Measurement of Ultra Fine Structure – Effect of Degassing

When measuring organic radicals, the signal may be broader than expected from the chemical structure. A possible cause is oxygen dissolved in the solvent. In water, dissolved oxygen is about 250 µmole/l. As oxygen is a radical, when the sample concentration is low, the unpaired electron (spin) of the sample and the spin of the oxygen generate a dipolar magnetic interaction, which causes line broadening. Therefore, to measure the spectrum without this effect, it is necessary to degas the solution. The degassing process is normally done by connecting the sample tube with the sample to a vacuum line. However, in some cases, simple degassing with nitrogen may be sufficient.

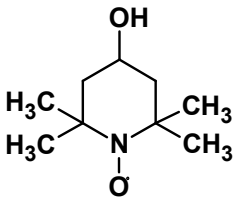

Fig. 1

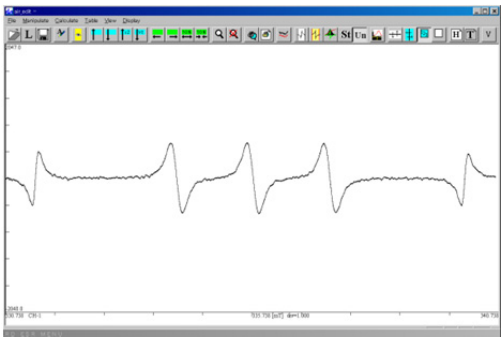

Fig. 2 Before degassing

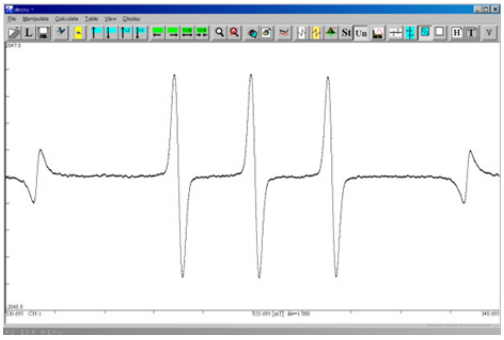

Fig. 3 After degassing

Here, we show the ultra fine structure of TEMPOL in Benzene solution, a stable radical, before and after degassing. The 4 methyl-groups are coupled with carbons on both sides of the N-O where the spin is localized. However, in an oxygen-saturated solution as shown in Fig. 2, the fine structure on the methyl group by H is not observed. After degassing with a vacuum line, the result was the spectrum shown in Fig. 3. As the line broadening arising from the dipole interaction was reduced by the degassing, the lines became sharper and the S/N improved. If we reduce the magnetic field modulation width (Mod width) from 0.1 mT to 0.01mT, the over-modulation phenomenon disappears and the fine structure shown in Fig. 4 is observed. The low magnetic field group is expanded in Fig. 5.

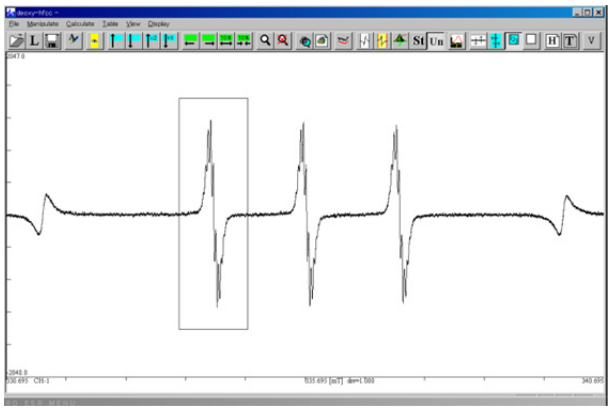

Fig. 4 After Degassing (Mod.width:10µT)

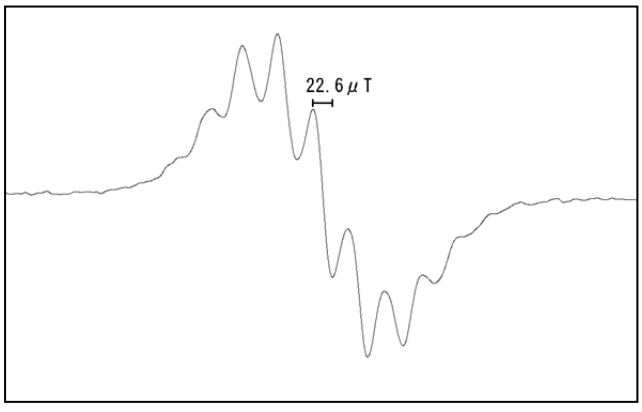

Fig. 5 Fine Structure after Degassing

In cases where samples are expected to show fine structure, we recommend measurement after degassing. There is a simple glass-free degassing cell available. Please check with us for details.