"Metabolomics" of NMR solvents

Attachment to the entry of April 11, 2010, on **Stan's NMR blog** (www.ebyte.it/stan/blog.html)

The Figures below show **one-dimensional 500 MHz proton spectra of three common deuterated solvents** acquired in a routine way (the operator was just asked to measure the solvent, without any compound, following the standard procedure used for most incoming samples. **What one expects** is the spectrum of the traces of partially deuterated isotopomers, plus a peak of water due to a trace of unavoidable humidity in the solvent. In particular:

In d_6 - DMSO (di-methyl-sulfoxide):

a) The pentuplet of the proton in–CD_2H groups at about 2.5 ppm
b) The 13C satellites of the above (each 0.55% of the main multiplet)
c) The triplet of the proton in –CDH_2 groups (very small; its ^{13}C satellites are never seen)
d) The water peak at about 3.3 ppm

In d - chloroform:

a) The singlet peak of the proton in non-deuterated $HCCl_3$ at about 7.26 ppm
b) The 13C satellites of the above (each 0.55% of the main peak)
c) The water peak at about 1.5 ppm

In d_4 - methanol:

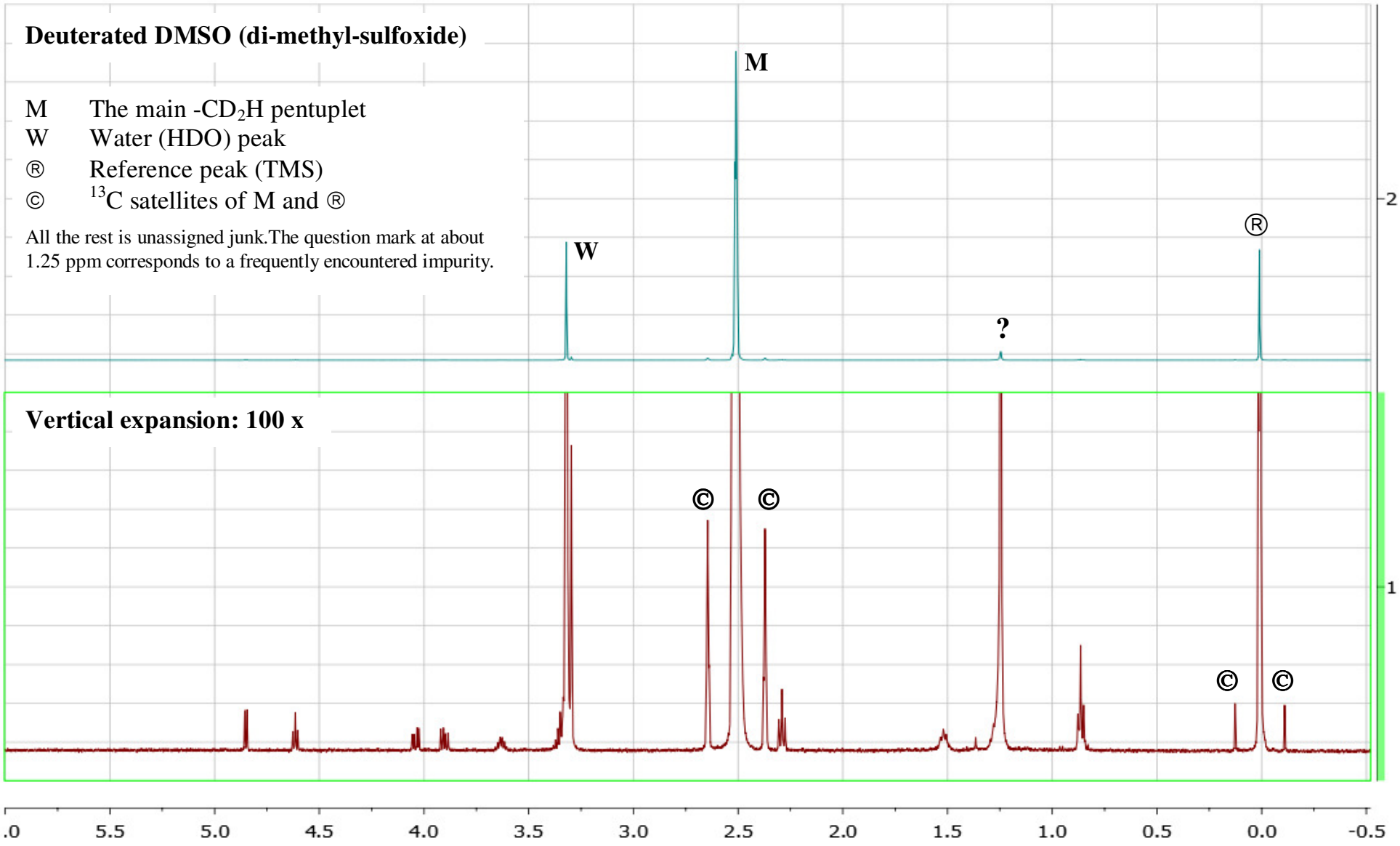
a) The pentuplet of the proton in–CD_2H groups at about 3.3 ppm
b) The 13C satellites of the above (each 0.55% of the main multiplet)
c) The triplet of the protons in –CDH_2 groups (very small; its ^{13}C satellites are never seen)
d) The water & -OH peak at about 4.8 ppm (a bit less in the present case because the solvent was extremely wet)
e) There could be also a heptuplet of the proton in CD_3OH groups but only in extremely dry methanol, and it would be very difficult to resolve

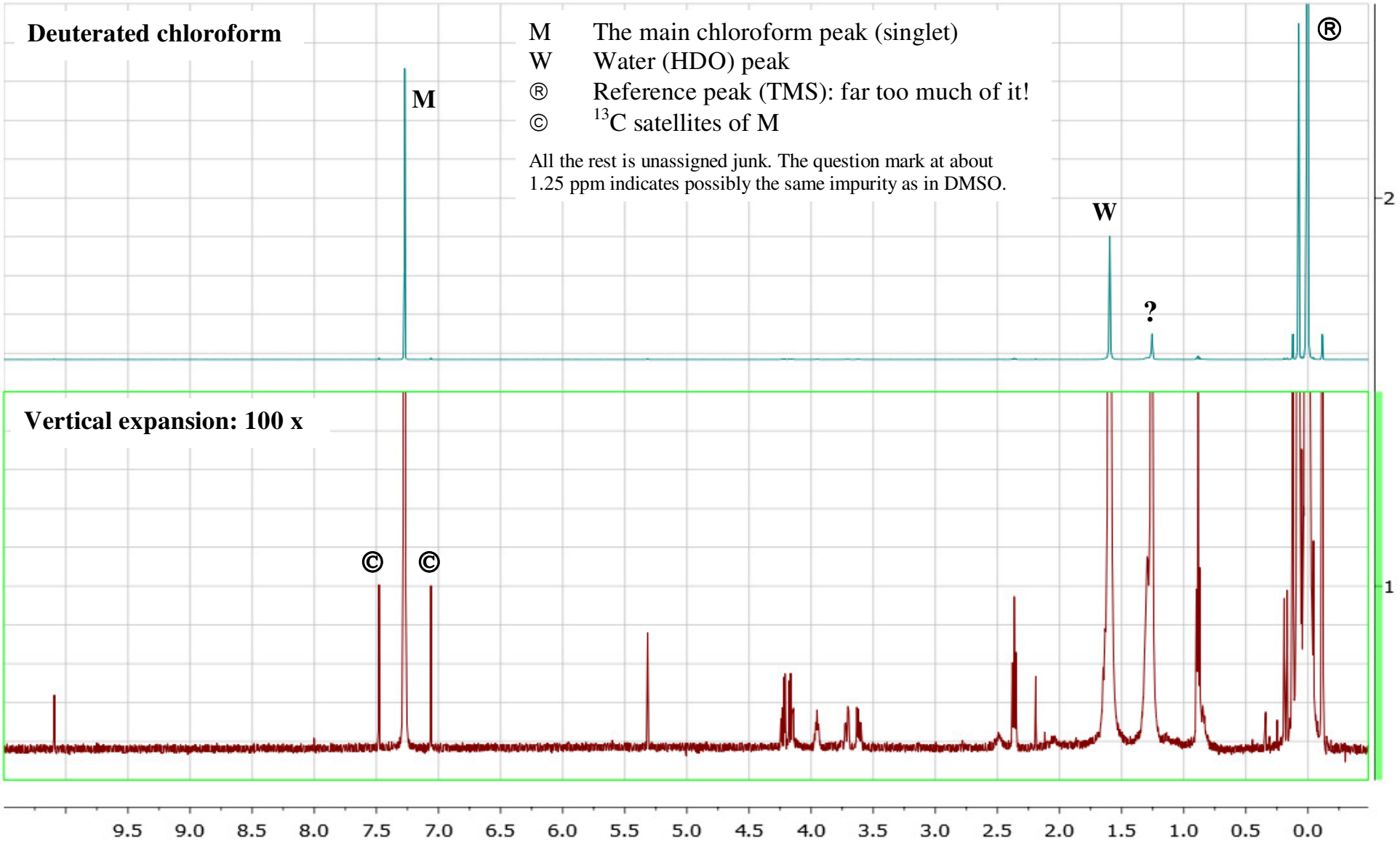
What one gets, however, can be quite a different story. The real spectra illustrate an evident high degree of contamination of the solvents. The impurity peaks are mostly sharp and thus should belong to dissolved impurities of small molecular weight (though some broad humps *might* be fat from fingerprints). The probable cause of the contamination, at least in the case of methanol, is a careless use of a communal storage bottle for the solvent or a contaminated pipette tip. In this case, probe contamination is not likely since there are too few peaks appearing in all three samples.

The strong impurity peak at 1.25 ppm found both in DMSO and in chloroform is not specific to the laboratory which ran the spectra – I encounter it in spectra measured in DMSO coming from many different places. It looks as an isolated (uncoupled) and totally protonated methyl. Personally, I have no idea about the compound to which it might belong.

This kind of “test” on a lab’s practices, when carried out without any prior warning, is no doubt a bit mean thing to do. But then, would you like your spectra measured in the “solvents” shown here? Perhaps **laboratories should make it a rule to actually measure their solvents once a month or so**.

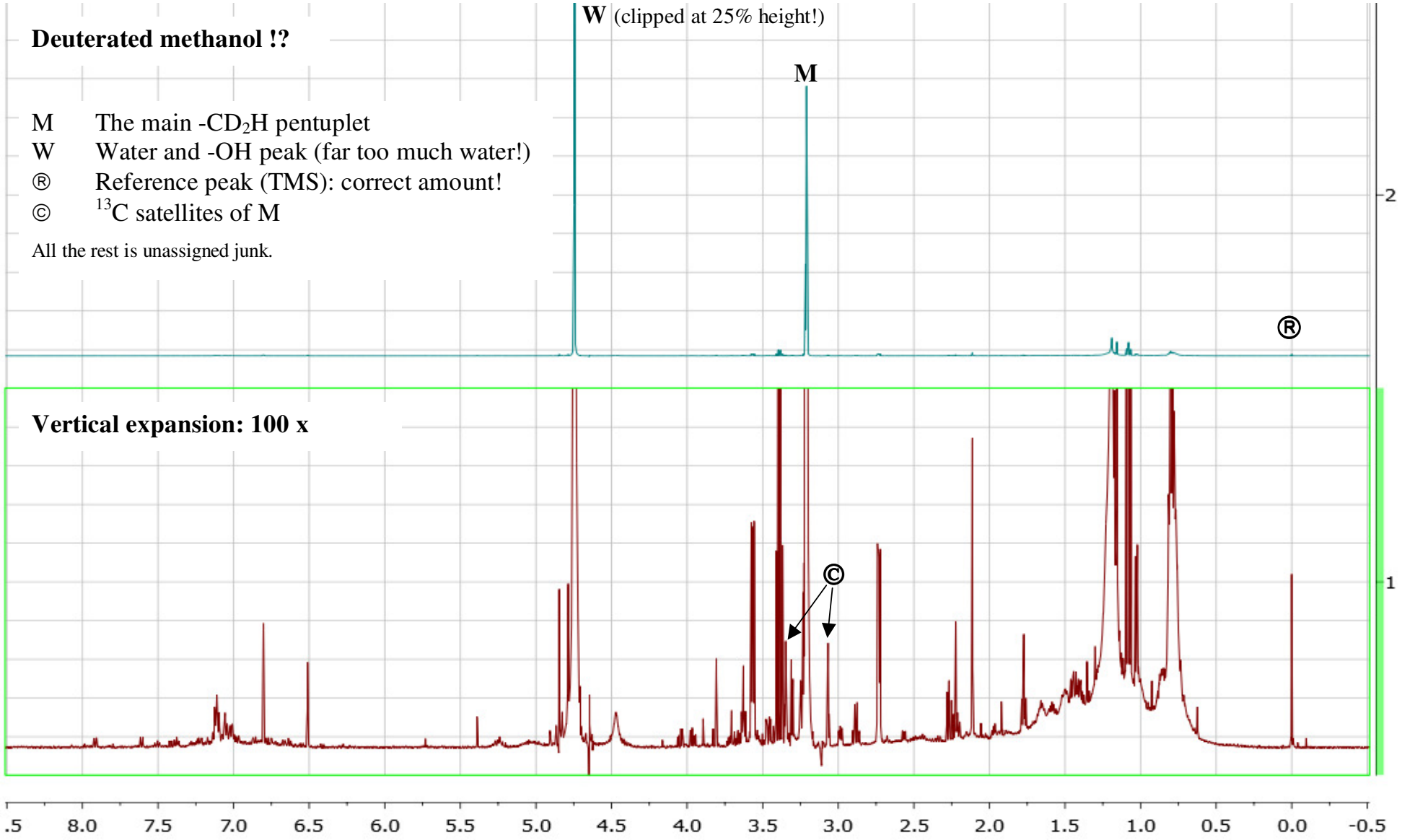
Stan Sykora, April 2010

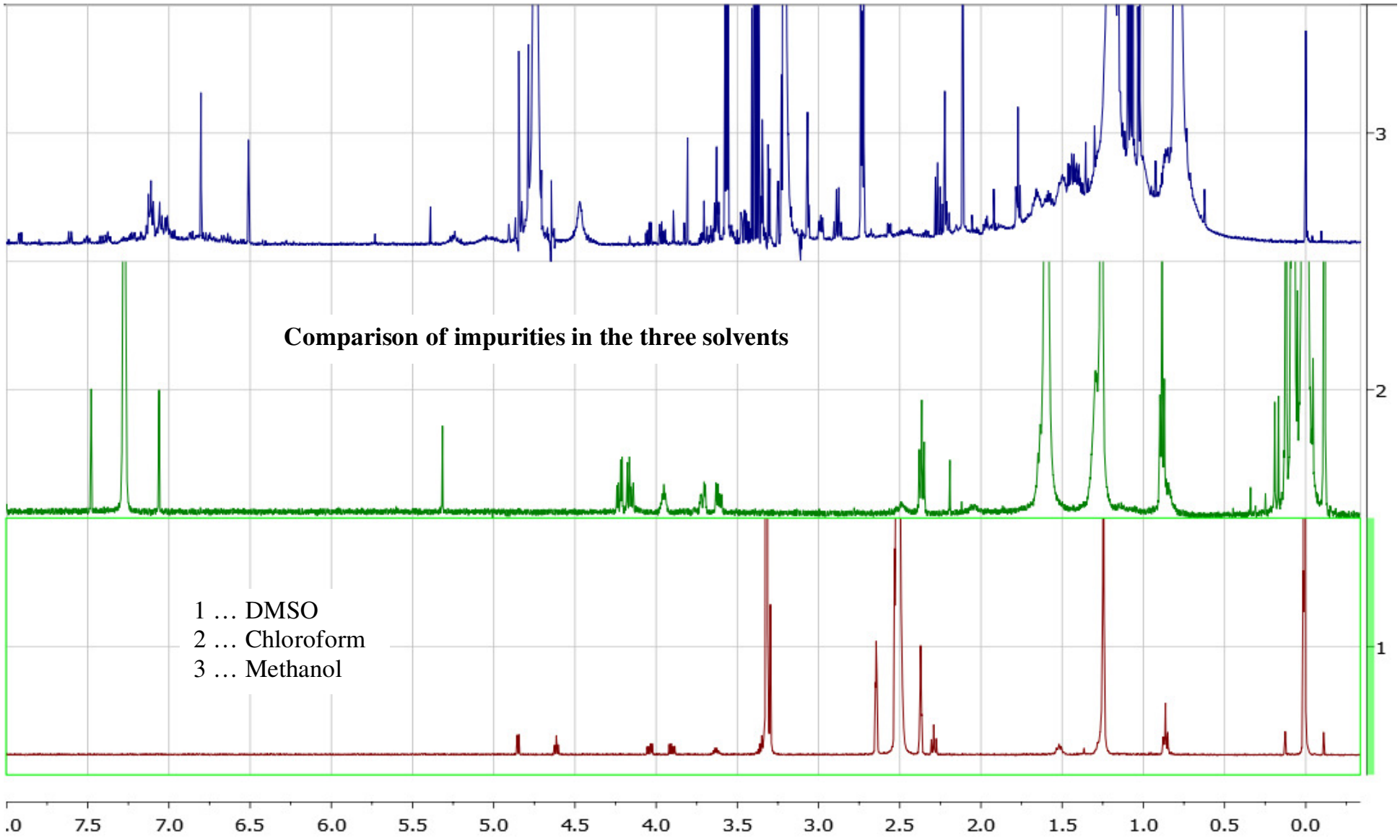

Deuterated DMSO (di-methyl-sulfoxide)
M The main -CD2H pentuplet
W Water (HDO) peak
® Reference peak (TMS)
© 13C satellites of M and ®
All the rest is unassigned junk.The question mark at about 1.25 ppm corresponds to a frequently encountered impurity.
M
W
?
®
Vertical expansion: 100 x
©
©
©
©
2
1
.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5



M The main chloroform peak (singlet)
W Water (HDO) peak
® Reference peak (TMS): far too much of it!
© ^{13}C satellites of M

All the rest is unassigned junk. The question mark at about 1.25 ppm indicates possibly the same impurity as in DMSO.


Deuterated methanol !?
M The main -CD2H pentuplet
W Water and -OH peak (far too much water!)
® Reference peak (TMS): correct amount!
© 13C satellites of M
All the rest is unassigned junk.
W (clipped at 25% height!)
M
®
Vertical expansion: 100 x
©
2
1
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


Comparison of impurities in the three solvents
1 … DMSO
2 … Chloroform
3 … Methanol
3
2
1
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0