Technical Information

Valve Tubes and Air Sensitive Samples in NMR

Keeping samples sensitive to air or moisture from making contact with atmospheric oxygen or moisture requires equipment designed especially for this purpose. Otherwise, samples must be handled under an inert atmosphere like a glovebox. When NMR studies of such samples are required, the tube must be compatible with the handling system you're using. In a glovebox, one might use standard NMR tubes with a serum cap, such as the WILMAD 521-S; or a tube that attaches to a vacuum rack for transfer of a sample into the NMR tube. This report describes the diversity of products available for handling air or moisture sensitive samples, the advantages of each, and their application to NMR studies. The table on the last page summarizes the applications of WILMAD Valve NMR Sample Tubes.

Drying Samples

If your samples are sensitive to moisture, then your solvents must be dry. Resonance Report NMR-004 provides details on selecting and handling solvents for best results, including steps for drying. Molecular sieves, like Linde 3A or 4A (non-spherical in shape), work well with most NMR solvents. But their use with sample solutions could catalyze degradation reactions, so test these or any other drying agents to see that your samples aren't adversely affected before drying any NMR sample.

Freeze-Pump-Thaw Cycles

Freeze-pump-thaw (FPT) cycles can be used to remove residual oxygen, which is paramagnetic and decreases T2s, or other unwanted gases from the sample solution. Build a vacuum rack using a WILMAD Tip-Off Manifold such as 552-5. A dry ice/slush bath (-56.64° C) is usually sufficient to freeze most samples in the tube. Liquid Nitrogen (-210° C) will also work, but using this stringent cryogen can lead to problems like oxygen condensation and tube failure even when making temperature changes slowly. After freezing the sample, bring the pressure above the sample to 10-4 torr or less, close the stopcock above the tube, and let the solution warm to room temperature to complete a cycle. After three cycles, tube can be flame sealed after refreezing the sample solution and assuring a moderate vacuum (<1 torr) above the solution. Valve tubes can be kept closed after the last Freeze-Pump-Thaw.

Sealed Sample Tubes

The most reliable method of preserving valuable samples for NMR is sealing the sample into a WILMAD NMR tube. When samples are introduced via vacuum transfer and the tube is sealed in vacuo, the sample isn't exposed to air or moisture until the tube seal is broken. For longevity, no other method of conserving a sample is as reliable. That's why NMR Reference Standards continue to be made in sealed NMR tubes.

To make a symmetrical seal, use a sample tube constricted at the point of the seal. WILMAD constricted NMR tubes are tapered to a 1mm ID 25mm from the top of the tube. A microtorch works best, but one can be made from copper tubing. Firmly seal one end of a 75mm length of copper tubing, punch 6-8 holes 0.5mm in diameter along one side, spaced about 8-10mm apart. Then, curl the tubing into a hook around a 25mm diameter pipe with the holes on the inside. When a gas/oxygen mixture is supplied to the tube, gas lighted at the punched holes will form a cylindrical array of flames that will evenly heat the constriction. Adjust the diameter of the hook to your requirements. Using this 'torch,' symmetrical seals can be easily made. All samples should be frozen before applying heat at the constriction of the tube.

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1-800-220-5171 • Email: cs@wilmad-labglass.com
www.wilmad-labglass.com

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LPV (Low Pressure/Vacuum) Valve NMR Sample Tubes

WILMAD's LPV tubes are the best value on the market today. Like the gas-tight piston valves in laboratory glassware used with air-sensitive chemicals, the LPV Valve is easy to use. Its redesigned sealing surface (4X's larger) eliminates leaks and greatly increases its lifetime compared to traditional gas-tight tubes while the PTFE piston provides a contamination free seal.

Since the valve is made with O-Rings covered with PTFE sheaths, the sample sees only Pyrex® and PTFE. No need to worry about material incompatibilities. After fusing the Glass Valve Adapter (GVA) under a stopcock on your vacuum rack, just slide the LPV valve into the adapter to position it on the rack. Open the stopcock and NMR Valve and you're connected to a vacuum making Freeze-Pump-Thaws easy. Even samples that generate moderate pressure can be studied with this tube. It's ideal for T studies. Vacuum transfers are as easy as air-sensitive sample studies. Before using NMR tubes in pressure applications, refer to Resonance Report NMR-003. Maximum temperature for the tube body is 230°C (glass) and 1300°C (quartz). During the experiment, do not directly heat or cool down the valve section which has a different thermal expansion rate than the tube body.

Pressure/Vacuum Valve NMR Sample Tubes

By combining a pressure rated valve with an NMR tube, the WILMAD Pressure/Vacuum Valve NMR Sample Tube lets you obtain spectra or study reactions of solutions under controlled gaseous atmospheres. Vacuum transfers can be made with plastic connectors and a Pyrex® adapter fused to a stopcock on your vacuum rack, both available from WILMAD. The PV tube can be attached to the regulator of a gas cylinder through Swagelok® fittings (1/8" OD tubing nut and ferrule) too, so you can add most any gas to an evacuated Pressure Valve NMR Tube. Before using any NMR tube in pressure applications, read the precautions included in Resonance Report NMR-003.

Sample compatibility is excellent, since only PTFE, Viton®, or Pyrex® are used in the PV Tube. Adapters for a vacuum rack add a Polyethylene component to the list, though. With the PV Tube, sample size is limited to solutions or low viscosity suspensions that can pass through a 0.8mm constriction without clogging. Powder samples, viscous liquids, or course suspensions will clog the valve. Use care when tightening the Pressure Valve; PTFE threads can easily cold flow or strip. Replacements are readily available if the valve gets damaged. Maximum temperature for tube body is 230°C (glass) and 1300°C (quartz). During the experiment, do not directly heat or cool down the valve section which has a different thermal expansion rate than the tube body.

Omni-Fit Valve NMR Sample Tubes

To study the reaction of an air-sensitive sample with a compound that gets added in aliquots to your NMR tube between spectra, many other valve tubes and sealed sample tubes just won't do. However, the Omni-Fit® Valve is ideal as it seals with a double protection system that includes a plastic stopcock and septum.. just slip it on the top of a special 5mm NMR Tube. Due to the tight fit of valve to tube, the Omni-Fit tube has a 50mm medium wall section at the top.

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To add aliquots of a reactant to the sample tube, rotate the stopcock to the open position with a small screw-driver so a syringe needle can be passed through both the septum and valve. Remember to dry the syringe carefully and flush it with dry nitrogen before drawing up the reactant so no moisture or oxygen is injected into your sample. Septa can be replaced even during experiments. Close the stopcock, remove the old septum, flush the top of the valve in a stream of dry nitrogen, then replace the septum cap with a new septum in place.

The components of the Valve and Adapters are made from PTFE, Kel-F®, Tefzel®, Polypropylene, and Pyrex®, so chemical compatibility of the Omni-Fit NMR Tube is excellent. It's also the lowest cost approach to the study of air-sensitive samples available today.

Vacuum transfers can be done through the Omni-Fit Valve with plastic connectors and a Pyrex® adapter fused under a stopcock on a vacuum rack. The Omni-Fit valve would be pushed off the tube by internal pressure, so it is not recommended for pressurized samples. Because the valve is not axially symmetrical, the Omni-Fit Valve NMR Tube system is best used for non-spinning experiments.

Screw-Cap NMR Sample Tubes

While not a 'valve' tube, the WILMAD Screw-Cap NMR Tube still provides many advantages. It's the same security as storing in vials. Solid or open caps with septa are available for most NMR tube sizes. Injecting or withdrawing samples is as easy as with a vial, just use a longer needle (available from Hamilton) to reach the bottom of an NMR tube.

It's also the only NMR tube used to perform air-sensitive coaxial studies, since coaxial inserts (and vortex plugs) can still be inserted into these tubes as long as their length is shorter than the tube length (load tubes under an inert atmosphere). Because it's relatively easy to mount perfusion assemblies on an adapter that screws to the top of these tubes, they have also found occasional use in perfused cell NMR studies.

For	Sealed	TR	LPV	PV	OF
Evacuations/Vacuum Transfer	Yes (i.)	No	Yes	Yes (ii.)	Yes (ii.)
Pressure (iii.)	No	No	Yes	Yes	Yes
Syringe Fill	No	Yes	No	No	Yes

TR = Screw-Cap NMR Tube
LPV = Low Pressure/Vacuum Valve NMR Tube
PV = Pressure Valve NMR Tube
OF = Omni-Fit Valve NMR Tube

(i) when used with Tip-Off Manifold
(ii)when used with optional adapter
(iii)see Resonance Report NMR-003 before doing NMR pressure experiments.

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