

Solvents, NMR Tubes, and Susceptibility Matched Plugs Sets

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Solvents

The deuterated stockroom solvents are fine for all standard experiments. See Aldrich or CIL for specialized deuterated solvents.

Achieving optimal line shapes in an NMR experiment depends critically on the amount of solvent used. The recommendation is:

Varian 5mm probes	≥ 0.6 ml solvent
older Bruker 5mm probes (ACs, broadband)	≥ 0.5 ml solvent
newer Bruker inverse 5mm probes (NMRFAM)	≥ 0.6 ml solvent

In general, what is needed is for the solvent column to extend the *rf coil length* both above and below the coil (i.e., total height = 3 times the coil length). Different probes have different coil lengths, so there is no universal guideline to apply. The above-recommended volumes are derived as follows:

Varian 5mm coil length	= 16 mm	→ 48 mm recommended solvent length = 650 μ l.
older Bruker 5mm coil length	= 12 mm	→ 36 mm recommended solvent length = 500 μ l.
newer Bruker 5mm coil length	= 18 mm	→ 54 mm recommended solvent length = 700 μ l.

For variable-temperature experiments, when using expensive solvents, and to maximize concentration, minimum solvent volume is preferred. Empirically, we find that using less solvent than the above-recommended volumes can safely be done, but only within certain limitations, and with a price to be paid of increasing the shimming effort needed to achieve a desired linewidth. Going less than 0.45 ml without susceptibility plugs (see below) on a Varian 5mm probe is almost certain to be fatal to achieving reasonable line shapes. Similarly, going to less than 0.35 ml on an older Bruker 5mm probe will almost certainly prevent optimal line shapes from being achieved. [*Facility experiments show very similar sensitivities with both vendors' probes for identical sample amount—e.g., ^{13}C of 10mg sucrose in D_2O . Thus, Varian probes are not less sensitive because the concentration is lower; the longer coil makes up for the lower concentration.*] Since sensitivity decreases with degraded line shape, ***the user should never push solvent volume too low for sensitivity reasons (i.e., to maximize concentration).***

Susceptibility plugs allow the solvent volume to be reduced to $\sim 1/3$ that stated above by removing the susceptibility gradients occurring at the solvent-air interface. Susceptibility plugs have been successfully used in our facility for ^1H and ^{13}C experiments. In these experiments, we have always seen the expected factor of 3^2 (=9) improvement in experiment time for identical S/N. Thus, an overnight experiment without susc. plugs gives the same S/N as a 1.5 h experiment with the susc. plugs! **USE SUSC. PLUGS WHEN SAMPLE AMOUNT IS LIMITED!!!**

Note that when using susceptibility plugs, the solvent volume should equal the length of the rf coil + 2mm on each end of the column. Thus, a solvent length of 20mm is recommended for use with Varian 5mm probes. The facility director has various sets of susc. plugs that are available on loan for students to try. See him for additional details about these extremely useful items.

Wilmad NMR tubes (800-229-5171 or www.wilmad.com):**for 250/300 MHz work:**

routine work	WG-5mm-ECONOMY-8	\$1.70/ea	(OK for routine & ^{13}C)
recommended	507-PP-8	7.00	(current stock room tubes)

for 360 MHz work:

recommended	507-PP-8 (or ECONOMY)	7.00	(current stock room tubes)
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for 500/600 MHz work:

routine work	507-PP-8 (or ECONOMY)	7.00	(OK for routine & X nucleus)
recommended	528-PP-8	12.60	(stockroom now has)
best	535-PP-8	17.45	(for solvent suppression)
best(er)	541-PP-8	25.75	(for 750 work?)
best(crest)	542-PP-8	30.90	(for 800/900?)

The ECONOMY tubes are consistently “good enough” on the 250/300 spectrometers; similar with 507 tubes on the 500s (*cgf*: seems ECONOMY are working ok even at 500 MHz for routine use). Use 528s for best ^1H spectra at 500 and at 600 MHz. If the bulk of your group’s work is routine intermediate checks on the 300s, the ECONOMY tubes likely will be fine. Groups performing water suppression are strongly urged to use 535, or 528 as a minimum, tubes. Keep in mind while shimming that *the most common problems with resolution are not the tube type, but rather insufficient solvent height (see previous pg), “floaters” in the solvent, or scratches on the tube.* Even so, using the wrong tube (e.g., a 507 for high-quality water suppression) can present insurmountable problems. Spending a few dollars more for the right tubes is the right purchasing decision: using additional spectrometer time for shimming adds up in usage fees!

NMR tubes come in 7”, 8” and 9” lengths. Pricing (in 2004) for 8”, but for flame sealing, use 9” tubes; they allow the resulting sealed tube to easily be long enough for the spinners.

See Wilmad’s NMR-010 technical note at their web site (www.wilmad.com) for suggestions on how to correctly clean and dry tubes.

Other vendors sell similar products; I cannot comment on relative quality of the other vendors, but know the Wilmad tubes give consistently good results.

Susceptibility Inserts (Shigemi):

(phone # 724-444-3011)

Shigemi tube sets are generally regarded as optimum for precision/best quality work (e.g., when needing water suppression). The disadvantages are slightly higher cost (glass is more chemically durable, however), and susceptibility matching to the solvents shown below. Change V (15mm length) to J (12mm) or B (8mm) for Bruker probes, and 005 to 003, 008 or 010 (\$150-160 ea) for tube diameter. Order a cap (\$7.50 ea) to hold the upper plug stationary.

CDCl_3 :	CMS-005V	clear (etched)	\$85.00 per set
CD_3OD :	MMS-005V	blue	\$85.00 per set
DMSO:	DMS-005V	green	\$85.00 per set

D₂O: BMS-005V clear (etched) \$95.00 per set

Properties of Solvents (from Wilmad and/or Shigemi—neither provide a source reference):

Solvent	-c (cgs)	Density (g/cc)
Glycerol	0.78	1.26
Chloroform	0.74	1.48
Water	0.72	1.00
Deuterium Oxide	0.70	1.10
Carbon Tetrachloride	0.69	1.58
Dimethylsulfoxide	0.68	1.10
Acetonitrile	0.68	
Toluene	0.62	0.86
Benzene	0.61	0.87
Ethanol	0.58	0.79
Diethyl Ether	0.53	0.71
Methanol	0.53	0.79
Acetone	0.46	0.78

Susceptibility Inserts (Wilmad):

Doty Susceptibility Plugs from Wilmad (<http://www.wilmad.com/html/nf/DotyPlugs.html>)

These inserts are polymeric (except Zirconia), and thus chemical compatibility with solvent/solute combination must be taken into account for their use. The 1st line following the price indicates the susceptibility match to the solvent; the 2nd line indicates the chemical compatibility with the solvent and solute combination.

5mm kel-f positioning rod \$24.00
5mm sealing clamp \$62.00

Aurum plug set \$72.00
susceptibility match to D2O/water (as solvents)
excellent chem compatibility with alcohols, aliphatics, aromatic H-C, esters, ketones

Glass filled PEEK set \$40.00
susceptibility match to methanol, MEK, ethyl ether (as solvents)
excellent chem compatibility with alcohols, aliphatics, aromatic H-C, esters, ketones

G-10 plug set \$30.00
susceptibility match to acetone, MEK, methanol (as solvents)
excellent chem compatibility with strong bases, alcohols, aliphatics, aromatic H-C,
esters, ketones

Kel-f plug set \$28.00
susceptibility match to glycerol (as solvents)

excellent chem compatibility with strong acids and bases, alcohols, aliphatics, aromatic H-C, esters, ketones

PPS plug set \$50.00

susceptibility match to CDCl_3 , water (as solvents)

good chem. compatibility with strong acids and excellent compatibility with strong bases, alcohols, aliphatics, aromatic H-C, esters, ketones

Ultem plug set \$24.00

susceptibility match to D_2O , water (as solvents)

excellent chem. compatibility with alcohols, aliphatics, esters, ketones

Zirconia plug set \$240.00

susceptibility match to D_2O , CCl_4 , DMSO, benzene (as solvents)

excellent chem. compatibility with strong acids and bases, alcohols, aliphatics, aromatic H-C, esters, ketones