Technical Information

NMR Sample Devices and Magnetic Susceptibility

Traditionally, NMR sample tubes have been made from commercial glasses. For many years, WILMAD has used Corning 7740 Pyrex, which has many important properties needed for NMR spectroscopy:

rigidity (for precise structure)
excellent chemical resistivity
compatibility with valves, joints, vacuum lines, etc.
Until recently, the magnetic properties of the glass sample tube have not been a concern. Typical sample sizes were 3-5 times the height of the probe Rf coil. This kept all distortions in the magnetic field, caused by magnetic susceptibility discontinuities at the upper and lower ends of the sample, far from the sensitive volume of the probe. Magnetic field homogeneity at the sample could easily be controlled with careful shimming.

As spectrometer field strength rose over the last 10 years, smaller and smaller samples became accessible to NMR analysis. Today, complex multi-dimensional spectra can routinely be taken on samples as small as 10-20µg. Diluting samples this tiny to nearly 1ml in volume results in concentrations too low for adequate NMR spectra. Dissolving small samples to volumes just equal to or even smaller than the Rf coil results in poor resolution in today's high field spectrometers. It's simply impossible to shim away the effects of magnetic susceptibility discontinuities at the upper air/sample and lower sample/tube interface so close to the Rf coil.

New Materials Deliver the Desired Properties

It's not surprising that new sample devices have been developed to accommodate small samples in today's spectrometers. Now, for the first time, the magnetic susceptibility of the sample device is a critical factor . Specially formulated glasses, carefully selected polymers, or high purity ceramic materials are used in NMR sampling of small samples. By using materials that match (within 5%) the magnetic susceptibility of the microsample solvent, exceptional spectra can be obtained on samples which would normally be too small for NMR. Confining small samples between 'plugs' of materials with a magnetic susceptibility that matches the solvent yields at least three-fold sensitivity improvements over conventional sample devices. Of course, the dimensions and solvent compatibility of the plugs must be carefully selected.

Doty Scientific has developed a series of susceptibility plugs or inserts, used with 3, 5, and 8mm NMR tubes, that match the susceptibility of the most common and a few uncommon NMR solvents. Compared to the glass alternative currently available, Doty susceptibility plugs are easier to use and usually less expensive. And because they're used with the sample tubes you already have, you don't need an entirely new set of NMR tubes.

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Better Design Means Better Results

Plugs machined to fit the NMR tube snugly are difficult to use. They can swell in certain solvents, trap air bubbles, and break tubes. Doty plugs made from polymeric materials are designed with a slightly 'loose' fit inside the tube. Doty's Ceramic plugs, which don't swell, fit the tube a bit more snugly. The loose fit allows you remove air bubbles more easily. And the plugs can be removed after the spectra are obtained and used with other samples while your sample remains in the tube. A tiny amount of sample (1-2%) fills the space between the tube and plugs. Filling factor loss is minimal. Doty Susceptibility Plugs are provided in sets of two, an upper and lower plug. The lower plug is shaped to fit the round bottom of the NMR tube. The upper plug has a flat bottom that defines the upper edge of the sample volume. The upper face of both plugs has a thread1 that lets you firmly attach a positioning rod. The upper plug is held in the tube by the positioning rod. The rod, in turn, is held by a collar, provided with each rod, that you rests atop the tube.

Seal Samples in the Tube

You can now obtain a collar equipped with two O-Rings that lets you seal the tube as well as holding the positioning rod at the right height in the tube. This collar is ideal for long-term acquisitions, where solvent evaporation is a concern. You can also store samples in the tube between NMR studies, if you choose.

Selecting the Right Plug

In addition to the susceptibility match, it's important to appreciate the solvent compatibility of the plug and rod. Kel-F rods provide the widest variety of solvent resistance, so Kel-F rods should be used if you plan to employ organic solvents. You'll find solvent compatibilities and other physical properties of Doty Susceptibility Plugs in Table 1, below. Choose Aurum for compatibility with Chloroform-d, Water, Deuterium Oxide and Water/Organic Solvent mixtures. Ultem is better if you plan to use only Water or Deuterium Oxide, since Aurum can swell in Water. Other properties of the plugs you'll need to study before you select the plug best for your experiment are Susceptibility and Interference Resonance for certain nuclei that originate from the plugs. Table 2 shows these properties. WILMAD's products listings provide solvent recommendations for each plug material.

Since one length can't be used with all probes, Doty offers two plug lengths for 5 and 8mm probes. Which plug length will meet your need? That depends upon your sample volume (height) and your probe. Check the position of the Rf coil of your probe and the depth from the bottom of the coil to the bottom of the probe head. Certain probes, e.g. certain Varian and Bruker 5mm probes, have short probeheads. The NMR tube might bottom out before a sample 12-15mm high is centered in the Rf coil. Short plugs (8mm long) allow you to center your sample properly in such probes. Unfortunately, WILMAD and Doty have not compiled a compendium of probe configurations for which short plugs are needed. You may want to consult the operation manual for your probe or contact your probe manufacturer for guidance.

The Position Rod

It's important to store positioning rods in a flat position. Otherwise, you may find the rods develop a bend (or camber). It's difficult to thread or 'capture' the lower plug with a bent positioning rod. The threads at the end of the rod may not align with the threads in the plug. Although the rods can be straightened, you'll find properly handling the rods is easier. Use a long (9 inch) WILMAD NMR tube box or the original packing to store your positioning rods!

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The Bottom Line

If you select the wrong plug, your results will suffer. So follow these steps in selecting your plug.

1) Select the tube size.
2) Determine the sample solvent.
3) If the solvent is viscous, decide if you will want plugs with vent grooves.
4) Compare the plug materials that match your solvent and select the one that's recommended for the nuclide you'll study.
5) Select the rod material
6) Order the plug sets you need.

And if you need very high resolution spectra, you can also use Doty Susceptibility Plugs to reduce the resolution loss associated with thermal gradients.

1 J. Lounila, et. al., J. Mag. Res. Ser. A, 118 (1996)

Table 1: NMR Solvent Compatibility Data

Material	Solvent Susceptibility* ($X\ 10^{-6}$)	Viscosity (cp, 20C)	Density (g/cm^3)	Plug for ^{1}H-NMR	Plug for ^{13}C-NMR	Plug for ^{19}F-NMR
Acetone	0.46	0.32	0.78	GFP**, G-10	GFP**, G-10	GFP**, G-10
Benzene	0.61	0.65	0.61	Zirconia	Zirconia	Zirconia
Carbon Tetrachloride	0.69	0..97	1.58	Zirconia	Zirconia, Pyrex	Zirconia
Chloroform	0.74	0.58	1.48	Zirconia	Zirconia, Pyrex	Zirconia
Deuterium Oxide	0.7	1	1.1	PEEK, Aurum, PPS	PEEK, Aurum, Ultem	PEEK, Aurum, Ultem, PPS
Dimethylsulfoxide	0.68	N/A	1.19	Zirconia, Aurum	Zirconia, Aurum	Zirconia, Aurum
Ethanol	0.58	1.2	0.79	Zirconia, GFP**	Zirconia, GFP**	Zirconia, GFP**
Methanol	0.53	0.6	0.79	Zirconia, GFP**	Zirconia, G-10	Zirconia, GFP**
Toluene	0.62	0.59	0.86	Zirconia	Zirconia	Zirconia
Water	0.72	1	1	PEEK, Aurum, PPS	PEEK, Aurum, Ultem	PEEK, Aurum, Ultem, PPS

** cgs units - chivc X 10-6, **GFP = Glass-filled PEEK, N/A = Not Available*

Doty Susceptibility Plug Properties and Chemical Compatibilities

Property	Kel-F(for ref.)	Pyrex (for ref.)	PPS	Aurum	Ultem	Zirconia	GFP	G-10
$\chi vc\ X\ 10^{-6}$	0.92	0.86	0.73	0.71	0.71	0.7	0.52	~0.5
Wideline NMR Backgrounds	F, Cl, C	Si, B, Al, Na	H, CS	H, CN	H, C, N	Zr	H, C, Al, Si, F	H, C, Al
H_2O absorp. %	0.02	0.01	0.03	0.8	0.7	0.01	0.2	0.15
Density (g/cm^3)	2.1	2.5	1.35	1.42	1.27	5.7	1.45	1.88
Maximum Temperature (C)	150	400	120	240	205	700	250	160
Color	Clear	Glass	Ivory	Black	Amber	White	Grey	Green
Strong Acids	E	E	G	G	G	E	P	E
Strong Alkali	E	E	E	G	G	E	G	E
Alcohols and Aliphatics	E	E	E	E	E	E	E	E
Aromatic Hydrocarbons	E	E	E	E	G	E	E	E
Esters and Ketones	E	E	E	E	E	E	E	E
Organochlorides	E	E	E	G	F	E	G	G

Chemical Resistance:
E = Excellent
G = Good, usually acceptable
F = Fair, sometimes acceptable
P = Poor

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