# Technical Information

## $^{29}$Si and $^{11}$B NMR Spectroscopy & Tube Selection

$^{29}$Si and $^{11}$B NMR Spectroscopy and Tube Selection Pyrex is a Borosilicate glass containing approximately 80% Silicon Dioxide and 12% Boron Oxide. Quartz glass is essentially 100% Silicon Dioxide. Because quality NMR sample tubes are made from Pyrex, they often contribute substantial and broad signals in 11B and/or 29Si NMR Spectroscopy. The insert of most broad band probes is made from Quartz, which can also contribute background signals to 29Si spectra. These background signals can make important spectral features of your sample impossible to discern. Overcoming them adds another challenge to NMR, particularly 29Si NMR, because of the low abundance and relative sensitivity of this spin 1/2 nucleus. A few approaches are available for reducing or eliminating background signal inteRference. Some involve the sample tube. Others require modifying the probe, which can be more costly to implement in your laboratory. Often, though, a simple adjustment in the pulse sequence you employ can overcome background signals.

Boron NMR Spectroscopy Eliminating the boron signal contributed by a Pyrex NMR Tube is a simple matter of changing to a Quartz sample tube. Products like the WILMAD Clear Fused Quartz 5mm NMR tubes 507-PP-7QTZ and 528-PP-7QTZ or 10mm NMR tube 513-7PP-7QTZ are suitable choices. These can be substituted for the most commonly used NMR tubes prepared from Pyrex.

Probe manufacturers have mostly used Quartz inserts in probes that access 11B NMR. If you find that, after changing to a Quartz tube, you still have a background signal, confirm the insert material by contacting the manufacturer or carefully examining the insert. If the insert has the Rf coils mounted on it, then replacing the insert with one made from Quartz should be attempted only by highly skilled individuals.

Silicon NMR Spectroscopy Contending with background signals is more challenging when 29Si is the nucleus of interest. That's because all commonly employed sample tube and insert materials contain a substantial amount of silicon in the form of Silicon Dioxide. There seems to be no single solution to this problem that is universally accepted; rather, a number of methods are available that may help with 29Si-NMR. In one approach, employed at Dow-Corning1, the sample isplaced in a WILMAD PTFE-FEP tube liner. But instead of being inserted into a standard NMR tube, the liner is allowed to dangle from an NMR tube from which the bottom 50 - 60mm has been removed. Tape or a short length of rubber tubing is wrapped around the top of the liner so it doesn't fall through the open bottom NMR tube.

In this set-up, the glass tube is used only as a bushing to hold the liner in the spinner turbine. Since only the liner is long enough to reach into the Rf coils of the probe, the tube doesn't produce a signal in the spectrum. Only the probe insert remains a source of background signal. At Dow-Corning, a special probe has been employed which uses a polymeric material in place of the glass insert.

In a second approach, a sample with a signal whose relaxation time is short or can be shortened with the addition of relaxation agents, such as Cr(ACAC)3, can be studied in a quartz tube in a probe with a quartz insert. Although this means the tube and insert have higher concentrations of Silicon Dioxide than standard Pyrex tubes and inserts, the goal in this approach is to change the relaxation characteristics of the background signal, not to reduce the concentration of the offending material. Since Clear Fused Quartz is essentially 100% Silicon Dioxide, the relaxation time of the signal generated by a Quartz tube and insert is long. By setting a fast pulse repetition rate, it is often possible to saturate the background signal from the insert and sample tube prior to collecting data. Some large molecular systems incorporating Silicon, such as Zeolites, may not be amenable to this approach, since the Silicon atoms may be held more rigidly in the structure and their relaxation times may be correspondingly long.

Incorporating a BIRD sequence at the start of the acquisition pulse train is another approach that has been used when the relaxation time of your sample and the quartz tube or insert are different. When the proper t is selected, this 180-t-180 sequence refocuses only sample magnitization, while that associated with the tube and insert are not refocused. The result is a background-free spectrum of your 29Si NMR sample.Inverse detection has found increasing use recently and could be employed if your sample has protons structurally close to the Silicon atoms of interest in the structure. If inverse detection is accessible, it may be the simplest approach to use, since it requires no additional supplies or equipment.

*1 Analytical Chemistry of Silicones, A. Lee Smith, ed., J. Wiley and Sons, Inc., 1991, pp. 347-419.*
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Wilmad-LabGlass SP SCIENCEWARE™

1172 NW Blvd., Vineland, NJ 08360 USA
1-800-220-5171 • Email: cs@wilmad-labglass.com
www.wilmad-labglass.com