

Solvents, NMR Tubes, and Susceptibility Matched Plugs Sets

Tubes and Caps Compatible with New Bruker Spectrometers (and their robots)

- A. Choose tubes compatible with 400 and 500 MHz NMR: see the 2 sections below.
- B. The 400 robot requires either 4" or 7" tubes with special caps: for more information, see http://www.chem.wisc.edu/~cic/nmr/Guides/Ba3vug/Av400UG_IconNMR.pdf.
- C. Our 500s and 600 can handle 7 to 8" tubes. Do not use 9" tubes, as they are too long for some of the sample changers.
- D. J-Young tubes: request **528-LPV-209M** from Wilmad (this is not a standard item, but Wilmad will make to this specification), which are compatible with our 500 and 600 MHz Bruker robots and are long enough for work on Varian spectrometers. 9" J-Young tubes will not work on these spectrometers under automation: -209M (8.5") is the longest possible. Note that the (standard item) -200M tubes will be OK on our Bruker spectrometers but may not work on other vendors' equipment.

Solvents

The deuterated stockroom solvents are fine for all standard experiments.

Glass tubes often have acetone and/or water residues that are easily observed on more sensitive spectrometers. Rinse tubes carefully prior to any work at lower concentrations (sub-millimolar).

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, 360)	≥ 0.45 ml solvent
newer Bruker 5mm probes	≥ 0.6 ml solvent

In general, what is needed to achieve best line shape is for the solvent column to equal 3 times the *rf coil length*. Different probes have different coil lengths, so there is no fixed length guideline to apply. The above-recommended volumes roughly fit the rule-of-thumb:

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. [*Longer rf coils have been found to be more sensitive, in general, for fixed amounts of compound: i.e., although the concentration is lower, the overall sensitivity*

is higher. That is why all modern probes (to our knowledge) have longer coil lengths (which require more solvent).] 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 up to 1/3 that stated above by removing the susceptibility gradients occurring at the solvent-air interface. Susceptibility plugs are regularly used in our facility: one gains the expected factor of up to 3² (=9) times reduction 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!!!**

The rule-of-thumb when using susceptibility plugs is to have the solvent volume 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, and 22mm on our Bruker 5mm cryoprobes.**

Wilmad NMR tubes :

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 our Bruker spectrometers. If the bulk of your group’s work is routine intermediate checks, the ECONOMY tubes are fine. Groups performing water suppression are encouraged to use 535 or 528 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., an ECONOMY tube for high-quality water suppression) can present insurmountable problems. Spending a few dollars more for the right tube is the right purchasing decision: obtain better data in a consistent manner.

NMR tubes come in 7”, 8” and 9” lengths. Avoid the 9” tubes for use in our facility.

Cleaning and Drying NMR tubes :

See Wilmad's NMR-010 technical note at their web site (www.wilmad.com) for suggestions on how to correctly clean and dry tubes. In particular, the following is from that note:

Drying tubes at elevated temperatures can reshape and ruin precision NMR tubes. If you dry tubes in an oven, WILMAD recommends placing tubes on a perfectly flat tray at 125° C for only 30-45 minutes. Better is the use of a vacuum oven that will remove water at lower temperatures. In a flat position, tubes that do reshape could be out-of-round and may not fit the spinner turbine as well. But they'll not affect the spectrometer probe adversely. Tubes placed in an oven in a beaker, flask, or tube rack can bend, increasing Camber (lack of straightness)1. *Bent tubes may still fit the spinner turbine, but can damage or break the NMR probe insert, a costly repair with many probes.*

Other vendors sell similar products; we'll not comment on relative quality of the other vendors. The Wilmad tubes give consistently good results.

Susceptibility Inserts (Shigemi):

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 (xxx-CAP for \$9.30 ea) to hold the upper plug stationary.

CDCl ₃ :	CMS-005V	clear (etched)	\$94 per set
CD ₃ OD:	MMS-005V	blue	\$106 per set
DMSO:	DMS-005V	green	\$106 per set
D ₂ O:	BMS-005V	clear (etched)	\$94 per set

Properties of Solvents (likely from Doty Scientific).

Solvent	tube	tube color	-c (cgs)	Density (g/cc)
Glycerol			0.78	1.26
Chloroform	CMS	clear	0.74	1.48
Dichloromethane			0.73	1.36
Water			0.72	1.00
Deuterium Oxide	BMS	clear	0.70	1.10
Carbon Tetrachloride			0.69	1.58
Dimethylsulfoxide	DMS	green	0.68	1.10
Acetonitrile			0.68	0.78
Toluene			0.62	0.86
Benzene			0.61	0.87
Ethanol			0.58	0.79
Diethyl Ether			0.53	0.71
Methanol	MMS	blue	0.53	0.79
Acetone			0.46	0.78