6.4: Answers to Questions in the Practical Aspects section

Question 1

A quantitative NMR experiment is performed to quantify the amount of isopropyl alcohol in a D_2O solution. Sodium maleate (0.01021 M) is used as an internal standard. The integral obtained for the maleate resonance is 46.978. The isopropanol doublet at 1.45 ppm produces an integral of 104.43. What would you predict for the integral of the isopropanol CH resonance as 3.99 ppm. What is the concentration of isopropanol in this solution?

Solution

The isopropanol CH resonance is produced by a single proton whereas the doublet is produced by the 6 methyl protons. Therefore, the CH integral should be 1/6th that of the methyl doublet, or 17.405.

To find the isopropanol concentration we first have to calculate normalized areas for isopropanol and our standard, maleate. The isopropanol(IP) doublet is comprised of 6 protons due to the two equivalent methyl groups of this compound.

$$\text{Normalized Area (IP)} = \frac{104.43}{6} = 17.405 \tag{6.4.1}$$

Similarly, the normalized area for maleate (MA) is:

$$\text{Normalized Area (MA)} = \frac{46.978}{2} = 23.489 \tag{6.4.2}$$

The concentration of the isopropanol can be calculated using the known the maleate concentration.

$$[\text{IP}] = \frac{[\text{MA}] \times \text{Normalized Area (IP)}}{\text{Normalized Area (MA)}} \tag{6.4.3}$$

$$[\text{IP}] = \frac{0.01021\ \text{M} \times 17.405}{23.489} = 0.007565\ \text{M} \tag{6.4.4}$$

Because the accuracy of the determination depends on how well the maleate concentration is known, the standard solution should be prepared with care, using dried sodium maleate of high purity, weighing carefully a mass that is known to an appropriate number of significant figures (in this case 4), transferring the maleate quantitatively to a volumetric flask and finally dilution to the mark. Again, an appropriate solution volume must be selected to produce the desired number of significant figures given the manufacturer specifications for the glassware used.

Question 2

A solution prepared for quantitative analysis using NMR was acquired by coaddition of 8 FIDs produces a spectrum with an S/N of 62.5 for the analyte signals. How many FIDs would have to be coadded to produce a spectrum with an S/N of 250?

Solution

S/N increases in NMR experiments as the square root of the number of scans coadded.

$$\text{S/N} \propto (\text{n})^{0.5} \tag{6.4.5}$$

To increase the S/N from 62.5 to 250 (a factor of 4 increase in S/N) would require coaddition of 16 times as many FIDs as was used to produce a spectrum with S/N of 62.5. The answer is that coaddition of 128 FIDs (8 x 16) would be required to achieve an S/N of 250.

Question 3

A ^{1}H NMR spectrum was measured using a 400.0 MHz instrument by acquisition of 8192 total data points (8192 real points) and a spectral width of 12.00 ppm. What was the acquisition time? Calculate the digital resolution of the resulting spectrum? Is this digital resolution sufficient to accurately define a peak with a width at half height of 0.5 Hz?

Solution

We can calculate the acquisition time knowing the spectral width and the total number of data points.

$$\mathrm{AT} = \frac{\mathrm{NP}}{2\ \mathrm{SW}} = \frac{16384}{2 \times 400 \times 12} = 1.707\ \mathrm{sec} \tag{6.4.6}$$

$$\mathrm{DR} = \frac{\mathrm{SW}}{\mathrm{NP(real)}} = \frac{2 \times 400 \times 12}{8192} = 1.172\ \mathrm{Hz/pt} \tag{6.4.7}$$

This would not be adequate digital resolution to accurately define a peak with a 0.5 Hz width at half height. A longer acquisition time would allow for collection of more points. Also, zero-filling could also be used to help increase the digital resolution.
