CHEMISTRY 133
Spring, 2017 Homework Set 2.2 Solutions

Set 2.2 – Complete for quiz on April 13th

Ch. 20: 1, 2, 4, 7, 14, 21

1. In which technique, atomic absorption or atomic emission is flame temperature stability more critical? Why? *It is more critical for atomic emission because the emission flux is depends on the flame temperature, while the atomization, which affects both methods, is less dependent on temperature.*

2. State the advantages and disadvantages of a furnace compared with the use of a flame in atomic absorption spectroscopy.
The main advantages is greater sensitivity (concentration and especially mass). The main disadvantages are greater instrument complexity and instrument cost. The sample throughput (number of samples that can be analyzed per hour) will also be somewhat lower due to the required temperature cycle.

4. State the advantages and disadvantages of inductively coupled plasma compared with conventional flames in atomic spectroscopy.
The main advantages are faster multielement analyses and fewer interferences. The main disadvantages are higher costs.

7. Explain what is meant by spectral, chemical, ionization, and isobaric interference.
Spectral interference arises from overlapping spectra (between different metal atoms or between metal atoms and molecules)
Chemical interference occurs when a species is present in the sample matrix that affects the atomization of the element of interest.
Ionization interference occurs when an analyte tends to ionize producing free ions instead of free atoms.
Isobaric interference occurs in atomic mass spectrometry when ions with the same nominal mass (or mass to charge ratio) are present.

14. Derive the entries for 500 nm in Table 20-3. Find N^*/N_0 at 6000 K if $g^* = 3$ and $g_0 = 1$.
$E = hc/\lambda = (6.626 \times 10^{-34}\ J\cdot s)(2.998 \times 10^{8}\ m/s)/5.00 \times 10^{-7}\ m = 3.973 \times 10^{-19}\ J/atom$
$N^*/N_0 = g^*/g_0 e^{-E/kT} = 3\exp[-(3.9729 \times 10^{-19}\ J)/(1.381 \times 10^{-23} J/K\cdot 6000\ K)] = 3e^{-4.795} =$ **0.025**

21. Using Excel, one can get an equation for the line through the data as A = 0.07049C + 0.1579. The x-intercept occurs where y (A) = 0. Or – x-intercept = - (-b/m) = 0.1579/0.0749 = 2.3397. Using equation 5-10 for the uncertainty gives 0.0652 μg/mL
Now, we just need to account for dilution. Since 5.00 mL aliquots were added to 50 mL, the original aliquot had 50/5 or 10 x the conc. – namely 23.4 $\pm$ 0.7 μg/mL. Since 100 mL was generated, the 0.5216 g sample had (100 mL)(23.4 μg/mL) = 2.34 mg Ca. Thus the sample was (2.34 mg/521.6 mg)100 % Ca = 0.4294%. % unc. = 0.012% (using propagation of uncertainty)
% Ca = 0.43% $\pm$ 0.01%

NMR (R&R Ch. 11): 1, 3, 4, 5, 7
Rubinson and Rubinson Text Ch. 11: 1, 3, 4, 5, 7

1. A 250 MHz ^{1}H NMR spectrum was run, and six peaks with equal integral areas were found. The peaks were at 0, 346, 408, 467, 950, and 1787 Hz downfield relative to TMS. In the sample are tetramethyl silane, acetone, benzene, cyclohexane, t-butanol, and dioxane. The hydroxyl proton of the alcohol could not be seen.

a) Assign the six peaks to the six compounds.

First, we can convert from Hz to ppm by $(\nu - \nu_{TMS})\cdot 10^6/\nu_{TMS}$ (e.g. = 346·1,000,000/250,000,000 = 1.384 ppm) 6 peaks: 1.384, 1.632, 1.868, 3.800, 7.148

Assignment

Peak (ppm)	*0*	*1.384*	*1.632*	*1.868*	*3.800*	*7.148*
compound	*TMS*	*cyclohexane*	*t-butanol*	*acetone*	*dioxane*	*benzene*

b) If the spectrum were a 500 MHz ^{1}H NMR spectrum, at what frequencies relative to TMS would the six resonances be?

Example for cyclohexane: ν = (346 Hz)(500 MHz/250 MHz) = 692 Hz
All others: 0, 692, 816, 934, 1900, and 3574 Hz.

c) If the TMS is assigned a concentration of 10.0, what are the concentrations of the other five components of the mixture?

compound	*TMS*	*cyclohexane*	*t-butanol*	*acetone*	*dioxane*	*benzene*
Mole H/ mole	*12*	*12*	*9*	*6*	*8*	*6*
concentration	*10.0*	*10.0*	*13.3*	*20.0*	*15.0*	*20.0*

Calculation for t-butanol: (10.0)(12/9) = 13.3 This is based on equal signals, meaning greater concentrations for compounds with fewer than 12 protons per mole.

3. Assign spectra I through V in Figure 11.3.1. The possible compounds are
A. 1-chloropropane, $CH_3CH_2CH_2Cl$, B. 1, 2-dichloropropane, $CH_3CH(Cl)CH_2Cl$, C. 1,3-dichloropropane, $Cl(CH_2)_3Cl$, D. isopropanol, $(CH_3)_2CHOH$, E. Allyl chloride, $H_2C{=}CHCH_2Cl$, F. 1-propanol, $CH_3CH_2CH_2OH$

I. Shows left triplet at 3.5 ppm, multiplet at 1.8 ppm, and right triplet at 1.05 ppm. This indicates an alkyl methyl group at 1.05 ppm split by a neighboring –CH_2– group. This limits it to A or F. The triplet at 3.5 ppm is in between that expected for a CH_2Cl and a CH_2OH group, but no other peak for OH is seen, indicating that it must be ***A (1-chloropropane)***

II. Shows ugly multiplets at 5.7 ppm to 6.2 ppm, a doublet at 5.3 ppm, and another doublet at 5.1 ppm (with a small coupling constant) followed by another doublet at 4.0 ppm. The presence of no groups upfield of 4.0 ppm indicate plenty of electron withdrawing groups or a double bond in the molecule. This rules out A, B, C, D, and F. Therefore, it must be ***E (Allyl chloride)****. The -CH_2Cl protons are at 4.0 ppm and split by the =CH- proton. The other protons absorb between 5 and 6 ppm. The CH_2= group protons should show a doublet of doublets (split by each other and by the =CH-proton). The =CH- proton shows even more complex splitting (split by doublets of doublets by the CH_2= group protons and into triplets by the -CH_2Cl protons). The combined olefinic ^{1}H spectra is complicated by overlapping spectra making exact interpretation difficult.*

III. Shows a multiplet at 4.1 ppm, possibly a doublet at about 3.6 ppm and a strong doublet at 1.6 ppm. The doublet at 1.6 ppm is split by one equivalent proton. This is indicative of a methyl group next to a CH group as in B and D. The doublet at 3.6 ppm can correspond to another set of protons split by the

one equivalent proton as the peak at 1.6 ppm. Thus this corresponds to the -CH_2Cl protons, as the chemical shift is close to that expected (3.4 ppm) and indicates structure ***B (1, 2-dichloropropane)****. The large multiplet at 4.1 ppm is the from the CH group split by the methyl and the -CH_2Cl group (a triplet of quartets or close to a quintet).*
IV. Shows a clear triplet at 3.7 ppm and a quintet at 2.2 ppm. The triplet is split by two equivalent protons and the quintet is split by four equivalent protons. This indicates structure ***C. (1,3-dichloropropane)*** *with the quintet from the middle –CH_2- group and the triplet from the four protons that are equivalent in the outer –CH_2- groups.*
V. Shows a triplet at 3.6 ppm, a singlet at 3.1 ppm, a multiplet (sextet?) at 1.5 ppm and a triplet at 0.9 ppm. The triplet at 0.9 ppm indicates a methyl group far from an electron withdrawing group with a neighboring –CH_2- group which indicates F. (1-propanol). The peak at 1.5 ppm is what is expected for the middle –CH_2- group (split into a quartet of triplets. The singlet is for the OH proton, and the peak at 3.6 ppm is from the –CH_2OH protons.

4. Assign spectra I through VI in Figure 11.4.1 The possible compounds are A.ethylbenzene, $CH_3CH_2C_6H_5$, B. p-cresol, $CH_3C_6H_4OH$, C. p-xylene, $CH_3C_6H_4CH_3$, D. benzene, C_6H_6, E. toluene, $C_6H_5CH_3$, F. anisole, $C_6H_5OCH_3$, G. p-dimethoxybenzene, $CH_3OC_6H_4OCH_3$.
I. Shows only two peaks: one at 7.0 ppm and another at 2.3 ppm. This can only be due to ***p-xylene*** *because it has only two sets of equivalent protons and they would be expected a little less than 7.1 ppm (listed for toluene) and 2.3 ppm (methyl on benzene).*
II. Shows a singlet at 7.2 ppm and at 2.35 ppm. This is very similar to structure I but shows a higher peak at 7.2 ppm and a lower group at 2.35 ppm, indicative of more aromatic protons and fewer alkyl protons (integrated areas would be useful for confirmation, though). This can be from ***toluene****.*
III. Shows a multiplet at 6.8 ppm, a singlet at 5 ppm, and a singlet at 2.3 ppm. The 6.8 ppm peak is indicative of aromatic protons in a para benzene group with non-equivalent functional groups. The 2.3 ppm peak is indicative of an aromatic methyl and the 5 ppm peak could be from an OH group. This leads to ***p-cresol****.*
IV. Shows a singlet at 7.1 ppm, a quartet at 2.6 ppm and a triplet at 1.2 ppm. Based on the triplet and quartet, an ethyl group is likely, indicating ***ethylbenzene****.*
V. Shows a messy peak at 7 ppm and a singlet at 3.8 ppm. The singlet at 3.8 ppm is indicative of a methoxy group. Since the peak at 7 ppm is not a singlet, G can be ruled out leaving ***anisole****.*
VI. Looks similar to V. except with a singlet at 6.8 ppm. The singlet indicates equivalent aromatic protons which is given by ***p-dimethoxybenzene****.*

5. A new sulfonate drug was being developed that contained the following group in its structure -(CO)-C_6H_4-SO_3^-
Running a conventional mass spectrum was not possible because the compound degrades when heated, so it was decided to find the molecular mass by NMR. To do this, 10.0 mg of the compound was weighed into an NMR tybe. To the tube was added 5.00 mg of anhydrous sodium acetate (FW 82.04). Both compounds were dissolved in D_2O. An NMR spectrum was run. The sodium acetate peak at 1.90 ppm had an integral area of 82.0 units (average of 3 runs). A singlet at 8.0 ppm (no other peaks in the region had an integral of 30.5 units (average of 3 runs). What is the formula weight of the analyte?
1) Calculate mmol $NaCH_3CO_2$ and mmol H: 5.00 mg/(82.04 mg/mmol) = 0.06095 mmol or 0.1828 mmol protons
2) Determine area/mmol proton ratio: 82.0 area units/0.182 mmol proton = 448 area units/mmol proton

3) Determine mmol proton in unknown: 30.5 area units/(448 area units/mmol proton) = 0.06801 mmol proton
4) Determine mmol unknown: (0.06801 mmol proton)(1 mmol compound/4 mmol aromatic proton) = 0.01700 mmol
5) Determine FW: 10.0 mg/0.01700 mmol = ***588 g/mol***

7. Figure 11.20 shows the proton NMR spectrum of 2-iodo-1,1,1-trifluoroethane. If you were to obtain the F NMR of the compound, what kind of multiplet splitting would the fluorines exhibit?
They would be split by the two protons on the #2 carbon. Thus, they would be split into a triplet with the same coupling constant observed in Figure 11.20.