CHEM 3590 Test 2, answers VERSION A.

1.a) As a general rule in GC compounds elute in order of boiling points.

As another general rule the b.p of compounds increases with MW
If two compounds are of the same size but one is more polar, the latter will have a higher b.p.

lowest boiling point : pyridine (115.2 °C)

then the choice is between naphthalene and acetophenone.

naphthalene is a solid at room temperature (moth balls) but is non polar.
and acetophenone is a liquid. B.Ps could be either way but more polar.
real boiling pts for reference: acetophenone 202°C,
naphthalene 218°C.

Benzophenone is the largest compound and it is polar. Should elute last. (bp = 305.4°C)

accepted orders:

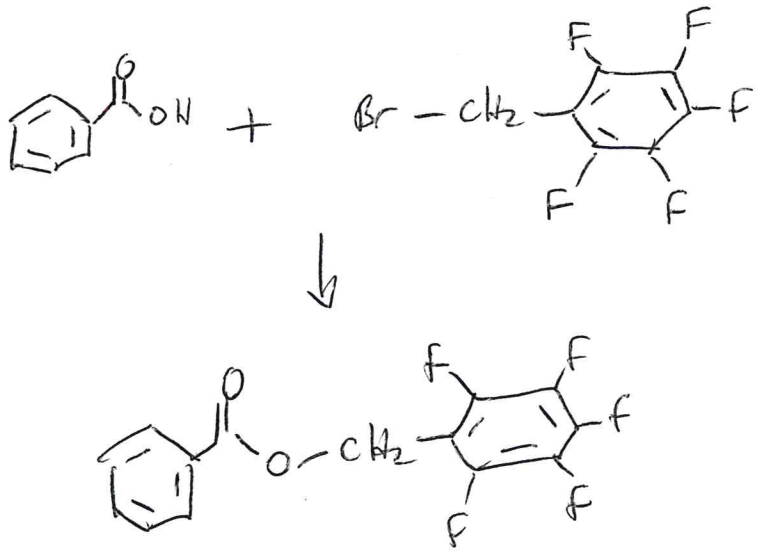
- pyridine, naphthalene, acetophenone, benzophenone

real order → pyridine, acetophenone, naphthalene, benzophenone

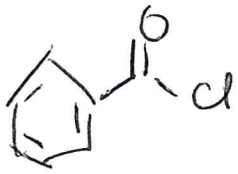
b) Increase flow rate of gas; increase temperature; speed up T gradient; shorten column; change stationary phase; change gas for mobile phase; decrease stationary phase film thickness.

2 The addition of a label containing halogens is needed.

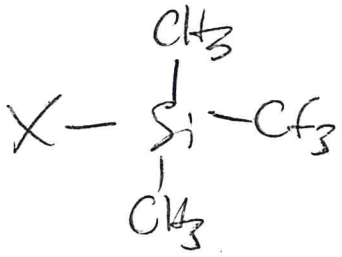
The best reaction is



but replacement of -OH by Cl is also good, to lead



or one can also use a silalytalin reagent that has halogens, example



3.

a) $M + e^- \rightarrow M^{+\bullet} + 2e^-$

↑ electron generated by a tungsten filament and accelerated to 70 eV so it can collide with molecules M and ionize them.

b) Good for small, volatile, thermostable molecules.
(coupled with GC so molecules need these characteristics)

4. a) Elution order 2, 1, 3 in reverse order of polarity.

b) Only the carboxylic acid is ionizable and will pair up with the ⊕ charged reagent. The effect will be to slow down the elution of compound 2. Others are not affected. The alcohol does not form anions in solution.

5.

Excitation spectrum:

this is to know the maximal (optimal) λ_{exc} to conduct a fluorescence experiment.

$\lambda_{fluo.}$ is constant (second monochromator is fixed) and λ_{exc} is scanned.

Fluorescence spectrum:

Using $\lambda_{exc.\ max}$, and keeping it constant with the first monochromator, $\lambda_{fluo.}$ is scanned by rotating the second monochromator. The spectrum obtained will be a higher λ values and will often look like the mirror image of the excitation spectrum.

6. Say the pair of peaks $1364.82 = (m/z)_1$

$1137.53 = (m/z)_2$

$$(m/z)_1 = \frac{M+n}{n} \Rightarrow M = n(m/z)_1 - n$$

$$(m/z)_2 = \frac{M+n+1}{n+1} \Rightarrow M = n(m/z)_2 + (m/z)_2 - n - 1$$

$$n(m/z)_1 = n(m/z)_2 + (m/z)_2 - 1$$

$$n = \frac{(m/z)_2 - 1}{(m/z)_1 - (m/z)_2} = \frac{1136.53}{1364.82 - 1137.53} = 5$$

$$M = n(m/z)_1 - n = 5(1364.82) - 5 = 6819.1$$

7. V_r = retention volume of an analyte

Measured during the experiment when peak is observed.

V_m = volume of mobile phase inside and outside pores.

Calculated from manufacturers' specification about % swelling volume of dry beads.

V_o: void volume or volume of mobile phase outside pores.

Measured by passing a large molecule (unretained) through the column and measuring its elution volume.

8. The amino acid with the lower pI (phe) is more acidic, so more negatively charged, and more retained on ⊕ charged beads used for anion exchange chromatography.

⇒ Phenylalanine will elute second because it has stronger interactions with beads.

9. A beta emitter (^{63}Ni) emits electrons (beta particles) causing a constant current between two electrodes (baseline). When halogenated compounds elute and arrive between the electrodes, they capture electrons and the current decreases → this is the origin of the signal.

10. Each compound has a different UV spectrum. The absorptivity (ε) at $\lambda = 254$ differs for all molecules so peak heights or areas obtained at that wavelength cannot be compared directly for different compounds. A calibration curve for each compound must be done, and slopes will be different as ε is different.