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:

(a) it is easier to interface a GC with a mass spec

(b) a GC is cheaper to purchase

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

(d) it is more difficult to scale up (from analytical to preparative scale) a GC

(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).

(a) 0.135 V

(b) -0.126 V

(c) -0.274 V

(d) -0.422 V

(iii) Concentration polarisation means the electrochemical voltage generated:

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

(b) decreases over time as material plates on the electrode

(c) is limited by the initial concentration in the double layer

(d) will be larger than the theoretical $E°$ value

(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%).

(a) 0.0113%

(b) 0.317%

(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?

(a) infrared (IR) absorption

(b) mass spectrometry

(c) refractive index (RI)

(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?

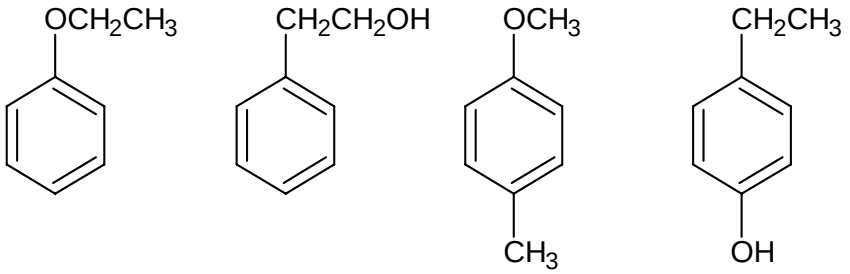
(a) Am (*s*)

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

(c) Am^{4+} (*aq*)

(d) AmO_2^{+} (*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?



(a) (b) (c) (d)

(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?

(a) 51 s

(b) 244 s

(c) 353 s

(d) cannot say without knowing the peak widths

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*.

(a) 5.15×10^{-7} *M*

(b) 0.000732 *M*

(c) 0.00230 *M*

(d) 0.00729 *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?

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

(c) Explain the difference between fluorescence and phosphorescence.

(d) Explain how to reverse electroosmotic flow.

(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 1.955×10^6 g/s^2.

(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.

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).

(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.

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

(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?

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:

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

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

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)

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

Question 7 For *2 of the 3* cases below, choose an analytical method or methods that would allow you to perform the analysis described. Give SPECIFIC DETAILS on experimental parameters (including justification), *e.g.*, detector, stationary phase, etc. You may also want to comment on any preliminary sample preparation that might be necessary. (5 points each, 10 points total)

(a) You are a weapons inspector for the International Atomic Energy Commission. Iran claims that it is not developing a uranium enrichment program (required for making nuclear weapons). You have obtained a metallic uranium sample from an Iranian source. How would you determine if it has been enriched in ^{235}U, the isotope used in weapons? Naturally occurring uranium is 1% ^{235}U and 99% ^{238}U.

(b) Scrubbers are installed on smokestacks (like the ones at Bowater and hospital incinerators) to trap noxious volatile (gaseous) substances. Unwanted gasses are usually acid-rain causing sulfur-based (SO_2, SO_3) or nitrogen-based (NO_2) compounds, ozone-depleting CFC's ($C_xCl_yF_z$), or greenhouse gasses (CO, CO_2, NO). How would you detect whether exhaust emitting from a smokestack contains any of these substances? Water is allowed to come out; is water likely to interfere with the identification of any of these substances?

(c) Some partially decomposed human remains are found in a bog. There is evidence of violence on the body. The police need to know if they should open a murder case, or if the body has been in the bog for a long time (bogs can preserve remains for hundreds of years). How could you determine the age of the body? Hint: Living DNA is in the L-form. After organism death, it gradually isomerises to racemic (50/50 L/D ratio) DNA.