

**Chem 136 Spring 2003**

**Handouts**

**NMR Solvents & Impurities**

is changed from  $\text{CDCl}_3$  to  $\text{C}_6\text{D}_6$ , whereas downfield shifts are sometimes observed for  $\text{CD}_3\text{CN}$ . The solvent used should always be specified when reporting  $^1\text{H}$  chemical shifts. This is not as important when reporting  $^{13}\text{C}$  shifts, because they vary only slightly when the solvent is changed from  $\text{CDCl}_3$  to  $\text{C}_6\text{D}_6$ . These and other deuterated solvents are commercially available in high percentages (typically greater than 99.9%) of deuterium enrichment. The small amount of residual hydrogen does not usually obscure regions of interest in  $^1\text{H}$  NMR. A summary of the  $^{13}\text{C}$  and  $^1\text{H}$  chemical shifts for a variety of solvents relative to TMS can be found in Table 2.3. The standard shifts shown in this table can be assigned to a solvent peak, so it can be used as an internal chemical shift reference, which would substitute for adding TMS as an internal standard.

The best way to assess the quality of a spectrum is to examine the signal height relative to the noise, and the sharpness of peaks. Narrow line widths are observed for  $^1\text{H}$  and can be measured by examining the width of a peak at its half-height. This parameter is called the *half-width* ( $\Delta\nu_{\frac{1}{2}}$ ), as shown in Figure 2.10. For  $^1\text{H}$ , the half-width of singlets ought to be less

TABLE 2.3 Some Useful NMR Solvents

Solvent	$\delta^1\text{H}$ (ppm) (mult.)	$\delta^{13}\text{C}$ (ppm) (mult.)	Liquid Range ( $^\circ\text{C}$ )	Dielectric Constant	$\delta^{\text{HOD}}$ (ppm) in $^1\text{H}$ NMR
Acetic Acid- $\text{d}_4$	11.65 (1) 2.04 (5)	179.0 (1) 20.0 (7)	17 – 118	6.1	11.6
Acetone- $\text{d}_6$	2.05 (5)	206.7 (13) 29.9 (7)	-94 – 57	20.7	2.0
Acetonitrile- $\text{d}_3$	1.94 (5)	118.7 (1) 1.4 (7)	-45 – 82	37.5	2.1
Benzene- $\text{d}_6$	7.16 (1)	128.4 (3)	5 – 80	2.3	0.4
Chloroform- $\text{d}$	7.27 (1)	77.2 (3)	-64 – 62	4.8	1.5
Cyclohexane- $\text{d}_{12}$	1.38 (1)	26.4 (5)	6 – 81	2.0	–
$\text{D}_2\text{O}$	4.80		4 – 101	78.5	4.8
Dichloromethane- $\text{d}_2$	5.32 (3)	54.0 (5)	-95 – 40	8.9	1.5
<i>p</i> -Dioxane- $\text{d}_8$	3.53 (m)	66.7 (5)	12 – 101	2.2	2.4
DMF- $\text{d}_7$	8.03 (1) 2.92 (5) 2.75 (5)	163.2 (3) 34.9 (7) 29.8 (7)	-61 – 153	36.7	3.5
DMSO- $\text{d}_6$	2.50 (5)	39.5 (7)	18 – 189	46.7	3.3
Methanol- $\text{d}_4$	4.87 (1) 3.31 (5)	49.2 (7)	-98 – 65	32.7	5.0
Pyridine- $\text{d}_5$	8.74 (1) 7.58 (1) 7.22 (1)	150.4 (3) 135.9 (3) 123.9 (5)	-42 – 116	12.4	5.0
THF- $\text{d}_8$	3.58 (1) 1.73 (1)	67.6 (5) 25.4 (1)	-109 – 66	7.6	2.5
Toluene- $\text{d}_8$	7.09 (m) 7.00 (1) 6.98 (m) 2.09 (5)	137.9 (1) 129.2 (3) 128.3 (3) 125.5 (3) 20.4 (7)	-95 – 111	2.4	0.4
TFA- $\text{d}$	11.50 (1)	164.2 (4) 116.6 (4)	-15 – 72	39.5	11.5

Also see <http://www.isotope.com>

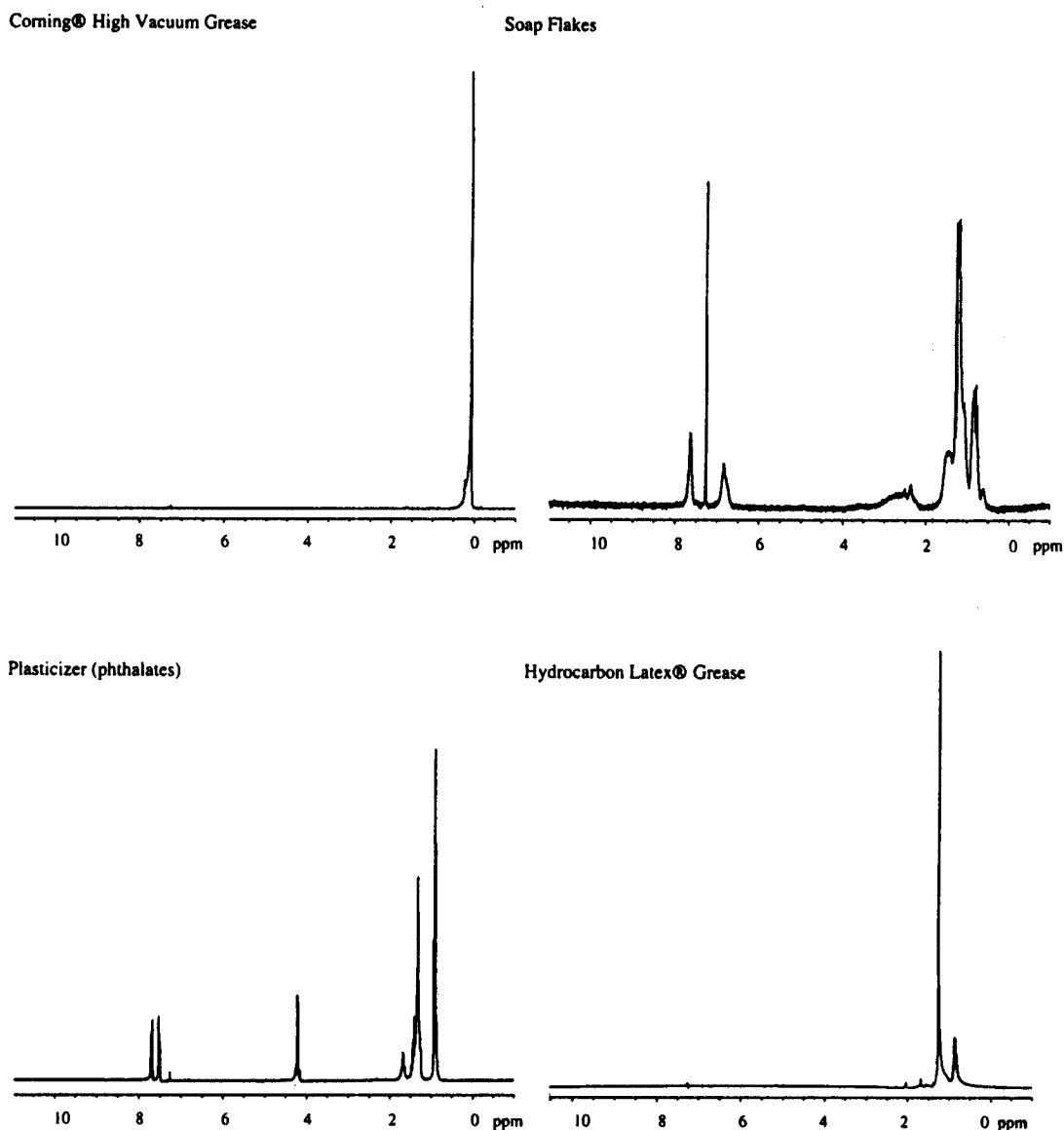


FIGURE 2.17 Some common impurities in  $^1\text{H}$  NMR.

NMR impurities. Water can be troublesome and is often present in  $\text{CDCl}_3$ , as well as most other NMR solvents, but can be minimized by storing the solvent in a desiccator. The chemical shift of the water peak in various solvents is shown in Table 2.3. The water level can be reduced with drying agents, but molecular sieves are not recommended because they contain very fine dust, which can affect the resolution. Other commercial products routinely used in the laboratory can creep into samples and give rise to unexpected peaks. Two common examples are the phthalates from Tygon® tubing and grease used to lubricate ground glass joints. Acetone is frequently used to wash out NMR tubes and it can persist even when the tubes are placed in an oven (a simple rinse with  $\text{CDCl}_3$  will solve this problem). The spectra of these and other relevant compounds appear in Figure 2.17. A list of shifts of common impurities in various solvents is shown in Table 2.4.

TABLE 2.4 <sup>1</sup>H NMR Shifts of Common Impurities in Various Solvents [ $\delta$  ppm (mult)]

Impurity	Chloroform- <i>d</i>	DMSO- <i>d</i> <sub>6</sub>	Pyridine- <i>d</i> <sub>5</sub>	Benzene- <i>d</i> <sub>6</sub>	D <sub>2</sub> O
Acetic Acid	2.13 (s)	1.95 (s)	2.13 (s)	1.63 (s)	2.16 (s)
Acetone	2.17 (s)	2.12 (s)	2.00 (s)	1.62 (s)	2.22 (s)
Acetonitrile	1.98 (s)	2.09 (s)	1.85 (s)	0.67 (s)	2.05 (s)
Benzene	7.37 (s)	7.40 (s)	7.33 (s)	7.30 (s)	7.44 (s)
<i>t</i> -Butanol	1.28 (s)	1.14 (s)	1.37 (s)	1.06 (s)	1.23 (s)
Chloroform	7.27 (s)	8.35 (s)	8.41 (s)	6.41 (s)	ns
Cyclohexane	1.43 (s)	1.42 (s)	1.38 (s)	1.40 (s)	ns
Dichloromethane	5.30 (s)	5.79 (s)	5.62 (s)	4.46 (s)	ns
Diethyl Ether	3.48 (q)	3.42 (q)	3.38 (q)	3.27 (q)	3.56 (q)
	1.20 (t)	1.13 (t)	1.12 (t)	1.10 (t)	1.17 (t)
DMF	8.01 (s)	7.98 (s)			7.91 (s)
	2.95 (s)	2.92 (s)	2.72 (s)	2.40 (s)	3.00 (s)
	2.88 (s)	2.76 (s)	2.66 (s)	1.98 (s)	2.86 (s)
DMSO	2.62 (s)	2.52 (s)	2.49 (s)	1.91 (s)	2.70 (s)
<i>p</i> -Dioxane	3.70 (s)	3.61 (s)	3.61 (s)	3.38 (s)	3.75 (s)
Ethanol	3.72 (q)	3.49 (q)	3.86 (q)	3.39 (q)	3.64 (q)
	1.24 (t)	1.09 (t)	1.29 (t)	0.97 (t)	1.16 (t)
Ethyl acetate	4.12 (q)	4.08 (q)	4.06 (q)	3.91 (q)	4.14 (q)
	2.04 (s)	2.02 (s)	1.94 (s)	1.68 (s)	2.08 (s)
	1.25 (t)	1.21 (t)	1.10 (t)	0.94 (t)	1.23 (t)
Methanol	3.48 (s)	3.20 (s)	3.57 (s)	3.09 (s)	3.35 (s)
Petroleum Ether	1.28 (bs)	1.28 (bs)	1.20 (bs)	1.22 (s)	ns
	0.90 (t)	0.89 (t)	0.86 (t)	0.89 (t)	
<i>i</i> -Propanol	4.03 (m)		4.16 (m)	3.76 (m)	
	1.22 (d)	1.06 (d)	1.29 (d)	1.01 (d)	1.18 (d)
<i>n</i> -Propanol	3.60 (t)		3.75 (t)	3.76 (t)	3.61 (t)
	1.60 (m)	1.45 (m)	1.70 (m)	1.40 (m)	1.57 (m)
	0.93 (t)	0.87 (t)	0.97 (t)	0.80 (t)	0.89 (t)
Pyridine	8.60 (m)	8.61 (m)	8.71 (m)	8.50 (m)	8.50 (m)
	7.69 (m)	7.83 (m)	7.58 (m)	7.05 (m)	7.90 (m)
	7.28 (m)	7.21 (m)	7.21 (m)	6.70 (m)	7.47 (m)
THF	3.74 (m)	3.63 (m)	3.67 (m)	3.01 (m)	3.75 (m)
	1.85 (m)	1.78 (m)	1.64 (m)	0.87 (m)	1.88 (m)
Toluene	7.19 (m)	7.22 (m)	7.22 (m)	7.10 (m)	ns
	2.34 (s)	2.32 (s)	2.22 (s)	2.13 (s)	
Triethylamine	2.56 (q)	2.47 (q)	2.43 (q)	2.40 (q)	2.59 (q)
	1.03 (t)	0.99 (t)	0.96 (t)	0.95 (t)	1.02 (t)

ns = not soluble.

### Sources for Further Reading

1. See 1–3 of "Sources for Further Reading" in Chapter 1.
2. E. Breitmaier and W. Voelter, *Carbon-13 NMR Spectroscopy* (VCH, Weinheim, 1990). Chapter 2 of this text gives an excellent description of the pulse sequences that can be used to determine  $T_1$  and  $T_2$  relaxation times for <sup>13</sup>C nuclei. Chapter 1 contains a very good description of the effect of applying a magnetic field on a set of nuclear spins. Events leading up to phase coherence and after a single pulse are covered in detail.