Question 1 Multiple Choice. Answer all questions (2 points each, 18 points total).

(i) Which of the following is NOT TRUE when comparing GC with HPLC:

(c) a GC can be used with more classes of compound, including gasses, salts, and large biomolecules

(ii) At what voltage will a solution of Pb^{2+} be quantitatively reduced ($[Pb^{2+}] \leq 1.00 \times 10^{-5}$ *M*)? For $Pb^{2+} + 2e^- \rightleftarrows Pb(s)$, $E° = -0.126$ V (*vs.* SHE).

(c) -0.274 V

(iii) Concentration polarisation means the electrochemical voltage generated:

(a) is limited by the rate of new material getting to the electrode

(iv) What is the size of the M + 2 peak for the fatty acid linoleic acid, $C_{18}H_{32}O_2$? Natural abundances are: ^{16}O & ^{1}H (100%), ^{12}C (98.9%), ^{13}C (1.1%).

(d) 1.6%

Q1 (cont'd) (v) Which of the following HPLC detectors is the LEAST appropriate for detecting a saturated (all single bonds) hydrocarbon?

(d) UV-visible absorption

(vi) Americium is a synthetic element used as a radioactive source in smoke detectors. The oxidation states +6, +5, +4, +3, and 0 are stable. Acyclic voltammogram was run in which AmO_2^{2+} (*aq*) was reduced. If the peak-to-peak height was 0.0197 V, which is the likely product of the reduction?

(b) Am^{3+} (*aq*)

(vii) The following species all have the empirical formula $C_8H_{10}O$. The mass spec fragmentation peaks are *m*/*z* 105, 76, 29, and 17. Which of the following is the most likely structure?

(d) (*p*-ethylphenol)

(viii) Two molecules have retention factors (k_A and k_B) of 3.1 and 3.8 and are fully resolved (R_s = 1.5). On a 10 cm HPLC column, how long will the separation take if the plate height is 0.01 cm and unretained mobile phase comes off in 30 s?

(b) 244 s

Q1 (cont'd) (ix) The octanol-water partition constant (k_D) of a PCB is 8.62. How much PCB will be left in 0.400 L of water after 3 extractions with 100 mL of octanol? Initial concentration of PCB was 0.0230 *M*.

(b) 0.000732 *M*

Question 2 Short answer. Answer 5 of the following 6. (2 points each, 10 total)

(a) Chemical companies sell "HPLC grade" solvents. Why is this necessary?

HPLC columns have very small pore sizes and are easily clogged. Therefore, solvents must be free of anything that might precipitate and/or build up in the column over time (*e.g.* metal ions).

(b) Explain how an electron-impact source for mass spec works.

A gas phase ion enters a stream of high energy electrons. If an electron impacts the molecule, it has enough energy to ionise it and possibly also to break it up (it is a hard source).

(c) Explain the difference between fluorescence and phosphorescence.

Both are emission of light, but phosphorescence has a longer lifetime because of intersystem crossing. This causes the excited state to get "stuck" in a situation where the decay (electron decreasing in energy level and emitting the photon) process is spin forbidden. Therefore, the spin forbidden transistion is longer lived.

(d) Explain how to reverse electroosmotic flow.

You must have a capillary coated with something positively charged (*e.g.*, -Si-CH_3^+) and reverse the potential (voltage) applied across the capillary.

(e) Calculate the IR frequency (in cm^{-1}) of an inorganic salt's nitrile stretch. Remember that the nitrile anion is $C{\equiv}N^-$. The force constant (k) is 1.955 x 10^6 g/s^2.

using the formula $\Delta E = h/2\pi*(k/\mu)^{1/2}$, you get 2266 cm^{-1}

(g) For a mass spec sample, briefly explain the difference between a spectrum obtained using a hard source and one using a soft source. You may assume the mass spec was of an organic molecule.

Soft source mostly gives just the molecular ion, M^+
Hard source breaks the molecule up to give molecular fragments. May not even show M^+.

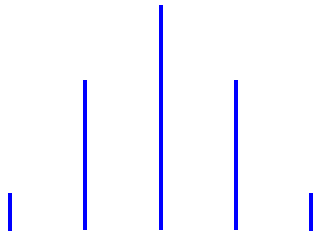
Question 3 Longer answer. Answer 3 of the following 4. (3 points each, 9 total)

(a) Explain the difficulties in linking a mass spectrometer to a liquid chromatographic instrument (such as an HPLC or CZE).

- liquid chromatograms operate at 1 atm, MS at 10^{-7} atm; dropping the pressure is not trivial
- analyte in low concetration, how do you get all the solvent and buffer molecules out of there so they don't interfere?

(b) Carbon tetrabromide, CBr_4, was formerly used as a solvent, but is now generally banned due to its toxicity (both to humans and the ozone layer). Sketch the isotope pattern for the molecular ion(s). The isotopic abundance for ^{79}Br is 50.7% and for ^{81}Br is 49.3%. Assume ^{12}C is 100% abundant.

Because the two isotopes are almost 50/50, you can actually use Pascal's triangle to solve this. If so you'd get the following 1:4:6:4:1 ratio:



m/*z* 328 330 332 334 336

You could also plug each one into the $C_x^4(0.507^x)(0.493^{4-x})$ formula.

(c) Explain how a gas-permeable electrode works (to detect gaseous species).

Electrode has a material that is hydrophobic so that non-polar molecules (like O_2, CO_2, etc.) can pass through but H_2O can't. Inside the electrode is usually a solvent that will react with the incoming gas. The product of this reaction can be measured for concentration (*e.g.* CO_2 dissolves in water to create an acidic solution, the pH of which is measured).

(d) In size-exclusion chromatography, two peaks elute at *exactly the same time*, at the end of the chromatogram (*i.e.* they are the last peak). How would you change the gel to separate these two peaks?

The gel is of the wrong pore size - further if the peaks are at the end of the chromatogram, they are both fully retained, which means that both peaks are smaller than the size range of the gel. Therefore, a gel with smaller pores (smaller molecular weight range) is needed.

Question 4 Determine $E°$ for the following reaction (4 points):

$$AgIO_3\,(s) + e^- \rightleftarrows Ag\,(s) + IO_3^-\,(aq)$$

The following information might be useful:

$$Ag^+\,(aq) + e^- \rightleftarrows Ag\,(s) \qquad E° = 0.799\ V$$

$$AgIO_3\,(s) \rightleftarrows Ag^+\,(aq) + IO_3^-\,(aq) \qquad K_{sp} = 3.1 \times 10^{-8}$$

Solve for the effective concentration of Ag^+ in the presence of IO_3^-:

$k_{sp} = [Ag^+][IO_3^-]$ or $[Ag^+] = k_{sp}/[IO_3^-]$
but $[IO_3^-] = 1\ M$, therefore $[Ag^+] = k_{sp}$

Voltage generated at that concentration:

$E_{Ag/AgIO3} = E°_{Ag+/Ag} - (0.0592/n)\log(1/[Ag^+])$
$= 0.799 - (0.0592/1)\log(1/3.1 \times 10^{-8}) = 0.354\ V$

Question 5 Describe the design of a pH meter, including specific materials. Be sure to describe each of the three principle parts: the reference electrode, the indicator electrode, and the junction. (4 points)

Indicator electrode: made with a membrane (soda glass) that exchanges Na^+ with H^+ in solution.
Reference electrode: usually Ag/AgCl or SCE (SHE never used because don't want H_2 blowing up the lab)
Junction: usually a slat bridge of some sort with KCl in it.

Question 6 Describe a MALDI-ToF mass spectrometer. (5 points)

MALDI source = matrix-assisted laser desorption/ionisation. Analyte (solid or possibly liquid) mixed with a dye. Laser light excites the dye, the energy then transfers from the dye to the analyte. This energy is sufficient to cause the analyte to desorb and ionise, at which point the ions are introduced into the ToF mass analyser.

ToF mass analyser = time of flight. All ions pushed through a voltage which imparts on them the same kinetic energy. Because K.E. = 1/2 mv^2, the heavier the particle, the slower it moves. These ions are introduced into a long drift tube, with a detector at the end. The time it takes the ion to reach the detector will be related to its speed, which is related to its mass.

Question 7 There may be many correct answers for all of these. Just make sure you create complete answers, including the type of column you would use if you are doing a separation, the time of ionisation source you would use if using a mass spec, the types of detectors (these would have to be appropriate detectors - both for the instrument and for the type of molecule you are looking at). Also, a comment on sample prep might be appropriate (*e.g.*, not contaminating the bog body with your own DNA) or the use of standards (*e.g.*, if you used an FID detector, you'd first have to calibrate it to know the retention times of the gases you are looking for).