Name ____

Equations and constants that you may find useful: $0^{\circ}C = 273 \text{ K}$; Planck's constant $h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s}$ Boltzmann Distribution: $N^*/N_o = (g^*/g_o)e^{-E/kT}$ with Boltzman Constant $= k = 1.38 \times 10^{-23} \text{ J/K}$ NMR frequency equation: $v = (\gamma/\pi)B_o$ (v = frequency and $B_o =$ magnetic field at the nucleus) Pascal's triangle:

1 1 1 2 1 1 3 3 1 1 1 4 6 4 1 1 10 10 5 1 5 1 6 15 20 15 6 1 Chromatography Equations: retention factor = $k = (t_r - t_m)/t_m$ $\alpha = k_y/k_x$ for components x and y (eluting in that order) N = plate number = $16(t_r/w^2)$ (w = width at base)

SHORT ANSWER SECTION: (Each question worth 4 points)

- 1. In inductively coupled plasma-atomic emission spectroscopy (ICP-AES), spectral interference from molecular species is usually less than in flame atomic absorption (AA) spectroscopy because:
 - a) ICP atomization is more complete
 - b) AA doesn't use a monochromator
 - c) atoms and molecules have different mases
 - d) emission bands are narrower than absorption bands

BONUS. (3 pts) A proton NMR is obtained on CH_3CDCl_2 (where $D = {}^{2}H$, an I = 1 nucleus). The presence of D instead of ${}^{1}H$ will:

- a) have no effect on the NMR spectrum
- b) cause a large change in the chemical shift of the CH₃ protons
- c) cause a change in the splitting observed by CH₃ protons
- d) cause a large increase in the intensity of the CH₃ protons

2. In NMR, knowledge of spin-lattice relaxation is important because it affects:

- a) the rate at which sample can be irradiated without causing saturation
- b) the frequency where nuclei absorb
- c) the number and type of splitting nuclei undergo
- d) the ability of other nuclei to absorb light

3. Give the name or describe an ionization method that can be applied as a detector for GC-MS. Method = _____

4. Aromatic hydrogens (hydrogens on benzene rings) in NMR absorb at downfield (lower magnetic frequencies or higher ppm values) primarily because:

a) the benzene ring is an electron withdrawing region leading to deshielding

b) the high electron density leads to a high degree of shielding

c) electron circulation induced in the benzene ring leads to an increased magnetic field at protons

d) all ringed compounds fix the orientation so protons get the full magnetic field

5. Alkyl amines are what make tuna fish smell bad. These compounds are weak bases and are volatile as molecules but non-volatile in the ion form. To reduce the smell from alkyl amines, one should prepare tuna fish under:

a) acidic conditions b) basic conditions c) pH has no effect.

6. Two compounds are being separated by reversed phase HPLC using a mobile phase of 60% methanol and 40% water and a C8 stationary phase. The separation is not good because of insufficient retention. To increase retention, the chemist should:

a) increase the percent methanol

b) increase the percent water

c) go with a C4 stationary phase (similar polarity but less volume)

d) use a faster flow rate

7. Name or describe one source of band broadening. Source of band broadening:

SECTION II. PROBLEM SECTION. Show work – use the back side if needed

1. A soil sample (4.00 g) is digested and analyzed for Cd by atomic absorption analysis. The digestion results in 25.0 mL of extract. Because there is concern of matrix effects, standard addition is used. A portion of the extract is analyzed directly by AA and gives an absorbance of 0.211. Another 10.0 mL portion of the extract is spiked with 50.0 μ g of Cd (ignore any added volume from Cd spiking) and gives an absorbance of 0.539.

a) Calculate the Cd concentration in the (unspiked) extract (in μ g/mL). (10 pts)

b) Calculate the Cd concentration in the soil in ppm (by mass). (4 pts)

c) A Cd standard prepared in dilute nitric acid to a concentration of 1.00 μ g/mL is analyzed and gives an absorbance of 0.191. Was the standard addition justified? (4 pts)

- 2. Sketch an NMR ¹H spectrum for methyl isopropyl ketone (CH₃COCH(CH₃)₂).
- (15 points) Indicate:
- a) the number of groups of equivalent nuclei.
- b) the relative position (higher vs. lower field) of the different groups of equivalent nuclei.
- c) the splitting pattern (number of peaks) for each group of equivalent nuclei.

2 - BONUS) if the CH proton and the left CH_3 protons are located 0.32 ppm apart, will their peaks overlap on a 200 MHz spectrometer? Assume a 10 Hz coupling constant for splitting if needed. Show work. (3 pts)

3. A scientist is trying to produce 2-chloroacetophenone ($C_6H_5C(O)CH_2Cl$) but is worried that chlorination occurred on the benzene ring instead (producing $ClC_6H_4C(O)CH_3 - e.g.$ 4'chloroacetophenone – instead). Atomic weights: ${}^{1}H - 1.008$ amu, ${}^{12}C - 12.000$ amu, ${}^{16}O - 15.995$ amu, and ${}^{35}Cl - 34.969$ amu.

a) Given that ketones tend to fragment between the α carbon and the carbonyl carbon, indicate two fragment peaks (give the mass to charge ratio and structure) that would be indicative of 2-chloroacetophenone. (6 pts)

b) What two related fragments would be expected from $ClC_6H_4C(O)CH_3$ instead? (4 pts)

4. Upon analysis by mass spectrometry 1,1-bromo-chloro-ethane (CHBrClCH₃) gives a most common isotope peak of 142. Given information for less common isotopes below, give ratios of peak intensities for M+1/M (e.g. ratio of intensity of 143 peak to 142 peak), M+2/M and M+4/M ratios. The most common isotopes are: ¹²C, ³⁵Cl, and ⁷⁹Br

| | | l l | |
|-----------------|------|------|------|
| Isotope/Element | С | Cl | Br |
| М | 100 | 100 | 100 |
| M+1 | 1.08 | none | none |
| M+2 | none | 32 | 97 |

You can ignore the contribution of 2^{13} Cs to any ratios. (9 pts)

5. Two columns, a non-polar DB-1 column and a moderately polar DB-17 column, were tested to separate methyl stearate – MS or $CH_3O_2C(CH_2)_{16}CH_3$ from methyl oleate – MO or $CH_3O_2C(CH_2)_7CH=CH(CH_2)_7CH_3$ (cis form) using GC in two trial chromatograms with retention times and peak widths listed below. The columns had similar dimensions (length, diameter and film thickness) and were run using the same temperature program.

| Peak | DB-1 Retention | DB-1 Peak width | DB-17 Retention | DB-17 Peak width |
|--------------|----------------|-----------------|-----------------|------------------|
| | Time (min) | at base (min) | Time (min) | at base (min) |
| CH_4 | 1.71 | - | 1.83 | - |
| (unretained) | | | | |
| MO | 8.53 | 0.185 | 10.31 | 0.213 |
| MS | 8.79 | 0.190 | 8.84 | 0.186 |

a) Determine the retention factor (k) for MO on the DB-1 column. (4 pts)

b) Determine the plate number (N) for each column using MS. (6 pts)

c) Calculate relative retention (α) for MO and MS for each column. For which column is this better? (6 pts)

d) Based on their separations, which compound (MS or MO) is more polar? Explain your answer. (4 pts)