Determination of %C-13 in Natural Carbon

As you know, naturally occurring carbon consists of three isotopes, C-12, C-13, and C-14. Of these, C-14 (the carbon used for carbon dating) is present in only trace amount. Since C-12 has an atomic mass of exactly 12, there must be about 1% C-13 present. NMR allows you to estimate this value experimentally. Carbon-12 has a spin of zero and does not split the hydrogens attached to it. In contrast, C-13 has a spin of ½, and thus splits just like hydrogen nuclei. In a normal spectrum, you don't see the C-13 resonances because, at 1% abundance, they are each only about 0.5% as tall has the peaks coming from the hydrogens bound to C-12 carbons.

However, if the right compound is chosen, for example one with only one hydrogen in the molecule, it becomes possible to get a rough estimate of the C-13 abundance. Conceptually it works like this. Consider $CHCl_3$. A ^1H NMR spectrum yields a singlet at about 7.3 ppm, but any C-13 splits the singlet into a doublet. If you find those peaks and compare their total integration to the integration of the 7.3 ppm peak, you can estimate the abundance of C-13 indirectly. Why is it only an estimate? The reason has to do with the sensitivity of NMR. As you have learned, NMR has poor sensitivity and so yields noisy spectra. It takes many scans to have the C-13 peaks come out of the noise. In addition to that, as you have seen digital integration is not perfectly accurate either. In combination, these effects limit the accuracy of the experimental determination.

Use sample the sample labeled "1% chloroform 99% acetone-d6" on a clear label (not white like usual). Collect a normal proton spectrum, but **select acetone as your solvent**. (If you don't, your peaks will appear in unexpected places.) You will see two groups of resonances: the chloroform peak (7.26 ppm) and the residual hydrogen attached to acetone (2.04 ppm).

Begin with the chloroform resonances centered at 7.26 ppm. The large peak arises from the protons in chloroform, $CHCl_3$ (~99%), that are attached to C-12. Look very closely to see the two peaks arising from the hydrogen attached to C-13. These will be very small peaks about 0.25 ppm upfield and downfield of the C-12 H peak.

1) Plot this part of the spectrum and interpret the peaks.
2) Measure the distance between them in ppm and use the conversion factor 1 ppm = 400 Hz to calculate the CH one-bond coupling constant, $^1J_{CH}$. (It is possible that you will see similar, small peaks 0.05 ppm on either side of the central peak. Ignore them for now, they are spinning side bands.)
3) Zoom in on the central and satellite (^{13}C) peaks and integrate them. Set the integration of the central (^{12}C) peak to 100. There are also spinning side bands and the frequency is equal to the rate at which the sample spins. Print a copy of the entire region and locate each of the 5 peaks on it and label them.
4) From the integration, calculate the %C-13 in natural carbon. For example, if your integrations are 1.04, 100, and 0.59; then the %C13 = $2(0.82 \pm 0.22) = 1.64 \pm 0.44$ %. Show your calculation on your spectrum. [Make sure you understand how to get from the measured integrations provided here to the calculated percentages.]

5) Compare your results to the actual percentage of 1.11% and discuss possible sources of error.
6) Returning to the peaks you ignored in (2), calculate the rate at which the sample is spinning in the instrument from the spinning sidebands and compare it with the spin rate that is part of the instrument settings.

Write a brief summary of your results and tell how this relates to the relative difficulty of obtaining C-13 spectra relative to the difficulty of obtaining H-1 spectra.

Bonus: The acetone multiplet, a 1:2:3:2:1 pentet, should be centered at 2.04 ppm. Also, expand the spectrum around the CHD_2 peak of the acetone and calculate the 2 bond coupling constant between deuterium and hydrogen. Explain why this is a 1:2:3:2:1 pentet.