

Technical Information

Tube Closures and Vortex Plugs in NMR

WILMAD offers an enviable variety of sample tubes for NMR spectroscopists. Often, the difference between one tube and another is simply the closure. To better understand the use of these different tubes and how the closures affect the way each is used, we've assembled information about NMR tube caps, valves, joints, etc. that will help you select NMR tubes that best meet your needs.

Many of today's spectrometers deliver such good magnetic field homogeneity that spectra are accumulated non-spinning. Indeed, many long-term accumulations, such as multi-dimensional experiments, yield better results when samples aren't spun. However, in laboratories where large numbers of samples are analyzed, sample spinning often yields faster results and greater sample throughput.

If sample spinning creates vortexes in your samples, then vortex plugs are the recommended solution. There are a variety of vortex plugs available and this report explains the appropriate use of each type of vortex plug.

The tables at the end of the report summarize the advantages and disadvantages of the various vortex plugs and closures available for WILMAD NMR tubes.

NMR Tube Caps

WILMAD's standard NMR tubes are delivered with a disposable Ethylene Vinyl Acetate cap. Low-cost replacements make it more practical to cut these caps from your NMR tubes at the end of your experiment than risk breaking the tube pulling the cap from the sample tube.

Disposable caps are easy to use. Careful application helps prevent spinning instability that results when the cap isn't straight. But, because Chloroform can leach unreacted monomers from these caps into your sample, you should replace these disposable caps with WILMAD's WG-1264 series PTFE NMR tube caps when using CDCl₃. WILMAD's 5mm tube cap 521-PC is Polyethylene and molded with ribs on the inner surface that help the cap grip a 5mm tube. The size and tapered shape of this cap are such that only the lower rib of the cap fits over the tube. This is sufficient to make a firm fit, but the 521-PC does not provide as effective a vapor seal as the disposable caps supplied with WILMAD NMR tubes. Unfortunately, the 521-PC cap is not available for tube sizes other than 5mm OD.

Instead, we recommend the WG-1264 Series of PTFE caps. Carefully tapered, these caps provide excellent chemical resistivity and a tight fit against rapid evaporation of volatile solvents. In addition, these caps, because they're machined, are more symmetrical than molded caps, like the disposable or 521-PC caps. This leads to exceptional spinning stability. If you must spin your samples during long acquisitions, these caps help reduce modulation sidebands and T₁ noise. This benefit outweighs the cost of the cap, since spectrometer time is considerably more expensive than quality PTFE caps.

The best cap for sealing 5mm tubes is the 521-S, a natural gum rubber serum-type cap that is easily slipped over the top of the tube. With air-sensitive samples you load in a glovebag or glovebox, this cap is ideal. It doesn't add weight to the top of the tube like screw-cap closures . . . has reasonably good resistance to the most common NMR solvents . . . but should not be used for long term storage of samples, since the cap can oxidize and harden over time when exposed to the air or can swell when exposed to certain solvent vapors for extended periods of time.

If handled carefully, it is even possible to inject chemicals into a sample tube through the 521-S Serum Cap.

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Other NMR Tube Closures

In addition to simple tube caps, there are a host of closures that work with modified NMR tubes, such as valves and joints. The simplest is the Screw Cap for WILMAD's unique Screw Cap NMR Tube. These are available in either a solid cap, which makes storing NMR samples in the tube easy, or a hollow cap that incorporates a PTFE-coated Silicone Septum, which allows addition of reagent aliquots to the sample with a syringe. They're easy to use and interchangeable. Your sample comes in contact with only PTFE and the tube glass. Any appropriately sized septum can be used with the open-top cap. Screw-caps and tubes are available in many sizes and replacement caps are standard X-425 or X-400 sizes (where X=8, 13, 15, or 24), available from WILMAD or any supplier of vials. Since the plastic caps and NMR tube will expand at different rates in response to heat, Screw Cap NMR tubes shouldn't be used in variable temperature (VT) experiments.

The Omni-Fit Valve, which slips over and is tightened onto a special 5mm NMR tube, also allows addition of reagents to your NMR sample. It incorporates both a septum and a miniature plastic stopcock, so you get double protection against exposure to air or atmospheric moisture. Your sample comes in contact with only PTFE, Tefzel®, and the NMR tube glass. And it's the lowest-cost approach to handling air sensitive NMR samples. However, the Omni-Fit Valve has a built-in dissymmetry which makes spinning stability difficult to assure. On low-field spectrometers (60 - 100MHz), it's an economical alternative to other approaches to handling air-sensitive samples. The Omni-Fit Valve should not be used in variable temperature experiments. The Valve fits snugly onto the tube and changes size with temperature faster than glass. At elevated temperatures, the valve can crush the tube and reduced temperatures could cause the valve seal with the tube to leak.

Other valves for WILMAD NMR tubes include the Pressure Valve (PV) and the Low Pressure/Vacuum NMR Tube Valve (LPV). Both are piston valves that expose your sample to only PTFE or the Pyrex NMR tube.

The glass portion of the PV valve is heavy, so the valve is capable of withstanding higher pressures than the LPV valve or any NMR tube. All samples for use in the PV tube must pass through a 0.8mm orifice at the center of the valve. The LPV valve has a larger orifice, so sample restrictions are not as severe with this valve.

Both the PV and LPV valves can be connected to vacuum racks using adapters available for each tube. The PV valve can even be connected to a regulator, so you can add a controlled amount of a specific gas above your sample solution, ideal for studying homogenous catalysis, for instance. Read WILMAD's Resonance Report NMR-003 prior to conducting any experiments in glass NMR tubes under pressure, though.

Because the PV and LPV valves are a mixture of plastic and glass, they're not recommended for variable temperature studies.

Which Vortex Plug is Best?

For simplicity, finned vortex plugs offer the best performance. PTFE is soft and the flexible fins make the fit into precision NMR tubes snug. The fit of WILMAD finned vortex plugs can't be guaranteed in other manufacturers' NMR sample tubes, which may not have precisely the same diameter as WILMAD tubes. Even small differences in tube diameter will create problems with the fit of finned vortex plugs.

Cleaning PTFE Finned Vortex Plugs is easy and the plugs are interchangeable. A simple plastic positioning rod is all that's needed to place the plug at the correct height in the NMR tube. An air vent in the plug's center assures easy insertion. And because finned vortex plugs are available for many sizes of NMR tubes, you'll find they're the most commonly used.

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If you perform variable temperature experiments, you should avoid finned plugs. The tolerance for the fit of finned vortex plugs are tight and even slight deviations from room temperature can cause this fit to vary. The result is a plug that slips at reduced temperature or that bursts the NMR tube at elevated temperatures. If the tube bursts in the instrument, contamination will require you disassemble the probe for cleaning, a time-consuming and delicate chore that is best avoided.

For variable temperature studies, WILMAD's piston plugs are recommended. Two kinds are available, one made from PTFE, the other from Pyrex. With no fins, these plugs must be held in position in the tube using a string running under the tube cap or with dimples pushed into the side wall of the tube. The glass plug, WG-805-GP series, fits the NMR tube more snugly than the PTFE version, the WG-805-PT. But the glass plug weighs more. Although it can be permitted to 'float,' the buoyancy depth of the glass plugs may be well into the sample volume and interfere with the experiment. Piston plugs are available from WILMAD only for the most common sizes of NMR tubes.

A type of NMR tube plug introduced in the last seven years is Varian's susceptibility plug. They're designed to eliminate volume magnetic susceptibility discontinuities when confining a small sample into the critical volume of a 5mm NMR tube. Try this with vortex plugs and you'll soon discover that PTFE's susceptibility is radically different than that of the common NMR solvents. See WILMAD's Resonance Report NMR-008 for more details about microsampling in NMR.

NMR Sample Tube Plugs

Product	Advantages	Disadvantages
WG-805	Large variety of sizes. Ease of use.	Not for variable temperature (VT) studies.
WG-805-PT Series	Ideal for VT studies	Must be held by string or dimples in tube wall. Limited size availability.
WG-805-GP Series	Fits more snugly than PT series. Ideal for VT studies.	Must be held by string or dimples in tube wall. Limited size availability.
Doty Susceptibility Plugs	Limits or eliminates susceptibility discontinuities in microsampling.	Low cost vs. altered glass tubes. Ease of Use

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