Friday Worksheet **Name: …….**
Analytical chemistry revision 5

You will need to answer this worksheet on a separate piece of paper.

1) An organic compound with the molecular formula was analysed using HPLC. Five standard solutions of the organic compound were analysed and the area under the peak measured. The results are shown on the right.
a) Draw a calibration curve, using the graph below, to express the relationship between concentration and area under the peak.

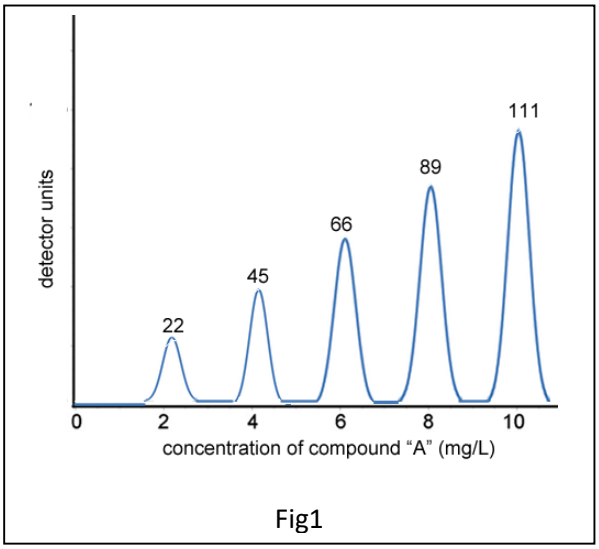
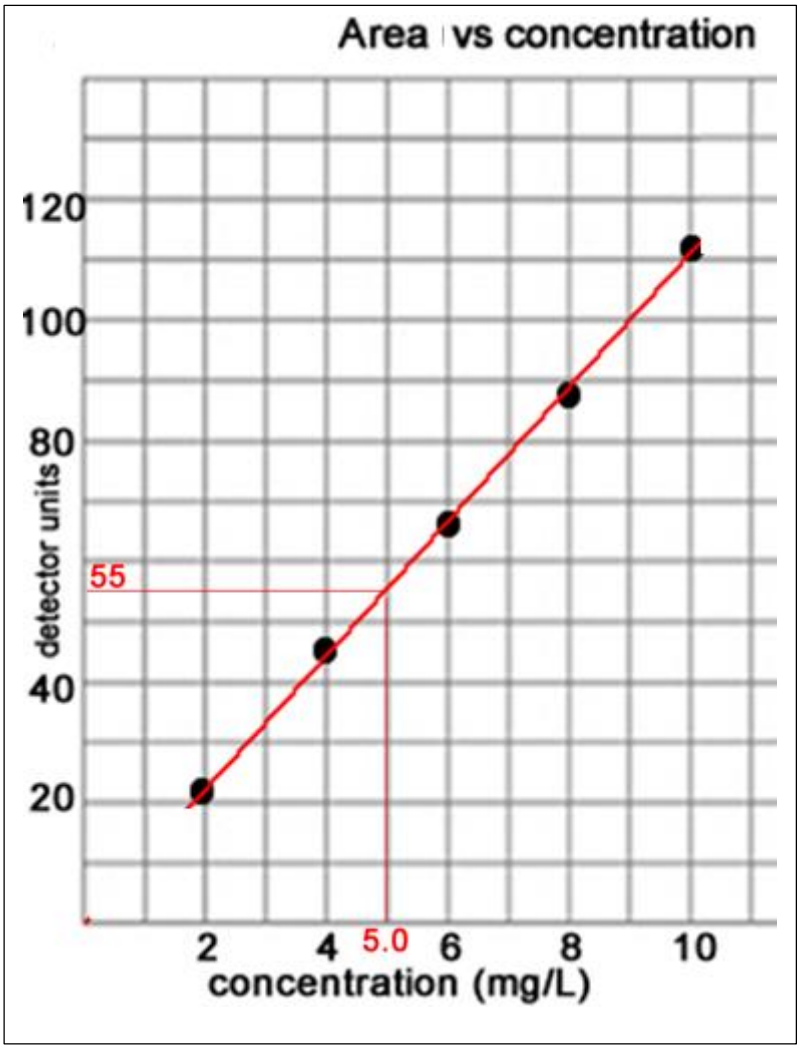


Fig1



b) The following compounds, with the molecular formula $C_4H_{10}O$, were put through the column.

A = $CH_3CH_2OCH_2CH_3$

B = $CH_3CH_2CH_2CH_2OH$

C = $CH_3CHOHCH_2CH_3$

Given that ethers are not as soluble as alcohols in water and that secondary alcohols are less soluble in water than primary alcohols discuss whether the mobile phase is polar or non-polar?

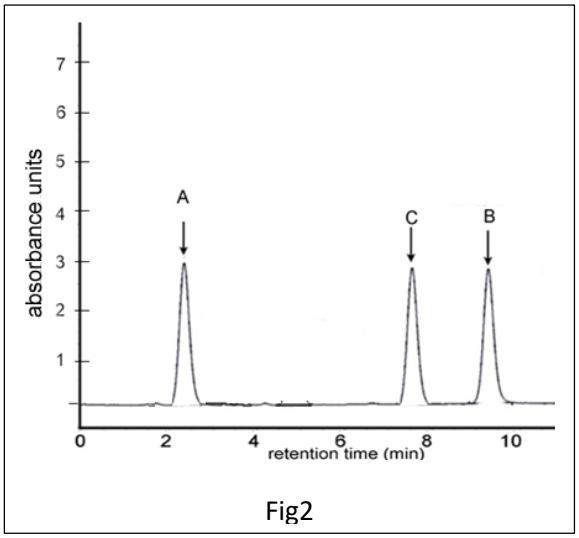


Fig2

A is an ether whereas B and C are primary and secondary alcohols, respectively. The less soluble substances have a lower retention time than the more soluble primary alcohol (B). The mobile phase is therefore non-polar. In order to obtain a higher retention time, the more soluble, primary alcohol must be interacting more with the stationary phase than the mobile phase, suggesting that the mobile phase is non-polar.

c) A sample of an organic mixture was placed in the column and allowed to run through the column creating the chromatogram shown on the right (fig 3).

i. Which of the three compounds A, B and C are present in the mixture?

From fig 2 we can see that A has a retention time of 2.4, while B and C have retention times of 9.5 and 7.8 respectively. In fig 3 the only matching compounds are 1 whose R_t is 2.4 and 7 with an R_t of 7.8. Compounds A and C are present.

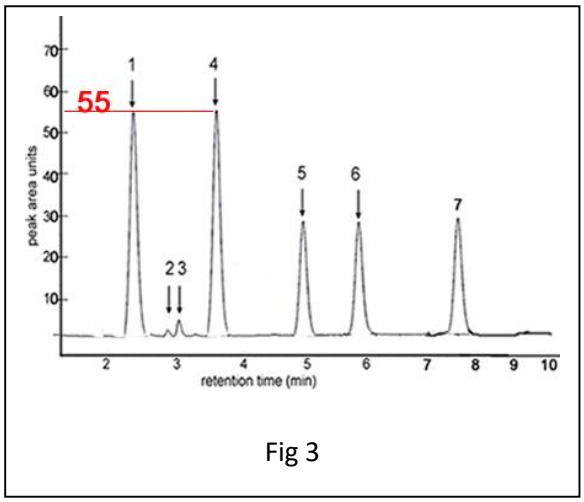


Fig 3

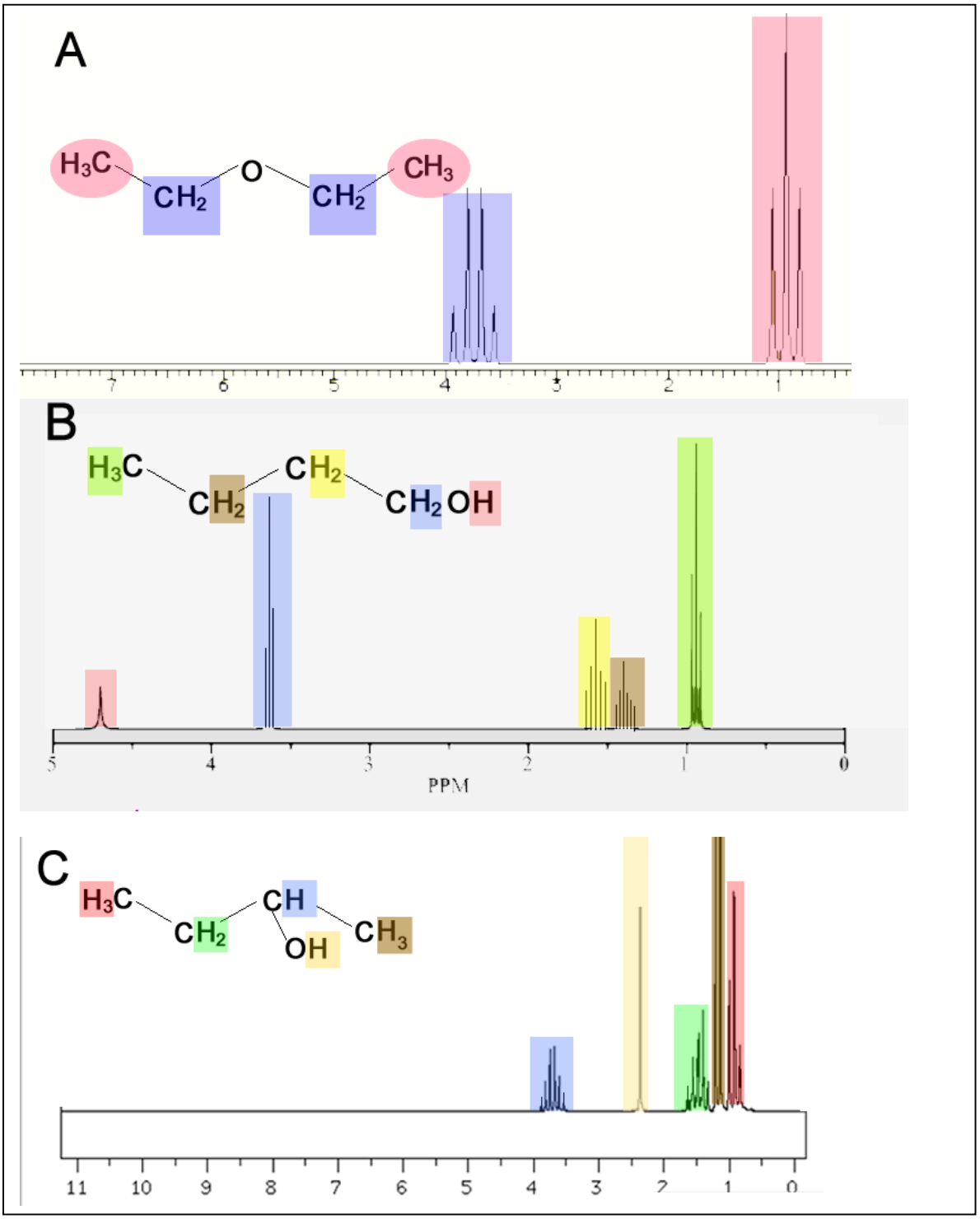
ii. Substance 4 was the compound that was analysed in question a) above. What is the concentration of compound 4, shown in figure 3, opposite?

The area under the peak is approximately 55 units. Reading from the calibration curve the concentration must be approximately 5.0 mg/L

iii. Explain how you can distinguish between the
^{1}HNMR of A, B and C.

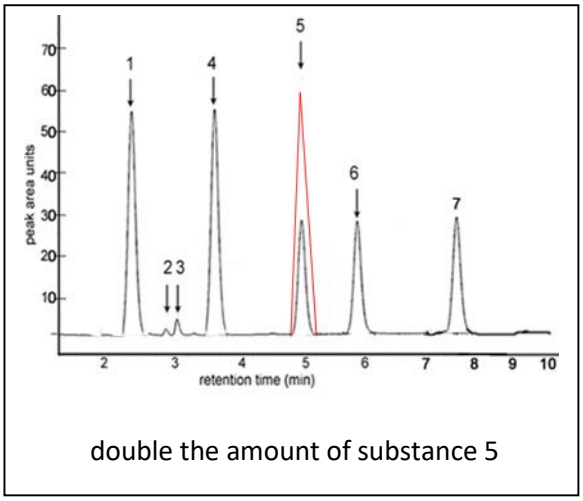
The ^{1}HNMR spectrum of A diethyl ether will have two hydrogen environments and hence two signals in its HNMR spectrum, a triplet and a quartet.

The ^{1}HNMR spectrum of B butan-1-ol and C butan-2-ol each have 5 hydrogen environments and hence5 signals in their HNMR spectra. The spectrum of butan-2-ol will have doublet whereas the spectrum of butan-1-ol will not. The spectra are shown below.



d) Draw, on figure 3, how the peak representing compound 5 would change if its concentration in the mixture had doubled.

See image on the right.



double the amount of substance 5

2) Figure 4 shows the chromatogram when a mixture of alcohols and carboxylic acids are separated using GC. If the mixture contained propan-1-ol, butan-1-ol, hexan-1-ol, ethanoic acid and propanoic acid, identify the peaks that belong to each. Give a reason.

Carboxylic acids are generally more polar and hence more soluble than the similar size primary alcohol. For example ethanoic acid is more soluble than ethanol in a polar solvent such as water. Size, however, also plays a part in a molecule's solubility. The bigger the molecule the less soluble it becomes.

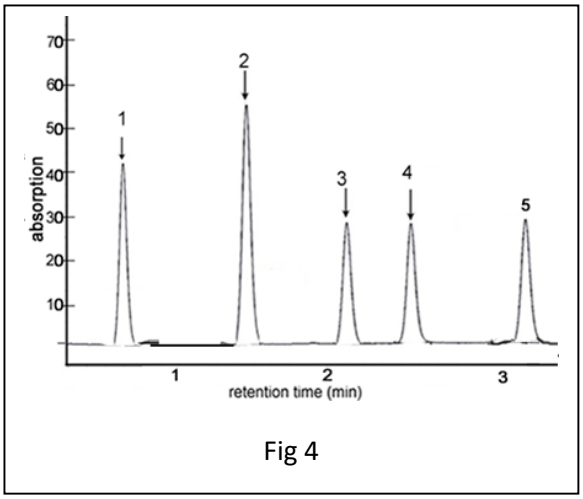


Fig 4

Also the bigger the molecule the slower it travels through the column at a given temperature. Heavier molecules are not pushed along the column by the carrier gas as well as smaller molecules, which vaporise with ease and have a greater speed.

Similarly, some compounds may dissolve in the liquid stationary phase more readily than others. The more soluble compounds will spend more time in the stationary phase than the less soluble ones which spend more time in the carrier gas being pushed through the column.

So retention time depends on:

- the solubility of the compound in the liquid phase. A compound that is highly in the liquid phase, the less time it will spend being carried through the column by the gas. High solubility in the liquid phase results in a high retention time.
- the boiling point of the compound. A high boiling temperature results in a long retention time because the compound spends more of its time in the liquid phase in the column and so is not carried by the gaseous mobile phase.
- the temperature of the column. The higher the temperature the easier it is for molecules to enter the gas phase. This applies to all molecules so a high column temperature results in a low retention time for all compounds in the column.

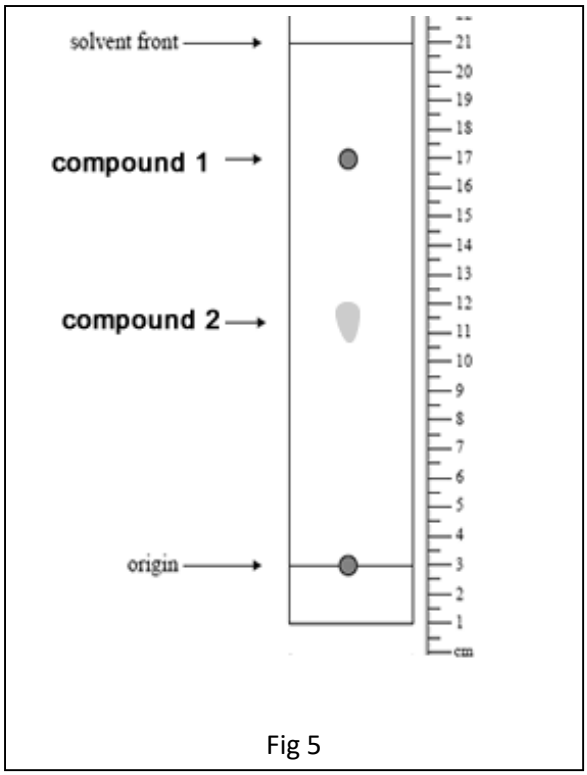


Fig 5

3) A thin layer chromatography (TLC) plate was set up with a non-polar solvent, hexane, and a polar stationary phase, silica gel. The chromatogram, on the left (fig 5), was obtained using a mixture of two compounds. A ruler was then placed next to the plate, as shown.

a) Which compound is the most polar? Explain

A compound which is highly soluble in the mobile phase will be carried further up the plate. Since the mobile phase is hexane, a non-polar compound, the less polar compound will be carried further up the plate. Compound 2 is the most polar of the two.

b) A compound of interest has an R_f value of 0.47 when run through the plate . Is this compound present? Yes Explain.

Compound 2 has an R_f value of 8.5 / 18.0 = 0.47