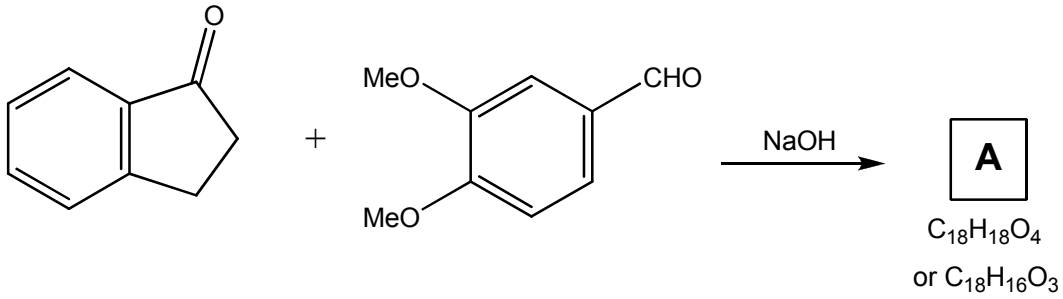
PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

An Environmentally Friendly Aldol Condensation

In attempts to become more environmentally friendly, increasing attention is being paid to minimising the large amounts of solvents used in chemical reactions. In the following experiment, an aldol condensation reaction is carried out in the absence of solvent.



Chemicals

- 3,4-dimethoxybenzaldehyde, 0.50 g pre-weighed in vial,
- 1-indanone, 0.40 g pre-weighed in vial,
- NaOH, 0.10 g pre-weighed in vial,
- HCl, aqueous solution, c = 3.0 mol dm^{-3}, 10 cm^3 in a bottle,
- Diethyl ether : Heptane (1:1), 25 cm^3 in a bottle,
- Ethyl ethanoate, 1 cm^3 in a small vial,
- Sample of 1-indanone dissolved in ethyl ethanoate, 1.0 cm^3 in small vial,
- Sample of 3,4-dimethoxybenzaldehyde dissolved in ethyl ethanoate, 1.0 cm^3 in small vial,
- Ethyl alcohol (9:1 mixture with H_2O): 100 cm^3 in a bottle.

Procedure

(a) Add 3,4-dimethoxybenzaldehyde (DMBA 0.50 g, 3.0 mmol) and 1-indanone (0.40 g, 3.0 mmol) to a 25 cm^3 beaker. Use a metal spatula to scrape and crush the two solids together until they become a clear oil.

(b) Add NaOH (0.1 g, 2.5 mmol) to the reaction mixture, crush any lumps formed and continue scraping and crushing until the mixture becomes solid.

(c) Allow the mixture to stand for 20 minutes. Then add 4 cm^3 of aqueous HCl solution (c = 3 mol dm^{-3}) and scrape around the beaker so as to dislodge all product from the walls. Use a flat-ended glass rod to crush any lumps present.

1.1 Measure and record the pH of the solution.

(d) Isolate the crude product using vacuum filtration through a Hirsch funnel. Rinse out the beaker with 2 cm^3 of aqueous HCl solution (c = 3 mol dm^{-3}) and pour over the crude product in Hirsch funnel to wash, continuing to pull air through the solid for 10 minutes to facilitate drying.

1.2 Report the mass of the crude product (which may still be a little wet), using the vial labelled 'CPA' as a container.

(e) Take a TLC to assess whether the reaction is complete, using Et_2O : heptane (1 : 1) as the eluant. Solutions of both starting materials in ethyl ethanoate are provided. The crude product is soluble in ethyl ethanoate.

[Note: Three TLC plates are provided. You may use them all, but you must only submit *one* in your labelled Ziploc bag. This should be the plate that you draw in your answer booklet.]

1.3 Using UV light to visualize, draw around the spots on the plate in pencil to show where they are, copy your plate onto the answer sheet, and place your plate in the Ziploc bag labelled with your student code.

Determine and record the relevant R_F values.

(f) Using a 100 cm^3 conical flask with a stir bar in the bottom, recrystallize the product from a mixture of EtOH : H_2O (9 : 1). (N.B. A hot filtration, using the glass funnel provided, is required as part of this process to remove small amounts of insoluble

impurities.) Any lumps may be crushed using the flat-ended glass rod. Allow the conical flask containing the filtered solution to cool to room temperature and then cool in an ice bath (use the polystyrene tray to make the ice bath in) for one hour before filtration through a Büchner funnel to collect your product. Suck air through for 10 minutes to dry the product. Place your product in the vial marked with your code and labelled 'RPA'.

1.4 Report the mass of the purified product.

Product **A** could have one of the two formulae: $C_{18}H_{18}O_4$ or $C_{18}H_{16}O_3$.

1.5 Draw the structure of every geometrical and/or stereoisomer with formula:

i) $C_{18}H_{18}O_4$,

ii) $C_{18}H_{16}O_3$

that could be formed in this reaction. Indicate how many peaks you would expect in total in the ^{13}C NMR spectrum of each.

1.6 The ^{13}C NMR spectrum for **A** is shown in the practical instructions. Peaks due to the solvent, $CDCl_3$, are marked with an asterisk. With the aid of the spectrum, decide which is the correct formula for **A**. Mark on the answer sheet one of the two boxes below to indicate which you have chosen:

$C_{18}H_{18}O_4$: ❑ $C_{18}H_{16}O_3$: ❑

1.7 Report the mass and calculate the percentage yield of the purified product, based on the formula you gave for its structure.

SOLUTION

1.1 Values of pH = 1 – 2 are accepted.

1.2 Because the sample is not completely dry, often this mass is above 100 % of that expected. Usual range is 800 – 1000 mg (94 – 117 %). Zero points for any less than 400 mg (product has been lost).

1.3 Evaluation:

Maximum points if both standards plus crude product are present and no starting materials remain and student has co-spotted crude product with one or both starting materials and solvent front is marked and plate is not over- or under-loaded.

Minus points if:

- plate has no co-spots,
- substantial amount of either or both starting materials remain,
- over- or under-loading occurs which does not interfere with evaluation,
- over- or under-loading occurs and does interfere with evaluation,
- over- or under-loading occurs and prevents evaluation,
- any sample is missing.

The relevant R_F values:

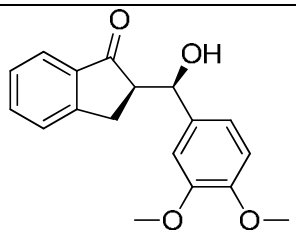
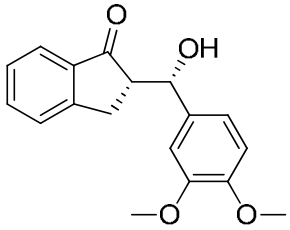
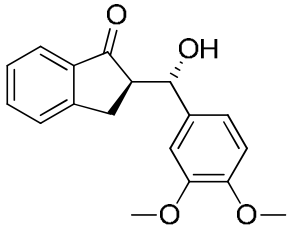
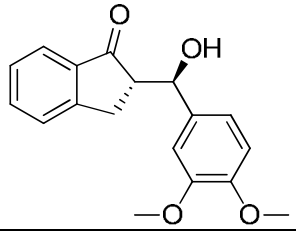
Chemical	R_F
3,4-DMBA	0.16 – 0.25
1-Indanone	0.34 – 0.43
CPA	0.11 – 0.20

Maximum points if both starting materials and reaction product are present with R_f values which fall within those given.

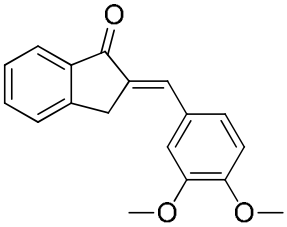
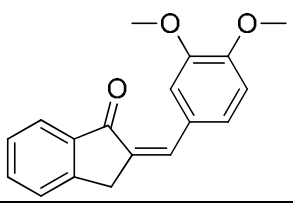
Minus points if:

- R_F values are missing for one or more chemicals,
- both starting materials and reaction product are present with R_F values which fall outside those given due to the plate running too long or the student having marked the solvent front incorrectly,
- both starting materials and reaction product are present with R_F values which fall outside those given, due to an inability to calculate R_F values.

1.4 For $C_{18}H_{18}O_4$:

Structure	Number of ^{13}C NMR signals expected:
	18
	18
	18
	18

For $C_{18}H_{16}O_3$:

Structure	Number of ^{13}C NMR signals expected:
	18
	18

1.5 $C_{18}H_{16}O_3$: ☑

1.6 Mass: 0.5 g (example mass of product)

Calculation:

For formula **$C_{18}H_{18}O_4$**: Molar mass = 298.324 g mol^{-1}

Expect: 0.3 mmol maximum = 0.895 g

$$\frac{0.5\,\text{g}}{0.895\,\text{g}} \times 100 = 56\,\%$$

For formula **$C_{18}H_{16}O_3$**: Molar mass = 280.308 g mol^{-1}

Expect: 0.3 mmol maximum = 0.841 g

$$\frac{0.5\,\text{g}}{0.841\,\text{g}} \times 100 = 59.5\,\%$$

YIELD:

The samples were also weighed by the organizer, before and after drying for one hour in a vacuum desiccator. Sample purity was then checked by ^{1}H and ^{13}C NMR. The evaluations of the results were adapted to the results obtained by the above measurements.

PROBLEM 2 (Practical)

Analysis of a Copper(II) Complex

You are provided with a sample of an inorganic copper(II) complex, the anion of which is made from copper, chlorine, and oxygen. The counter ion is the tetramethyl ammonium cation. There is no water of crystallisation. You are required to determine proportions of copper ions and chloride ions by titration and hence determine the composition of the complex.

Chemicals

- Inorganic complex: three samples of approximately 0.1 g, accurately pre-weighed in vials labelled 'Sample 1', 'Sample 2', 'Sample 3'.
- Inorganic complex: three samples of approximately 0.2 g, accurately pre-weighed in vials labelled 'Sample 4', 'Sample 5' and 'Sample 6'.
- pH 10 ammonia buffer, 10 cm^3.
- Murexide indicator, solution in H_2O, 10 cm^3.
- EDTA disodium salt, aqueous solution, c = 0.0200 mol dm^{-3}, 150 cm^3.
- Ethanoic acid, 10 cm^3.
- 2,7-Dichlorofluorescein indicator, solution in 7 : 3 EtOH : H_2O), 10 cm^3.
- Dextrin, 2 % solution in H_2O, 25 cm^3.
- Silver nitrate, aqueous solution, c = 0.1000 mol dm^{-3}, 150 cm^3.

Procedure

<u>Titration to determine the proportion of copper ions</u>

(a) You are provided with three accurately pre-weighed samples of copper complex, each of approximately 0.1 g. These are labelled "Sample 1", "Sample 2", "Sample 3", together with the exact mass of the copper complex. Take the first of these, note down the mass of the sample and quantitatively transfer the contents to a 250 cm^3 conical flask using approximately 25 cm^3 of water.

(b) Add pH 10 ammonia buffer solution until the precipitate which forms initially just redissolves (about 10 drops).

(c) Add 10 drops of the murexide indicator.

(d) Titrate with the 0.0200 mol dm^{-3} EDTA solution until the solution turns violet and the colour persists for at least 15 seconds. Record the volume of solution used in the titration.

(e) Repeat if necessary with samples 2 and 3.

Note: You will be marked only on a single value you report in the answer booklet. This may either be an average value, or a single value you feel most confident in.

2.1 Calculate the volume of EDTA solution needed to react completely with 0.100 g of complex.

2.2 Give an equation for the titration reaction.

2.3 Calculate the percentage by mass of copper in the sample.

You will need to wash out your burette before you start the titration for the determination of chloride ions. Any remaining EDTA solution may be disposed of into the waste containers labelled 'EDTA'.

Titration to determine the proportion of chloride ions present

(f) You are provided with three accurately pre-weighed samples of copper complex each of approximately 0.2 g. These are labelled "Sample 4", "Sample 5", "Sample 6", together with the exact mass of the copper complex. Take the first of these, note down the mass of the sample and quantitatively transfer the contents to a 250 cm^3 conical flask using approximately 25 cm^3 of water.

(g) Add 5 drops of ethanoic acid, followed by 10 drops of dichlorofluorescein indicator and 5 cm^3 dextrin (2 % suspension in water). Shake the bottle well before adding the dextrin suspension.

(h) Titrate with the 0.1000 mol dm^{-3} silver nitrate solution, swirling constantly until the white suspension turns pink and the colour does not disappear after swirling.

(i) Repeat if necessary.

Note: You will be marked only on a single value you report in the answer booklet. This may either be an average value, or the value you feel most confident in.

2.4 Calculate the volume of silver nitrate solution needed to react completely with 0.200 g of complex.

2.5 Give an equation for the titration reaction.

2.6 Calculate the percentage by mass of chloride ions in the sample.

The percentage of carbon, hydrogen and nitrogen in the complex was determined by combustion analysis and found to be as follows:

Carbon: 20.87 %; Hydrogen: 5.17 %; Nitrogen: 5.96 %.

2.7 Mark in the answer booklet, which element in the complex has the greatest percentage error in the determination of its proportion.

Cu Cl O C H N

2.8 Determine the formula of the copper complex. Show your working.

_____

SOLUTION

2.1 Full marks if answer is $V_{corr.} \pm 0.1$ cm^3. Zero marks if answer is less than ($V_{corr.} - 0.5$ cm^3) or greater than ($V_{corr.} + 0.5$ cm^3), linear point scale is applied in between.

2.2 $Cu^{2+} + EDTA^{4-} \rightarrow [Cu(EDTA)]^{2-}$

2.3 n(EDTA) = 0.0200 mol dm^{-3} $\times$ V(EDTA) (in dm^3) = (0.0200 mol dm^{-3} $\times$ V) mol

$n(Cu^{2+})$ = (0.0200 mol dm^{-3} $\times$ V) mol

m(Cu) = M(Cu) $\times$ n(Cu) = 63.55 g mol^{-1} $\times$ (0.0200 mol dm^{-3} $\times$ V) mol

$$\% \text{ Cu} = \frac{m(\text{Cu})}{m(\text{sample})} \times 100$$

2.4 Full marks if answer is $V_{corr.} \pm 0.1$ cm^3.

Zero marks if answer is less than ($V_{corr.} - 0.5$ cm^3) or greater than ($V_{corr.} + 0.5$ cm^3), linear point scale is applied in between.

2.5 $Ag^+ + Cl^- \rightarrow AgCl$

2.6 $n(Ag^+)$ = 0.100 mol dm^{-3} $\times$ $V(Ag^+)$ (in dm^3) = (0.100 mol dm^{-3} $\times$ V) mol

$n(Cl^-)$ = (0.100 mol dm^{-3} $\times$ V) mol

m(Cl) = M(Cl) $\times$ n(Cl) = 35.45 g mol^{-1} $\times$ (0.100 mol dm^{-3} $\times$ V) mol

$$\% \text{ Cl} = \frac{m(\text{Cl})}{m(\text{sample})} \times 100$$

2.7 If the percentage of oxygen is calculated by subtracting all the others from 100, it has all the errors from the determination of the other elements combined. In practice this leads to a large error which affects the subsequent calculation of the formula unless this point is appreciated.

Cu Cl (O) C H N

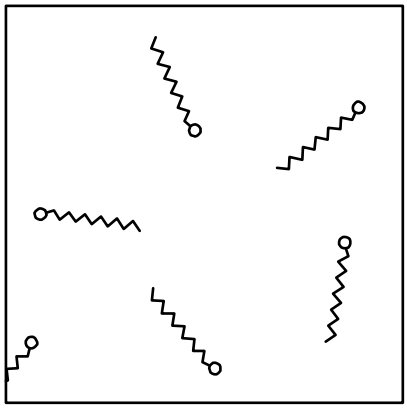
2.8 Full marks if the formula is correctly calculated from the student data and the large error in oxygen is taken into account (either by using one of the proportions of the other elements to determine the elemental ratios, or by a consideration of charge balance).

PROBLEM 3 (Practical)

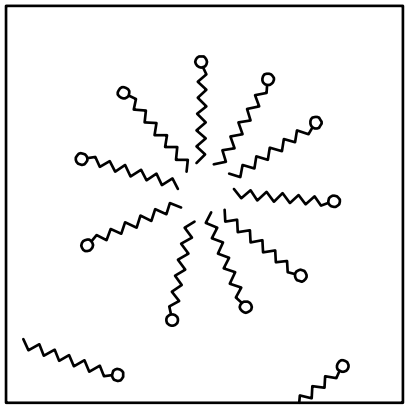
The Critical Micelle Concentration of a Surfactant

Surfactants are used extensively in many everyday cleaning products, such as shampoos or detergents for washing clothes. One such surfactant is SDS, sodium *n*-dodecyl sulfate, $CH_3(CH_2)_{11}OSO_3Na$ (Relative Molecular Mass: 288.37).

Very dilute aqueous solutions consist of solvated individual molecules of SDS. However, if the concentration is gradually increased beyond a specific concentration, the concentration of monomeric SDS does not change, but instead the surfactant begins to form clusters known as *micelles*. It is these micelles that assist in the removal of grease and dirt. The concentration at which the micelles form is called the *critical micelle concentration*. This process is shown schematically in the figure below.



low SDS concentration
free monomer only



high SDS concentration
micelles and some free monomer

In this experiment, you will determine the critical micelle concentration of SDS by measuring the conductivity of different concentrations of SDS.

Chemicals

- Sodium dodecyl sulphate, (99%), approximately 4.3 g, accurately pre-weighed in vial labelled ‘SDS’.
- Conductivity solution ‘HI 70031’, 20 cm^3 in pouch.

Procedure

(a) You are provided with approximately 4.3 g SDS, accurately pre-weighed in a vial, a 250 cm^3 volumetric flask, a 50 cm^3 burette, 50 cm^3 bulb pipette, a conductivity meter, conductivity solution (used only for calibration), and a tall plastic vessel.

(b) You need to measure the conductivity (σ, in $\mu S\ cm^{-1}$) of various concentrations of aqueous SDS (c, up to 30 mmol dm^{-3}). [Note: You may assume that all volumes are additive.]

3.1 Give the concentration of your stock SDS solution.

3.2 Use the table given in the answer booklet to record your results and plot a suitable graph to determine the critical micelle concentration (CMC) on the paper provided.

3.3 State the concentration at which micelles begin to form (the critical micelle concentration).

Notes

1) Solutions of SDS readily form bubbles if shaken.

2) The conductivity meter needs at least 50 cm^3 of solution to be inside the plastic vessel in order to work correctly.

3) To calibrate the conductivity meter:

- Switch the meter on by pressing the ON/OFF button once.
- Press and hold the ON/OFF button again, this time for about 3 seconds, until you see the letters 'CAL' on the screen, indicating that the calibration mode has been entered. Let go of the ON/OFF button and '1413' will start blinking on the display. To calibrate, carry out the next step immediately, before the meter has reverted back to reading '0' on the screen (meaning you have exited the calibration mode)
- Immerse the probe in the pouch containing the 'HI 70031' calibration solution, without exceeding the maximum immersion level.
- Stir gently and wait for about 20 seconds to confirm the reading.
- Once the display stops blinking, the meter is calibrated and ready for use.
- Rinse the meter with distilled water and dry before making measurements.

4) To record the reading:

- Switch the meter on by pressing the ON/OFF button.
- Immerse the probe in the sample without exceeding the maximum immersion level and being above the minimum immersion level.

- Stir gently and wait for the reading to stabilize. The meter automatically compensates for temperature variations.
- The conductivity value of the sample will be shown on the LCD.

SOLUTION

3.1 Correct concentration with correct units is expected - full points.

Correct concentration but with missing or incorrect units - 1/2 points.

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Note:

The evaluation of the graphs, constructed by competitors in this practical problem, differs from that used for grading especially titration results in the other practical problems. That is the reason why the evaluation in this particular case is given here more in detail.

3.2 Number and spread of data points

The graph should show two distinct gradients and the point at which the gradients change is the critical micelle concentration (CMC). The region where the concentrations are lower than the point at which the gradients change is referred to as “Region 1”; “Region 2” refers to the region where the concentrations are higher than this point. The gradient change will be taken from the data presented. If no gradient change is obvious the literature value of 8.3 mmol dm^{-3} will be used to distinguish between the two Sections.

Maximum marks are allotted if:

a) in Region 1 at least three points are distributed with a spacing of approx CMC/(n+1) mmol (where n is the number of points).

b) in Region 2 at least three points are distributed through a range of at least 10 mmol with a spacing of approx c/(n+1) mmol (where n is the number of points and c the concentration range and $c \geq$ 10 mmol dm^{-3}).

Indicating gradients

Straight lines plotted through experimental points with different gradients and extended to identify crossing points are expected.

Alternative graphs with marks allotted are shown below.

Accuracy of data

A transparent overlay will be used to judge the accuracy of the experimental measurements as plotted on the graph. If a systematic error in calculation can be

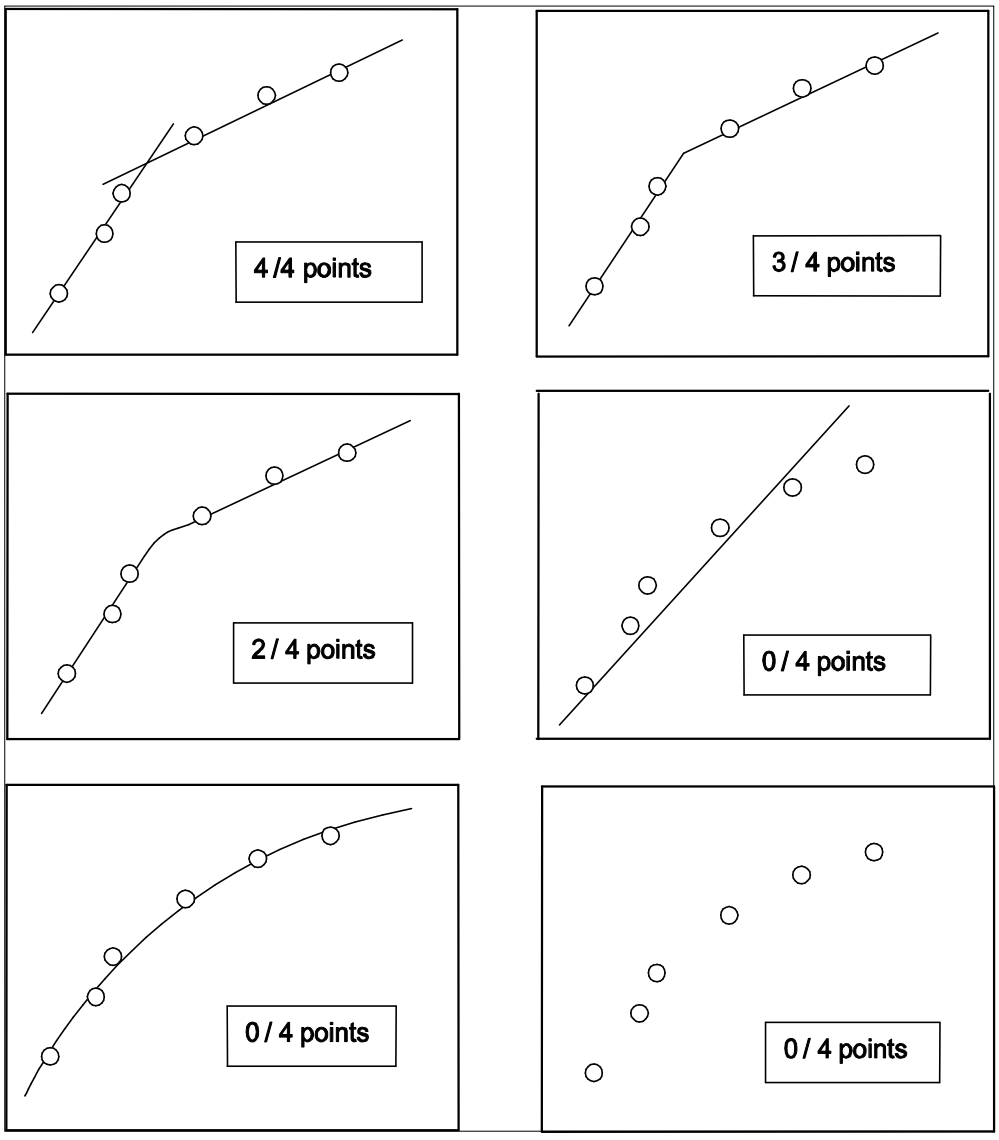
determined from the table of data the graph will be re-plotted by the organisers for the purposes of this part of the marking.

The overlay has a number of bands marked and the marking scheme has been devised to reward careful experimental technique. There is one set of bands for Region 1 and another for Region 2. The bands are numbered from the innermost (band 1) to the outermost (band 5) (see Fig. 3.1).

The maximum number of points for each band is shown in the following table:

Band	1	2	3	4	5	Outside 5
Maximum number of points	10	8	6	4	2	0

Alternative graphs with marks allotted

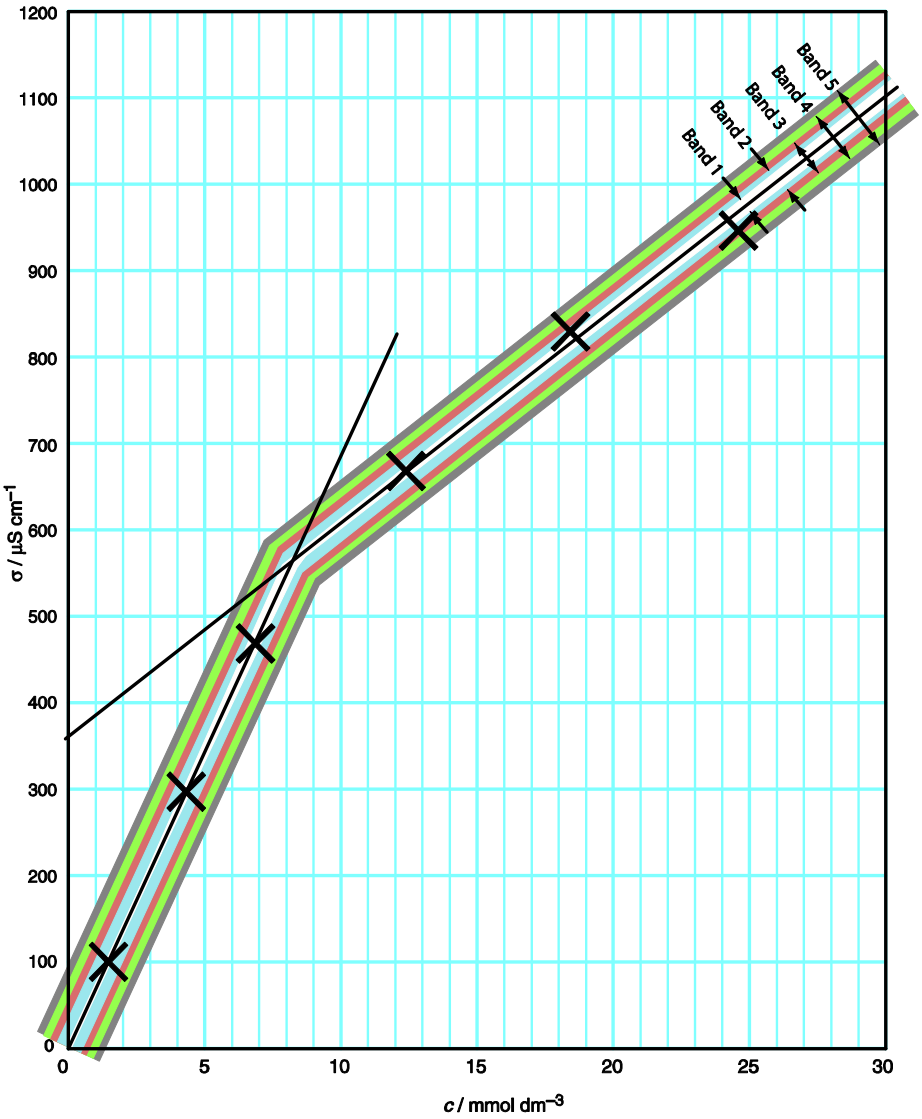


Points will be awarded as follows:

If there are three or more points in a Region and 50 % are in band *m* (where *m* is the number of the band) with none falling in band *m*+2 or beyond, the full marks for band *m* are awarded.

If *n*, the number of points in the Region, is less than 3, only (*n*/3) of the relevant band marks will be given (and rounded up to the nearest half-integer when necessary).

Fig. 3.1. Examples



In Region 1 all of the datapoints lie in Band 1 (cross hatched) so 10 points scored for that Region.

In section 2 one of the three datapoints lies in Band 1 (not 50%) but two lie in band 2. The remaining point does not lie in Band 4 (*m*+2) so full 8 points are scored.

3.3 Correct concentration as read from graph with correct units is expected.