AQA A-LEVEL CHEMISTRY · 7405

CHEMISTRY



MARK SCHEME

3.3.16 CHROMATOGRAPHY

SCORE	PERCENTAGE
/84	%

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Q1.

(a) **M1** Moles of cyclohexanol = (10 × 0.96)/100.0 = 0.096

Correct answer scores all 3 marks

1

M2 Max mass of cyclohexene = 0.096 × 82.0 = 7.87(2)

= *M1 × 82.0 (process mark)*

1

M3 % yield = (5.97 / 7.87) × 100 = 76% (Allow range 75.8 – 76)

= *(5.97 / M2) × 100 (process mark)*

1

Alternative method

M1 Moles of cyclohexanol = (10 × 0.96)/100.0 = 0.096

M2 Moles of cyclohexene = 5.97/82.0 = 0.0728

M3 % yield = 0.0728 / 0.096 × 100 = 76% (allow range 75.8 – 76)

= *(M2 / M1) × 100*

Allow 1/3 for 62(.2)%

(b) Add bromine (water)

If M1 not correct then only allow M2 if reagent involves bromine (water)

1

Would turn (from orange to) colourless / decolourise

Do not allow incorrect starting colour, but allow brown/red/yellow

Not discolour.

Ignore clear

1

(c) Na_2CO_3 would neutralise/react with/remove (phosphoric) acid/H_3PO_4/H^+

1

(d) avoid pressure build-up / release pressure / release CO_2/air/gas / prevent stopper blowing out

Ignore explosion

Do not allow an incorrect named gas

Allow idea that build-up of gas/CO_2 would lead to increased pressure/stated effect of increased pressure

1

(e) Does not dissolve in/react with the cyclohexene

Allow remains a solid/is inert in cyclohexene

Allow organic product/organic compound formed/ organic layer/distillate instead of cyclohexene

Do not allow if answer implies cyclohexanol

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Do not allow if answer says does not react with products

Ignore references to filtration

Do not allow insoluble/unreactive unless qualified by implied reference to cyclohexene

1

(f) If diagram drawn:

M1 diagram of basic set up to include flask or tube with side-arm/Buchner flask, flat-bottomed funnel/Buchner funnel, filter paper

M2 apparatus should work, flow through, air-tight connection between flask and funnel, arrow/label/description (to vacuum pump)

Do not allow "standard" Y-shaped funnel

1

If description given:

M1 Buchner funnel/flat-bottomed funnel containing filter paper

M2 Buchner flask/side-arm flask connected to vacuum pump

Do not allow just "funnel"

Penalise M2 if described apparatus would not actually work.

1

(g) Cyclohexene is less polar than cyclohexanol / cyclohexanol is more polar than cyclohexene

It = cyclohexene

Allow cyclohexene is non-polar and cyclohexanol is polar

1

Cyclohexene has a greater affinity/attraction for the mobile phase/hexane / cyclohexanol has a greater affinity/attraction for the stationary phase/silica

Allow cyclohexanol held in the stationary phase for longer

Allow cyclohexene is more soluble in the mobile phase/hexane or converse for cyclohexanol

Allow references to hydrogen bonds between cylcohexanol and silica

1

(h) Would be no peak at 3230 – 3550 cm^{-1} due to O—H((alcohol))

OR

There would be no additional peaks in the fingerprint region compared to a pure sample / fingerprint region exactly matches cyclohexene

Need wavenumber and bond for mark

1

[13]

Q2.

(a) $HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$

Allow $H_2SO_4 + HNO_3 \longrightarrow NO_2^+ + HSO_4^- + H_2O$

Allow a combination of equations which produce NO_2^+

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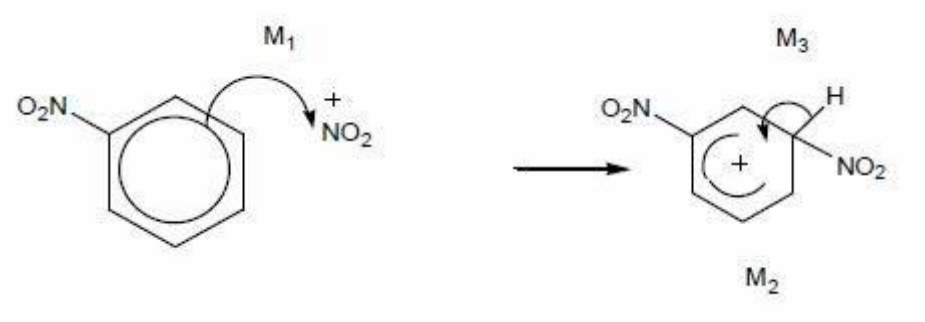
Penalise equations which produce SO_4^{2-}

1

(b) Electrophilic substitution.

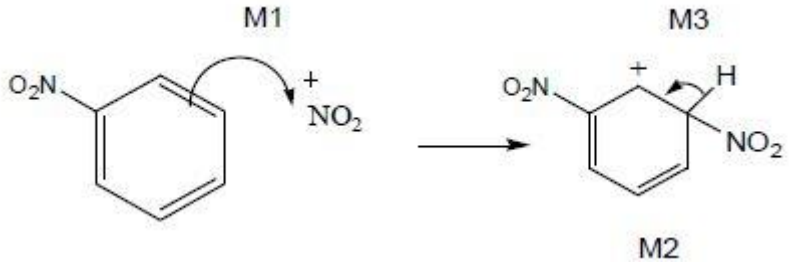
Ignore nitration

1



3

OR Kekule



M1 Arrow from inside hexagon to N or + on N (Allow NO_2^+)

M2 Structure of intermediate

- *horseshoe centred on C1 and must not extend beyond C2 and C6, but can be smaller*
- *+ in intermediate not too close to C1 (allow on or "below" a line from C2 to C6)*

M3 Arrow from bond into hexagon (Unless Kekule)

- *Allow M3 arrow independent of M2 structure*
- *+ on H in intermediate loses M2 not M3*

(c) D

1

(d) (Balance between) solubility in moving phase and retention by stationary phase

OR (relative) affinity for stationary / solid and mobile / liquid / solvent (phase)

(e) Solvent depth must be below start line

Ignore safety

1

(f) 1,2- is more polar **OR** 1,4- is less polar
OR 1,2 is polar, 1,4- is non-polar

1

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1,4- (or Less/non polar is) less attracted to (polar) plate / stationary phase / solid **OR** (Less/non polar is) more attracted to / more soluble in (non-polar) solvent / mobile phase / hexane

1

M2 dependent on correct M1

If M1 is blank then read explanation for possible M1 and M2

Allow converse argument for 1,2

(g) No CE = 0

Yes - mark on but there is **NO MARK FOR YES**

Mark independently following yes

Solvent (more) polar or ethyl ethanoate is polar

1

Polar isomer more attracted to / more soluble in / stronger affinity to the solvent (than before)

Penalise bonded to mobile phase in M2

1

[12]

Q3.

(a) **Gas chromatography explanation**

Different retention times / dipeptides appear at different times.

1

Different balance between solubility in the moving phase / gas carrier **and** retention by the stationary phase / column **OR** different relative affinity for mobile and stationary phases.

1

Mass spectrometry explanation

Same *m/z* values.

1

(Both) dipeptides / **J** and **K** have same molecular formula / M_r.

1

(b) ser-ala

1

ala-lys

1

ser-ala-lys

This order only.

1

[7]

Q4.

(a) **Wear plastic gloves:**

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Essential – to prevent contamination from the hands to the plate

1

Add developing solvent to a depth of not more than 1 cm^3:

Essential – if the solvent is too deep it will dissolve the mixture from the plate

1

Allow the solvent to rise up the plate to the top:

Not essential – the R_f value can be calculated if the solvent front does not reach the top of the plate

1

Allow the plate to dry in a fume cupboard:

Essential – the solvent is toxic

Allow hazardous

1

(b) Spray with developing agent or use UV

1

Measure distances from initial pencil line to the spots (*x*)

1

Measure distance from initial pencil line to solvent front line (*y*)

1

R_f value = *x* / *y*

1

(c) Amino acids have different polarities

1

Therefore, have different retention on the stationary phase or different solubility in the developing solvent

1

[10]

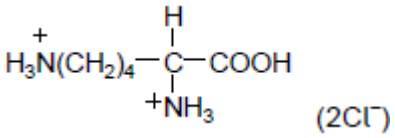
Q5.

(a) <u>2,6-diaminohexanoic acid</u>

Ignore additional , or – or spaces.

1

(b) (i)



NB both N must be protonated.

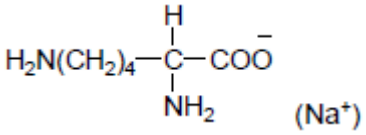
Allow $-NH_3^+$ allow CO_2H Allow $-^+H_3N$.

Penalise – C_4H_8 – here.

1

(ii)

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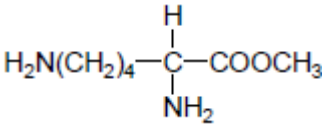
Allow CO_2^-.

Allow $-H_2N$.

Allow –COONa but penalise O–Na bond shown.

1

(iii)

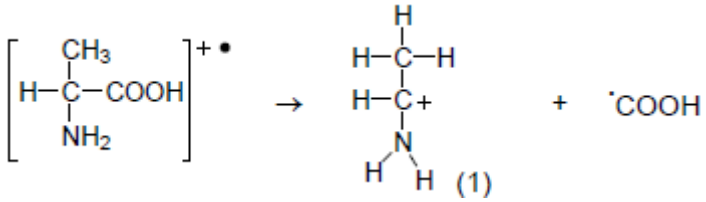


Allow CO_2CH_3.

Allow $-NH_3^+$ or $-H_2N$.

1

(c)



1 for displayed formula of fragment ion.

1 for molecular ion of alanine AND radical.

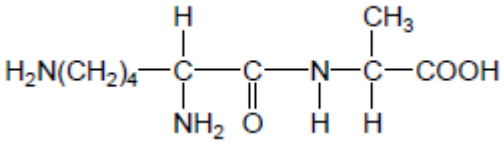
Allow molecular ion without brackets and fragment ion in brackets with outside +.

Allow dot anywhere on radical.

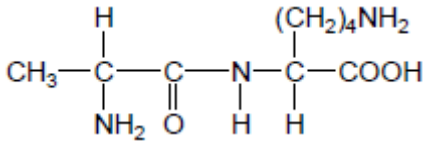
Allow $[C_3H_7NO_2]_+^{\bullet}$ for molecular ion.

2

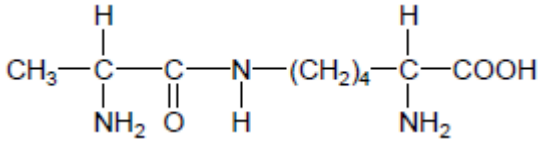
(d)



OR



OR



Dipeptide, not repeating unit /.

Allow CO_2H Allow $-H_2N$.

Allow –CONH–.

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1

(e) M1 In acid lysine has double positive or more positive charge

1

M2 (Lysine ion) has greater affinity / greater attraction / adheres better / sticks better to polar / stationary phase

M2 only scores after a correct M1.

Ignore greater retention time.

1

[9]

Q6.

(a) (i) Two rings only around nitrogen or sulfur

Lose this mark if more than 2 atoms are ringed.

Do not allow two atoms at the same end of the ion.

1

(ii) 275.8

Accept this answer only. Do not allow 276

1

(iii) Carboxylate / COO^-

Allow salt of carboxylic acid or just carboxylic acid.

1

(b) (32.1 / 102.1) = 31.4%

Do not penalise precision but do not allow 1 significant figure.

1

(c) Zineb is mixed with a solvent / water

Max=2 if M1 missed

1

Use of column / paper / TLC

Lose M1 and M2 for GLC

1

Appropriate collection of the ETU fraction
OR Appropriate method of detecting ETU

Allow ETU is an early fraction in a column or collecting a range of samples over time, lowest retention time / travels furthest on paper or TLC (allow 1 mark for having the longest retention time in GLC).

1

Method of identification of ETU (by comparison with standard using chromatography)

If method completely inappropriate, only M1 is accessible

1

[8]

Q7.

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(a) **If 2 stage test for one compound, award no marks for that compound, eg no mark for ROH or RX to alkene then Br_2 test. If reagent is wrong or missing, no mark for that test; if wrong but close/incomplete, lose reagent mark but can award for correct observation. In each test, penalise each example of wrong chemistry, eg $AgClr_2$**

propan-1-ol

acidified
potassium
dichromate

sodium

Named acid + conc H_2SO_4

named acyl chloride

PCl_5

M1 **1**

(orange) turns green

effervescence

Sweet smell

Sweet smell /misty fumes

Misty fumes

M2 **1**

propanal

add Tollens or Fehlings / Benedicts

acidified
potassium
dichromate

Bradys or 2,4-dnph

if dichromate used for alcohol cannot be used for aldehyde

M3 **1**

Tollens: silver mirror or Fehlings/ Benedicts: red ppt

(orange) turns green

Yellow or orange ppt

M4 **1**

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propanoic acid

Named carbonate/ hydrogencarbonate

water and UI (paper)

Named alcohol + conc H_2SO_4

sodium or magnesium

PCl_5

if sodium used for alcohol cannot be used for acid

M5 **1**

effervescence

orange/red

Sweet smell

effervescence

Misty fumes

if PCl_5 used for alcohol cannot be used for acid

M6 **1**

1-chloro propane

NaOH then acidified $AgNO_3$

$AgNO_3$

If acidification missed after NaOH,
no mark here but allow mark for observation

M7 **1**

white ppt

white ppt

M8 **1**

(b) oxidation (of alcohol by oxygen in air)

M1 **1**

absorption at <u>1680 -1750</u> (due to C=O)

Must refer to the spectrum

M2 **1**

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comparison of polarity of molecules or correct imf statement:
propanone is less polar OR propan-2-ol is more polar
OR propanone has dipole-dipole forces
OR propan-2-ol has hydrogen bonding

M3

1

about attraction to stationary phase or solubility in moving phase
Propan-2-ol has greater affinity for stationary phase or vice versa
OR propanone is more soluble in solvent/moving phase or vice versa

M4

1

[12]

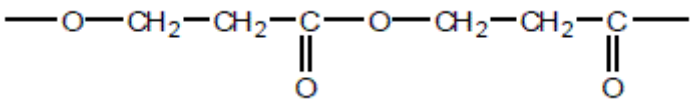
Q8.

(a) 3-hydroxypropanoic acid

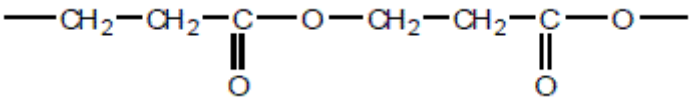
allow 3-hydroxypropionic acid
must be correct spelling

1

(b) (i) must show trailing bonds



or can start at any point in the sequence, e.g.



not allow dimer
allow –O–$CH_2CH_2COOCH_2CH_2CO$–
or –$CH_2CH_2COOCH_2CH_2COO$–
ignore ( ) or n
NB answer has a total of 6 carbons and 4 oxygens

1

(ii) condensation (polymerisation)

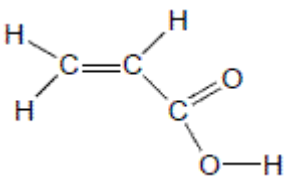
Allow close spelling

1

(c) (i) C=C or carbon-carbon <u>double</u> bond

1

(ii)

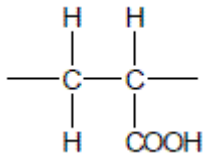


*must show **ALL** bonds including O–H*

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1

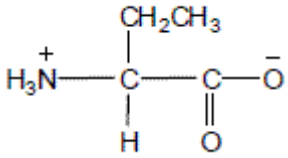
(iii) must show trailing bonds



allow polyalkene conseq on their c(ii)
ignore n

1

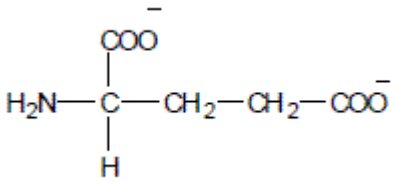
(d)



allow NH_3^+—
allow COO^-

1

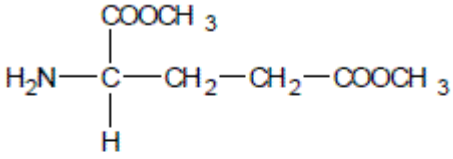
(e) (i)



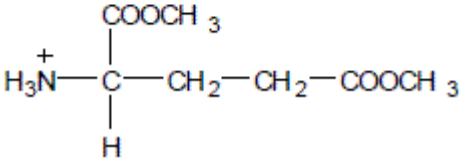
In (e), do not penalise a slip in the number of carbons in the $-CH_2CH_2-$ chain, but all must be bonded correctly
NB two carboxylate groups
Allow COONa or COO^- Na^+ but not covalent bond to Na
allow NH_2–

1

(ii)



OR



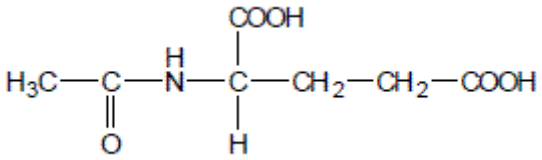
In (e), do not penalise a slip in the number of carbons in the $-CH_2CH_2-$ chain, but all must be bonded correctly
NB two ester groups

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allow NH_2– or $^+NH_3$–

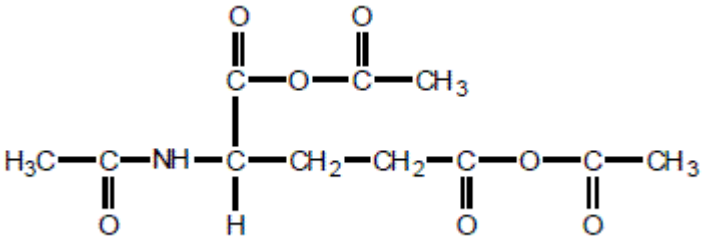
1

(iii)



In 4(e), do not penalise a slip in the number of carbons in the $-CH_2CH_2-$ chain, but all must be bonded correctly

allow anhydride formation on either or both COOH groups (see below) with or without amide group formation



1

(f) **M1** phase or eluent or solvent (or named solvent) is <u>moving or mobile</u>

1

M2 stationary phase or solid or alumina/silica/resin

1

M3 separation depends on balance between solubility or affinity (of compounds) in each phase
OR
different adsorption or retention
OR
(amino acids have) different R_f values
OR
(amino acids) travel at different speeds or take different times

1

[13]

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Q1.

(a) Most students coped with the need to convert volume to mass and gave 9.6 g of cyclohexanol at the start, but too many then assumed that this meant the maximum possible yield of cyclohexene would be 9.6 g and so divided 5.97 by this. 47.5% of students completed the calculation successfully.

(b) Most students (70.2%) were able to suggest the use of bromine water, with only very few getting the colour change the wrong way round. The most common wrong answer was the suggestion of a test for the absence of alcohol rather than a positive test for the presence of an alkene.

(c) This was not answered as well as expected (42% correct), with many vague references to 'removing impurities' or 'separating the layers'.

(d) The key to questions like this about understanding the method of a practical is to relate the answer to the position of the process in the overall method. The reference to periodic opening of the tap preceded the actual separation of the layers in the method, yet many answers referred to opening the tap to run off one of the layers. It was interesting that more students (57.4% correct) were able to suggest that this was to release pressure of CO_2 (due to reaction with acid) than were able to suggest, in part (c), that the carbonate had been added in order to react with acid.

(e) The low success rate in this question (28.2% correct) is explained by a lack of specificity in students' answers; the mark required a reference to a lack of reactivity with, or solubility in, **cyclohexene**.

(f) Most students chose to draw a diagram rather than write a description; the former is the recommended approach. However, clear, simple cross-sectional line diagrams of a Buchner funnel and filter paper on top of a Buchner flask (with side-arm attached to a vacuum pump) were seldom seen. Tubes were often shown as sealed, bungs and side-arms were missing and the side-arm was often drawn on the funnel rather than the flask. Only 28.7% of students gained both marks; 37.1% failed to score.

(g) This part gave numerous examples of repeating the question, with many answers seen along the lines of "the retention time is shorter because the retention time is shorter". Some students also inverted the question and tried to describe why cyclohexene had a longer retention time, while others thought incorrectly that cyclohexene is polar due to the C=C bond. An inversion of reasoning that was often seen was the incorrect idea that cyclohexanol has hydrogen bonding, which is why it is polar. 34.9% of students scored zero here.

(h) Too many students failed to remember the need always to mention both the wavenumber range **and** the bond responsible in questions of this type. Most correctly stated that a peak in the range 3230−3550 would not be visible, but many then failed to state that this peak relates to the O−H bond in an alcohol. As a result, only 43.7% of students gained the mark.

Q2.

(a) This was well known; most students gave an equation for a 1:1 mole ratio, although a 1:2 ratio and a two-step process were also seen and credited.

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(b) This was also well known and 35% of students scored full marks. In the mechanism, some students incorrectly showed a lone pair on the electrophile, or the horseshoe was sometimes drawn in an incorrect orientation relative to C1. Some students started from benzene and formed nitrobenzene first.

(c) Only the very weakest 7% of students failed to calculate the correct R_f value.

(d) This question tested understanding of the balance between solubility in the moving phase and retention by the stationary phase. Both parts were needed in the answer.

(e) This question was found very easy by most, although weaker students discussed safety issues.

(f) A third of students scored both marks, but sadly 7% of students made no attempt at the question. They were asked to deduce the answer to an unfamiliar practical situation, but one which is similar to those they will have met in Required Practical Activity 12. Many deduced that the 1,4 isomer was less polar, but then attempted to explain this relative polarity rather than answering the question asked.

(g) This final part to the question was not attempted by 10.2% of students. The best answers demonstrated the ability of candidates to deduce that the student was correct, and to explain their deduction.

Q5.

Parts (a), (b)(i), (b)(ii) and (d) were very well answered, but formation of the ester in part (b)(iii) was less well understood. Just over a third of students scored both marks in part (c), but a mark was often lost where a displayed formula for the fragment ion was not shown. Other errors included omitting the charge and the radical dot on the molecular ion or including two positive charges on the fragment ion, ie writing C+ in the structure and also writing + outside brackets around the ion. There were very few correct answers to part (e). Only a small number of students recognised that the amino acids would become protonated in acidic solution and so the protonated lysine would have twice the charge of the protonated alanine.

Q6.

(a) In part (i), most students were able to identify two appropriate atoms in the structure, but the ionic nature of Zineb resulted in many students failing to calculate its M*r* correctly in part (ii).In part (iii) proved to be demanding too, ester being the most common error.

(b) The simple calculation in this part proved straightforward for most students.

(c) This part highlighted the difficulties students face when applying theoretical ideas. Many students ignored the specific references to Zineb and ETU and wrote at length about the theory of chromatography. It was not uncommon to see long answers that did not specify the type of chromatography to be used, or make any mention of Zineb or ETU. Students were similarly reluctant to use the information in the questions to predict the outcomes for this particular separation. Such non-specific answers received few marks. A significant number of students chose gas chromatography, and even then could not make any use of the information at hand.

Q7.

There were many excellent answers to part (a) of this question. Common errors in what were otherwise correct answers for part (a) included incomplete reagents such as

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omission of the acid with potassium dichromate or simply stating “carbonate” rather than the full name or formula of a carbonate such as sodium carbonate or Na_2CO_3.

The haloalkane proved to be the most difficult to identify, with students often treating it as an acyl chloride and assuming that addition of water would give misty fumes.

A single test was required for each compound so answers which involved a preliminary step before a test did not score.

In part (b), the first two marks were often gained but few students gained both of the other two. This was often because of incorrect or missing statements about polarity in propanone or propan–2–ol or because of a lack of knowledge of what is happening in this type of chromatography. Many students thought that the substances would rise in the column while others thought that the M_r would affect retention time.

Q8.

Part (a) was answered well by two thirds of the candidates. In part (b)(i), half gave a correct structure; many wrong answers showed too many repeating units or included an extra oxygen atom. The type of polymerisation in part (b)(ii) and the required bond in part (c)(i) were both very well known. In part (c)(ii) the answer was required as a displayed formula, ie it must show **all** the bonds. Many candidates have still not realised that all includes the O–H bond. Part (d) was correctly answered by fewer than a fifth of the candidates. Many simply drew 2-aminobutanoic acid rather than its zwitterion. In parts (e)(i) and (e)(ii), many candidates did not recognise that both acid groups in glutamic acid would react. Two thirds of candidates answered part (e)(i) correctly, but parts (e)(ii) and (e)(iii) were found more difficult. In part (f), some candidates explained clearly how column chromatography worked and just under a third gained full marks in this section. Others described paper chromatography or were obviously unfamiliar with the topic.

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