**CHEM 3590  Test 2, Version A**
November 9, 2018, 10:30-11:30 in Machray 124
Answer all five (5) questions directly on the exam paper.

Name: _Answers_
Student no.:_____

## Question 1

a) According to data shown below for butanal (butyraldehyde) and 1-methyl cyclopentene, predict the retention order of these compounds on a DB-1 GC capillary column and justify.

| Compound name | Butanal | 1-methyl cyclopentene |
|---|---|---|
| Boiling point °C | 75 | 75 |
| Vapour pressure* (mmHg) | 90 | 36 |

*at room temperature

Both compounds have the same boiling pt, but as butanal has a higher vapour pressure it is more volatile, so butanal will elute first.

With DB-1 columns interactions with the stationary phase are minimal and elution order depends essentially on boiling point and vapour pressure.

b) Determine the column selectivity if the two peaks are just resolved at baseline (draw your own chromatogram).
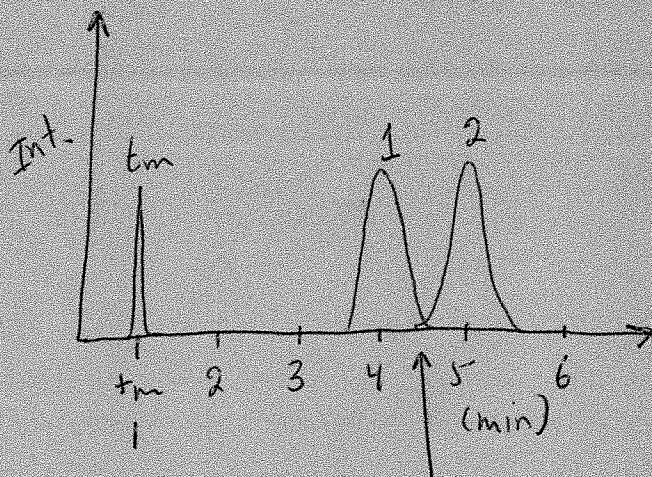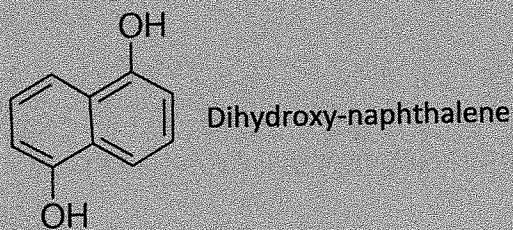


$$\alpha = \frac{k_2'}{k_1'} = \frac{5-1}{4-1} = \frac{4}{3}$$

$$\left( k_2' = \frac{5-1}{1}, \; k_1' = \frac{4-1}{1} \right)$$

just resolved at baseline

## Question 2

Prior to a GC/MS experiment, a sample of dihydroxy-naphthalene is derivatized with chlorotrimethylsilane.
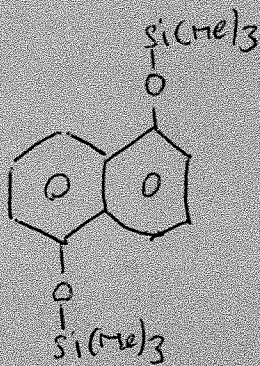


Dihydroxy-naphthalene

a) What is the purpose of this reaction?

- To make the compound more volatile and remove potential interactions of −OH groups with the stationary phase
- This will reduce analysis time and yield sharper peaks.

b) What is the molecular mass of the product to be measured by GC/MS?
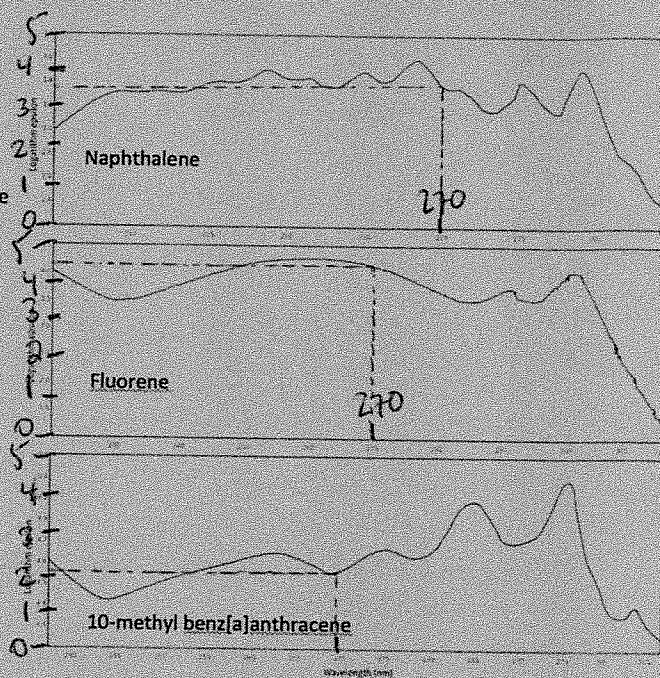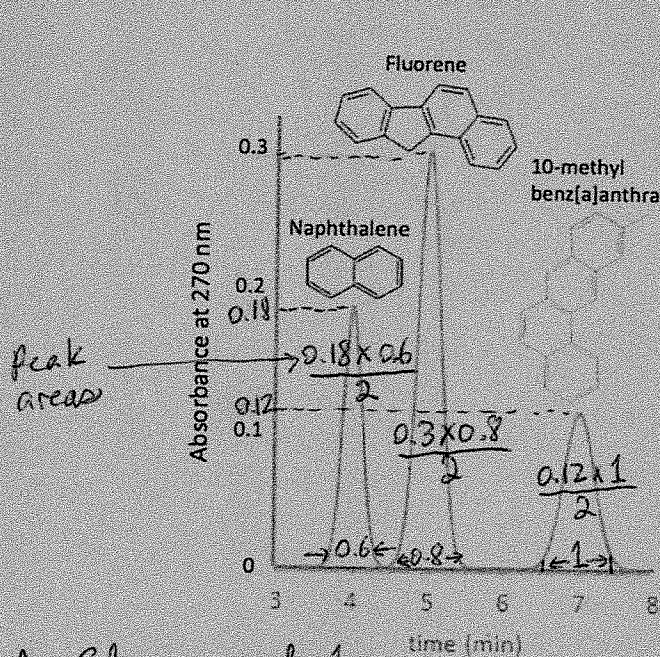
Each −OH group reacts with TMS-Cl by losing HCl:

$$R-OH + Cl-TMS \rightarrow R-OTMS + HCl.$$



formula: $C_{16} H_{24} O_2 Si_2$

$MW = 304\ g/mol$

## Question 3

a) The HPLC-UV chromatogram shown below was obtained at 270 nm. Based on the UV spectra of the three compounds of interest, determine their relative concentrations. Assume that the HPLC peaks are perfect triangles.



Fluorene

Naphthalene

10-methyl benz[a]anthracene

peak areas → $\frac{0.18 \times 0.6}{2}$

$\frac{0.3 \times 0.8}{2}$

$\frac{0.12 \times 1}{2}$

→0.6← ←0.8→ ←1→

at $\lambda = 270$ nm

$\varepsilon = 10^{3.6}$ — Naphthalene — 270

$\varepsilon = 10^{4.5}$ — Fluorene — 270

$\varepsilon = 10^{2}$ — 10-methyl benz[a]anthracene

$A = \varepsilon l c$, given $l = 1$

$\Rightarrow C = \dfrac{A}{\varepsilon}$

270

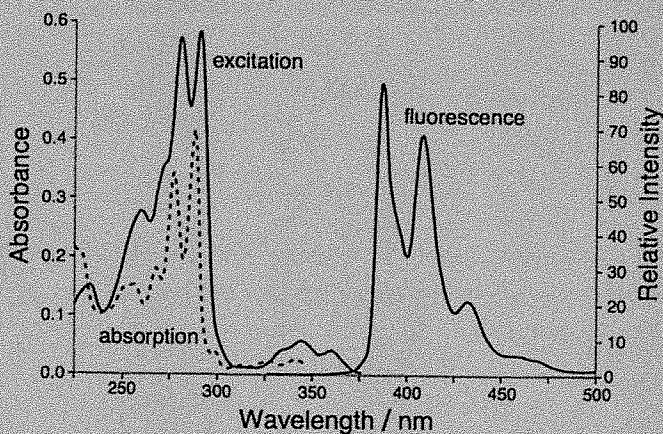Naphthalene $\quad C = \dfrac{0.18 \times 0.6}{2} \div 10^{3.6} = 1.35 \times 10^{-5} \rightarrow 2.25\%$

fluorene $\quad C = \dfrac{0.3 \times 0.8}{2} \div 10^{4.5} = 3.8 \times 10^{-6} \rightarrow 0.63\%$

10-methyl b $\quad C = \dfrac{0.12 \times 1}{2} \div 10^{2} = 6 \times 10^{-4} \rightarrow 100\%$

} are the relative concentrations

b) Based on the figure below for 10-methyl benz[a]anthracene, comment on the most possible sensitive detection method for this compound.



fluorescence, using $\lambda_{exc} \widetilde{=} 285$ nm

$\lambda_{em} \simeq 385$ nm

would provide the most sensitivity.

↓

needed to be specified.

## Question 4

a) It is proposed to use an ion-exchange column to separate three tripeptides: tri-glycine (pI 5.98), tri-lysine (pI 9.54) and tri-aspartic acid (pI 3.05). If the mobile phase has a constant pH of 6, what would be the elution order?

At pH 6: Triglycine is neutral (very slightly negative)

Tri lysine is positive ⊕

Tri aspartic acid is neg. ⊖

∴ If cation exchange: order is Tri Asp, trigly, trilys

If anion exchange: " " Trilys, Trigly, Triasp.

b) Besides UV and fluorescence, which detectors would be suitable for this experiment? Justify.

• Conductivity detection if pH is changed to charge triglycine

• Refraction index detector is no gradient of mobile phase is used

• Amperometric could be used, set for reduction of carboxylate or Carboxyl

• Mass spectrometry, especially APCI or ESI, could be used to obtain $(M+H)^+$ or $(M-H)^-$ ions.

• Light scattering could give info on concentration but not on molecular shape or size (too small).

note that detectors was plural, so I gave full marks for 2 or more detectors mentioned (not FID, which is only for GC!)

## Question 5

There are two main types of nylon polymers, nylon-6 and nylon-2. They differ in the number of carbon atoms in each monomer.
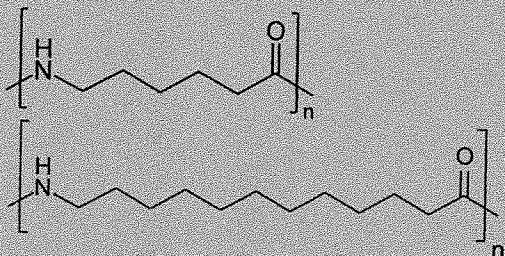


a) A chemist prepares a nylon polymer with an average "n" of 500, without knowing if nylon-6 or nylon-12 monomers were present in solution. Suggest a method to verify which of the two starting materials was used and justify.

As nylon-6 and nylon-12 have significantly different MW's, Size Exclusion (chrom-) would be the best method for their characterisation by comparison with a calibration curve.

Mass spectrometry is also a good technique.

⟹ NO GC! Nylons are way too big and non volatile for GC.

b) Comment on the type of detector(s) used in polymer analysis.

- The best is MALS. Can provide info on concentration, shape and size of the molecules, i.e. MW.

- Other LS detectors are also OK if coupled with size exclusion column.

- Mass spectrometry also a good detector.

- RI also if coupled with SEC.
⟹ NO FID! as FID's only work for GC, not possible to use these detectors for polymers.