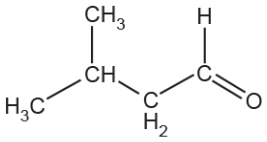
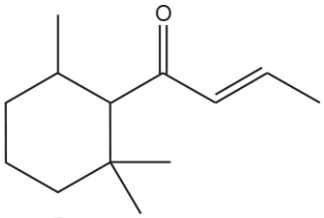
Chromatography and Qualitative Analysis

1. The carbonyl compounds, **F** and **G**, shown below, contribute to the flavour of coffee.



F



G

Describe suitable chemical tests, with observations, that would confirm the presence of the functional groups in **F** and **G**.

---

[4]

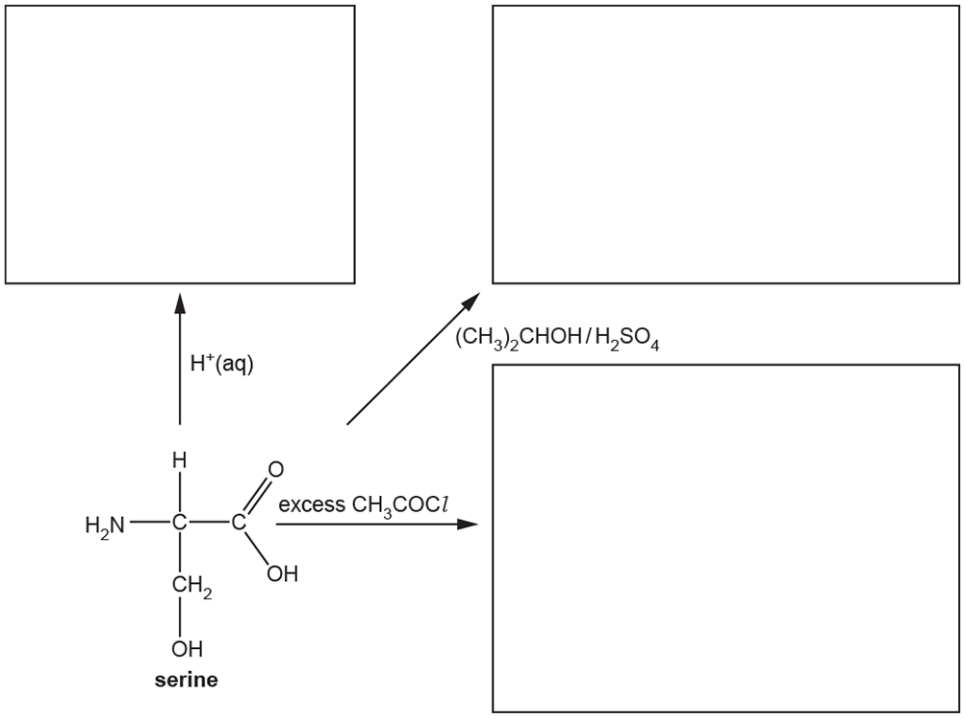
2(a). This question is about α-amino acids, $RCH(NH_2)COOH$.

Table 17.1 shows the R groups in four amino acids.

Amino acid	R group
alanine (ala)	CH_3–
serine (ser)	$HOCH_2$–
leucine (leu)	$(CH_3)_2CHCH_2$–
glycine (gly)	H–

Table 17.1

i. In the boxes, draw the organic products for the reactions of serine shown below.



[4]

ii. A student is provided with one of the four amino acids in **Table 17.1.**

A student carries out a titration with a standard solution of hydrochloric acid to identify the amino acid. The student's method is outlined below.

- The student dissolves 5.766 g of the amino acid in water and makes the solution up to 250.0 cm^3 in a volumetric flask.
- The student titrates this solution with 25.0 cm^3 of 0.150 mol dm^{-3} hydrochloric acid.
- 21.30 cm^3 of the amino acid solution were required for complete neutralisation of the hydrochloric acid.

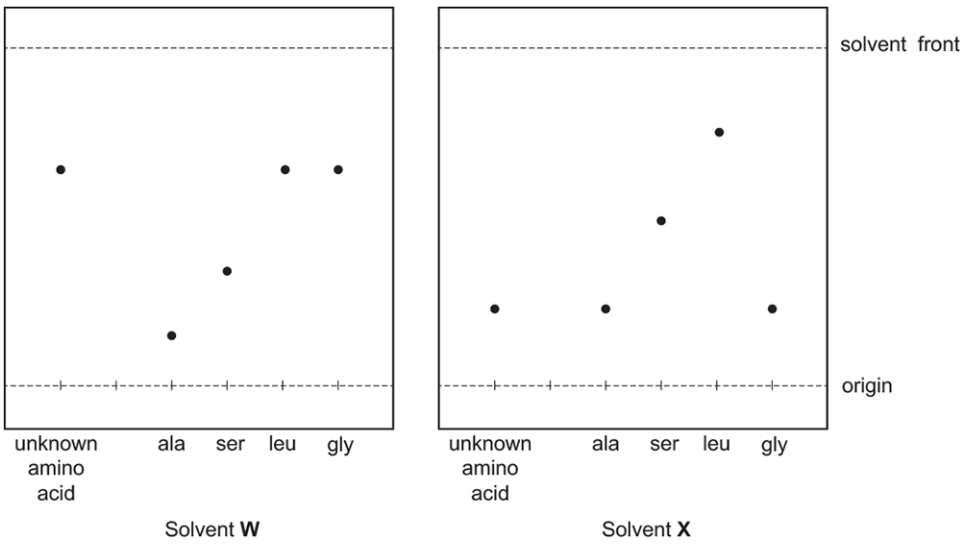
Determine which amino acid the student used.

[4]

(b). The student is provided with another amino acid.

The student attempts to identify the unknown amino acid using chromatography.

The student obtains two TLC chromatograms of the unknown amino acid and the four amino acids in **Table 17.1**, using two different solvents, **W** and **X**.



i. What is the R_f value of serine (ser) in solvent **W**?

R_f = ... **[1]**

ii. Analyse the chromatograms to identify the unknown amino acid.

Explain your reasoning.

Name of unknown amino acid

Explanation

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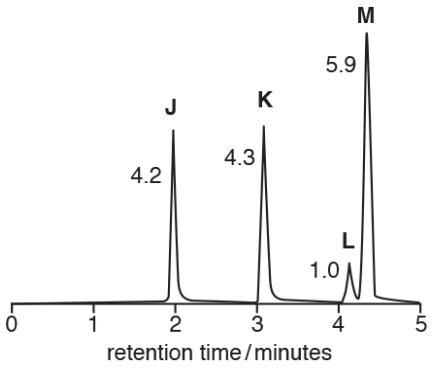
[2]

3. A cosmetic product containing four esters, **J**, **K**, **L** and **M**, is analysed by gas chromatography and mass spectrometry. The results are shown below.

Gas chromatogram



The numbers by the peaks are the relative molar proportions of the compounds in the mixture.

Mass spectrometry

ester	*m/z* of molecular ion peak
J	152
K	166
L	180
M	180

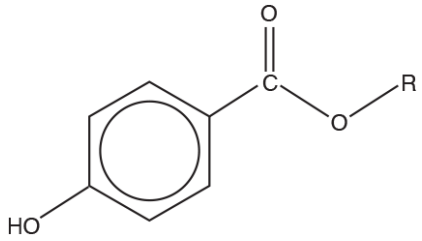
i. The concentration of ester **K** in the cosmetic product is 9.13×10^{-2} g dm^{-3}.

Using the results, calculate the concentration, in mol dm^{-3}, of ester **M** in the cosmetic product.

Give your answer to **two** significant figures.

concentration of ester **M** = _____ mol dm^{-3} **[2]**

ii. A general structure for esters **J**, **L** and **M** is shown below.



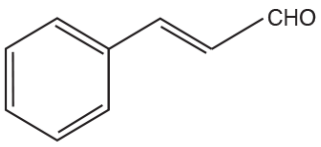
Where 'R' is an alkyl group.

Use the mass spectrometry results to deduce possible structures for esters **J**, **L** and **M**.

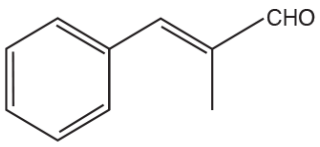
J	**L**	**M**

[3]

4. A student plans to carry out some chemical tests on both cinnamaldehyde and methylcinnamaldehyde.



cinnamaldehyde



methylcinnamaldehyde

i. Suggest a suitable chemical test to confirm that both compounds contain an unsaturated carbon chain.

Your answer should include the reagent and observations.

---

[1]

ii. Describe a chemical test to confirm that both compounds contain an aldehyde functional group.

Your answer should include the reagent and observations.

---

[1]

iii. Describe a chemical test to confirm that cinnamaldehyde and methylcinnamaldehyde contain a carbonyl group.

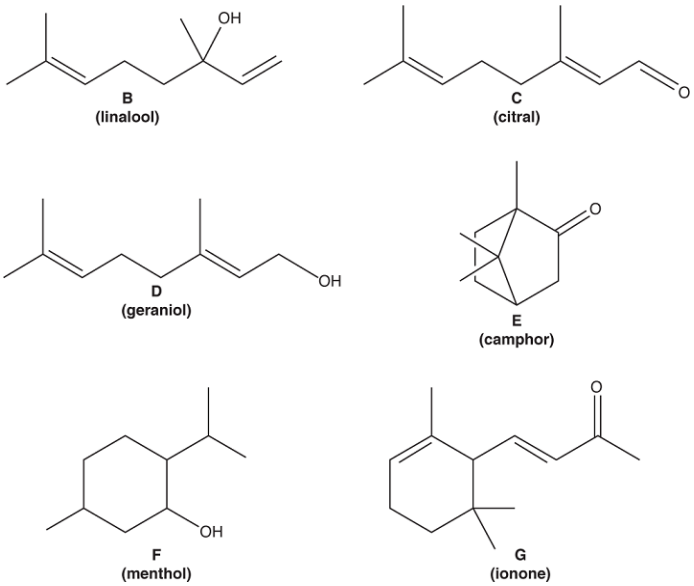
How could the products of this test be used to distinguish between the two compounds?

Your answer should **not** include spectroscopy.

---

[3]

5. The structures for six naturally occurring organic compounds with pleasant smells, **B–G**, are shown below. The common names in brackets relate to their source and smell.



Explain how chemical tests would allow each compound to be distinguished from the other compounds.

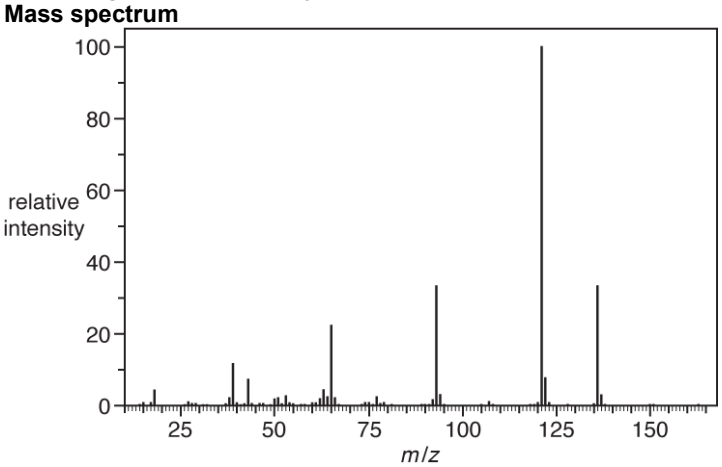
In your answer, include essential details for all test procedures and observations.

Details of apparatus and quantities are **not** required.

[6]

6(a). A chemist analyses a naturally occurring aromatic compound.

The percentage composition and mass spectrum of the compound are shown below.
Percentage composition by mass: C, 70.58%; H, 5.92%; O, 23.50%.
Mass spectrum



Determine the molecular formula of the compound.
Show your working.

molecular formula = ... **[3]**

(b). Qualitative tests are carried out on the aromatic compound. The results are shown below.

Test	**Acidity**	**Na_2CO_3(aq)**	**2,4-DNP**	**Tollens' reagent**
Observation	pH = 5	No observable change	Orange precipitate	No observable change

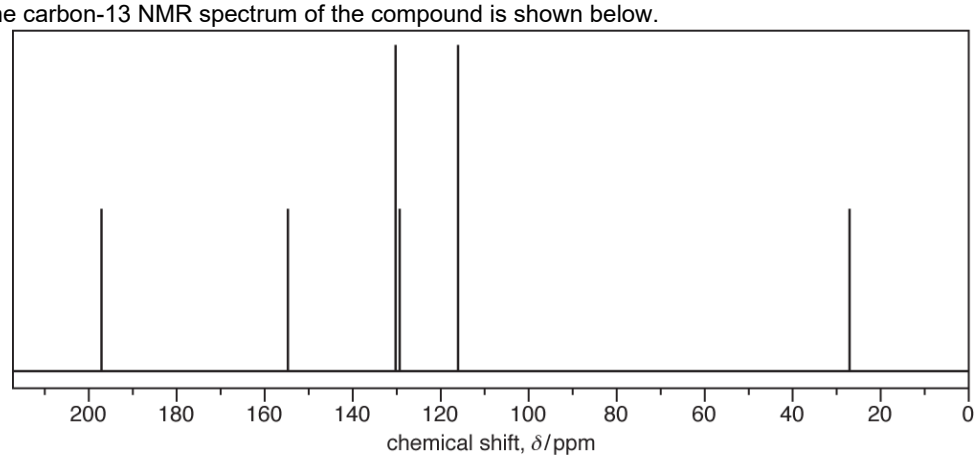
Determine the functional groups in the compound. Explain your reasoning.

Functional groups ----------

Explanation ----------

--- **[3]**

(c). The carbon-13 NMR spectrum of the compound is shown below.



Using the spectrum and the results from **(a)** and **(b)**, determine the structure of the compound. Explain your reasoning.

Structure of compound

[3]

7(a). A student was provided with five compounds: an aldehyde, a ketone, a carboxylic acid and two esters. The student decides to identify the type of compound by carrying out some chemical tests.

Suggest chemical tests to identify the carboxylic acid and aldehyde.

For each test, include essential reagent(s), observation(s) and a balanced equation.

In your equations, use 'R' for the alkyl group.

i. Test for carboxylic acid.

Reagent(s)

……

……

Observation(s)

……
……

Equation

[2]

ii. Test for aldehyde.

Reagent(s)

……
……

Observation(s)

……
……

Equation

[2]

(b). Suggest a chemical test to distinguish the ketone from the two esters.

Reagent(s)

……
……

Observation(s)

……
……

---

[1]

(c). The student wants to confirm that the other two compounds are esters. Unfortunately there is no direct test for an ester group.

The esters are $CH_3COOC(CH_3)_3$ and $(CH_3)_3CCOOCH_3$.

The student plans the following:

- hydrolyse the two esters using aqueous sodium hydroxide.
- separate the hydrolysis products.
- carry out tests on the hydrolysis products.

i. Write an equation for the hydrolysis of one of the two esters with aqueous sodium hydroxide.

Show the structures for the organic compounds.

[2]

ii. Suggest a chemical test on the hydrolysis products that would allow the two esters to be identified.

Write an equation for one reaction that takes place.

Show the structures for the organic compounds.

Reagent(s)

……

……

Observation(s)

……

……

Equation

[2]

iii. The student thought that NMR spectroscopy could be used to identify the two esters without the need to carry out chemical tests.

The esters are $CH_3COOC(CH_3)_3$ and $(CH_3)_3CCOOCH_3$.

Explain whether the student is correct for ^{13}C and ^{1}H NMR spectroscopy. Your answer should also clearly state any differences between the spectra of the two esters.

[3]

(d). The ketone and aldehyde provided to the student both contain five carbon atoms.

The ^{1}H NMR spectrum of the aldehyde contains two singlet peaks only:
a large peak at δ = 1.2 ppm and smaller peak at δ = 9.6 ppm.

Suggest **all** possible structures for the ketone and identify the aldehyde.

Show **all** your reasoning.

[5]

8. A student hydrolyses a sample of protein and uses Thin-Layer Chromatography (TLC) to analyse the mixture of amino acids produced.

The chromatogram obtained is shown in **Fig. 17.1**.

Table 17.1 shows the R_f values for different amino acids in the solvent used.

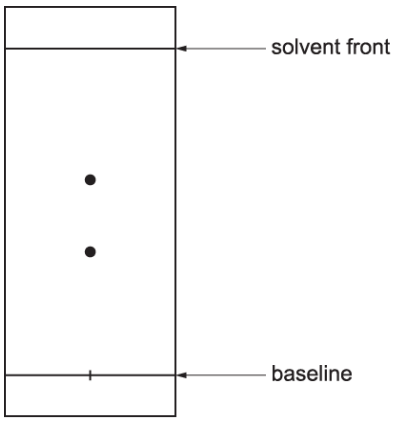


Fig. 17.1

Amino acid	R_f value
Threonine	0.65
Valine	0.60
Histidine	0.53
Serine	0.45
Leucine	0.38

Table 17.1

i. Analyse the chromatogram to identify the amino acids.

---

[1]

ii. The student runs a second chromatogram on the sample using a more polar solvent.

Predict the effect, if any, on the R_f values of the amino acids. Explain your reasoning.

---

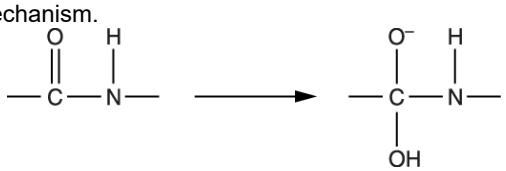
[2]

9(a). The building blocks of peptides and proteins are α-amino acids.

A tripeptide is hydrolysed to form a mixture of three different α-amino acids.

The first step of an incomplete mechanism for the alkaline hydrolysis of the tripeptide is shown below.

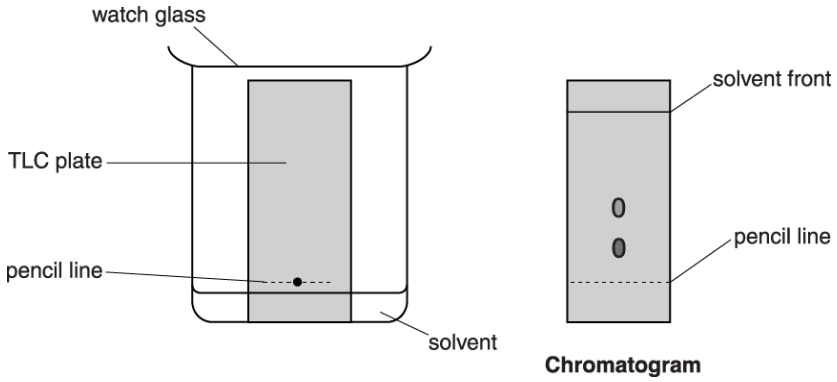
Add curly arrows and relevant dipoles to the diagram to suggest how the hydroxide ion takes part in the first step of this mechanism.



[2]

(b). The tripeptide is hydrolysed and the resulting mixture containing the three amino acids is neutralised.

A student tries to separate and identify the three amino acids in the mixture using thin-layer chromatography (TLC). The diagram below shows the apparatus for the experiment and the chromatogram produced.



Explain how the chromatogram can be used to identify amino acids.
The student thinks that there should be three spots on the chromatogram.

Suggest why there are only two spots.

---

[3]

(c). The three α-amino acids in the tripeptide are aspartic acid, glycine and isoleucine.

The general formula for an α-amino acid is $RCH(NH_2)COOH$.

α-amino acid	**R-group**
aspartic acid	$–CH_2COOH$
glycine	–H
isoleucine	$–CH(CH_3)CH_2CH_3$

i. Aspartic acid has an isoelectric point of 2.77.

What is meant by the term *isoelectric point*?

In your answer you should use the appropriate technical terms spelled correctly.

---

[1]

ii. Draw the structure of aspartic acid when it is dissolved in a solution with a high pH.

[1]

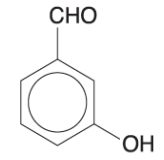
iii. Suggest a structure for the tripeptide.

On your structure, mark each chiral centre with an asterisk (*).

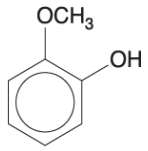
[2]

10(a). A student analysed a mixture of compounds found in red wine using gas chromatography followed by mass spectrometry (GC-

Two of the compounds found to be present in the mixture are shown below.



compound A



compound B

The column in the gas chromatogram is packed with solid beads coated with a liquid polymer.

How does gas chromatography (GC) separate the compounds in the mixture?

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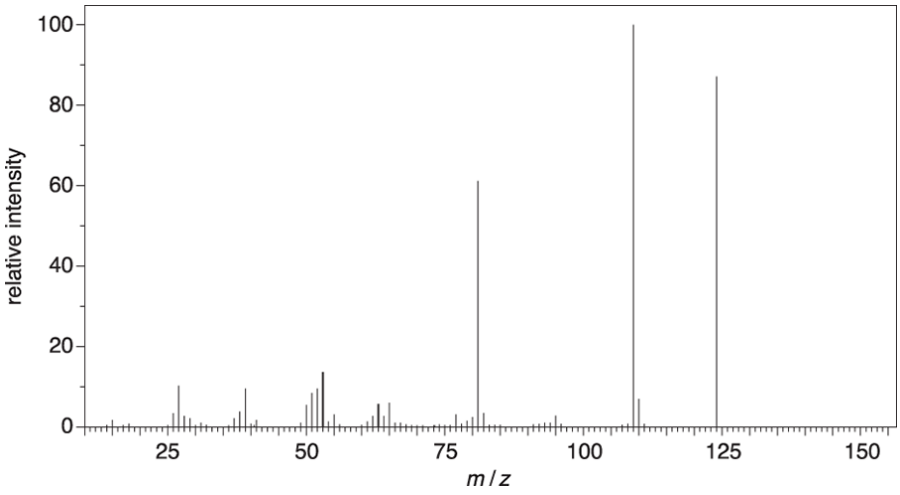
[1]

(b). The mass spectrum (of the **first** compound to emerge from the column is shown below.



i. Identify the compound responsible for this spectrum.

Give a reason for your answer.

---

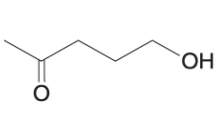
[1]

ii. What does your answer to **(b)(i)** suggest about the interaction of this compound with the phases present in the column?

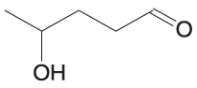
---

[1]

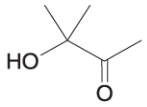
11. The following three carbonyl compounds are structural isomers of $C_5H_{10}O_2$.



compound C



compound D



compound E

Describe chemical tests that you could carry out in test-tubes to distinguish between compounds **C**, **D** and **E**.

Include appropriate reagents and any relevant observations. Also include equations showing structures for the organic compounds involved.

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[4]

12(a). Cyclohexanone can be prepared in the laboratory by reacting cyclohexanol with concentrated sulfuric acid and sodium dichromate.

Ethanedioic acid is added to the reaction mixture to react with any excess dichromate.

The mixture is then distilled. The impure distillate is a mixture of cyclohexanone and water.

You will need to refer to some or all of the following data to answer these questions.

	Boiling point / °C	**Density / g cm^{-3}**	***M*$_r$**
Cyclohexanol	161	0.962	100.0
Cyclohexanone	156	0.948	98.0

* Draw a labelled diagram to show how you would safely set up apparatus for distillation and describe a method to obtain a pure sample of cyclohexanone from the distillate.

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____ **[6]**

(b). Ethanedioic acid removes excess dichromate ions, $Cr_2O_7^{2-}$, as in the equation below.

$$3(COOH)_2 + Cr_2O_7^{2-} + 8H^+ \rightarrow 6CO_2 + 2Cr^{3+} + 7H_2O$$

Suggest how you could tell when the excess dichromate has completely reacted with the ethanedioic acid.

_____

_____ **[1]**

(c). A student monitors the course of this reaction using thin-layer chromatography (TLC).

Outline how TLC could be used to monitor the course of the reaction.

_____

_____

_____

_____ **[2]**

(d). Plan an experiment that would allow the student to confirm the identity of the pure organic product by means of a chemical test.

---

[3]

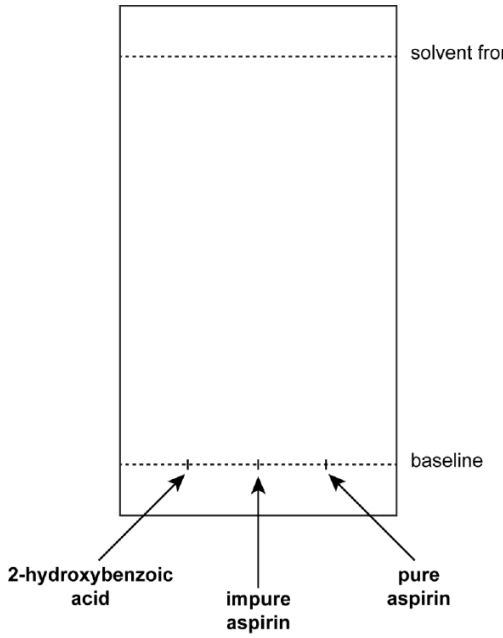
13. The R_f values and melting point ranges of 2-hydroxybenzoic acid and pure aspirin are shown in the table.

Compound	R_f	Melting point range / °C
2-Hydroxybenzoic acid	0.30	158–161
Pure aspirin	0.75	138–140

i. A student analyses the purity of their impure aspirin by thin-layer chromatography (TLC).

From the results the student concludes that the impure aspirin is contaminated with a small amount of unreacted 2-hydroxybenzoic acid.

Draw spots on the chromatogram below to show how the student arrived at this conclusion.



[2]

ii. Predict the melting point range of the impure aspirin.

---

[1]

14(a). Compound **F** has the molecular formula C_4H_8.

Compound **F** is reacted with steam in the presence of an acid catalyst, to form a mixture of three alcohols, **G**, **H** and **I**.

Compound **G** is oxidised with acidified potassium dichromate(VI) to form compound **J**.

Compound **J** reacts with Tollens' reagent to form compound **K**.

Compounds **H** and **I** are optical isomers.

Draw the structures of the compounds **F**, **G**, **H**, **I**, **J** and **K**.

[6]

(b). Explain, with reference to a suitable chemical test, how compound **J** could be identified.

Your answer should **not** include spectroscopy.

---

[3]

END OF QUESTION PAPER