analysis of our fluorocarbon compounds. Though I had no background in NMR, I had read the published papers; apparently protons offered no such opportunities. As my initial fluorine work was poorly reproducible, I phoned John Zimmerman at the Magnolia Petroleum Co. in Dallas, Texas; his advice, which was by far the most important help I received, was to get a frequency counter to measure the audio sidebands. These were used to determine the position of any signal relative to a reference.

Subsequently, when a coworker asked me to look at some unusual solid proton

compounds, I found to my great surprise that similar structural features had highly reproducible peak positions relative to the solvent, though not to the traditional external reference. Within a day or two I knew that internal referencing was extremely broadly applicable and (thanks to the frequency counter) gave amazingly reliable measurements.

The choice of a reference substance was next and took about half an hour. Remembering a comment made at a meeting (by H.S. Gutowsky) that methyls on silicon were highly shielded and knowing the stability of silanes made this easy. Very shortly an American Chemical Society abstract was submitted, followed by this paper. Its importance is attested to by the fact that, despite 30 years of fabulous improvements in NMR equipment, tetramethylsilane (TMS) remains the standard internal reference for proton NMR spectroscopy. Furthermore, publication of this paper appears to have aided NMR to move from the realm of the physical chemists into the organic lab. Indeed, TMS and internal referencing have been so universally used¹ that there is no need for modern references² to this paper. (The third contribution was the creation and precise definition of the TMS-based τ -scale of chemical shifts, now in disuse. By contrast, the symbol δ was then, and is, today, still used indiscriminately in a variety of units and zeroed to various reference substances!)

As it turned out, Nugent F. Chamberlain, at the Humble Oil Co. in Baytown, Texas, had for some time been using internal referencing (albeit without TMS and less precisely). He had sent in a paper to *Analytical Chemistry* that had repeatedly been rejected for its presumably faulty technique. It was only after he could cite my publication that his was accepted.³ Such was the state of NMR in the late 1950s.

1. Jackson L M & Sternhell S. *Applications of nuclear magnetic resonance spectroscopy in organic chemistry*. Oxford, England: Pergamon Press, 1969. 456 p. (Cited 2,670 times.)
2. Eischenbroich C, Schneider J & Mellinghoff H. Metall- π -Komplexe von Benzolderivaten XXIX (Metal- π -complexes of benzene derivatives XXIX). *J. Organometal. Chem.* 333:37-45, 1987.
3. Chamberlain N F. Determining molecular structure by nuclear magnetic resonance of hydrogen. *Anal. Chem.* 31:56-77, 1959. (Cited 95 times.)