SECTION 15 Analytical Chemistry

Qualitative Analysis

AL96(II)_04b

For each of the following pairs of compounds, suggest a test to distinguish one compound from the other:

(i) $Na_2CO_3(s)$ and $NaHCO_3(s)$

(2 marks)

(ii) $KCl(s)$ and $MgCl_2(s)$

(2 marks)

AL98(I)_07a

Briefly describe how you would test for the presence of the all constitute ions and molecule in a sample of iron alum, $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$.

(4 marks)

AL99(I)_07

(a) Describe the procedure for a flame test.

(3 marks)

(b) Describe how to distinguish between a sodium salt and a potassium salt of the same anion by flame test.

(1 mark)

(c) Describe how to detect the presence of water of crystallization in an inorganic salt.

(1 mark)

AL99(II)_01

For each of the following pairs of substances, suggest a chemical test to distinguish one from the other. For each test, give the reagent(s) used and the expected observation.

(a) $CsCl(s)$ and $NH_4Cl(s)$

(2 marks)

(b) $Na_2SO_3(aq)$ and $Na_2S_2O_3(aq)$

(2 marks)

ASL00(I)_02

In the laboratory, there are three bottles labelled A, B and C. Each bottle contains one of the following reagents:

$Cl_2(aq)$, $NaI(aq)$ and $KBr(aq)$

Three tests were carried out using the reagents in the bottles. The results are summarized in the table below:

Test	Observation
Mixing reagent in bottle *A* with reagent in bottle B	No observable change
Mixing reagent in bottle *A* with reagent in bottle C	Mixture turned brown
Mixing reagent in bottle *B* with reagent in bottle C	Mixture turned brown

(a) Deduce which bottle contains $Cl_2(aq)$. Write the relevant chemical equations.

(3 marks)

(b) If hexane is also provided, suggest how you would carry out an experiment to identify the contents of the other two bottles.

(2 marks)

(c) State ONE safety precaution which should be taken when performing the experiment you have suggested in (b).

(1 mark)

AL00(I)_08

In order to establish the functional groups present in an acyclic compound F (C_4H_6O), three chemical tests were carried out. The test results are listed in the table below.

(a) Complete the table by giving the inference of each test.

Test reagent	Test result	Inference
Acidified $K_2Cr_2O_7(aq)$	Positive	Function group(s) that may be present:
Tollen's reagent	Negative	Functional group(s) absent:
Br_2 in CH_3CCl_3	Positive	Functional group(s) that may be present:

(3 marks)

(b) Based on the above information, draw four possible structure of F.

(2 marks)

ASL00(II)_07

X, Y and Z are three isomeric cyclic compounds with molecular formula $C_6H_{10}O$. Two chemical tests were carried out on the compounds. The results are summarized in the table below :

Chemical test	X	Y	Z
Fehling's test	No observable change	Red precipitate	No observable change
Adding the compound to bromine water	No observable change	No observable change	Decolorization

(a) What is the red precipitate formed in the Fehling's test?

(1 mark)

(b) Deduce a possible structure for each of the compounds, X, Y and Z.

(5 marks)

ASL00(II)_11

Suggest a chemical test to distinguish one solution from the other in each of the following pairs Equations should be given where appropriate.

(a) $Mg(NO_3)_2(aq)$ and $Al(NO_3)_3(aq)$

(4 marks)

(b) $Na_2SO_3(aq)$ and $Na_2SO_4(aq)$

(3 marks)

ASL01(I)_07

Suggest tests to show the identities of the cations and anion in KCl(s), and state the expected observation.

(4 marks)

AL02(II)_05c

Consider the substances listed below:

Butane
Ethanoic acid
Propanone
Benzoic acid
Hexane
Tetrachloromethane
Dichlorodifluoromethane
Polystyrene
Triethylamine

For each of the descriptions of physical properties from (a) to (h) below, choose from the above list, one substance which best fits the description.

(i) A colorless, flammable gas
(ii) A colorless liquid with a sour odour
(iii) A colorless, water miscible, flammable liquid
(iv) A colorless, non-flammable liquid
(v) A colorless liquid with a fishy smell
(vi) A colorless, water immiscible, flammable liquid
(vii) A white solid which is insoluble in both cold and hot water
(viii) A white solid which is insoluble in cold water, but soluble in hot water

(8 marks)

AL02(II)_01c

You are provided with a sample of blackboard chalk made from hydrated calcium sulphate(VI) powder.

(i) The presence of calcium in the sample can be shown by conducting a flame test.

  (I) Give the essential steps in a flame test.

(3 marks)

  (II) State the origin of the flame color.

(1 mark)

(ii) Devise an experiment, using chemicals and apparatus commonly available in a school laboratory, to determine the number of water of crystallization per formula unit of CaSO4 in the sample of blackboard chalk.

(4 marks)

AL03(I)_07

Outline how you would show the presence of Ba^{2+} and Ag^{+} ions in a sample of water-soluble inorganic mixture. Give confirmatory test(s) for these ions if necessary.

(4 marks)

AL04(I)_07a

You are provided with three unlabeled bottles each containing one of the white powders listed below:

$KBr(s)$, $SiO_2(s)$ and glucose

(i) Outline the physical tests that you would perform to distinguish unambiguously the three substances from one another.

(2 marks)

(ii) Describe how you would carry out a chemical test to distinguish $KBr(s)$ from glucose.

(2 marks)

ASL05(I)_06

Compound A has the following composition by mass:

C 81.8%, H 6.1% and O 12.1%

Its relative molecular mass is in the range of 130 to 140.

(a) Calculate the molecular formula of A.

(3 marks)

(b) A is an aromatic compound. It gives positive results when treated with Tollen's reagent. Deduce all functional groups present in A.

(3 marks)

(c) State a type of isomerism that A can exhibit. Illustrate your answer with the appropriate structures.

(2 marks)

AL05(II)_01

Each of six reagent bottles labeled **A**, **B**, **C**, **D**, **E** and **F** contained one of the following solutions.

$AgNO_3(aq)$, $BaCl_2(aq)$, $H_2SO_4(aq)$, $NH_3(aq)$, $NaOH(aq)$ and $Na_2S_2O_3(aq)$

In an attempt to identify the contents of the bottles, a series of tests were conducted by mixing two of the solutions. The table below lists the observations in these tests.

Solution being mixed	Observations
A and C	A brown precipitate is formed
A and E	A white precipitate is formed
A and F	A brown precipitate is initially formed and the precipate dissolves when F is in excess.
B and C	Only heat is liberated
B and D	A pale yellow precipitate is formed slowly
B and E	A white precipitates is formed

Identify, with explanation, the contents of the six reagent bottles based on the above information.

(8 marks)

AL07(I)_03

A mixture of $Fe^{3+}(aq)$ and $Cu^{2+}(aq)$ is separated by paper chromatography using a mixture of propanone and 6M $HCl(aq)$ as the mobile phase. Suggest how you would identify chemically the $Fe^{3+}(aq)$ and $Cu^{2+}(aq)$ on the chromatographic paper.

(3 marks)

AL08(I)_08

Propenamide, the monomer of polypropenamide (also known as polyacrylamide), is a potential carcinogen. The melting point of propenamide is 84 °C and its solubility in water is 2.16 g cm^{-3} at 30 °C.

(a) Polyacrylamide gel (PAAG) is polyacrylamide saturated with water. A sample of PAAG for breast augmentation is suspected to contain about 1 % of propenamide. Suggest a chemical test to show the presence of propenamide in the sample.

(2 marks)

(b) Propenamide can be identified by converting it to a solid derivative and determining the melting point of the derivative. With the help of a chemical equation, suggest ONE solid derivative of propenamide suitable for this purpose.

(1 mark)

(c) Suggest an instrumental method for the further characterization of the derivative suggested in (b). State clearly the expected results.

(2 marks)

AL08(II)_07

Compounds **M**, **N**, **P**, **Q** and **R** are all colorless liquids. Without the aid of instrumental analysis, suggest how you would differentiate the five compounds from one another.

CH_3CH_2OH	CH_3COCH_3	$(CH_3)_3COH$	$CH_3(CH_2)_3NH_2$	$CH_3(CH_2)_7OH$
M	**N**	**P**	**Q**	**R**

ASL10(I)_05

State the expected observation(s) in each of the following experiments, and account for the observation with the aid of chemical equation(s).

Adding a solution of 2,4-dinitrophenylhydrazine to $CH_3CH_2CHO(l)$.

(2 marks)

AL11(I)_07a

Copper(II) sulphate(VI) crystallizes from its aqueous solution as $CuSO_4{\bullet}5H_2O(s)$.

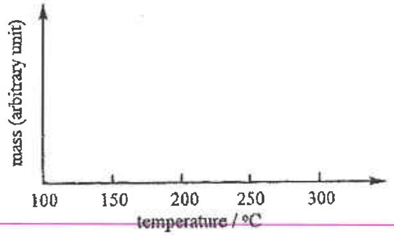
(i) The water of crystallization of the salt can be liberated upon heating. Suggest a chemical test to show that water is being liberated.

(1 mark)

(ii) Outline an experimental method to establish that the salt is a pentahydrate.

(3 marks)

(iii) When $CuSO_4{\bullet}5H_2O(s)$ is heated slowly such that the temperature rises steadily, it will lose four water molecules at about 110 °C, and then the last water molecule at about 250 °C. Using the axes below, sketch the change of mass when a sample of $CuSO_4{\bullet}5H_2O(s)$ is heated slowly.



(2 marks)

AL11(I)_07b

For each of the following pairs of species, suggest a chemical test to distinguish between them and write the chemical equation(s) of the reaction(s) involved.

(i) $Ba^{2+}(aq)$ and $Pb^{2+}(aq)$

(2 marks)

(ii) $Cl^-(aq)$ and $Br^-(aq)$

(2 marks)

ASL12(II)_06 (modified)

(a) Based on the information given below, deduce the structures of two isomeric compounds:

(1) Both compounds contain carbon, hydrogen and oxygen only.

(2) Both compounds have the same relative molecular mass of 58.0.

(3) Both compounds can react with 2,4-dinitrophenylhydrazine to give an orange precipitate.

(3 marks)

(b) Suggest a chemical test to distinguish between the two isomers in (a).

(2 marks)

AL13(I)_08b

For each of the following, given an example of its use in an inorganic experiment:

(i) A flame test

(1 mark)

(ii) Acidified $BaCl_2(aq)$

(1 mark)

(iii) Starch solution

(1 mark)

DSE12_03a

Compound **X** (molar mass < 118 g) contains a $-C_6H_5$ group. Two chemical tests are performed on **X** and the results are as follows:

Test (1) : **X** turns acidified potassium dichromate solution green.

Test (2) : **X** gives a negative result when tested with 2,4-dinitrophenylhydrazine.

(i) With reference to the result of Test (1) only, suggest TWO functional groups that **X** may have.

(2 marks)

(ii) (1) What is the purpose of using 2,4-dinitrophenylhydrazine in Test (2)?

(1 mark)

(2) State the expected observation if **X** gives a positive result in Test (2).

(1 mark)

(iii) With reference to the results of both Test (1) and Test (2), suggest one functional group that may be present in **X**.

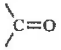
(1 mark)

DSE14_03a

Suggest a chemical test to show the presence of each of the following:

(i) HCl(g)

(2 marks)

(ii)  functional group

(2 marks)

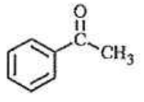
DSE15_03a

Suggest a chemical test to show the presence of $Br^-(aq)$.

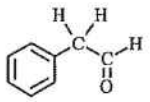
(2 marks)

DSE15_03b

Compounds **X** and **Y** shown below are isomers with relative molecular mass 120.



X



Y

(i) Each of **X** and **Y** can react with 2,4-dinitrophenylhydrazine solution to give a similar observation. State the observation.

(1 mark)

(ii) Suggest a chemical test to distinguish between **X** and **Y**.

(2 marks)

DSE16_03a

Suggest a chemical test to show the presence of hypochlorite ions in an aqueous solution.

(2 marks)

DSE17_03a

Answer the following short questions:

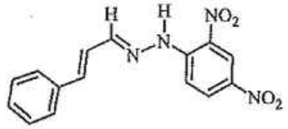
(i) Suggest a test to distinguish between sodium ions and potassium ions.

(2 marks)

(ii) Suggest a chemical test for detecting sulphur dioxide gas.

(2 marks)

(iii) An organic compound **X** reacts with 2,4-dinitrophenylhydrazine to form a yellow solid **Z**. The structure of **Z** is shown below:



Given that the molecular of **X** is C_9H_8O, draw the structure of **X**.

(1 mark)

DSE18_03a

Answer the following short questions:

(i) An ionic compound gives a brick red flame in a flame test. Suggest one cation the compound may contain.

(1 mark)

(ii) Suggest a chemical test to distinguish between $K_2SO_3(aq)$ and $K_2SO_4(aq)$.

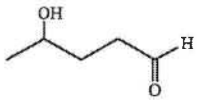
(2 marks)

DSE19_03a ii iii

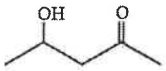
(ii) Organic compounds can be extracted by suitable solvents from their aqueous solutions. The solvents should dissolve the organic compounds to be extracted without reacting with them. State one other property these solvents should have.

(1 mark)

(iii) Suggest a chemical test to show how compounds **A** and **B** below can be distinguished :



A



B

(2 marks)

DSE20_03a

3. (a) Answer the following short questions :

(i) Suggest how $Na_2CO_3(s)$ and $Na_2CO_3 \cdot 10H_2O(s)$ can be distinguished.

(2 marks)

(ii) In an acidified medium, $I_2(aq)$ in a conical flask is titrated with $Na_2SO_3(aq)$ using starch solution as indicator. State the colour change at the end point of the titration.

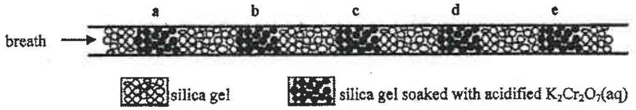
(1 mark)

(iii) Suggest a chemical test to show how hex-1-ene and hexanal can be distinguished.

(2 marks)

DSE20_03c i

(c) Road checking on ethanol intake of a driver can be done by having the driver exhale a breath into the tube as shown below :



(i) (1) Suggest the colour change of the silica gel soaked with acidified $K_2Cr_2O_7(aq)$ if enough ethanol-contained breath is exhaled into the tube. Write a half equation for the colour change involved.

(2) A breath from driver **A** only changes colour at positions **a** and **b**; while a breath from driver **B** changes colour at positions **a**, **b** and **c**. Assuming the checking is performed in a fair manner, explain which driver has a higher ethanol intake.

(3) Suggest how the checking can be performed in a fair manner.

(4 marks)

Marking Scheme

AL96(II)_04b

(i) **Dissolve the solid in water**, add Mg(NO$_3$)$_2$(aq) or Ca(NO$_3$)$_2$(aq) to the solutions. [1]
Only Na$_2$CO$_3$(aq) give a white precipitate; but NaHCO$_3$(a) does not. [1]

(ii) Carry out a **flame test, KCl(s) give a lilac flame**, while MgCl$_2$(s) gives no characteristic flame color. [1] [1]
OR, Add NaOH(aq) to aqueous solution of the substance.
Only MgCl$_2$ gives white precipitate, while KCl does not.

AL98(I)_07a

(i) NH$_4^+$: Heat the sample with NaOH(aq); [½]
Evolution of a gas with pungent smell, which can turn wet red litmus paper to blue indicates the presence of NH$_4^+$. [½]

(ii) Fe^{3+}: Add KNCS(aq) [½]
Appearance of red color indicates the presence of Fe^{3+} [½]
OR, NaOH – forming brown precipitate
K$_4$[Fe(CN)$_6$](aq) – appearance of deep blue color

(iii) SO$_4^{2-}$: Add acidified BaCL$_2$(aq) / Ba(NO$_3$)$_2$(aq) to the solution of salt; [½]
Appearance of white precipitate indicate the presence of SO$_4^{2-}$ [½]

(iv) Water of crystallization
Heat a sample of salt; water vapor will turn anhydrous CoCl$_2$ from blue to pink / [½]
anhydrous CuSO$_4$ from white to blue. [½]

AL99(I)_07

(a) Clean a platinum wire. [1]
Stick a sample of the salt on the Pt wire with conc. HCl. [1]
Heat the wire with the sample in a non-luminous flame. [1]

(b) Na salt gives a persistent yellow flame [½]
K salt gives a lilac flame [½]

(c) Heat the sample [½]
Water vapor will turn anhydrous CoCl$_2$ from blue to pink / anhydrous CuSO$_4$ from white to blue. [½]

AL99(II)_01

(a) Heat the compounds separately with NaOH(aq). [1]
NH$_4$Cl(s) gives an alkaline gas / a gas which forms white fumes with HCl(g) but CsCl(s) not. [1]

(b) Treat the compounds separately with HCl(aq). [1]
Na$_2$S$_2$O$_3$(aq) gives white / yellow precipitate of sulphur (+SO$_2$) [½]
Na$_2$SO$_3$(aq) gives a gas with choking smell (SO$_2$) and a clear solution. [½]
OR, Only Na$_2$S$_2$O$_3$(aq) gives a white / yellow precipitate.

ASL00(II)_07

(a) Bottle C [1]
Because solution A and B can only be give brown mixture after mixing with solution C. [1]

$$Cl_2(aq) + 2Br^-(aq) \longrightarrow 2Cl^-(aq) + Br_2(aq) \quad [½]$$
$$Cl_2(aq) + 2I^-(aq) \longrightarrow 2Cl^-(aq) + I_2(aq) \quad [½]$$

(b) Add hexane in the solution A and B. [1]
The one can give a purple solution after mixing with solution C is NaI(aq). [1]

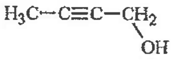
(c) Hexane is flammable and the experiment should be carried inside the fumehood. [1]

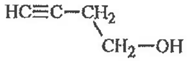
AL00(I)_08

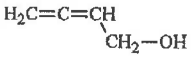
(a)

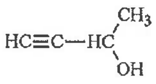
Test reagent	Test result	Inference	
Acidified K$_2$Cr$_2$O$_7$(aq)	Positive	Functional group(s) that may be present:	
		–CH$_2$OH (primary alkanol)	[½]
		CHOH (secondary alkanol)	[½]
		–CHO (aldehyde)	[½]
Tollens' reagent	Negative	Functional group(s) absent:	
		–CHO (aldehyde)	[½]
Br$_2$ in CH$_3$CCl$_3$	Positive	Functional group(s) that may be present:	
		C=C (alkene)	[½]
		C≡C (alkyne)	[½]

(b)


$H_3C{-}C{\equiv}C{-}CH_2{-}OH$


$HC{\equiv}C{-}CH_2{-}CH_2{-}OH$


$H_2C{=}C{=}CH{-}CH_2{-}OH$

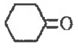

$HC{\equiv}C{-}CH(CH_3){-}OH$

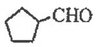
[2]

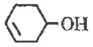
ASL00(II)_07

(a) Copper(I) oxide / Cu$_2$O(s) [1]

(b) D.B.E. of C$_6$H$_{10}$O is 2. Compound **X**, **Y** and **Z** are cyclic compounds with one double bond.
From the Fehling's test, only compound **Y** can give a red precipitate. **Y** should be a cyclic aldehyde, while others are not. [1]
Only compound **Z** can decolorize the bromine water. Compound **Z** possess a carbon-carbon double bond, while others do not. [1]
Possible structure:


X


Y


Z

[3]

ASL00(II)_11

(a) Dropwise addition of NaOH(aq) into two solutions respectively, until in excess. [1]

Mg(NO$_3$)$_2$(aq) gives white precipitate while Al(NO$_3$)$_3$(aq) firstly forms white precipitate and it redissolves in excess NaOH(aq). [1]

$Mg^{2+}(aq) + 2OH^-(aq) \longrightarrow Mg(OH)_2(s)$ [1]

$Al^{3+}(aq) + 3OH^-(aq) \longrightarrow Al(OH)_3(s)$ [½]

$Al(OH)_3(s) + OH^-(aq) \longrightarrow Al(OH)_4^-(aq)$ [½]

(b) Dropwise addition of acidified KMnO$_4$(aq) into two solutions respectively. [1]

Only Na$_2$SO$_3$(aq) can decolorize purple KMnO$_4$(aq), while Na$_2$SO$_4$(aq) cannot. [1]

$5SO_3^{2-}(aq) + 2MnO_4^-(aq) + 6H^+(aq) \longrightarrow 5SO_4^{2-}(aq) + 2Mn^{2+}(aq) + 3H_2O(l)$ [1]

ASL01(I)_07

By flame test / dip the sample on the platinum wire with conc. HCl and heat the sample in a non-luminous flame. [1]

Potassium cations will give lilac flame in the flame test. [1]

Add few drop of acidified silver nitrate solution in the KCl(aq). [1]

White precipitate AgCl(s) is given. [1]

AL02(II)_05c

(i)	Butane	(ii)	Ethanoic acid	[2]
(iii)	Propanone / ethanoic acid	(iv)	Tetrachloromethane	[2]
(v)	Triethylamine	(vi)	Hexane	[2]
(vii)	Polystyrene	(viii)	Benzoic acid	[2]

AL02(II)_01c

(i) (I) Clean a Pt wire / use a clean Pt wire (silica rod for flame test). [1]

Stick sample of the salt onto the Pt ware with concentrated HCl. [1]

Heat the wire with the sample in a non-luminous Bunsen flame. [1]

(II) Electron transition from a higher energy level to a lower energy level leads to the emission of a photo with wavelength in the visible (red) region. [1]

(ii) Heat a sample of the blackboard chalk (with a known mass) in a crucible [1]

until there is no further reduction in mass. [1]

Assuming that the initial mass and the final mass of the sample are m1 and m2 respectively.

$$\text{moles of } CaSO_4 = \frac{m2}{40 + 32 + 16 \times 4} = \frac{m2}{136}$$ [½]

$$\text{moles of } H_2O = \frac{m1 - m2}{18}$$ [½]

moles of water of crystallization per formula unit of CaSO$_4$

$$= \frac{m1 - m2}{18} / \frac{m2}{136}$$ [1]

AL03(I)_07

Dissolve the mixture in deionized water (water free from Cl$^-$ ions)

Add HCl(aq) to the solution. The silver ions in the solution will react with Cl$^-$(aq) ions to form a white precipitate. [1]

Confirmatory test for Ag$^+$ ions: AgCl(s) is solution in aqueous ammonia. [1]

Filter the mixture obtained. Add (NH$_4$)$_2$SO$_4$(aq) / H$_2$SO$_4$(aq) to the filtrate. Formation of a white precipitate shows the presence of Ba^{2+}(aq) ions. [1]

Confirmatory test for Ba^{2+} ions: apple green color in a flame test. [1]

AL04(I)_07a

(i) Add water to the white powder. Only SiO$_2$(s) is insoluble. [1]

Test the electrical conductivity of the solutions obtained. [½]

KBr(aq) conducts, but glucose solution does not. [½]

OR, Conduct a flame test. Only KBr(s) gives a lilac flame.

OR, Determine the melting points of the solid. KBr(s) has a very high melting point.

OR, Use IR spectroscopy. Only glucose shows absorption peak at 2800 – 3400 cm^{-1}.

(ii) Heat the solids strongly. Only glucose becomes char. [2]

OR, Add conc. H$_2$SO$_4$. Glucose gives a black mass, while KBr(s) gives brown fumes.

OR, Add acidified AgNO$_3$(aqq). KBr(aq) gives a pale yellow precipitate.

OR, Treat compounds with Tollens' reagent. Only glucose gives a silver mirror.

ASL05(I)_06

(a) $$\text{mole ratio of } C : H : O = \frac{81.8}{12} : \frac{6.1}{1} : \frac{12.1}{16} = 6.81 : 6.1 : 0.756 = 9 : 8 : 1$$ [1]

empirical formula is C$_9$H$_8$O

molecular formula is (C$_9$H$_8$O)$_n$ [1]

$130 < n(9 \times 12 + 8 + 16) < 140$

$\therefore n = 1$

molecular formula is C$_9$H$_8$O [1]

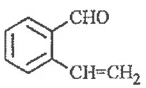
(b) A reacts with Tollens' reagent. ∴ A possess an aldehyde functionality / the –CHO group. [1]

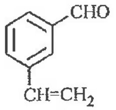
A is an aromatic compound with molecular formula C$_9$H$_8$O. it has a double-bond equivalence of 6. [1]

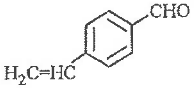
A is likely to possess a C=C bond or alicyclic structure. [1]

(c) Possible types of isomerism: Position isomerism: [1]

Structure (Any TWO of the following)



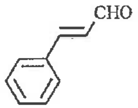


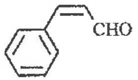


[1]

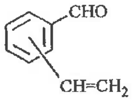
OR, Geometrical isomers:

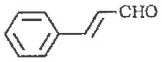
Structure

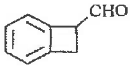




OR, Structural isomerism (Any TWO of the following)







AL05(II)_01

A is $AgNO_3(aq)$ [1]

C and F are alkali because $AgNO_3(aq)$ reacts with alkalis to give brown $Ag_2O(s)$. [1]

$2Ag^+(aq) + 2OH^-(aq) \longrightarrow Ag_2O(s) + H_2O(l)$

C is NaOH(aq), while F is $NH_3(aq)$. [1]

$Ag_2O(s)$ reacts with excess $NH_3(aq)$ to give $[Ag(NH_3)_2]^+(aq)$.

$Ag_2O(s) + H_2O(l) + 4NH_3(aq) \longrightarrow 2[Ag(NH_3)_2]^+(aq) + 2OH^-(aq)$

B is $H_2SO_4(aq)$ as it undergoes neutralization with C. (Heat is evolved) [1]

$H_2SO_4(aq) + 2NaOH(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O(l)$

E is $BaCl_2(aq)$ as it reacts with $SO_4^{2-}(aq)$ ions (in B) to give a white precipitate. [1]

$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$

E also reacts with $AgNO_3(aq)$ to give a white precipitate AgCl(s) [1]

$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$

D is $Na_2S_2O_3(aq)$ because it reacts with acid (B) to give a pale yellow precipitate. [1]

$S_2O_3^{2-}(aq) + 2H^+(aq) \longrightarrow S(s) + SO_2(g) + H_2O(l)$

The six solutions are

A : $AgNO_3(aq)$ B : $H_2SO_4(aq)$ C : NaOH(aq) D : $Na_2S_2O_3(aq)$ E : $BaCl_2(aq)$ [1]

F : $NH_3(aq)$

AL07(I)_03

Place the chromatographic paper in the atmosphere of ammonia. [1]

$Fe^{3+}(aq)$ reacts with $OH^-(aq)$ to give brown $Fe(OH)_3(s)$ [1]

$Cu^{2+}(aq)$ reacts with $NH_3(aq)$ to give deep blue complex $[Cu(NH_3)_4]^{2+}(aq)$. [1]

AL08(I)_08

(a) Add Br_2/H_2O or Br_2/CCl_4 [1]

The presence of propenamide causes the reddish brown reagent to turn colorless. [1]

OR, Add $ICl/CHCl_3$

The presence of propenamide causes the reddish brown reagent to turn colorless. (accept other test for alkene)

(b) $Br_2 + CH_2{=}CHCONH_2 \longrightarrow CH_2BrCHBrCONH_2$ [1]

(c) Mass spectrometry [1]

Expected result: There are three peaks for the molecular-ion at m/z = 229, 231 and 233 respectively. The intensities of the three peaks should be in the ratio of 1 : 2 : 1. (relative abundance of the isotopes of bromine ^{79}Br and ^{81}Br is 1 : 1). [1]

(Also accept compare the fragmentation patterns of the derivative obtained with that of an authentic sample).

OR, NMR spectroscopy (1)

Run NMR spectrum of the derivative and that of an authentic sample of the derivative. Compare the two spectra. (1)

AL08(II)_07

Q is the compound with a fishy smell (foul smell) / Only **Q** is basic [1]

R is the only compound which is immiscible with water. [1]

Only **N** reacts with 2,4-dinitrophenylhydrazine to give a red precipitate. [1]

M is more readily oxidized by $Cr_2O_7^{2-} / H^+$ than **P**. [2]

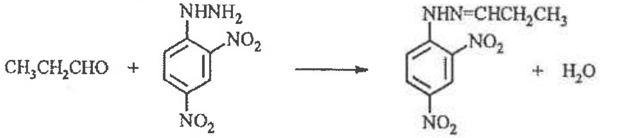
(or when **M** and **P** are treated with conc. $HCl/ZnCl_2$ (Lucas Reagent), **P** reacts more readily to give a cloudy mixture.)

(or when M and R are treated with I_2 in NaOH (iodoform test), only M give yellow precipitate.)

(award 1 mark for distinguishing one compound from the others.)

ASL10(I)_05

Orange / red precipitate [1]



[1]

AL11(I)_07a

(i) Treat the vapor with anhydrous $CoCl_2$ / dry cobalt(II) chloride paper. A change of color from blue to pink shows the presence of water. [½] [½]

OR, Treat the vapor with anhydrous $CuSO_4$. A change of color from white to blue shows the presence of water.

(ii) Weigh an empty crucible and its lid (m_1). [½]

Put a sample of the salt in the crucible and weigh the crucible, its content and the lid (m_2). [½]

Heat the crucible and its content, not completely covered by the lid, to allow water vapor to escape until the sample turns white. [½]

Allow the crucible and its content to cool in a desiccator and then weigh the crucible, its content and the lid.

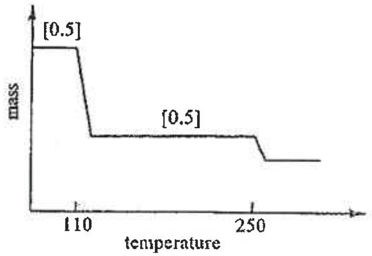
Repeat the heating and weighing processes until a constant mass (m_3) is reached. [½]

No. of molecules of water of crystallization

$$= \frac{(m_2 - m_3)}{(m_3 - m_1)} \times \frac{(63.5 + 32.1 + 16 \times 4)}{(2 \times 1 + 16)}$$ [½]

Should be equal to 5. [½]

(iii) [2]



(1 mark for showing two 'steps' in the curve; 1 mark for showing that the heights of two 'steps' are in 4 : 1 ratio.)

AL11(I)_07b

(i) Adding of dil. HCl(aq) to two solutions. The one gives white precipitate is $Pb^{2+}(aq)$, the one does not give white precipitate is $Ba^{2+}(aq)$. [1]

$Pb^{2+}(aq) + 2Cl^-(aq) \longrightarrow PbCl_2(s)$ [1]

OR Adding few drops of NaOH(aq) / $NH_3(aq)$ [not in excess] into the two solutions. The one gives white precipitate is $Pb^{2+}(aq)$, the one has no precipitate is $Ba^{2+}(aq)$.

$Pb^{2+}(aq) + 2OH^-(aq) \longrightarrow Pb(OH)_2(s)$

(ii) Adding of chlorine water into the two solutions. The one gives brown solution is $Br^-(aq)$, the one has no observable change is $Cl^-(aq)$. [1]

$Cl_2(aq) + 2Br^-(aq) \longrightarrow 2Cl^-(aq) + Br_2(aq)$ [1]

OR Adding acidified $AgNO_3(aq)$ into the two solutions. The one gives white precipitate is $Cl^-(aq)$, the one give pale yellow precipitate is $Br^-(aq)$.

$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$

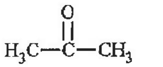
$Ag^+(aq) + Br^-(aq) \longrightarrow AgBr(s)$

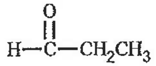
ASL12(II)_06 (modified)

(a) Both compounds contain C=O carbonyl group because they give positive result with 2,4-dinitrophenylhydrazine. [1]

A carbonyl group has a mass unit of 28. (58 – 28) = 30. These compounds can have 2 other C atoms. Their formula should be C_3H_6O. [1]

Possible structure


$H_3C-\overset{\overset{\displaystyle O}{||}}{C}-CH_3$


$H-\overset{\overset{\displaystyle O}{||}}{C}-CH_2CH_3$ [1]

(b) Reagents: $Cr_2O_7^{2-}(aq)$ / $H^+(aq)$ [1]

Observation: Only propanal will turn the color of the reaction mixture from orange to green. [1]

(Also accept Tollens' test; Fehling's reagent; iodoform reaction etc.)

(1 mark for reagents; 1 mark for observation)

AL13(I)_08b

(i) Identification of some metal and their ions, e.g. Na (golden yellow flame), K (lilac flame), Ca (brick red flame) etc. [1]

(ii) Confirmation of $SO_4^{2-}(aq)$ ions. [½]

$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$ [½]

(iii) Testing of iodine [½]

I_2 + starch $\longrightarrow$ blue complex [½]

DSE12_03a

(i) hydroxyl (group) / –OH / alcohol [1]

aldehyde (group)/ –CHO / aldehyde [1]

(ii) (1) Test for aldehyde (group) or ketone (group)/ carbonyl (group)/ aldehyde (group)and ketone (group). [1]

(2) 2,4-dinitrophenylhydrazine reacts with aldehyde or ketone to give yellow, orange or red precipitate. [1]

(iii) hydroxyl (group)/ –OH [1]

DSE14_03a

(i) Place HCl(g) near NH_3(g / conc.) [1]

Dense white fume is observed. [1]

OR Dissolve HCl(g) in deionized water.

+ Na_2CO_3 (s/aq) give a gas

+ $AgNO_3/H^+$ gives a white ppt.

OR HCl + Na_2CO_3(aq) gives a gas

HCl + $AgNO_3/H^+$ gives a white ppt

(ii) Add 2,4-dinitrophenylhydrazine [1]

Yellow / orange / red precipitate is formed. [1]

DSE15_03a

Addition of (acidified) silver nitrate solution (acidified by nitric acid). [1]

Pale yellow precipitate formed (which is insoluble in aqueous ammonia) [1]

[Add Cl_2(aq). Next, add an organic solvent. The solution turns brown. The organic solvent becomes orange/brown.]

DSE15_03b

(i) yellow / orange / red precipitate (solid/ppt) [1]

(ii) Add acidified $K_2Cr_2O_7$(aq). [1]

Only Y turns the solution from orange to green. [1]

OR Only Y turns MnO_4^-/H^+ from purple to colourless.

OR Only Y gives a silver mirror in Tollens' test.

OR Only X gives a yellow precipitate with I_2/NaOH(aq).

DSE16_03a

Add a few drops of HCl(aq) /a dilute acid / acid. [1]

Pale (yellowish-)green gas evolved / which turns (moist) blue litmus paper red and then bleaches it / gas evolved which turns colorless iodide solution brown / yellow / orange. / a yellow gas is evolved which turns blue litmus paper red and then bleaches it. [1]

WITHOUT the use of dilute acid

Reasonable test of the bleaching property with correct observation

e.g. use a red litmus paper;	red → (blue) → white (NOT colorless)
use a blue litmus paper;	blue → white (NOT colorless)
use a pH paper;	yellow → (green / blue) → white (NOT colorless)
use litmus solution;	purple → (blue) → colorless (NOT white) blue → colorless (NOT white)
colored flowers (petals);	decolorize

DSE17_03a

(i) Flame test(s) are carried out. [1]

Sodium ions give an intense golden yellow flame while potassium ions give a lilac flame. [1]

(ii) Add a piece of filter paper which is soaked with acidified $K_2Cr_2O_7$ to the gas, [1]

the paper turns from orange to green. [1]

OR Pass the gas to $Cr_2O_7^{2-}/H^+$ (or MnO_4^-/H^+).

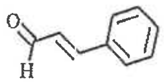
The solution turns from orange to green (or purple to colorless / pale pink) [No acidification: 0 mark]

OR It decolorizes petals temporarily.

OR It turns Br_2(aq) from brown / orange to colorless.

1 mark for correct reagent and 1 mark for correct observation

(iii) [1]



DSE18_03a

(i) calcium (ion) / Ca^{2+} [1]

(ii) Add $Ba(NO_3)_2$(aq) acidified with HNO_3(aq) to the sample, [1]

white precipitate forms for K_2SO_4(aq) whereas no precipitate will form for K_2SO_3(aq). [1]

[Accept other answers: 1 mark for the reagent and 1 mark for the observation]

Reagent	Observation
H^+(aq) / acid	Only SO_3^{2-} gives a gas, SO_2, with pungent smell
$Cr_2O_7^{2-}/H^+$(aq)	Only SO_3^{2-} turns the solution from orange to green
MnO_4^-/H^+(aq)	Only SO_3^{2-} turns the solution from purple to colorless
I_2(aq)	Only SO_3^{2-} turns the solution from brown to colorless

Not accept Br_2 / Br_2(l)

DSE19_03a

3. (a) (i) • IR Peak at 2070 – 2250 cm^{-1} corresponds to C≡C. 1

• Relative molecular mass of 40.0 confirms it to be HC≡CCH_3. 1

(ii) immiscible with water / low boiling point / easily evaporate 1

(iii) • Heat with Tollen's reagent. 1

• Only **A** gives silver mirror. 1

DSE20_03a

3. (a) (i) Heat the solid samples in a test tube and place a piece of anhydrous/dry cobalt chloride paper near the mouth of the tube. 1
The anhydrous/dry cobalt chloride paper turns from blue to pink. The solid is $Na_2CO_3 \bullet 10H_2O(s)$. The colour of cobalt chloride paper does not change for $Na_2CO_3(s)$. 1
(A comparative sense)
(OR
Heat both samples.
Condensed liquid can only be found in $Na_2CO_3 \bullet 10H_2O(s)$.
OR
Heat both samples.
Only $Na_2CO_3 \bullet 10H_2O(s)$ will have condensed liquid that can turn anhydrous/dry copper(II) sulphate from white to blue.)
(A comparative sense)

(ii) From blue to colourless 1

(iii) Hex-1-ene turns Br_2 (in organic solvent/aq) (not accept $Br_2(l)$) (1)
from reddish-brown to colourless but hexanal does not. (1)
OR
Warm hexanal with Tollen's reagent. 1
It gives a silver mirror but hex-1-ene does not. 1
(A comparative sense)
(1 mark for the reagent and 1 mark for observation)
(Accept other possible chemical tests with comparative sense.
Hexanal :
 $Cr_2O_7^{2-}(aq)/H^+(aq)$: from orange to green but hex-1-ene does not
 2,4-dinitrophenylhydrazine: a yellow / red / orange precipitate but hex-1-ene does not)
(Not accept:
Hex-1-ene :
 $MnO_4^-(aq)/H^+(aq)$: from purple to colourless)

DSE20_03c i

3. (c) (i) (1) orange to green 1
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ 1

(2) Driver **B** has a higher ethanol intake because the breath can also change the colour of the gel in position **c** while Driver **A** cannot. 1
(A comparative sense and similar meaning)

(3) (Exhale the) same amount / volume / strength of breath (into the tube). 1

(ii) No. of mole of ethanol = $0.025 \times 4.38 \times 10^{-3} \times 3 = 0.0003285$ mol (0.00033 / 0.000329) 1*
Mass of the ethanol = 0.0003285×46 (× 46) 1*
$= 0.01511$ g = 15.11 mg
The mass of ethanol in 100 cm^3 of serum sample = 15.11 mg ÷ 10 × 100 (÷ 10 × 100) 1*
= 151.1 mg
(The mass is) 151.1 mg (which exceeds 55 mg. The driver would be found) guilty. 1
(Range of answer: 150 – 152, max. 3 dec. places)

Separation and Purification Methods

AL97(I)_08

You are provided with a mixture of two liquids, hexan-1-amine (**U**) and ethyl ethanoate (**W**). Outline an experimental procedure, based on a solvent extraction process, to enable **U** to be separated from **W**.

(3 marks)

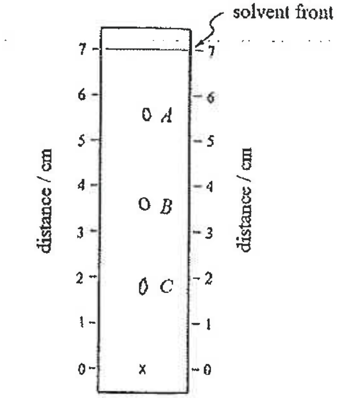
AL98(I)_08

You are provided with a mixture of tow liquids, heptanoic acid and hexan-3-one. Outline an experimental procedure, based on a solvent extraction process, to isolate pure heptanoic acid in good yield.

(3 marks)

AL99(I)_02c

A mixture of amino acids, *A*, *B* and *C*, was separated by paper chromatography using an appropriate solvent. The chromatogram obtained is shown below:



(x is the starting point of the mixture.)

(i) Briefly describe the principle underlying the separation of *A*, *B* and *C* by paper chromatography.

(2 marks)

(ii) The amino acid spots are invisible to naked eyes. Suggest how to make them visible.

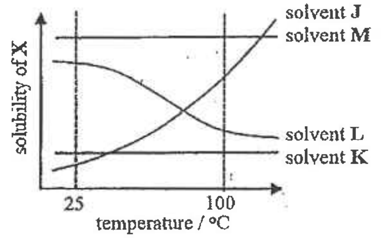
(1 mark)

(iii) Calculate the R_f value for *A*.

(1 mark)

AL01(I)_08a

The graph shows the solubility curves of a solid organic compound **X** in four mutually miscible solvents **J**, **K**, **L** and **M**.



(i) (I) Which solvent among **J**, **K**, **L** and **M** is the best for the recrystallization of **X**?

(1 mark)

(II) You are provided with a sample of **X** contaminated with some colored impurities. Outline the procedure to purity **X** by recrystallization.

(3 marks)

(ii) Decide which two of these solvents form the best solvent system for the recrystallization of X at 25°C.

(1 mark)

AL01(I)_08b

In an experiment to prepare propanal from propan-1-ol,

$$CH_3CH_2CH_2OH \xrightarrow[\text{heat}]{Cr_2O_7^{2-}/H^+} CH_3CH_2CHO$$

a side-product N ($C_6H_{12}O_2$) was formed

(i) What is N? Suggest how N is formed.

(2 marks)

(ii) Suggest one method to separate propanal from a mixture of propanal and N.

(1 mark)

(iii) Suggest two methods to confirm the identity of propanal.

(2 marks)

ASL01(II)_11

2-chloro-2-methylpropane can be prepared by reacting 2-methylpropan-2-ol with concentrated hydrochloric acid.

$$(CH_3)_3COH + HCl \longrightarrow (CH_3)_3CCl + H_2O$$

This preparation consists of four stages as outlined below:

Stage 1: Add concentrated hydrochloric acid slowly into a vessel containing 2-methylpropan-2-ol while shaking until the acid is in excess.

Stage 2: Allow the mixture to settle into two layers. Separate the organic layer and add to it sodium hydrogencarbonate solution to neutralize the excess acid.

Stage 3: Transfer the organic layer obtained at the end of *Stage 2* into a conical flask. Add enough anhydrous sodium sulphate(VI) and swirl the flask.

Stage 4: Filter off sodium sulphate(VI) from the mixture obtained in *Stage 3*. Distil the filtrate and collect 2-chloro-2-methylpropane in the temperature range from 47°C to 53°C.

(a) A turbid mixture is formed in *Stage 1*. Explain.

(2 marks)

(b) How can one know that the excess acid has been neutralized in *Stage 2*?

(1 mark)

(c) Why is anhydrous sodium sulphate(VI) used in *Stage 3*? State the expected observation at the end of this stage.

(2 marks)

(d) Draw a labelled diagram for the experimental set-up that is used in the distillation process in *Stage 4*.

(2 marks)

(e) The boiling point of 2-methylpropan-2-ol is 82°C. Explain why the boiling point of 2-methylpropan-2-ol is higher than that of 2-chloro-2-methylpropane.

(1 mark)

AL02(I)_08a

In an attempt to prepare 1-methylcyclopenten e, 1-methylcyclopentanol was allowed to react with phosphoric(V) acid. The reaction mixture was then subjected to simple distillation. a side-product

(i) Draw a labelled diagram to show the set-up of apparatus used in a simple distillation.

(2 marks)

(ii) Suggest a chemical test, giving the expected observation, to show the presence of an alkene in the distillate.

(2 marks)

(iii) The distillate was known to contain a small amount of unreacted 1-methylcyclopentanol. Suggest a method to separate it from the desirable product.

(1 mark)

(iv) Is 1-methylcyclopentene the only compound obtained after the suggested separation method in (iii)? Explain.

(1 mark)

AL03(I)_08b

The following compounds can be used as drying agents:

$Na_2SO_4(s)$, $NaOH(s)$, $CaCl_2(s)$ and $P_2O_5(s)$

Choose, from the above, one compound which is most suitable and effective

(i) for drying a solution of $C_6H_5CO_2H$ in $CHCl_3$.

(1 mark)

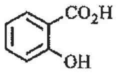
(ii) for drying a moist solid sample of $C_6H_5CO_2H$.

(1 mark)

AL03(II)_05

A student carried out an experiment to extract 4-nitrophenylamine and 2-hydroxylbenzoic acid from a solution of the two compounds in ethoxyethane. The solution contained 1.5 g each of the compounds in 20 cm^3 of ethoxyethane.

4-nitrophenylamine



2-hydroxybenzoic acid

The student shook the solution with 12 cm^3 of 0.50 M $NaHCO_3(aq)$ in a separating funnel. The mixture in the separating funnel was allowed to settle, and the aqueous layer was then separated from the organic layer. Evaporation of the aqueous layer gave a solid residue, which was water-soluble and had a melting point higher than 200 °C. Evaporation of the organic layer gave another solid residue, which melted over a wide temperature range of 140 °C to 160 °C.

(a) Why was $NaHCO_3(aq)$ used in the extraction?

(1 mark)

(b) While the student was shaking the separating funnel, the stopper of the funnel popped out, spilling part of the mixture on the bench. With the help of equation(s), explain why this happens.

(2 marks)

(c) Was the solid residue obtained from the organic layer a pure compound? Support your answer by stoichiometric calculation.

(3 marks)

(d) State TWO reasons why ethoxyethane is commonly used to extract organic compounds from an aqueous solution.

(2 marks)

(e) State ONE safety precaution necessary in the evaporation of ethoxyethane.

(1 mark)

AL04(I)_08

(a) A sample of N-phenylethanamide is contaminated with some colored impurities. Outline the procedures for the purification of this sample by recrystallization from water.

(3 marks)

(b) Draw a labelled diagram for the assembly of apparatus used in simple distillation.

(2 marks)

AL04 (II)_03d

Chile saltpetre is a mineral with a high sodium nitrate(V) content.

(ii) Chile saltpetre also contains a small amount of sodium iodate(V), which is a source of iodine.

(I) Suggest one way to isolate $NaNO_3(s)$ from an aqueous solution of Chile saltpetre.

(1 mark)

(II) After removing $NaNO_3(s)$ from an aqueous solution of Chile saltpetre, the $NaIO_3(aq)$ that remains is divided into two parts. One part is treated with $NaHSO_3(aq)$ to reduce $NaIO_3(aq)$ to $I^-(aq)$. The resultant mixture is then mixed with the unreacted part of $NaIO_3(aq)$ to give iodine.

Use equations to describe the conversion of $NaIO_3$ to I_2 in the above process.

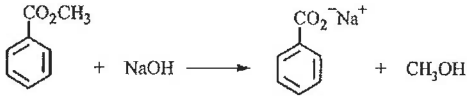
(2 marks)

(III) Suggest one method that can be used to purify a sample of sodium iodine.

(1 mark)

ASL04(II)_10

Preparation of benzoic acid ($C_6H_5CO_2H$) involves heating methyl benzoate ($C_6H_5CO_2CH_3$) with excess sodium hydroxide solution under reflux for some time. The resultant mixture contains sodium benzoate and methanol.



(a) Draw a labelled diagram for the set-up used for heating methyl benzoate with sodium hydroxide solution under reflux.

(2 marks)

(b) Suggest how a crude sample of benzoic acid can be obtained from the resultant mixture.

(2 marks)

(c) The crude sample of benzoic acid can be purified by recrystallization from hot water. Outline the procedures in the recrystallization process.

(2 marks)

(d) In an experiment, 3.0 g of methyl benzoate gave 1.9 g of benzoic acid. Calculate the percentage yield of benzoic acid.

(2 marks)

AL05(I)_07a

(i) Draw a labelled diagram for the assembly of apparatus that you would use to determine the boiling point of propan-2-ol.

(2 marks)

(ii) Suggest one hazard warning label which should be displayed on a bottle of proan-2-ol.

(1 mark)

AL05(I)_08c

Consider the conversion of 4-methylphenylamine to 4-methylphenol:

4-methylphenylamine 4-methylphenol

(ii) The identity of the 4-methylphenol obtained can be confirmed from the melting point of its solid derivative.
With the help of an equation, suggest a derivative of 4-methylphenol that would be suitable for this purpose.
(2 marks)

(iii) Suggest a method to purify the derivative in (ii) for melting point determination.
(1 mark)

AL06(I)_08b

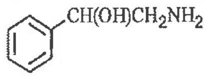
State a possible consequence from each of the following poor laboratory techniques:

(i) draining the lower layer from a separating funnel without removing the stopper
(1 mark)

(ii) determining the melting point of a compound without completely removing the solvent after recrystallization.
(1 mark)

AL06(II)_05b

Compound **B** is a strong stimulant. Its structural formula is as follows:

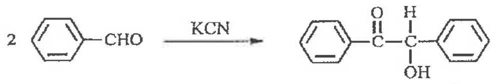


(i) It is known that among the two stereoisomers, only **B** has stimulant activity while the other one does not. Why?
(1 mark)

(ii) A person is suspected to have taken stimulant **B**. A urine sample of the person is sent for analysis. Suggest a method to establish whether **B** is present in the urine sample.
(2 marks)

AL07(I)_08

14.6 g of benzoin was obtained by heating 15.9 g of benzaldehyde with potassium cyanide in a solvent-free condition.



benzoin (m.p. 137 °C)

(a) Calculate the percentage yield of benzoin from benzaldehyde.
(2 marks)

(b) What is the function of potassium cyanide in this conversion?
(1 mark)

(c) Is this conversion an example of green chemistry? Explain.
(1 mark)

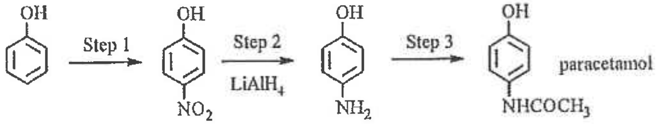
(d) Devise an experimental procedure to remove potassium cyanide from the crude product.
(2 marks)

(e) The benzoin obtained can be purified by recrystallization. Suggest three criteria for an appropriate solvent for the recrystallization.
(3 marks)

(f) Cyanide waste is usually treated with oxidizing agents. Explain whether acidified $KMnO_4(aq)$ is suitable for such a purpose.
(1 mark)

AL07(II)_07

Paracetamol is an over-the-counter analgesic drug. It can be synthesized from phenol in three separate steps as shown below:



(a) Consider Step 1.

(i) Give the reagent(s) used and the reaction conditions. (Out-of-syllabus)
(1 mark)

(ii) The reaction also gives 2-nitrophenol. The 4-nitrophenol formed can be separated from 2-nitrophenol by chromatography using powdered silica as the stationary phase, and a mixture of ethyl ethanoate and cyclohexane as the mobile phase.
Which of the two compounds, 2-nitophenol or 4-nitrophenol, would move faster in this chromatography? Explain. (Partial out-of-syllabus)
(3 marks)

(b) Name the type of reaction for the transformation in Step 2.
(1 mark)

(c) For Step 3, give the reagent(s) used and the reaction conditions.

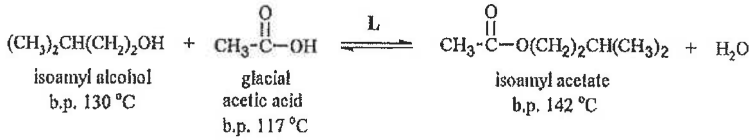
(1 mark)

(d) Outline the recrystallization procedure for the purification of a crude product of paracetamol by water.

(3 marks)

ASL09(I)_04

3-Methyl-1-butyl ethanoate, commonly known as isoamyl acetate, is a naturally occurring compound having a distinctive pleasant banana odor and is used in food flavoring. In an experiment to prepare the compound, 5.0 cm^3 of isoamyl alcohol is allowed to react with 15.0 cm^3 of glacial acetic acid in the presence of a reagent L.



$$(CH_3)_2CH(CH_2)_2OH + CH_3\text{-}\overset{\overset{O}{\parallel}}{C}\text{—}OH \overset{L}{\rightleftharpoons} CH_3\text{-}\overset{\overset{O}{\parallel}}{C}\text{—}O(CH_2)_2CH(CH_3)_2 + H_2O$$

(a) Suggest what reagent L may be and give the reaction conditions for this preparation.

(1 mark)

(b) Calculate the mole ratio of isoamyl alcohol to glacial acetic acid used in this preparation. (Given: density of isoamyl alcohol = 0.81 g cm^{-3}; density of glacial acetic acid = 1.05 g cm^{-3})

(2 marks)

(c) Draw a labelled diagram of the assembly of apparatus used in this preparation.

(2 marks)

(d) What are the major compounds present in the resulting mixture at the end of this preparation?

(2 marks)

(e) Outline the procedure to isolate isoamyl acetate from the resulting mixture. (It is known that isoamyl acetate cannot be effectively separated from the resulting mixture by fractional distillation.)

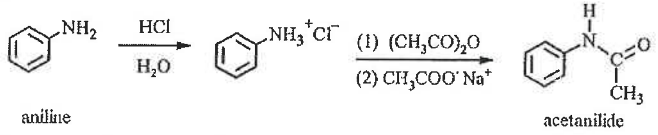
(2 marks)

(f) Suggest why isoamyl alcohol is NOT used in excess in this preparation.

(1 mark)

ASL10(I)_10

Acetanilide (N-phenylethanamide) is a white solid. It can be synthesized from aniline (phenylamine) according to the reaction scheme:



(a) The crude product from the above synthesis is collected by suction filtration. Draw a labelled diagram of the assembly of apparatus used.

(2 marks)

(b) The crude product appears yellow due to the presence of impurities. Outline the experimental procedure for the purification of the crude product by recrystallization from an ethanol-water mixture.

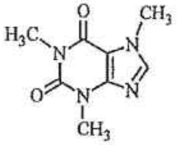
(3 marks)

(c) Suggest a method to verify or not the recrystallized sample of acetanilide is pure.

(1 mark)

ASL10(II)_06

Caffeine is a component of many over-the-counter analgesics.

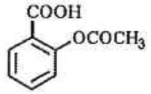


caffeine

(a) With reference to its structure, explain why caffeine is basic.

(2 marks)

(b) A brand of analgesic tablets contains aspirin, caffeine and a binder. The binder is insoluble in aqueous acids or alkalis, and in common organic solvents.



aspirin

Outline an experimental procedure to isolate caffeine and aspirin separately from the tablets.

(4 marks)

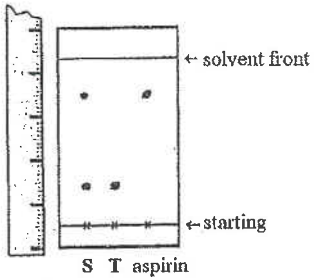
AL12 (I)_07

Outline how you would separate NH$_4$Cl(s), NaCl(s) and PbCl$_2$(s) from a mixture of the three compounds.

(3 marks)

AL12 (I)_08

An aspirin sample S was contaminated with an organic base T. A thin layer chromatography with silica as the stationary phase and ethyl ethanoate as the mobile phase was conducted to analyze S. the result obtained is shown below:



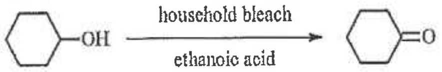
(a) (i) Calculate the R_f value of aspirin. (1 mark)

(ii) Explain why aspirin and T have different R_f values. (1 mark)

(b) Suggest how aspirin can be isolated from S without using chromatography. (2 marks)

ASL13(I)_09 (modified)

In an experiment to prepare cyclohexanone from cyclohexanol, a household bleach, containing 5.25% of sodium chlorate(I) by mass, was used as the oxidizing agent.



Density:	0.948 g cm^{-3}	0.947 g cm^{-3}
Solubility in water:	3.6 g / 100 cm^3	Very slightly soluble
Melting point:	25 °C	−16 °C
Boiling point:	160 °C	156 °C

5.0 cm^3 of cyclohexanol and 3 cm^3 of ethanoic acid were placed in a 250 cm^3 conical flask. A 25 cm^3 portion of the household bleach was added to the conical flask with vigorous stirring. Then additional 25 cm^3 portions of bleach were successively added into the reaction mixture until all cyclohexanol had reacted.

(a) (i) Assuming that the density of the household bleach is 1.0 g cm^{-3}, calculate the molarity of NaClO in the bleach used.
(Formula mass of NaClO = 74.5) (1 mark)

(ii) Given that the mole ratio between cyclohexanol and NaClO is 1 : 1, calculate the minimum number of 25 cm^3 portions of household bleach required for the complete reaction of cyclohexanol.
(Relative molecular mass of cyclohexanol = 100.0) (2 marks)

(b) What would be observed in the reaction mixture with the formation of cyclohexanone? (1 mark)

(c) Suggest how chromatography can be used to show that all cyclohexanol has reacted. (1 mark)

(d) You are provided with $Na_2S_2O_3$(aq) and $NaHCO_3$(aq). Outline the procedure for isolating cyclohexanone from the reaction mixture, and explain why these two chemicals are used. (3 marks)

(e) Draw the experimental set-up for the purification of the cyclohexanone isolated in (d). (2 marks)

DSE12PP_03a

A colorless compound X ($C_9H_8O_2$) is obtainable from cinnamon. X has a melting point of 134 °C and is insoluble in water.

An experiment to extract X from an impure sample, which contains non-polar organic impurities, involves the following five steps:

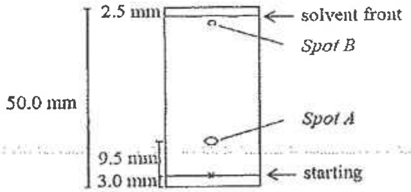
Step 1:	Dissolve the sample in excess NaOH(aq).
Step 2:	Shake the solution from Step 1 with hexane and discard the organic layer.
Step 3:	Add HCl(aq) to the aqueous layer obtained until a white precipitate forms and the solution becomes acidic.
Step 4:	Collect the white precipitate by filtration.
Step 5:	Using ethanol as solvent, recrystallize the precipitate collected to obtain X.

(i) From the above experimental steps, suggest ONE functional group present in X. (1 mark)

(ii) Name the apparatus used in Step 2. (1 mark)

(iii) Briefly explain the purpose of carrying out Steps 1, 2 and 3 respectively. (3 marks)

(v) Another sample of X is contaminated with a colorless organic compound. The sample is analyzed by thin-layer chromatography (TLC), and the result is shown below:



(1) Suggest ONE method that can be used to make the two spots on the chromatographic plate become visible.

(1 mark)

(2) Given that *Spot A* corresponds to X, calculate the R_f of X.

(1 mark)

(3) Based on the TLC results, suggest ONE method to separate X from the contaminated sample.

(1 mark)

DSE13_03a

Outline how hex-1-ene can be obtained from a mixture of hex-1-ene, octane and water by physical methods.

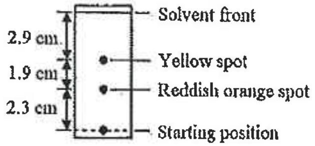
(Boiling points: hex-1-ene = 63°C, octane = 125°C, water = 100°C)

(4 mark)

DSE13_03c

The main pigments in a certain brand of tomato paste are lycopene (reddish orange) and β-carotene (yellow). In order to isolate lycopene from the tomato paste, and experiment involving solvent extraction, thin-layer chromatography (TLC) and column chromatography was performed.

(i) The result of TLC is shown below:



Calculate the R_f value for the lycopene spot.

(1 mark)

(ii) With reference to the result of TLC, explain whether the first-collected colored fraction in the column chromatography is lycopene or β-carotene, if the same stationary phase and mobile phase are used.

(1 mark)

DSE14_03a

Which of the following chemicals is most suitable for drying ethyl ethanoate?

Anhydrous magnesium sulphate, concentrated sulphuric acid, solid sodium hydroxide.

(1 mark)

DSE14_03c

Under room temperature, T ($C_xH_yO_z$) is a colorless oily liquid and is immiscible with water. Moreover, T does not react with $NaHCO_3(aq)$.

(i) A sample of T contains an organic acid as impurity. Outline the experimental steps for purifying the sample by using $NaHCO_3(aq)$ and pentane.

(2 marks)

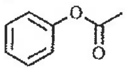
DSE15_03a

Suggest how copper powder can be obtained from a mixture of copper powder and iron(III) oxide by chemical method.

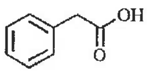
(2 marks)

DSE16_03c

X and Y are isomeric compounds with their structures shown below:



X



Y

(ii) The melting point of X is 50 °C while that of Y is 77 °C. Both of them are insoluble in water but soluble in dichloromethane. When treated with dilute $Na_2CO_3(aq)$, no reaction occurs for X but reaction occurs for Y to form a soluble salt.

(1) You are provided with dilute $Na_2CO_3(aq)$ and dilute $H_2SO_4(aq)$. Outline an experimental procedure, based on solvent extraction, to separate solid Y from a solution of X and Y in dichloromethane.

(4 marks)

(2) Suggest how you can identify that the solid obtained in (1) is pure compound Y.

(1 mark)

DSE17_03c

Many plants contain useful organic compounds which can be obtained by extraction using suitable solvents.

(i) The leaf of a certain plant contains a useful organic compound S. S can dissolve gradually in a warm organic solvent, and can be extracted from the leaves by using this solvent.

(1) 'Heating under reflux' is a method commonly used to carry out this kind of extraction. State the advantage of this method.

(1 mark)

(2) After extraction, the solvent can be removed from the extract by simple distillation. Draw a labelled diagram for the set-up required for this simple distillation.

(2 marks)

(3) S obtained from the extraction may contain other organic impurities. Suggest a method for separating S from these impurities.

(1 mark)

DSE18_03a

(iii) What is meant by the 'R_f value' of a substance in a paper chromatogram?

(2 marks)

DSE18_03c

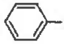
A liquid mixture consists of two organic compounds **X** and **Y**:

	X	Y
Molecular formula	C_4H_6O	C_4H_8O
Boiling point / °C	81.4	79.6

(i) Explain why fractional distillation is NOT a suitable method to separate **X** from the mixture.

(1 mark)

DSE19_03c i

3. (c) Chlorine reacted with ethylbenzene ($-CH_2CH_3$) under sunlight to give a mixture of different chlorinated compounds.

(i) Thin layer chromatography (TLC) was used to separate a small amount of the mixture.

(1) Explain briefly why chromatography can be used to separate a mixture.

(2) Based on the result in TLC, suggest a method to separate a large amount of the mixture.

(3 marks)

DSE20_03b i ii iii

(b) In order to determine the sodium contents (existing as NaCl) in a bacon sample, its Cl^- contents should first be found. 2.0 g of the bacon sample was added to 2.50 cm^3 of 1.0 M $AgNO_3$(aq). After that, excess dilute HNO_3(aq) was added to the mixture obtained. The AgCl(s) formed was then removed by filtration. The excess $AgNO_3$(aq) remaining in the filtrate was then titrated with 0.10 M KSCN(aq) to give AgSCN(s) in the presence of a suitable indicator until the end point was reached. All steps were repeated several times and the mean volume of the KSCN(aq) used to reach the end point was 9.42 cm^3.

(i) Why was excess dilute HNO_3(aq) added to the mixture ?

(1 mark)

(ii) Draw a diagram for the set-up to be used in the titration, labelling all apparatus and reagents.

(2 marks)

(iii) Assuming that all Cl^- comes from NaCl in the bacon sample, calculate the percentage by mass of sodium in the bacon sample.
(Relative atomic masses: Na = 23.0, Cl = 35.5, Ag = 107.9)

(4 marks)

Marking Scheme

AL97(I)_08

Add ether and dil HCl [1]

Shake in a separating funnel [½]

Ether layer will contain $CH_3CO_2C_2H_5$ [½]

Basify the aqueous layer with excess NaOH(aq) [½]

and then extract with ether. The ether layer will contain $CH_3(CH_2)_5NH_2$. [½]

AL98(I)_08

Add ether and dilute $NaHCO_3$(aq) / Na_2CO_3(aq). [1]

Shake in a separating funnel. [½]

Ether layer contains hexan-3-one; aqueous layer contains $CH_3(CH_2)_5COONa$.

Add dilute HCl to aqueous layer generate $CH_3(CH_2)_5COOH$. [½]

Extract with ether. [½]

Distill ether to obtain heptanoic acid. [½]

AL99(I)_02c

(i) There is a thin film of water on the chromatography paper. [½]

The amino acids distribute themselves between the stationary phase (water on the paper) and the moving phase (the solvent / eluent) [1]

A has a highest solubility in the moving phase. ∴ Its motion is fastest. [½]

OR, C has the lowest solubility in the moving phase. ∴ Its motion is slowest.

(ii) Spray chromatography paper with ninhydrin solution which reacts with amino acids to give purple-colored compounds. [1]

(Also accept using UV radiation / iodine vapor to detect the amino acid spots.)

(iii) $R_f = \frac{5.6}{7.0} = 0.8 \quad (Range: 0.77 \text{ to } 0.83)$ [1]

AL01(I)_08a

(i) (I) J [1]

(II) Add warm solvent J to X until X just dissolves. [½]

Heat with activated charcoal to remove colored impurities [1]

Filter when hot to remove charcoal particles [½]

Allow solution to cool to room temperature / scratch filtrate in the flask with a spatula. [½]

Collect X by filtration [½]

(ii) J and M [1]

AL01(I)_08b

(i) propyl propanoate / $CH_3CH_2COOCH_2CH_2CH_3$ [1]

Some propan-1-ol was oxidized to propanoic acid which reacts with excess propan-1-ol to give the ester [1]

(ii) Fractional distillation / chromatography [1]

2022

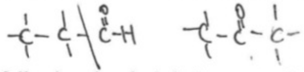
Section C Analytical Chemistry

Answer **ALL** parts of the question.

3. (a) Answer the following short questions :

(i) Suggest a chemical test to show how $SO_2(g)$ and $CO_2(g)$ can be distinguished.
(2 marks)

(ii) Illustrate how $CH_3CH_2CHO(l)$ and $CH_3COCH_3(l)$ can be distinguished from their respective mass spectra.



(2 marks)

(iii) Which one of the following chemicals is the most suitable for drying ethyl butanoate ?

concentrated sulphuric acid, solid sodium hydroxide, anhydrous sodium sulphate
(1 mark)

(b) A solid sample consists of a compound **Y** and a small amount of an impurity **Z**. The following steps were performed in an experiment to obtain pure **Y**(s) from this solid sample.
(Given : **Y** is more soluble in deionised water at 80 °C than at 25 °C.)

Step (1) : 1.40 g of this solid sample was added to 50 cm^3 of deionised water and heated to 80 °C.

Step (2) : Water-insoluble activated charcoal was then added to remove **Z**. The mixture obtained was filtered when it was still hot.

Step (3) : The hot filtrate obtained was allowed to cool slowly to 25 °C. **Y**(s) was formed.

Step (4) : The cooled mixture was filtered to collect **Y**(s). After washing and drying, 0.75 g of **Y**(s) was collected.

(i) It is given that no more than 3.04 g of **Y**(s) can dissolve in 100 cm^3 of deionised water at 80 °C. Show, by calculation, that all of **Y** in this solid sample should have dissolved in Step (1).
(1 mark)

(ii) Explain why the mixture was filtered in Step (2).
(1 mark)

(iii) Name the process of the formation of **Y**(s) in Step (3).
(1 mark)

(iv) Suggest one reason why the mass of **Y**(s) collected in Step (4) was smaller than the mass of **Y** in this solid sample.
(1 mark)

(v) **Y** and **Z** can be separated by chromatography. Thin layer chromatography (TLC) and column chromatography were performed separately with this solid sample using the same stationary phase and mobile phase.
(Given : R_f value of **Y** is greater than that of **Z**.)

(1) Sketch a labelled chromatogram of TLC to show the expected result.

(2) Explain whether the first-collected fraction in the column chromatography is **Y** or **Z**.
(3 marks)

(c) The major ingredient in a certain brand of iron supplement tablets is $FeSO_4$. Several pieces of these iron supplement tablets were dissolved in deionised water to obtain an aqueous solution **S**. The concentration of $Fe^{2+}(aq)$ ions in solution **S** was determined by using the following two methods :

(i) **Method (I) : using volumetric analysis**

The chemical equation for the reaction involved in the titration is as follows :

$$MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$$

25.00 cm^3 of solution **S** was acidified and then titrated with 0.0041 M $KMnO_4(aq)$. The mean volume of the $KMnO_4(aq)$ required to reach the end point was 32.35 cm^3.

(1) The colour of the reaction mixture changed from pale yellow to pale pink at the end point of the titration. Explain the colour change.

(2) Calculate the concentration of $Fe^{2+}(aq)$ ions in solution **S**.
(4 marks)

(ii) **Method (II) : using colorimetry**

$Fe^{2+}(aq)$ can completely react with a colourless organic reagent to form an orange-red species **W**(aq).
(Given : number of moles of $Fe^{2+}(aq)$ reacted : number of moles of **W**(aq) formed = 1 : 1)

Step (1) : Several standard $FeSO_4(aq)$ solutions of various concentrations were separately treated with the colourless organic reagent to form the corresponding orange-red solutions of **W**(aq).

Step (2) : The absorbances of these solutions of **W**(aq) were measured using a colorimeter and a calibration curve was plotted.

Step (3) : Solution **S** was diluted 100 times. A sample of this diluted solution was treated in the same way as described in Step (1) to give a solution **T** which contains **W**(aq).

Step (4) : The absorbance of solution **T** was measured.

(1) Sketch the calibration curve in Step (2) and label the axes. On this sketch, show how the concentration of **W**(aq) in solution **T** can be found.

(2) Hence, suggest how the concentration of $Fe^{2+}(aq)$ ions in solution **S** can be determined.
(4 marks)

DSE18_03a

(iii) What is meant by the 'R$_f$ value' of a substance in a paper chromatogram?

(2 marks)

DSE18_03c

A liquid mixture consists of two organic compounds X and Y:

	X	Y
Molecular formula	C_4H_6O	C_4H_8O
Boiling point / °C	81.4	79.6

(i) Explain why fractional distillation is NOT a suitable method to separate X from the mixture.

(1 mark)

DSE19_03c i

3. (c) Chlorine reacted with ethylbenzene ($-CH_2CH_3$) under sunlight to give a mixture of different chlorinated compounds.

(i) Thin layer chromatography (TLC) was used to separate a small amount of the mixture.

(1) Explain briefly why chromatography can be used to separate a mixture.

(2) Based on the result in TLC, suggest a method to separate a large amount of the mixture.

(3 marks)

DSE20_03b i ii iii

(b) In order to determine the sodium contents (existing as NaCl) in a bacon sample, its Cl^- contents should first be found. 2.0 g of the bacon sample was added to 2.50 cm^3 of 1.0 M $AgNO_3$(aq). After that, excess dilute HNO_3(aq) was added to the mixture obtained. The AgCl(s) formed was then removed by filtration. The excess $AgNO_3$(aq) remaining in the filtrate was then titrated with 0.10 M KSCN(aq) to give AgSCN(s) in the presence of a suitable indicator until the end point was reached. All steps were repeated several times and the mean volume of the KSCN(aq) used to reach the end point was 9.42 cm^3.

(i) Why was excess dilute HNO_3(aq) added to the mixture ?

(1 mark)

(ii) Draw a diagram for the set-up to be used in the filtration, labelling all apparatus and reagents.

(2 marks)

(iii) Assuming that all Cl^- comes from NaCl in the bacon sample, calculate the percentage by mass of sodium in the bacon sample.
(Relative atomic masses: Na = 23.0, Cl = 35.5, Ag = 107.9)

(4 marks)

Marking Scheme

AL97(I)_08

Add ether and dil HCl [1]

Shake in a separating funnel [½]

Ether layer will contain $CH_3CO_2C_2H_5$ [½]

Basify the aqueous layer with excess NaOH(aq) [½]

and then extract with ether. The ether layer will contain $CH_3(CH_2)_5NH_2$. [½]

AL98(I)_08

Add ether and dilute $NaHCO_3$(aq) / Na_2CO_3(aq). [1]

Shake in a separating funnel. [½]

Ether layer contains hexan-3-one; aqueous layer contains $CH_3(CH_2)_5COONa$.

Add dilute HCl to aqueous layer generate $CH_3(CH_2)_5COOH$. [½]

Extract with ether. [½]

Distill ether to obtain heptanoic acid. [½]

AL99(I)_02c

(i) There is a thin film of water on the chromatography paper. [½]

The amino acids distribute themselves between the stationary phase (water on the paper) and the moving phase (the solvent / eluent) [1]

A has a highest solubility in the moving phase. ∴ Its motion is fastest. [½]

OR, C has the lowest solubility in the moving phase. ∴ Its motion is slowest.

(ii) Spray chromatography paper with ninhydrin solution which reacts with amino acids to give purple-colored compounds. [1]

(Also accept using UV radiation / iodine vapor to detect the amino acid spots.)

(iii) $R_f = \frac{5.6}{7.0} = 0.8 \quad (Range: 0.77\ to\ 0.83)$ [1]

AL01(I)_08a

(i) (I) J [1]

(II) Add warm solvent J to X until X just dissolves. [½]

Heat with activated charcoal to remove colored impurities [1]

Filter when hot to remove charcoal particles [½]

Allow solution to cool to room temperature / scratch filtrate in the flask with a spatula. [½]

Collect X by filtration [½]

(ii) J and M [1]

AL01(I)_08b

(i) propyl propanoate / $CH_3CH_2COOCH_2CH_2CH_3$ [1]

Some propan-1-ol was oxidized to propanoic acid which reacts with excess propan-1-ol to give the ester [1]

(ii) Fractional distillation / chromatography [1]

(iii) Any TWO of the following: [2]

1. boiling point determination
2. Treat propanal with 2,4-dinitrophenylhydrazine / Brady's reagent, then determine the m.p. of the crystals formed.
3. Compare IR spectrum (finger print) of the propanal with that of an authentic sample.
4. Compare mass spectrum (finger print) of the propanal with that of an authentic sample.
5. Compare the H-NMR of the propanal with that of an authentic sample.

ASL01(II)_11

(a) Product $(CH_3)_3CCl$ is insoluble (immiscible) in the mixture of $(CH_3)_3COH$ and HCl(aq). [1]

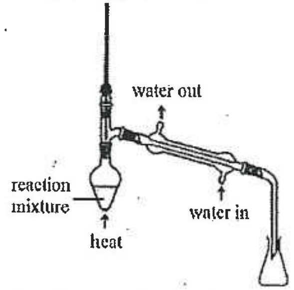
After shaking, an emission is formed which decrease the light transmittance. [1]

(b) Add $NaHCO_3$(aq) until no gas bubble formed. [1]

(c) To absorb water in the organic layer. [1]

A lump of Na_2SO_4 formed [1]

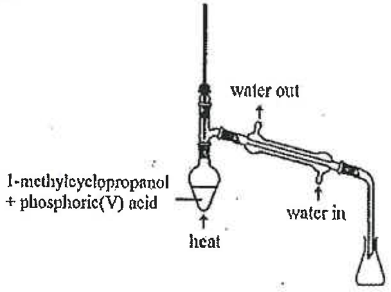
(d) [2]



(e) Both of them are simple molecule, while 2-methylpropan-2-ol molecules are held by strong hydrogen bond, while 2-chloro-2-methylpropane molecules are held by weak van der Waals' force. [1]

AL02(I)_08a

(i) [2]



(ii) Treat distillate with Br_2 in an appropriate solvent (e.g. CCl_4 or water). [1]

Observation: orange color of Br_2 solution changes to colorless. [1]

OR, Treat distillate with neutral $KMnO_4$

Observation: a brown precipitate is formed.

(iii), Fractional distillation [1]

(iv) No, the product contains another alkene such as [1]

OR, Gas chromatography

Yes, different compounds have different retention times.

∴ pure 1-methylcyclopentene can be isolated.

AL03(I)_08b

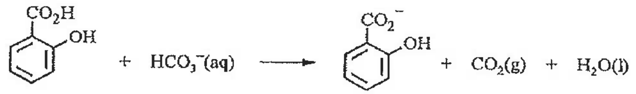
(i) $Na_2SO_4(s)$ [1]

(ii) $Na_2SO_4(s)$ / $CaCl_2(s)$ / $P_2O_5(s)$ [1]

AL03(II)_05

(a) To convert 2-hydroxybenzoic acid to the carboxylate salt which is soluble in water. [1]

(b) Carbon dioxide is formed.



[1]

Pressure therefore builds up inside the separating funnel. [1]

OR, Ethoxyethane is highly volatile. Vaporization of ethoxyethane leads to the building up of pressure in the funnel.

$CH_3CH_2OCH_2CH_3(l) \longrightarrow CH_3CH_2OCH_2CH_3(g)$

(c) no. of mole of 2-hydroxybenzoic acid $= \frac{1.5}{138} = 0.011$ [1]

no. of mole of $NaHCO_3 = 0.5 \times 12 \times 10^{-3} = 6 \times 10^{-3}$ [1]

no .of mole of 2-hydroxybenzoic acid > no. of moles of $NaHCO_3$

(0.011 – 0.006) = 0.005 mol of 2-hydroxybenzoic acid will remain in the organic layer. The residue is therefore not a pure compound. [1]

(d) Any TWO of the following: [2]

Ethoxyethane has a small dipole moment. It is a good solvent for most organic compounds.

Ethoxyethane is immiscible with water.

Ethoxyethane is volatile. It can easily be removed by distillation.

Ethoxyethane is chemically unreactive.

(e) Avoid naked flame / extraction should be carried out in a fume cupboard. [1]

AL04(I)_08

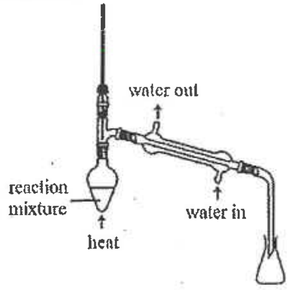
(a) Dissolve *N*-phenylethanamide in minimum volume of hot water. [1]

Heat the solution with activated charcoal. [1]

Filter the mixture while hot using a short stem funnel. [½]

Allow filtrate to cool to room temperature. Collect *N*-phenylethanamide crystal by filtration. [½]

(b) [2]



AL04 (II)_03d

(ii) (I) Fractional crystallization [1]

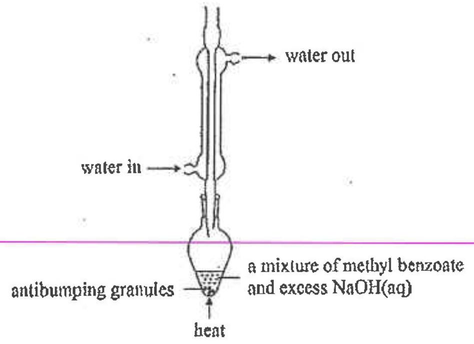
(II) $IO_3^- + 3HSO_3^- \longrightarrow I^- + 3SO_4^{2-} + 3H^+$ [1]

$5I^- + IO_3^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$ [1]

(III) Sublimation [1]

ASL04(II)_10

(a) [2]



(b) Add H_2SO_4(aq) and filter [1]

(c) Dissolve crude sample in minimum amount of hot water. [1]

Filter mixture while hot. [1]

Allow filtrate to cool and collect crystals by filtration. [1]

(d) no. of moles of methyl benzoate = $\frac{3.0}{136.0} = 0.022$ [½]

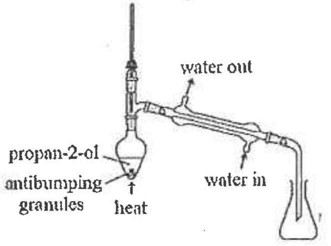
no. of moles of benzoic acid = $\frac{1.9}{122.0} = 0.0156$ [½]

% yield = $\frac{0.0156}{0.022} \times 100\% = 70.8\%$ [1]

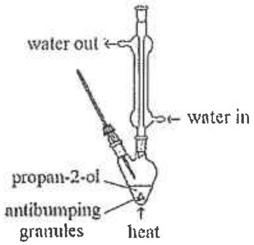
AL05(I)_07a

(i) [2]

simple distillation



heating under reflux

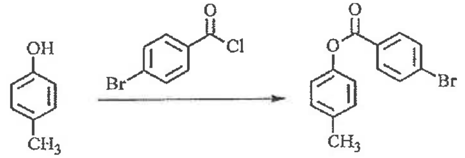


(1 M for a correct set-up and showing the bulb of the thermometer is slightly above the liquid level, 1 M for labels)

(ii) Flammable [1]

AL05(I)_08c

(ii) [2]



(iii) Recrystallization [1]

AL06(I)_08b

(i) Without releasing the pressure, the liquid in the separating funnel will not drain out of the funnel. [1]

(ii) The m.p. determined will be lower than the expected value. [1]

AL06(II)_05b

(i) The neuroreceptor is likely to be chiral. The reaction between compound **B** and the neuroreceptor is stereospecific. [1]

(ii) Conduct a chromatographic study. [1]

Compare the R_f value of the suspected stimulant with that of an authentic sample of **B**. [1]

AL07(I)_08

(a) $$\%\ \text{yield} = \frac{14.6}{15.9} \times 100\% = 91.8\%$$ [2]

(b) Catalyst [1]

(c) Open-end questions: [1]

Yes. Any ONE of the following:

1. The reaction does not involve the use of solvents
2. The reaction has a high atom economy
3. A catalyst is used.
4. No side product
5. One step reaction

No. The reaction requires the use of KCN which is highly toxic.

(d) Extract benzoin with an appropriate organic solvent, such as ethoxyethane. [1]

Wash the organic layer with water to remove KCN. [1]

(e) THREE of the following: [3]

1. Benzoin should have a high solubility in the solvent while the impurities should not.
2. The solubility of benzoin in the solvent should be high at elevated temperature but low at room temperature.
3. The solvent should be volatile.
4. The solvent should not react with benzoin.

(f) No. CN^- reacts with H^+ to give toxic HCN. [1]

AL07(II)_07

(a) (i) Diluted HNO_3; temperature <20 °C (stir reaction mixture for 2 hours). [1]

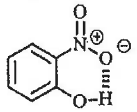
(accept conc. HNO_3 / mixture of conc. HNO_3 and conc. H_2SO_4)

(ii) 2-nitrophenol moves faster [1]

4-nitrophenol

4-nitrophenol has a large dipole moment and has a greater affinity for the polar silica / form intermolecular hydrogen bonds only, it has stronger attraction for silica. [1]

Intramolecular hydrogen bond occurs in 2-nitrophenol, but not in 4-nitrophenol. [½]



2-nitrophenol

2-nitrophenol is less polar and is more soluble in organic solvent (i.e. the mobile phase). [½]

(b) Reduction [1]

(c) CH_3COCl; at room temperature / warm. (Formation of amide) [1]

(d) Dissolve the sample in **minimum amount of hot water.** [1]

Filter, when hot, to remove any insoluble impurities. [1]

Allow the saturated solution to cool slowly and collect crystals of paracetamol by **filtration.** [1]

ASL09(I)_04

(a) Concentrated H_2SO_4 / conc. H_3PO_4 / P_4O_{10} [½]

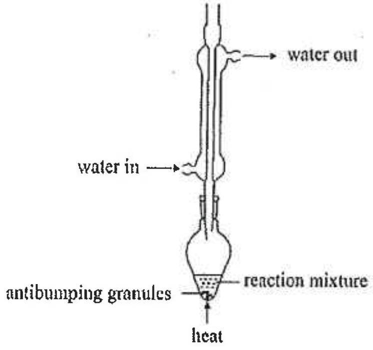
Reflux [½]

(b) $$\text{no. of moles of isoamyl alcohol} = \frac{5.0 \times 0.81}{88} = 0.046$$ [1]

$$\text{no. of moles of acetic acid} = \frac{15.0 \times 1.05}{60} = 0.26$$ [½]

Mole ratio of isoamyl alcohol : acetic acid = 1 : 5.7 [½]

(c) [2]



(d) Isoamyl acetate; acetic acid; water [1]

(e) **Shake mixture with $NaHCO_3(aq)$ in a separating funnel until no more gas is evolved.** [1] [½]

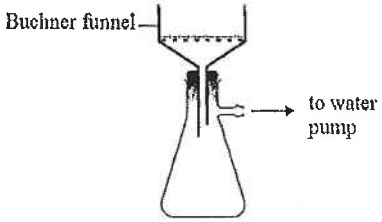
Extract isoamyl acetate from the organic layer using ethoxyethane (diethyl ether). [½]

Remove ethoxyethane (diethyl ether) by simple distillation. [1]

(f) It is difficult to remove isoamyl alcohol from isoamyl acetate as both substance do not react with alkali / their difference in boiling point is amll. [1]

ASL10(I)_10

(a) [1]



(b) Dissolve the crude product in minimum volume of hot ethanol-water mixture. [1]
Heat the solution with activated charcoal (to remove the color impurities). [1]
Filter the hot mixture (using a short-stem funnel). [½]
Allow the filtrate to cool to room temperature to obtain acetanilide. [½]

(c) Any ONE of the following: [1]
1. Determine the melting point of the product and compare the result with literature data.
2. Use the method of mixed melting point.

ASL10(II)_06

(a) Caffeine has amine / imine functional group. [1]
The lone pair on the N atoms can ready be donated to $H^+(aq)$ to form salt. [1]

(b) (use mortar and pestle to) grind analgesic tablets into fine powder. [½]
Add CH_2Cl_2 (any appropriate organic solvent) to dissolve caffeine and aspirin. [½]
Remove the (undissolved) binder by filtration. [½]
Add NaOH(aq) to filtrate. Aspirin will react to give a slat and dissolve in the aqueous layer. [½]
Using a separating funnel, separate the organic layer from the aqueous layer. (Dry the organic layer with $MgSO_4$(s).) [½]
Remove CH_2Cl_2 from organic layer by simple distillation to obtain caffeine. [½]
Add acid (HCl(aq)) dropwise to the aqueous layer (to pH~3) to regenerate aspirin. [½]
Cool the mixture and then filter to obtain aspirin. [½]
(1.5 marks for removing binder; 1.5 marks for isolation of the first ingredient; 1 mark for the second ingredient.)

AL12 I (7)

Heat the mixture. Only NH_4Cl(s) will sublime. [1]
It can be collected on a cold surface. [½]
Add water to the remaining solid mixture. [½]
$PbCl_2$(s) is insoluble. It can be collected by filtration. [½]
NaCl(s) can be obtained from its solution by filtration. [½]

OR, Add water to the mixture to dissolve NaCl(s) and NH_4Cl(s).
Remove undissolved $PbCl_2$(s) by filtration.
Separate NaCl(s) and NH_4Cl(s) from the solution by fractional crystallization / by (ion-exchange) chromatography.

AL12 (I)_08

(a) (i) $R_f = \frac{30}{38} = 0.79$ [1]

(ii) Any one of the following: [1]
- Aspirin is more soluble in ethyl ethanoate than T.
- T adsorbs more strongly to the stationary phase than aspirin does.
- Aspirin and T distribute differently between the stationary phase and the mobile phase.

(b) Dissolve the sample in an oragnic solvent such as CH_2Cl_2. [½]
Extract the solution obtained with an aqueous alkaline solution (e.g. NaOH / Na_2CO_3 / $NaHCO_3$). [½]
Collect the aqueous layer / decant the organic layer. [½]
Add HCl(aq) to the aqueous layer to regenerate aspirin and then collect the aspirin formed by filtration. [½]

OR, Dissolve the sample in an oragnic solvent such as CH_2Cl_2.
Extract the solution obtained with an aqueous acid (e.g. HCl).
Collect the organic layer / decant the aqueous layer.
Obtain aspirin from the organic layer by crystallization.

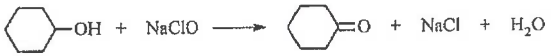
ASL13(I)_09

(a) (i)

$$\text{Molarity of NaClO} = \frac{\frac{5.25}{74.5} \times 1000}{100} = 0.705 \text{ M}$$

(acceptable range: 0.70 to 0.71 M) [1]

(ii)



[1]

$$\text{no. of moles of cyclohexanol used} = \frac{5.0 \times 0.948}{100} = 0.0474$$ [½]

no. of mole of NaClO in 25 cm^3 of bleach
$= 0.705 \times 25 \times 10^{-3} = 0.0177$ [½]

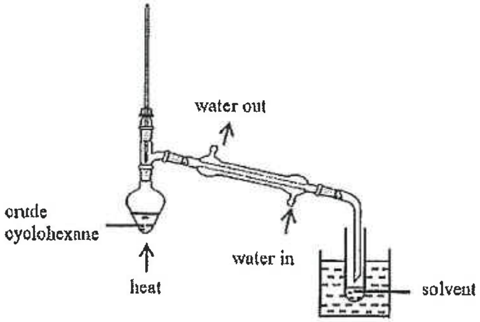
$$\text{Minimum no. of portions of bleach used} > \frac{0.0474}{0.0177} = 3$$ [½]

(b) Two immiscible layers / turbid / cloudy [1]

(c) Use TLC / GC / other appropriate chromatographic methods. Disappearance of the characteristic absorption peak for cyclohexanol indicates that all cyclohexanol has been reacted. [1]

(d) Using a separating funnel, separate the aqueous layer from the organic layer (upper layer). [½]
Shake the organic layer with $Na_2S_2O_3$(aq) and collect the upper / organic layer. [1]
$Na_2S_2O_3$(aq) reacts with excess NaClO(aq). [½]
Shake the collected organic layer with $NaHCO_3$(aq) until no more gas evolves from the mixture. [½]
$NaHCO_3$(aq) reacts with the CH_3COOH in the mixture. [½]

(e) Diagram (simple distillation / fractional distillation) [2]



DSE12PP_03a

(i) Carboxylic acid / carboxyl group (because X is soluble in NaOH(aq)) [1]
(Also accept phenol).

(ii) Separating funnel [1]

(iii) Step 1: Allow X to dissolve in NaOH(aq) to give (carboxylate) anions / a salt. [1]
Step 2: Allow the non-polar impurities to dissolve in hexane while the (carboxylate) anions / salt to stay in the aqueous layer. [1]
OR, Separate the non-polar impurities (in hexane) from the salt of X.
Step 3: Regenerate the (carboxylic) acid (which is insoluble in water) by adding acid. [1]

(v) (1) **Put the chromatographic plate into a jar that is saturated with iodine vapor.** The spot will appear brown. [1]
OR, **Irradiate the plate with UV.** The stationary phase is fluorescent while the two spots are not.

(2) $R_f = \dfrac{\text{distance travelled by X}}{\text{distance travelled by solvent}} = \dfrac{9.5}{(50 - 3 - 2.5)}$
$R_f = 0.21$ [1]

(3) Column chromatography (using the same moving phase and stationary phase) [1]

DSE13_03a

Use **separating funnel** to remove water (the lower liquid layer) from the mixture. [1]
The remaining upper / organic layer (remaining in the funnel) is hex-1-ene and octane. [1]
Carry out **fractional distillation / distillation** on the upper layer. [1]
The first distillated collected is hex-1-ene. The second distillate collected is octane. [1]

DSE13_03c

(i) $R_f = \dfrac{2.3}{2.3 + 1.9 + 2.9} = \dfrac{2.3}{7.1} = 0.32$ [1]

(Accept also 0.324 and 0.3239 BUT NOT 0.3)

(ii) β–Carotene
Lycopene has a smaller R_f value / lycopene moves slower. [1]
Lycopene takes a longer time to reach the bottom of the column.

DSE14_03a

(anhydrous) magnesium sulphate [1]

DSE14_03c

(i) Dissolve the sample in pentane and shake the solution with **$NaHCO_3$(aq)** in a **separating funnel.** [1] [1]
Collect the **organic layer** and carry out **fractional distillation / distillation.**
[Only fractional distillation / distillation: 0 mark]

DSE15_03a

Add **dilute** HCl(aq) / **dilute** H_2SO_4(aq) / **very dilute** HNO_3(aq) to the mixture (for dissolving the Fe_2O_3). [1]
Collect the copper powder from filtering the mixture obtained. [1]

DSE16_03c

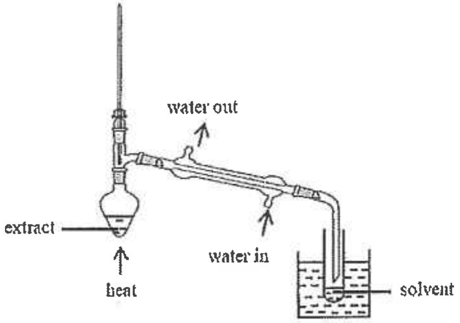
(ii) (1)
- Na_2CO_3(aq) is added to the dichloromethane solution of X and Y. [1]
- The mixture is shaken in a **separating funnel.** [1]
The mixture in the separating funnel is allowed to settle, and the aqueous layer was then separated from the organic layer.
- **Dilute H_2SO_4(aq)** is added to the aqueous layer / upper layer / lower aqueous layer / (until no more precipitate is formed.) / (the solution becomes acidic). [1]
- Solid Y can be obtained by **filtration.** [1]

(2) Measure the melting point of the solid obtained.
If the melting point of the solid is 77°C /a sharp m.p measured / a narrow melting point range, it may be pure compound Y. [1]
(mixed melting point technique → sharp melting point / m.p. 77 °C;
OR compare the IR spectrum / mass spectrum / NMR spectrum of the solid obtained with that of authentic sample, if they are identical → pure
OR run a TLC / paper chromatography for the sample; if only one spot is detected on the chromatogram → pure)

DSE17_03c

(i) (1) The solvent / product will not lose due to heating. [1]

(2) [2]



1 mark for correct experimental set-up, 1 mark for correct labels

Experimental set-up: 0 mark for closed system, wrong position of thermometer / delivery tube etc.

[Accept: No cold water to condense the solvent.]

1 mark for labelling heat, water in and water out

(3) (column) chromatography / thin layer chromatography / TLC / GCMS [1]

DSE18_03a

(iii) 'R_f value' of a substance is the ratio between the migration distance of the substance and the migration distance of the solvent front during chromatography. [2]

1 mark: indicating ratio; 1 mark: other parts correct

Can be represented by labelled diagram indicting 2 distances and correct mathematical expression.

DSE18_03c

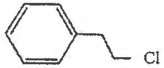
(i) Boiling points of **X** and **Y** are too close. [1]

DSE19_03c

(c) (i) (1)
- Different substances have different adsorptivity to the stationary phase. 1
- They have different solubility in mobile phase. 1

(2) column chromatography 1

(ii) The chemical species for the peak at m/z = 91 may be $C_6H_5CH_2^+$. 1
The chemical species for the peak at m/z = 140 may be $C_6H_5CH_2CH_2{}^{35}Cl^+$. 1
(or m/z = 142 may be $C_6H_5CH_2CH_2{}^{37}Cl^+$)
Possible structure :



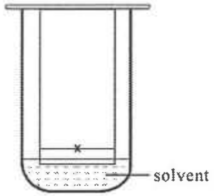
1

(iii) (1) High levels of dioxins may cause cancer. 1

(2) Modern instrumentation is accurate and sensitive enough to measure very low levels of dioxins. 1

DSE20_3b

(b) (i) 2



(1 mark for labelling: solvent
1 mark for the drawing: pencil line above solvent, spot of mixture, TLC plate and a container)

(ii) $R_f = 45 / (130-10-20) = 0.45$ 1
(Only mark the answer.)

(iii) Aspirin and Caffeine 1

(iv) (1) IR spectrum of Aspirin shows (strong absorption) peak at 2500 (cm^{-1}) to 3300 (cm^{-1}) / corresponding to O–H group of carboxylic acid while that of caffeine does not. 1
(A comparative sense)

(2) m/z = 43 corresponds to a CH_3CO^+ ion. 1
(Accept $CH_3CO\bullet^+$
Not accept $CH_3CO—^+$, CH_3CO)
Both aspirin and acetaminophen have this fragment, only this information cannot help confirm which one of the three chemicals the sample is. 1

AL96(I)_04c

In a titration experiment, a H_2O_2 solution was diluted 25 times. 25 cm^3 of the diluted H_2O_2 solution, in the presence of excess dilute H_2SO_4, required 26.45 cm^3 of 0.00995 M $KMnO_4$ solution for titration.

(i) Describe, with experimental details, how you would dilute the H_2O_2 solution.

(3 marks)

(ii) Write a balanced equation for the reaction involved in the titration.

(1 mark)

(iii) Describe the color change at the end point of the titration. .

(1 mark)

(iv) Calculate the molarity of the diluted H_2O_2 solution.

(2 marks)

(v) What reagent would be used to standardize the $KMnO_4$ solution in this experiment?

(1 mark)

AL96(I)_04d

In an experiment to determine the concentration of H_2O_2 contained in a rainwater sample, 5.0 cm^3 of the sample were mixed with an excess of a certain transition metal complex solution, giving a colored mixture. The absorbance of the mixture was measured by a colorimeter and was found to be 0.0273. When 5.0 cm^3 of 1.46×10^{-6} M H_2O_2 (instead of the rainwater sample) were treated in the same way, an absorbance of 0.0398 was recorded.

(i) Calculate the concentration of H_2O_2 in the rainwater sample assuming that concentration is directly proportional to absorbance.

(2 marks)

(ii) Why is the method of titration not suitable for the determination of the concentration of H_2O_2 in the rainwater sample?

(1 mark)

(iii) Why is it not suitable to collect the rainwater sample for this experiment in an iron container?

(1 mark)

AL98(I)_07 [Similar as DSE13]

The sulphur dioxide content in white wine was determined by an experiment described below:

1. 25.0 cm^3 of a sample of white wine was transferred to a conical flask
2. 15 cm^3 of 1 M NaOH(aq) was added to the flask and the mixture was allowed to stand for 15 minutes.
3. 15 cm^3 of 2 M H_2SO_4(aq) was added to the flask and the resulting solution was quickly titrated with 0.0050 M I_2(aq).
4. 12.9 cm^3 of the I_2(aq) was required to reach the titration end point.

(a) What is the purpose of adding the 2M H_2SO_4(aq)?

(1 mark)

(b) Why should the titration be carried out quickly?

(1 mark)

(c) Briefly describe how the end point of the titration can be determined.

(2 marks)

(d) Calculate the sulphur dioxide content, in mg dm^{-3}, in the sample of white wine.

(2 marks)

AL00(I)_03

In a titration experiment, 25.00 cm^3 of acidified $FeSO_4$(aq) required 32.15 cm^3 of 0.0203 M $K_2Cr_2O_7$(aq) for complete reaction.

(a) Write a balanced equation for the reaction involved.

(1 mark)

(b) Calculate the concentration, in mol dm^{-3}, of the $FeSO_4$(aq).

(2 marks)

ASL00(I)_03

The waste water from an electroplating factory contains chromium in the form of dichromate(VI) ions. In order to remove chromium from the waste water, green vitriol, $FeSO_4 \cdot 7H_2O$, was first added to reduce the dichromate(VI) ions to chromium(III) ions :

$$Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(l)$$

The chromium(III) ions formed were then precipitated as hydroxide.

(a) Suggest ONE reason why it is necessary to remove chromium from the waste water.

(1 mark)

(b) A sample of the waste water of volume 1.0×10^5 dm^3 contains 1.2×10^{-4} mol dm^{-3} of dichromate(VI) ions. Calculate the minimum mass of green vitriol required in the waste water treatment process.

(3 marks)

(c) Suggest an appropriate reagent for the precipitation reaction.

(1 mark)

(d) Name TWO chemicals present in the precipitate formed.

(2 marks)

ASL00(II)_12 [Similar as DSE13]

Sulphur dioxide is used to preserve wines. In an experiment to determine the sulphur dioxide content of a white wine, 25.00 cm^3 of a sample of the wine was titrated against 0.00480 M iodine solution. 14.80 cm^3 of the iodine solution was required to reach the end point.

(a) Explain why sulphur dioxide can be used to preserve wines.

(1 mark)

(b) In the titration, sulphate(VI) ions and iodide ions were formed. Using two half equations, establish the overall equation for the reaction involved.

(2 marks)

(c) What indicator should be used in the titration? State the color change of the indicator at the end point.

(2 marks)

(d) Calculate the concentration of sulphur dioxide, in mg dm^{-3}, in the sample of white wine.

(2 marks)

ASL00(II)_13 [Similar as DSE18]

A brand of mould-killer contains sodium chlorate(I) as the active ingredient. In an experiment to determine the sodium chlorate(I) content, 25.00 cm^3 of the mould-killer was treated with excess potassium iodide solution in the presence of an acid. The iodine liberated was then titrated against 0.680 M sodium thiosulphate solution. 31.10 cm^3 of the sodium thiosulphate solution was required to reach the end point.

(a) Write chemical equations for

  (i) the reaction of sodium chlorate(I) with potassium iodide solution under acidic condition, and

  (1 mark)

  (ii) the reaction of iodine with sodium thiosulphate solution.

  (1 mark)

(b) What indicator should be used in the titration? State the color change of the indicator at the end point.

(2 marks)

(c) Calculate the concentration of sodium chlorate(I), in g dm^{-3}, in the sample of mould-killer.

(3 marks)

ASL01(I)_03

In an experiment to determine the percentage by mass of iron in an iron wire, 0.160 g of a sample of the iron wire was added to 50 cm^3 of 2 M sulphuric(VI) acid. The solution obtained was then titrated against 0.0215 M potassium manganate(VII) solution. 24.30 cm^3 of the potassium manganate(VII) solution was required to reach the end-point.

(a) What would be observed when the iron wire was added to the sulphuric(VI) acid ?

(1 mark)

(b) Write the ionic equation for the reaction taking place during the titration. Hence, calculate the percentage by mass of iron in the sample of the iron wire.

(4 marks)

(c) Suggest how the end-point of the titration can be detected.

(1 mark)

ASL01(I)_07

Office paper contains calcium carbonate (up to 50%) as an additive to enhance its brightness, whiteness and opacity. Devise an experiment to estimate the percentage by mass of calcium carbonate in a sample of office paper.

(4 marks)

AL01(II)_01

A standard iodine solution was prepared by dissolving 0.953 g of KIO_3(s) in excess KI(aq) and H_2SO_4(aq) and then making up the solution to 250.0 cm^3.

(a) Why are standard iodine solutions not prepared directly from solid iodine?

(1 mark)

(b) Calculate the molarity of the standard iodine solution.

(2 marks)

(c) 25.00 cm^3 of the standard iodine solution was titrated against 0.0981 M $Na_2S_2O_3$(aq), 27.25 cm^3 of the $Na_2S_2O_3$(aq) was required to reach the end-point.

  (i) Deduce the stoichiometry of the reaction of I_2(aq) with $Na_2S_2O_3$(aq), and write a balanced equation for the reaction.

  (3 marks)

  (ii) Suggest an appropriate indicator for the titration and state the color change at the end-point.

  (1 mark)

AL02(I)_07

An experiment was carried out to determine the percentage by mass of tin in a sample of bronze, an alloy of copper and tin:

15.03 g of the finely divided sample was warmed with excess 1 M sulphuric acid to convert all the tin to tin(II) sulphate(VI). The mixture was filtered to remove copper which did not undergo reaction. The colorless filtrate was then diluted to 250 cm^3 with deionized water.
Four portions of the diluted tin(II) sulphate(VI) solution, each of volume 25.00 cm^3, were titrated against 0.0205 M potassium manganate(VII) solution. The titres were 23.90 cm^3, 23.35 cm^3, 23.40 cm^3 and 23.35 cm^3.

The equation for the reaction involved in the titration is as follows:

$$5Sn^{2+}(aq) + 2MnO_4^-(aq) + 16H^+(aq) \longrightarrow 5Sn^{4+}(aq) + 2Mn^{2+}(aq) + 8H_2O(l)$$

(a) Describe how the end point of the titration can be detected.

(1 mark)

(b) Calculate the reasonable volume of titre used in this titration.

(1 mark)

(c) Calculate the percentage by mass of tin in the sample of bronze.

(3 marks)

ASL02(II)_10 [Similar as DSE15]

A chemist carried out an experiment to determine the percentage by mass of nitrogen in a sample of nitrogenous fertilizer, which contained ammonium ions as the only source of nitrogen. The experiment consisted of three stages:

Stage 1: 1.64 g of the sample was dissolved in deionized water and then made up to 250.0 cm^3.

Stage 2: 25.00 cm^3 of this solution was heated with 25.00 cm^3 of 0.105 M sodium hydroxide solution until no more ammonia gas was evolved.

Stage 3: The resultant solution was titrated against 0.123 M hydrochloric acid. 10.80 cm^3 of the acid was required to reach the end point.

(a) Write a chemical equation for the reaction that occurred in *Stage 2*.

(1 mark)

(b) Suggest a suitable indicator for the titration in *Stage 3*. State the color change at the end point.

(2 marks)

(c) Calculate the percentage by mass of nitrogen in the sample.

(5 marks)

AL03(I)_01 modified

Phosphoric acid, $H_3PO_4(aq)$, a weak acid, ionizes in three stages to give $H_2PO_4^-(aq)$, $HPO_4^{2-}(aq)$ and $PO_4^{3-}(aq)$.

(a) Write an chemical equations to show the stepwise formation of $H_2PO_4^-(aq)$, $HPO_4^{2-}(aq)$ and $PO_4^{3-}(aq)$.

(3 marks)

(b) Explain why the ability of phosphoric acid to dissociate $H^+(aq)$ in each step progressively decreases.

(1 mark)

(c) Sketch the expected pH titration curve when $H_3PO_4(aq)$ is titrated with NaOH(aq).

(3 marks)

ASL03(II)_12 (I)

An experiment, consisting of the following two stages, was carried out to determine the content of ascorbic acid in a sample of grapefruit juice.

Stage 1: Excess KI(aq) and $H_2SO_4(aq)$ were added to 100.0 cm^3 of 0.0240 M $KIO_3(aq)$. The mixture was then diluted to 250.0 cm^3 using deionized water to give a standard iodine solution.

Stage 2: 25.0 cm^3 portions of the grapefruit juice were titrated against the standard iodine solution. The mean titre was 18.0 cm^3.

(a) The reaction in *Stage 1* can be represented by the following equation:

$$IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \longrightarrow 3I_2(aq) + 3H_2O(l)$$

Calculate the molarity of the standard iodine solution prepared.

(2 marks)

(b) Suggest how the end point of the titration in *Stage 2* can be detected.

(2 marks)

(c) The reaction of ascorbic acid, $C_6H_8O_6(aq)$, with iodine can be represented by the following equation:

$$C_6H_8O_6(aq) + I_2(aq) \longrightarrow C_6H_6O_6(aq) + 2H^+(aq) + 2I^-(aq)$$

Calculate the mass of ascorbic acid in 1.0 dm^3 of the sample of grapefruit juice.

(3 marks)

(d) Ascorbic acid is used as a preservative in packaged fruit juice. Suggest how ascorbic acid works.

(1 mark)

ASL03(II)_12 (II) [Similar as DSE18]

A sample of household bleach contains sodium chlorate(I) as the active ingredient. An experiment, consisting of the following three stages, was carried out to determine the concentration of sodium chlorate(I) in a sample of the bleach.

Stage 1: 25.0 cm^3 of the sample of bleach was diluted to 250.0 cm^3 with deionized water.

Stage 2: 25.0 cm^3 of the diluted sample was transferred to a conical flask. Excess KI(aq) and $H_2SO_4(aq)$ were then added.

Stage 3: The mixture in *Stage 2* was titrated against 0.105 M $Na_2S_2O_3(aq)$. 18.0 cm^3 of $Na_2S_2O_3(aq)$ was required to reach the end point.

(a) Outline the procedure for diluting the sample of bleach in *Stage 1*.

(2 marks)

(b) Write a chemical equation for the reaction in *Stage 2*.

(1 mark)

(c) Suggest how the end point of the titration in *Stage 3* can be detected.

(2 marks)

(d) Calculate the concentration of sodium chlorate(I), in g dm^{-3}, in the sample of bleach.

(3 marks)

AL04(I)_07

A student proposed a method to determine the concentration of citric acid in a sample of lemon juice by titration with standard sodium hydroxide solution. The method proposed consists of the following experimental procedures:

1. *Prepare a standard sodium hydroxide solution by dissolving a known mass of sodium hydroxide pellets in deionized water and then make it up to 250.0 cm^3.*
2. *Transfer a known volume of the sample of lemon juice to a clean conical flask.*
3. *Fill a burette, which has been well rinsed with deionized water beforehand, with the standard sodium hydroxide solution.*
4. *Titrate the lemon juice in the flask with sodium hydroxide solution using methyl orange as the indicator.*
5. *Using this titration result, calculate the concentration of citric acid in the sample.*

Point out four inappropriate practices in the method. Explain why they are inappropriate and suggest corrections for them.

(6 marks)

AL04(II)_04 [Similar as DSE11SP]

(a) Under acidic conditions, ethanol reacts with dichromate(VI) ions quantitatively to give ethanoic acid and chromium(III) ions.
Write an equation for the reaction of ethanol with dichromate(VI) ions under acidic conditions.

(1 mark)

(b) In an experiment to determine the concentration of ethanol in a brand of spirit, 10.0 cm^3 of a sample of the spirit was diluted to 250.0 cm^3. 25.0 cm^3 portions of the diluted spirit were withdrawn. To each portion, 25.0 cm^3 of 0.156 M $K_2Cr_2O_7(aq)$ and excess dilute $H_2SO_4(aq)$ were added. The mixtures obtained were allowed to stand at room temperature for about an hour. The excess $K_2Cr_2O_7$ in each mixture was then titrated against 0.118 M $(NH_4)_2Fe(SO_4)_2(aq)$ with an appropriate indicator. The mean titre was 12.23 cm^3.
Calculate the concentration of ethanol, in mol dm^{-3}, in this brand of spirit.

(4 marks)

ASL04(II)_08 [Similar as DSE18]

Household bleach contains NaClO as the active ingredient. In an experiment to determine the concentration of NaClO in a brand of household bleach, a sample of the bleach was diluted 50 times using deionized water. To 25.00 cm^3 of the diluted bleach, excess KI(aq) and $H_2SO_4(aq)$ were added. The mixture was then titrated against 0.0552 M $Na_2S_2O_3(aq)$. 16.00 cm^3 of the $Na_2S_2O_3(aq)$ was required to reach the end point.

(a) Describe how the sample of bleach can be diluted using apparatus available in a school laboratory.

(3 marks)

(b) Suggest how the end point of the titration can be detected.

(2 marks)

(c) The reaction of $ClO^-(aq)$ with $I^-(aq)$ under acidic conditions can be represented by the equations:

$$ClO^-(aq) + 2I^-(aq) + 2H^+(aq) \longrightarrow Cl^-(aq) + I_2(aq) + H_2O(l)$$

From the titration result, calculate the concentration of $ClO^-(aq)$, in mol dm^{-3}, in this brand of bleach.

(3 marks)

AL05(II)_01

X is a trivalent metal. When treated with hydrochloric acid, **X**(s) gives hydrogen, while its oxide $X_2O_3(s)$ undergoes neutralization.

(a) Write the chemical equation for the reaction of **X**(s) with HCl(aq) and that of $X_2O_3(s)$ with HCl(aq).

(2 marks)

(b) 16.5 g of a mixture of **X**(s) and $X_2O_3(s)$ is allowed to react with 6.0 M HCl(aq). 95.4 cm^3 of the acid is required for both the metal and its oxide to undergo complete reaction.
Deduce respectively the greatest possible value and the smallest possible value of the relative atomic mass of **X**.

(4 marks)

(c) With reference to the Periodic Table, deduce what **X** may be.

(1 mark)

ASL05(II)_11

An experiment was carried out to determine the amount of $K_2Cr_2O_7$ required to oxidize the organic matter present in a water sample. This provides an indication of the extent of organic pollution of the sample. The experiment consists of the following two stages:

Stage 1: 2.50 cm^3 of 0.0100 M $K_2Cr_2O_7(aq)$ and excess $H_2SO_4(aq)$ were added to 100.0 cm^3 of the sample. The mixture was heated under reflux until all the organic matter it contained was oxidized to $CO_2(g)$ and $H_2O(l)$. The resultant mixture was then allowed to cool to room temperature.

Stage 2: The unreacted $K_2Cr_2O_7$ in the resultant mixture was titrated against 0.0124 M $(NH_4)_2Fe(SO_4)_2(aq)$. 7.60 cm^3 of the $(NH_4)_2Fe(SO_4)_2(aq)$ was required to reach the end point.

(a) Draw a labelled diagram of the set-up used for heating the mixture under reflux in *Stage 1*.

(2 marks)

(b) Write an ionic equation for the reaction which occurred in *Stage 2*.

(1 mark)

(c) Calculate the number of moles of $K_2Cr_2O_7$ required to oxidize all of the organic matter present in 1.0 dm^3 of the sample.

(4 marks)

AL06(I)_02

Hard water contains $Mg^{2+}(aq)$ and $Ca^{2+}(aq)$ ions.

(a) Name a mineral that provides $Ca^{2+}(aq)$ ions in hard water.

(1 mark)

(b) An experiment as described below was carried out to determine the total hardness in a sample of hard water.

"50.0 cm^3 of the sample was allowed to pass through an ion-exchange column, in which the metal ions present in the sample were totally exchanged by hydrogen ions. The eluent collected required 15.0 cm^3 of 0.020 mol dm^{-3} $KOH(aq)$ for complete neutralization."

Assuming that the metal ions present in the sample are $Mg^{2+}(aq)$ and $Ca^{2+}(aq)$ only, calculate the total hardness, in mol dm^{-3}, of the sample.

(2 marks)

AL06(II)_07

The extent of oxidation of an oil can determined by iodometric analysis.

In a typical experiment, 4.85 g of a sample of oil is treated with excess $KI(aq)$ and $H_2SO_4(aq)$. The iodine liberated required 21.20 cm^3 of 0.012 mol dm^{-3} $Na_2S_2O_3(aq)$ for complete reaction.

Given that when treated with acidified $KI(aq)$, 1 mol of peroxide liberates 1 mol of I_2, calculate the number of moles of O_2 absorbed per kg of the oil.

(3 marks)

ASL06(II)_09c

A student carried out an experiment to determine the percentage by mass of iron in an iron wire. A sample of 0.212 g of the iron wire was added to 100 cm^3 of 2 M sulphuric aicd. The solution obtained was then titrated against 0.0208 M potassium manganate(VII) solution. 34.70 cm^3 of the potassium manganate(VII) solution was required to reached to the end-point.

(i) Write the ionic equation for the reaction taking place during the titration.

(1 mark)

(ii) Calculate the percentage by mass of iron in the iron wire sample.

(3 marks)

(iii) State one assumption for the experiment.

(1 mark)

(iv) Could hydrochloric acid be used instead of sulphuric(VI) acid in this experiment? Explain your answer.

(1 mark)

AL07(I)_07

(a) What is meant by 'primary standard' in titrimetric analysis?

(1 mark)

(b) Give one reason why each of the following chemicals is not used as a primary standard.

(i) liquid bromine

(1 mark)

(ii) potassium hydroxide pellets

(1 mark)

ASL07(II)_03

In an experiment to determine the percentage by mass of copper in a sample of copper ore, 3.00 g of the sample was warmed with excess $HNO_3(aq)$ to convert all copper-containing substances to $Cu^{2+}(aq)$ ions. The resulting solution was boiled to remove all nitrogen oxides formed. Upon cooling, the solution was diluted to 250.0 cm^3. 25.00 cm^3 of the diluted solution was withdrawn and then treated with excess $KI(aq)$ to liberate $CuI(s)$ and $I_2(aq)$. The titration of the $I_2(aq)$ liberated required 25.80 cm^3 of 0.102 M $Na_2S_2O_3(aq)$.

(a) Write chemical equation for

(i) The reaction of $Cu^{2+}(aq)$ and $I^-(aq)$, and

(1 mark)

(ii) The reaction of $I_2(aq)$ with $Na_2S_2O_3(aq)$.

(1 mark)

(b) Calculate the percentage by mass of copper in the sample of copper ore.

(3 marks)

(c) State one assumption made in the experiment.

(1 mark)

ASL09(II)_03

In an experiment to determine the relative atomic mass of magnesium, 0.420 g of magnesium ribbon was added to 25.0 cm^3 of 0.955 mol dm^{-3} $H_2SO_4(aq)$. When effervescence ceased, the resulting mixture was diluted to 250.0 cm^3 with deionized water. 25.0 cm^3 portions of the diluted solution were withdrawn and titrated against 0.0941 mol dm^{-3} $NaOH(aq)$ using methyl orange as indicator. The mean titre was 16.48 cm^3.

(a) State the color change at the end point of the titration.

(1 mark)

(b) Based on the titration results, calculate the relative atomic mass of magnesium.

(4 marks)

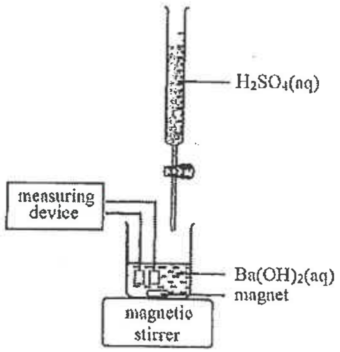
(c) Assuming that the experimental error is negligible, suggest ONE reason why the relative atomic mass of magnesium calculated in (b) is different from that found in the Periodic Table.

(1 mark)

AL10(I)_07

The diagram on the right shows the set-up of a titrimetric experiment involving the following reaction:

$$Ba(OH)_2(aq) + H_2SO_4(aq) \longrightarrow BaSO_4(s) + 2H_2O(l)$$



(a) What physical parameter of the reaction mixture is measured by this set-up?

(1 mark)

(b) $H_2SO_4(aq)$ is added gradually to $Ba(OH)_2(aq)$ until in excess.
Sketch a graph to show the variation of measured physical parameter with the volume of $H_2SO_4(aq)$ added. Explain your answer.

(2 marks)

AL11(I)_01

A water-soluble solid sample A contains iron(II) ions. The percentage by mass of iron(II) ions in A can be determined from the experimental data listed below:

25.00 cm^3 of 0.0326 mol dm^{-3} $Na_2C_2O_4(aq)$, after acidification, requires 24.35 cm^3 of a certain $KMnO_4(aq)$ for complete reaction.
An aqueous solution of 0.863 g of A, after acidification, requires 31.85 cm^3 of the same $KMnO_4(aq)$ for complete reaction.

(a) Write chemical equations for the above two reactions.

(2 mark)

(b) Calculate the percentage by mass of iron(II) ions in A. (Assume that A does NOT contain any other species that react with $KMnO_4(aq)$.)

(3 marks)

(c) Suggest why $KMnO_4(s)$ is NOT used as a primary standard.

(1 mark)

AL12(I)_07

Iodine-thiosulphate titrations involve the following reaction and the use of starch indicator.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

Suggest why

(a) starch indicator is only added near the end-point, and

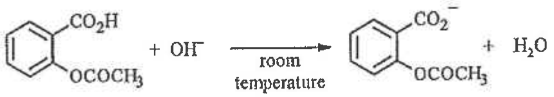
(1 mark)

(b) such titrations are NOT carried out under strongly acidic conditions.

(1 mark)

AL12(I)_08

A commercial aspirin sample U was known to contain about 90% by mass of aspirin, while the rest was an inert binder. Based on the following reaction, a student deigned an experiment and performed it at room temperature to determine the percentage by mass of aspirin in U.



The student added 2.25 g of U to 25.00 cm^3 of 3.05 mol dm^{-3} NaOH(aq), and then back titrated the excess NaOH(aq) with 2.50 mol dm^{-3} HCl(aq). The volume of HCl(aq) used was 23.10 cm^3.

(a) Suggest an indicator for the titration.

(1 mark)

(b) From the student's experimental results, calculate the percentage by mass aspirin in U. Suggest why the calculated percentage by mass of aspirin deviated greatly from 90%. (relative molecular mass of aspirin = 180.0)

(4 marks)

(c) Suggest ONE improvement to the design of the experiment to find the percentage by mass of aspirin in U.

(1 mark)

AL12(II)_01

Metal M forms a water-soluble bromide MBr_2. The following gravimetric analysis experiment was conducted to determine the formula mass of MBr_2.

A solution of MBr_2 was prepared by dissolving 0.400 g of $MBr_2(s)$ completely in deionized water. The solution was acidified with $HNO_3(aq)$ and then treated with excess $AgNO_3(aq)$. The AgBr(s) formed was separated from the mixture by filtration, washed and dried. Its mass was found to be 0.816 g.

(a) Given that the cation of M in MBr_2 does NOT react with $Ag^+(aq)$ ions, calculate the formula mass of MBr_2.

(3 marks)

(b) Calculate the relative atomic mass of M, and deduce what M is.

(2 marks)

(c) M also forms a water-soluble fluoride MF_2, Can the formula mass of MF_2 be determined by gravimetric analysis using $AgNO_3$(aq) as the precipitating agent? Explain.

(1 mark)

ASL13(II)_01

Orange juice contains ascorbic acid, also known as vitamin C. The following titrimetric experiment was conducted o estimate the amount of ascorbic acid in a sample of orange juice:

A standard iodine solution was prepared by dissolving 2 g of KI(s) in 100.0 cm^3 of 0.0100 mol dm-3 KIO_3(aq), adding in 25 cm^3 of 1 mol dm^{-3} H_2SO_4(aq) and then making up the resulting solution to 250.0 cm^3 with deionized water.

Several aliquots of 25.00 cm^3 of the sample of orange juice were titrated with the standard iodine solution. The mean titre was 7.60 cm^3.

(a) (i) Write the chemical equation for the reaction of KIO_3 with KI under acidic conditions.

(1 mark)

(ii) Suggest why the standard iodine solution was NOT prepared by weighing a sample of I_2(s) and then dissolving it in a known volume of KI(aq).

(1 mark)

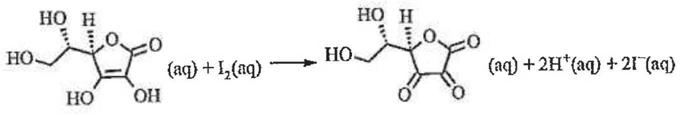
(iii) Calculate the concentration of the standard iodine solution prepared.

(1 mark)

(b) Suggest how the end point of the above titration can be detected.

(2 marks)

(c) The reaction of I_2(aq) with ascorbic acid can be represented by the following equation:



ascorbic acid

(i) From the titration results, calculate the mass of ascorbic acid in 100.0 cm^3 of this sample of orange juice.
(Relative molecular mass of ascorbic acid = 176.0)

(3 marks)

(ii) State ONE assumption in this experiment.

(1 mark)

DSE11SP_03b [Similar as AL04]

In an experiment to determine the concentration of ethanol in a brand of spirit, 10.0 cm^3 of a sample of the spirit was diluted to 250.0 cm^3. 25.0 cm^3 portions of the diluted spirit were withdrawn. To each portion, 25.0 cm^3 of 0.156 M $K_2Cr_2O_7$(aq) and excess dilute H_2SO_4 were added. The mixtures obtained were allowed to stand at room temperature overnight. The excess $K_2Cr_2O_7$ in each mixture was then titrated against 0.118 M $(NH_4)_2Fe(SO_4)_2$(aq) with an appropriate indicator. The mean titre was 12.23 cm^3.

(i) Write an equation for the reaction of ethanol with dichromate ions under acidic condition.

(1 mark)

(ii) Give TWO properties of $(NH_4)_2Fe(SO_4)_2$ rendering it to be used as primary standard in volumetric analysis.

(2 marks)

(iii) Suggest a method to test whether the oxidation of ethanol has been completed.

(2 marks)

(iv) Calculate the concentration of ethanol, in mol dm^{-3}, in this brand of spirit.

(5 marks)

DSE12PP_03b **[OUT, for reference]**

The percentage by mass of barium (Ba) in a barium salt can be determined by gravimetric method. In one such experiment, 0.305 g of a sample a barium salt was dissolved completely in about 100 cm^3 of deionized water. Excess dilute sulphuric acid was then added to the solution to precipitate out barium sulphate. After filtration and appropriate treatment, the barium sulphate was found to have a mass of 0.291 g.

(i) State TWO necessary treatment on the filtered barium sulphate precipitate before its mass is determined.

(2 marks)

(ii) Calculate the percentage by mass of barium in the sample.

(3 marks)

(iii) State TWO conditions under which gravimetric method is suitable for quantitative analysis.

(2 marks)

DSE12_03c **[OUT, for reference]**

An aqueous solution only contains HCl(aq) and HI(aq). Based on the fact that AgCl(s), but not AgI(s), can dissolve in excess NH_3(aq), you are required to plan a gravimetric analysis to determine the mole ratio of Cl^-(aq) to I^-(aq) in the solution.

(i) Suggest TWO reagents, other than deionized water, that should be used in the analysis.

(2 marks)

(ii) Outline the experimental steps involved in the analysis.

(4 marks)

(iii) Outline the steps in the calculation of the mole ratio of Cl^-(aq) to I^-(aq) in the solution using the data obtained from (ii) above.

(2 marks)

DSE13_03b [Similar as AL98, ASL00]

Both white wine and red wine contain SO_2 preservative which is fixed in different forms. A volumetric analysis experiment was performed to determine the total concentration of SO_2 in a sample of white wine. In the experiment, 25.00 cm^3 of the wine sample was transferred to a conical flask. Following certain stipulated procedure, NaOH(aq) and H_2SO_4(aq) were successively added to the flask to liberate all SO_2 from the wine. The resultant solution was immediately titrated with 0.00412 mol dm^{-3} I_2(aq) using freshly prepared starch solution as indictor. The experiment was repeated several times, and the mean volume of I_2(aq) required to reach the end point was 10.50 cm^3.

(i) A reaction must fulfill certain conditions in order that it can be used in volumetric analysis. State ONE such condition.

(1 mark)

(ii) Explain why the resultant solution needed to be titrated immediately.

(1 mark)

(iii) State the expected color change at the end point of the titration.

(1 mark)

(iv) The chemical equation for the reaction involved in the titration is as follows:

$$SO_2(aq) + I_2(aq) + 2H_2O(l) \longrightarrow 2HI(aq) + H_2SO_4(aq)$$

Calculate the total concentration of SO_2(aq), in mg dm^{-3}, in the white wine sample.

(4 marks)

(v) Explain whether the total concentration of SO_2 in a sample of red wine can be determined in such an experiment.

(1 mark)

DSE14_03b **[OUT, for reference]**

A powdered limestone sample mainly consists of $CaCO_3$, and a small amount of $MgCO_3$ and $FeCl_3$. The following steps were performed in an experiment to determine the percentage of $CaCO_3$ by mass in the sample.

Step 1: 2.025 g of the limestone sample was added to excess amount of 6 M HCl(aq).

Step 2: The mixture obtained was gently heated until no signs of further reaction. It was then allowed to cool to room temperature

Step 3: The cooled mixture was diluted with distilled water, and made slightly alkaline by adding NH_3(aq) to precipitate the Fe^{3+}(aq) ions present.

Step 4: The mixture obtained was filtered to collect the filtrate.

Step 5: Excess ammonium oxalate solution, $(NH_4)_2C_2O_4$(aq), was added to the filtrate, and the mixture obtained was then made slightly alkaline by using NH_3(aq) to selectively precipitate the calcium oxalate formed.

Step 6: The mixture was filtered. After washing and drying, 2.374 g of calcium oxalate solid was collected.

(i) Why is it necessary to heat the mixture in Step 2?

(1 mark)

(ii) (1) How does one know when the reaction involved in Step 2 has been completed?

(1 mark)

(2) State the observation in Step 3.

(1 mark)

(iii) It is given that magnesium oxalate is soluble in alkaline solutions but calcium oxalate is not. Calculate the percentage of $CaCO_3$ by mass in the limestone sample.

(3 marks)

(iv) State the quantitative analysis method used in this experiment.

(1 mark)

DSE15_03c [Similar as ASL02]

An experiment consisting of the following four steps was performed to determine the amount of nitrogen in a milk powder sample:

Step (1) : 3.00 g of the milk powder sample was heated with excess concentrated sulphuric acid so as to turn all nitrogen in it into $(NH_4)_2SO_4$(aq).

Step (2) : The reaction mixture obtained was heated with excess NaOH(aq) to liberate NH_3(g). All NH_3(g) liberated was then absorbed by 50.00 cm^3 of 1.00 M HCl(aq).

Step (3): The solution formed was diluted to 250.0 cm^3 with deionized water.

Step (4): 25.00 cm^3 portions of the diluted solution were titrated with 0.100 M KOH(aq) using methyl orange as an indicator. An average of 13.55 cm^3 of the KOH(aq) was required to reach the end point.

(i) Write the chemical equations for the following reactions in Step (2):

(1) The reaction of $(NH_4)_2SO_4$(aq) with NaOH(aq)

(1 mark)

(2) The reaction of NH_3(g) with HCl(aq)

(1 mark)

(ii) State the color change at the end point of the titration in Step (4).

(1 mark)

(iii) Calculate the percentage by mass of nitrogen in the milk powder sample.

(4 marks)

(iv) In finding out the protein content in a milk powder sample, a common method is to determine the amount of nitrogen, but not to directly determine the amount of protein in the sample. Suggest one limitation of this common method.

(1 mark)

DSE16_03a

Given one property of solid sodium hydroxide making it NOT suitable to be weighed for preparing a standard solution.

(1 mark)

DSE16_03b

The concentration of a $Na_2Cr_2O_7(aq)$ sample **A** was determined by volumetric analysis; while the concentration of another $Na_2Cr_2O_7(aq)$ sample **B** was determined by colorimetry.

(i) 25.00 cm^3 of sample **A** was transferred to a conical flask and acidified with dilute $H_2SO_4(aq)$. Then the mixture was titrated with 0.0642 mol dm^{-3} $Fe^{2+}(aq)$ solution with a suitable indicator. It required 26.88 cm^3 of the $Fe^{2+}(aq)$ solution to reach the end point.

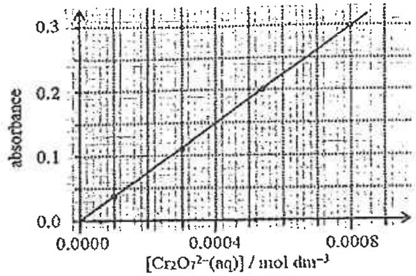
(1) Write a balanced equation for the reaction involved.

(1 mark)

(2) Calculate the concentration of $Na_2Cr_2O_7(aq)$ in **A**.

(2 marks)

(ii) In colorimetry, various standard $Cr_2O_7^{2-}(aq)$ solution were first prepared, and then the absorbance of these solutions were measured with a colorimeter installed with a blue filter. The calibration curve below shows the variation of absorbance with the concentration of $Cr_2O_7^{2-}(aq)$ ions.



(1) Suggest why a blue filter was used.

(1 mark)

(2) With reference to the above calibration curve, state the relationship between absorbance and $[Cr_2O_7^{2-}(aq)]$.

(1 mark)

(3) Sample **B** was diluted 100 times. The absorbance of the diluted solution was measured as 0.26 by the colorimeter. Based on the information given from the above calibration curve, calculate the concentration of $Na_2Cr_2O_7(aq)$ in **B**.

(2 marks)

(iii) Explain whether volumetric analysis or colorimetry is more appropriate in determining the concentration of a very dilute $Na_2Cr_2O_7(aq)$, such as around 10^{-4} mol dm^{-3}.

(1 mark)

DSE17_03b

Hydroxylamine ($HONH_2$) reacts with $Fe^{3+}(aq)$ ions under acidic conditions to form products including $Fe^{2+}(aq)$ ions and an oxide of nitrogen,. An experiment, consisting of the following two steps, was carried out to deduce the oxidation number of N in the oxide.

Step (1): An aqueous solution containing 0.875 g of $HONH_2$ and excess $Fe_2(SO_4)_3$ was heated under an acidic condition until the reaction was complete. The resulting solution was then dilute to 250.0 cm^3.

Step (2): 25.00 cm^3 of the diluted solution was acidified with excess $H_2SO_4(aq)$ and then titrated with 0.0282 mol dm^{-3} $KMnO_4(aq)$ until the end point was reached. The chemical equation for the reaction involved is as follows:

$$MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \longrightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$$

(i) State the color change at the end point of the titration.

(1 mark)

(ii) Four trials of the titration were carried out and the results are listed below:

Trial	1	2	3	4
Volume of $KMnO_4(aq)$ used / cm^3	38.34	37.62	37.58	37.60

(1) Calculate a reasonable average of the volume of $KMnO_4(aq)$ used in the titration.

(1 mark)

(2) Based on the experimental results, calculate the mole ratio of $HONH_2(aq)$: $Fe^{3+}(aq)$ required for the completion of the reaction in Step (1).
(Relative atomic masse: H = 1.0, N = 14.0, O = 16.0)

(3 marks)

(3) Given that the oxidation number of N in $HONH_2$ is −1, and the oxidation numbers of H and O remain unchanged, deduce the oxidation number of N in the oxide.

(2 marks)

(iii) According to (ii)(3), suggest a reasonable empirical formula for the oxide.

(1 mark)

DSE18_03b [Similar as ASL00, 03, 04]

An experiment was performed to determine the percentage by mass of $NaClO_3(s)$ in a sample. 1.63 g of the sample was dissolved in deionized water and then made up to 250.0 cm^3. 10.00 cm^3 of the solution was transferred to a conical flask. Then 10 cm^3 of 1 M KI(aq) and 20 cm^3 of 6 M HCl(aq) were added in the flask. The resulting mixture was titrated with 0.112 M $Na_2S_2O_3(aq)$, adding starch solution as indicator at appropriate time. The titration was repeated several times, and the mean volume of $Na_2S_2O_3(aq)$ required to reach the end point was 27.88 cm^3.

(i) Describe how the sample dissolved in deionized water can be made up to 250.0 cm^3.

(2 marks)

(ii) It is known that in the conical flask, $ClO_3^-(aq)$ reacts with $I^-(aq)$ in the presence of $H^+(aq)$ to form $I_2(aq)$ and $Cl^-(aq)$. Write an ionic equation for the reaction.

(1 mark)

(iii) State the color change at the end point of the titration.

(1 mark)

(iv) The chemical equation for the titration reaction is as follows:

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

Assuming that no other species in the sample would react with $I^-(aq)$, calculate the percentage by mass of $NaClO_3(s)$ in the sample.
(Relative atomic masses: O = 16.0, Na = 23.0, Cl = 35.5)

(3 marks)

DSE19_03b

(b) In order to determine the sodium contents (existing as NaCl) in a bacon sample, its Cl^- contents should first be found. 2.0 g of the bacon sample was added to 2.50 cm^3 of 1.0 M $AgNO_3(aq)$. After that, excess dilute $HNO_3(aq)$ was added to the mixture obtained. The $AgCl(s)$ formed was then removed by filtration. The excess $AgNO_3(aq)$ remaining in the filtrate was then titrated with 0.10 M KSCN(aq) to give AgSCN(s) in the presence of a suitable indicator until the end point was reached. All steps were repeated several times and the mean volume of the KSCN(aq) used to reach the end point was 9.42 cm^3.

(i) Why was excess dilute $HNO_3(aq)$ added to the mixture ?

(1 mark)

(ii) Draw a diagram for the set-up to be used in the titration, labelling all apparatus and reagents.

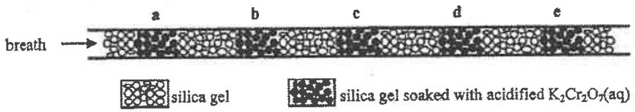
(2 marks)

(iii) Assuming that all Cl^- comes from NaCl in the bacon sample, calculate the percentage by mass of sodium in the bacon sample.
(Relative atomic masses: Na = 23.0, Cl = 35.5, Ag = 107.9)

(4 marks)

DSE20_03cii

(c) Road checking on ethanol intake of a driver can be done by having the driver exhale a breath into the tube as shown below :



(i) (1) Suggest the colour change of the silica gel soaked with acidified $K_2Cr_2O_7(aq)$ if enough ethanol-contained breath is exhaled into the tube. Write a half equation for the colour change involved.

(2) A breath from driver **A** only changes colour at positions **a** and **b**; while a breath from driver **B** changes colour at positions **a**, **b** and **c**. Assuming the checking is performed in a fair manner, explain which driver has a higher ethanol intake.

(3) Suggest how the checking can be performed in a fair manner.

(4 marks)

(ii) In a certain country, a driver would be found guilty if the ethanol content in his / her blood exceeds '55 mg of ethanol per 100 cm^3 of serum'. 10.0 cm^3 of a treated serum sample obtained from the blood of a driver requires 4.38 cm^3 of 0.025 mol dm^{-3} $K_2Cr_2O_7(aq)$ in an acidified medium for complete reaction. Given that the mole ratio of $C_2H_5OH(aq)$ to $K_2Cr_2O_7(aq)$ is 3 : 1 in the reaction, calculate the mass of C_2H_5OH, in mg, in the serum sample. Determine whether the driver would be found guilty.
(Relative atomic masses : H = 1.0, C = 12.0, O = 16.0)

(4 marks)

Marking Scheme

AL96(I)_04c

(i) Transfer the given H_2O_2 solution to beaker. [1]
Pipette 10 cm^3 of H_2O_2 solution to a 250 cm^3 volumetric flask. [1]
Dilute the solution by adding water until the bottom of the meniscus reach the graduation mark. [1]

(ii) $2MnO_4^- + 5H_2O_2 + 6H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 5O_2 + 8H_2O$ [1]

(iii) A permanent pink color appears at the end point / colorless to pink.

(iv) $\frac{\text{mole of } H_2O_2}{5} = \frac{\text{mole of } MnO_4^-}{2}$

$\frac{25 \times 10^{-3} \times [H_2O_2]}{5} = \frac{26.45 \times 10^{-3} \times 0.00995}{2}$ [1]

$[H_2O_2] = 0..263$ M [1]

(v) Sodium ethanedioate (oxalate) / ammonium iron(II) sulphate(VI) [1]

AL96(I)_04d

(i) $[H_2O_2]$ in the sample $= \frac{1.46 \times 10^{-6}}{0.0398} \times 0.0273 = 1.00 \times 10^{-6}$ M [2]

(ii) The concentration of H_2O_2 in rainwater is too low to be determined by titrimetric method. [1]

(iii) Fe can be oxidized by H_2O_2 [1]
OR, Transition metal ions can catalyze the decomposition of H_2O_2.

AL98(I)_07

(a) To convert all sulphite to SO_2 / to prevent the disproportionation of I_2 in alkaline medium. [1]

(b) SO_2 / I_2 is volatile [1]

(c) **Add starch solution** [1]
End point : solution changes from colorless to blue [1]

(d) $SO_2 + I_2 + 2H_2O \longrightarrow 2I^- + SO_4^{2-} + 4H^+$
$I_2 \equiv SO_2 \equiv SO_3^{2-}$

$[SO_2(aq)] = \frac{0.005 \times 12.9}{25} = 2.58 \times 10^{-3}$ M [1]

$[SO_2(aq)] = 2.58 \times (32.1 + 16 \times 2) = 165$ mg dm^{-3} [1]

AL00(I)_03

(a) $Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(l)$ [1]

(b) Mole of $Cr_2O_7^{2-}(aq) = 0.0203 \times 32.15 \times 10^{-3} = 6.526 \times 10^{-4}$ [1]

$[FeSO_4(aq)] = \frac{6 \times 6.526 \times 10^{-4}}{25 \times 10^{-3}} = 0.157$ mol dm^{-3} [1]

ASL00(I)_03

(a) Chromium(VI) is toxic. [1]
(b) No. of mole of $Cr_2O_7^{2-}(aq) = 1.2 \times 10^{-4} \times 1 \times 10^5 = 12$ [1]
No. of mole of $Fe^{2+}(aq)$ required $= 12 \times 6 = 72$ [1]
Mass of green vitriol $= 72 \times 277.8 = 200001.6$ g $= 20$ kg [1]
(c) Sodium hydroxide / ammonia [1]
(d) Cr(III) cation and hydroxide anion [1]

ASL00(II)_12

(a) Sulphur dioxide is used as anti-oxidant / reductant to prevent air oxidation of ethanol. [1]
(b) $SO_2(aq) + 2H_2O(l) \longrightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$ [½]
$I_2(aq) + 2e^- \longrightarrow 2I^-(aq)$ [½]
$SO_2(aq) + 2H_2O(l) + I_2(aq) \longrightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2I^-(aq)$ [1]
(c) Starch solution. Change from colorless to dark blue at the end point. [2]
(d) $SO_2(aq) + 2H_2O(l) + I_2(aq) \longrightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2I^-(aq)$
No. of mole of $SO_2(aq)$ = no. of mole of $I_2(aq)$ used
$= 14.8 \times 10^{-3} \times 0.0048 = 7.104 \times 10^{-5}$ [1]

$$[SO_2(aq)] = \frac{7.104 \times 10^{-5} \times 64}{25 \times 10^{-3}} = 0.182\ \text{g dm}^{-3} = 182\ \text{mg dm}^{-3}$$ [1]

ASL00(II)_13

(a) (i) $OCl^-(aq) + 2I^-(aq) + 2H^+(aq) \longrightarrow I_2(aq) + Cl^-(aq) + H_2O(l)$ [1]
(ii) $I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$ [1]
(b) Starch solution. [1]
Color changes from dark blue to colorless at the end point. [1]
(c)

$$\text{mole of } I_2(aq) \text{ formed} = \frac{1}{2} \times \text{mole of } S_2O_3^{2-} \text{ used}$$

$$= \frac{1}{2} \times 31.1 \times 10^{-3} \times 0.680 = 1.06 \times 10^{-2}$$ [1]

mole of $OCl^-(aq)$ = mole of $I_2(aq)$ formed $= 1.06 \times 10^{-2}$ [1]

$$[NaOCl(aq)] = \frac{1.06 \times 10^{-2} \times 74.5}{25 \times 10^{-3}} = 31.6\ \text{g dm}^{-3}$$ [1]

ASL01(I)_03

(a) A colorless bubbles and green iron(II) solution are given. [1]
(b) $MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \longrightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$ [1]
mole of $Fe^{2+}(aq) = 5 \times 24.3 \times 10^{-3} \times 0.0215 = 2.612 \times 10^{-3}$ [1]
mass of $Fe(s) = 2.612 \times 10^{-3} \times 55.8 = 0.146$ g [1]

$$\% \text{ by mass} = \frac{0.146}{0.160} \times 100\% = 91.1\%$$ [1]

(c) First appearance of permanent pink color [1]

ASL01(I)_07

Weigh a piece of office paper. [½]
Immerse paper in excess HCl(aq). [½]
When no CO_2 evolves from the mixture, decant acid and wash paper with distilled water. [1]
Dry the paper in an oven (110 °C). [½]
Weigh the paper again. [½]

$$\% \text{ by mass of } CaCO_3 = \frac{\text{change in mass of paper}}{\text{original mass of paper}} \times 100\%$$ [1]

Alternative answers

Weigh a piece of office paper. [½]
Immerse in a known volume of standard HCl (excess). [1]
Titrate excess HCl using standard KOH (aq) / NaOH (aq). [1]
Calculate mass of $CaCO_3$ from the titration result. [½]

$$\% \text{ by mass of } CaCO_3 = \frac{\text{mass of } CaCO_3}{\text{original mass of paper}} \times 100\%$$ [1]

Alternative answers

Weigh a piece of office paper [½]
Burn the paper completely (in a crucible) [1]
Weigh the CaO (s) produced, (m) [½]

$$\text{mass of } CaCO_3 = \frac{m}{40 + 16} \times 100\%$$ [1]

$$\% \text{ by mass of } CaCO_3 = \frac{\text{mass of } CaCO_3}{\text{original mass of paper}} \times 100\%$$ [1]

AL01(II)_01

(a) $I_2(s)$ is volatile. It is difficult to weigh accurately a sample of $I_2(s)$. [1]
OR, $I_2(s)$ reacts readily with reducing agents in the environment. $I_2(s)$ in the laboratory usually contains impurities.
(b) $IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$ [1]
$IO_3^- \equiv 3I_2$

$$[I_2(aq)] = 3 \times \frac{0.953}{214} \times 4 = 0.0534\ \text{M}$$ [1]

(c) (i) mole of I_2 used $= 0.0534 \times 25 \times 10^{-3} = 1.335 \times 10^{-3}$ [½]
mole of $S_2O_3^{2-}$ used $= 0.0981 \times 27.25 \times 10^{-3} = 2.673 \times 10^{-3}$ [½]
$I_2 : S_2O_3^{2-} = 1.335 \times 10^{-3} : 2.673 \times 10^{-3} = 1 : 2$ [1]
Equation: $I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$ [1]
(ii) Starch solution: color change: from blue to colorless [1]

AL02(I)_07

(a) No indicator is required. When the equivalence point is reached, the addition of a further drop of $KMnO_4(aq)$ will give a permanent pale pink color (end point) [1]
(b)

$$\text{mean titre} = \frac{23.35 + 23.40 + 23.35}{3} = 23.37\ \text{cm}^3$$ [1]

(c) mole of $MnO_4^-(aq)$ used $= 0.0205 \times 23.37 \times 10^{-3} = 4.79 \times 10^{-4}$ [1]

mole ratio of $MnO_4^-(aq)$: $Sn^{2+}(aq) = 5 : 2$

mole ratio of $Sn^{2+}(aq)$ in 250 cm³ $= 4.79 \times 10^{-4} \times \frac{5}{2} = 0.00120$

mole ratio of sample in sample bronze $= 0.00120 \times \frac{250}{25} = 0.0120$ [1]

% by mass of tin in the sample$= \frac{0.0120 \times 118.7}{15.03} = 9.46\%$ [1]

[deduct 1 mark if 23.90 cm³ is included in the calculation of the mean titre, i.e. % by mass of tin is 9.51']

ASL02(II)_10

(a) $NH_4^+(aq) + OH^-(aq) \longrightarrow NH_3(aq) + H_2O(l)$ [1]

(b) Methyl red / methyl orange; from yellow to orange [2]

Phenolphthalein; from pink to colorless

(c) mole of NaOH(aq) remained $= 0.123 \times 10.8 \times 10^{-3} = 1.328 \times 10^{-4}$ [1]

mole of NaOH(aq) reacted

$= 0.105 \times 25 \times 10^{-3} - 1.328 \times 10^{-4} = 1.297 \times 10^{-3}$ [1]

mole of $NH_4^+(aq) = 1.297 \times 10^{-3} \times \frac{250}{25} = 1.297 \times 10^{-2}$ [1]

mass of N $= 1.297 \times 10^{-2} \times 14 = 0.1815$ [1]

% by mass of N $= \frac{0.1815}{1.64} \times 100\% = 11.1\%$ [1]

AL03(I)_01 modified

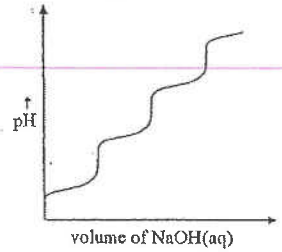
(a) $H_3PO_4(aq) \rightleftharpoons H_2PO_4^-(aq) + H^+(aq)$ [1]

$H_2PO_4^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H^+(aq)$ [1]

$HPO_4^{2-}(aq) \rightleftharpoons PO_4^{3-}(aq) + H^+(aq)$ [1]

(b) After the removal off a hydrogen ion, the remaining species has an additional negative charge that attracts the remaining hydrogen ions more strongly. [1]

(c) [3]



(2 mark for a curve showing the neutralization of H_3PO_4, $H_2PO_4^-$ and HPO_4^{2-}, 1 mark for labeling the axes.)

ASL03(II)_12 (I)

(a) $[I_2(aq)] = \frac{0.0243 \times 3}{2.5} = 0.0288$ mol dm^{-3} [2]

(b) Use starch solution as indicator [1]

Add iodine solution until a blue color is developed [1]

(c) Formula mass of ascorbic acid = 176 [1]

mass of ascorbic acid in 1.0 dm³ of grapefruit juice

$= \frac{0.0288 \times 18}{25} \times 176 = 3.65$ g [2]

(d) As an anti-oxidant [1]

ASL03(II)_12 (II)

(a) Use a pipette to transfer 25.0 cm³ of the bleach to a 250.0 cm³ volumetric flask. [1]

Add deionized water to the flask until the bottom of the meniscus reaches the mark on the flask. [1]

(b) $2H^+(aq) + ClO^-(aq) + 2I^-(aq) \longrightarrow Cl^-(aq) + I_2(aq) + H_2O(l)$ [1]

(c) Add $Na_2S_2O_3(aq)$ until the liquid in the conical flask turns pale yellow. [1]

Add starch solution and continue the titration until the color of the liquid changes from blue to colorless. [1]

(d) $I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$ [1]

$[ClO^-(aq)] = \frac{0.105 \times 18}{2 \times 25} = 0.0378$ mol dm^{-3} [1]

$[NaClO(aq)] = 0.0378 \times (23 + 35.5 + 16) \times 10 = 28.2$ g dm^{-3} [1]

AL04(I)_07

Step 1:

A standard NaOH(aq) should not be prepared using the method as described. [½]

Explanation: NaOH(s) is hygroscopic. [½]

Correction: It is necessary to standardize the NaOH(aq) before use. [½]

Step 3:

The burette should not be rinsed with water only. [½]

Explanation: Water that remains in the burette will cause a dilution of the NaOH(aq). [½]

Correction: The burette needs to be rinsed with deionized water and then with the NaOH(aq) prepared. [½]

Step 4:

Methyl orange is not a suitable indicator. [½]

Explanation: The experiment involves a titration of a week acid with a strong alkali. pH at the end point is about 8 to 9. [½]

Correction: Phenolphthalein should be used. [½]

Step 5:

Calculation should not be based on the result of one titration only. [½]

Explanation: There may be errors in the titration. [½]

Correction: Repeat the titration at least 3 times. Use the mean titre for the calculation. [½]

AL04(II)_04

(a) $3CH_3CH_2OH + 2Cr_2O_7^{2-} + 16H^+ \longrightarrow 3CH_3COOH + 4Cr^{3+} + 11H_2O$ [1]

(b) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$ [1]

moles of Fe^{2+} used in titration $= 0.118 \times 12.23 \times 10^{-3}$

moles of excess $Cr_2O_7^{2-} = \frac{1}{6} \times 0.118 \times 12.23 \times 10^{-3} = 2.405 \times 10^{-4}$ [1]

moles of excess $Cr_2O_7^{2-}$ added $= 0.156 \times 25 \times 10^{-3} = 3.9 \times 10^{-3}$ [1]

moles of excess $Cr_2O_7^{2-}$ that reacts with CH_3CH_2OH
$= 3.9 \times 10^{-3} - 2.405 \times 10^{-4} = 3.659 \times 10^{-3}$ [1]

$[CH_3CH_2OH]$ in the brand of spirit $= \frac{3.659 \times 10^{-3} \times 10}{10 \times 10^{-3}} \times \frac{3}{2} = 5.49 \text{ mol dm}^{-3}$ [1]

ASL04(II)_08

(a) Use a graduated pipette to transfer 5.0 cm³ of the household blech to a 250.0 cm³ volumetric flask. [1]

Add deionized water to the flask until the bottom of the meniscus reaches the mark on the flask. [1]

(b) Add $Na_2S_2O_3$(aq) until the color of the solution in the flask becomes pale yellow. [1]

Add starch indicator and continue the titration until the solution becomes colorless. [1]

(c) $I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$ [1]

moles of ClO^- in 25 cm³ of the diluted bleach $= \frac{1}{2} \times 0.0552 \times 16 \times 10^{-3}$ [1]

$[NaClO]$ in the bleach $= \frac{\frac{1}{2} \times 0.0552 \times 16 \times 10^{-3} \times 10}{5 \times 10^{-3}} = 0.883 \text{ mol dm}^{-3}$ [1]

AL05(II)_01

(a) $2X(s) + 6HCl(aq) \longrightarrow 2XCl_3(aq) + 3H_2(g)$ [1]

$X_2O_3(s) + 6HCl(aq) \longrightarrow 2XCl_3(aq) + 3H_2O(l)$ [1]

(b) According to the equations, $2X \equiv X_2O_3$

For complete reaction with 6 mole of HCl, the mass of X(s) required is less than that of X_2O_3.

Greatest possible value of RAM of X can be calculated by assuming that the sample contains X only.

moles of HCl(aq) used $= 0.0954 \times 6 = 0.5724$

Since the sample consists of pure X & 1 mole of X reacts with 3 moles of HCl

moles of X $= \frac{0.5724}{3} = 0.1908$ [1]

Greatest possible RAM of X $= \frac{16.5}{0.1908} = 86.5$ [1]

Smallest possible value of RAM of X can be calculated by assuming that the sample contains X_2O_3 only.

Since 1 mole of X_2O_3 reacts with 6 moles of HCl [1]

moles of $X_2O_3 = \frac{0.5724}{6} = 0.0954$

Let the RAM of X be A

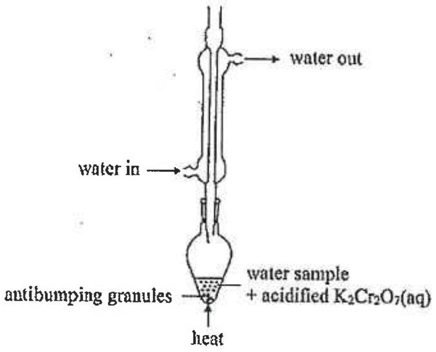
$\frac{16.5}{2A + 16 \times 3} = 0.0954$ [1]

Smallest possible RAM of X = 62.5

(c) The only trivalent metal with RAM in the range of 62.5 to 86.5 is gallium, Ga [1]

ASL05(II)_11

(a) [1]



(b) $Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(l)$ [1]

(c) moles of $Cr_2O_7^{2-}$ originally added $= 0.010 \times 2.5 \times 10^{-3} = 2.5 \times 10^{-5}$ [1]

moles of $Cr_2O_7^{2-}$ remaining $= \frac{1}{6} \times 0.0124 \times 7.6 \times 10^{-3} = 1.57 \times 10^{-5}$ [1]

moles of $Cr_2O_7^{2-}$ consumed $= 2.5 \times 10^{-3} - 1.57 \times 10^{-5} = 9.3 \times 10^{-6}$ [1]

mole of $K_2Cr_2O_7$ required to oxidize all organic matter in 1 dm³ of water sample
$= 9.3 \times 10^{-6} \times 10 = 9.3 \times 10^{-5}$ [1]

AL06(I)_02

(a) Limestone / marble / chalk / anhydrite / gypsum / fluorite [1]

(b) moles of H^+(aq) exchanged $= 0.020 \times 15 \times 10^{-3} = 3.0 \times 10^{-4}$ [1]

moles of Ca^{2+}(aq) / Mg^{2+}(aq) exchanged $= \frac{3.0 \times 10^{-4}}{2} = 1.5 \times 10^{-4}$

Total hardness of the waster sample $= \frac{1.5 \times 10^{-4}}{50 \times 10^{-3}} = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$ [1]

AL06(II)_07

Given that when treated with acidified KI(aq), 1 mol of peroxide liberates 1 mol of I_2

$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$

$I_2 \equiv 2S_2O_3^{2-}$

mole of $S_2O_3^{2-}$ used $= 0.012 \times 21.2 \times 10^{-3} = 2.54 \times 10^{-4}$ [1]

Mole of O_2 absorbed per kg of oil $= \dfrac{\frac{2.54 \times 10^{-4}}{2}}{4.85 \times 10^{-3}} = 26.2 \times 10^{-2}$ [2]

ASL06(II)_09c

(i) $MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \longrightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$ [1]

(ii) moles of Fe^{2+} present $= 5 \times$ moles of MnO_4^- reacted

$= 5 \times 34.7 \times 10^{-3} \times 0.0208 = 3.609 \times 10^{-3} =$ moles of Fe [1]

mass of Fe present in the sample $= 3.609 \times 10^{-3} \times 55.8 = 0.201$ g [1]

% by mass of Fe $= \dfrac{0.201}{0.212} \times 100\% = 94.8\%$ [1]

(iii) The impurities in the iron sample have no reaction with MnO_4^-. [1]

No air oxidation of Fe^{2+} to Fe^{3+}.

(iv) Not appropriate. MnO_4^- might oxidize Cl^- in the solution. [1].

AL07(I)_07

(a) Primary standard: a standard solution of the substance can be prepared by dissolving a known mass of the substance in a solvent and making up the solution to a known volume. [1]

(b) (i) $Br_2(l)$ is volatile. It is difficult to weigh a sample of $Br_2(l)$ accurately. [1]

(ii) KOH(s) absorbs water moisture/absorbs CO_2. [1]

ASL07(II)_03

(a) (i) $2Cu^{2+}(aq) + 4I^-(aq) \longrightarrow 2CuI(s) + I_2(aq)$ [1]

(ii) $I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$ [1]

(b) ∵ no. of mole of Cu^{2+} = no. of mole of $S_2O_3^{2-}$ [1]

mass of Cu^{2+} in the sample $= 25.8 \times 10^{-3} \times 0.102 \times 63.5 = 1.67$ g [1]

% by mass of Cu in the ore $= \dfrac{1.67}{3} \times 100\% = 55.7\%$ [1]

(c) Open-ended question. Possible answers [1]

The impurities in the sample do not react with KI(aq) to give $I_2(aq)$

$Cu^{2+}(aq)$ reacts quantitatively with $I^-(aq)$ to give CuI(s) and $I_2(aq)$.

ASL09(II)_03

(a) Red to orange [1]

(b) moles of NaOH used in the titration $= 0.0941 \times 16.48 \times 10^{-3} = 1.55 \times 10^{-3}$ [1]

moles of H^+ originally present $= 0.955 \times 25 \times 10^{-3} \times 2 = 0.0478$

moles of H^+ that react with Mg $= 0.0478 - 1.55 \times 10^{-3} = 0.0322$ [1]

$Mg + 2H^+ \longrightarrow Mg^{2+} + H_2$

moles of Mg in the ribbon $= \dfrac{0.0322}{2} = 0.0161$ [1]

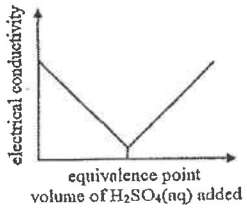
relative atomic mass $= \dfrac{0.420}{0.0161} = 26.05$ [1]

(c) Some of the Mg has been oxidized to MgO [1]

AL10(I)_07

(a) Electrical conductivity [1]

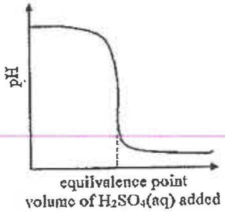
(b) [1]



Electrical conductivity decreases before the equivalence point because the concentration of the highly conducting $OH^-(aq)$ decreases as it reacts with $H^+(aq)$ to give $H_2O(l)$. [½]

After the equivalent point, the increase in conductivity is due to the increase in $[H^+(aq)]$. [½]

OR pH (1)



pH drops before the equivalent point because $OH^-(aq)$ ions are removed by $H^+(aq)$ ions. (1)

$OH^-(aq) + H^+(aq) \longrightarrow H_2O(l)$

When it is close to the equivalence point, both $[H^+(aq)]$ and $[OH^-(aq)]$ are small. (½)

Addition of a drop of $H_2SO_4(aq)$ can lead to a significant decrease in pH. (½)

AL11(I)_01

(a) $2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$ [1]

$MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \longrightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$ [1]

(b) $[MnO_4^-\ (aq)]\ \text{used} = \dfrac{0.0326 \times 25 \times 10^{-3}}{24.35 \times 10^{-3}} \times \dfrac{2}{5} = 0.0134\ \text{mol dm}^{-3}$ [1]

mole of Fe^{2+} in the solid sample $= 0.0134 \times 31.85 \times 10^{-3} \times 5 = 2.13 \times 10^{-3}$ [1]

% by mass of $Fe^{2+} = \dfrac{2.13 \times 10^{-3} \times 55.8}{0.863} \times 100\% = 13.8\%$ [1]

Acceptable range: 13.6% – 13.9 %

(c) Any ONE of the following: [1]

1. $KMnO_4(s)$ is a strong oxidizing agent. It readily reacts with reducing agents in the environment.
2. $KMnO_4(s)$ cannot be obtained in high purity.
3. $KMnO_4(aq)$ readily undergoes decomposition in the presence of light.

AL12(I)_07

(a) I_2 forms a very stable / water-insoluble complex with starch. Addition of starch right at the beginning will affect the accuracy of the titration. [1]

(b) $S_2O_3^{2-}(aq)$ will hydrolyze under acidic conditions. [1]

$S_2O_3^{2-}(aq) + 2H^+(aq) \longrightarrow SO_2(g) + S(s) + H_2O(l)$

AL12(I)_08

(a) Phenolphthalein / phenol red [1]

(b) mole of excess $OH^-(aq) = 2.50 \times 23.1 \times 10^{-3} = 5.78 \times 10^{-2}$ [½]

mole of $OH^-(aq)$ originally used $= 3.05 \times 25.0 \times 10^{-3} = 7.63 \times 10^{-2}$ [½]

mole of $OH^-(aq)$ reacted with aspirin $= 7.63 \times 10^{-2} - 5.78 \times 10^{-2} = 0.0185$ [½]

mass of aspirin $= 0.0185 \times 180 = 3.33$ [½]

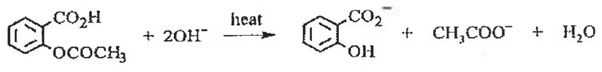
% by mass $= \dfrac{3.33}{2.25} \times 100\% = 148\%$ [1]

Reason: The ester group in aspirin undergoes alkaline hydrolysis. [½]

The amount of $OH^-(aq)$ consumed is greater than the expected value. [½]

(c) Any ONE of the following: [1]

- Use a smaller amount of aspirin so that a less concentrated NaOH(aq) can be used.
- Heat the reaction mixture to ensure complete hydrolysis of the ester so that the calculation can be based on the reaction:



AL12(II)_01

(a) mole of Br^- = mole of AgBr(s) formed $= \dfrac{0.816}{107.9 + 79.9} = 0.004345$ [1]

mole of MBr_2 formed $= \dfrac{0.004345}{2} = 0.00217$ [1]

formula mass of $MBr_2 = \dfrac{0.400}{0.00217} = 184.1$ [1]

(b) Relative atomic mass of M = 184.1 – 2×79.9 = 24.3 [1]

M is magnesium [1]

(c) No. AgF(s) is soluble in water. [1]

Ag(s) cannot be precipitated from $MF_2(aq)$ by adding $AgNO_3(aq)$. [1]

ASL13(II)_01

(a) (i) $IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \longrightarrow 3I_2(aq) + 3H_2O(l)$ [1]

(ii) $I_2(s)$ is volatile and cannot be weighed accurately. [1]

$I_2(s)$ readily reacts with reducing agents in the surrounding.

(iii) mole of KI used $= \dfrac{2}{39.1 + 126.9} = 0.012$

$I^-(aq)$ is in excess.

$[I_2(aq)]$ prepared $= 0.01 \times 3 \times \dfrac{100}{25} = 0.012\ \text{mol dm}^{-3}$ [1]

(b) Add starch indicator. [1]

The solution turns blue when the end point is reached. [1]

(c) (i) moles of $I_2(aq)$ used in the titration $= 7.6 \times 10^{-3} \times 0.012$ [1]

mass of ascorbic acid in 100 cm^3 of orange juice

$= \dfrac{7.6 \times 10^{-3} \times 0.012 \times 100}{25.00} \times 176.0$ [1]

$= 0.0642\ g$ [1]

(ii) Apart from ascorbic acid, the orange juice does not contain any other substances that react with I_2. [1]

DSE11SP_03b

(i) $3CH_3CH_2OH + 2Cr_2O_7^{2-} + 16H^+ \longrightarrow 3CH_3COOH + 4Cr^{3+} + 11H_2O$ [1]

(ii) Large formula mass [1]

Stable in air [1]

(iii) Retain some portions and allow a longer period of time, say 2 days. [1]

Perform the titration again. If the titre is consistent with the previous result, there has been complete oxidation of ethanol. [1]

(iv) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$ [1]

Mole of Fe^{2+} used in titration $= 0.118 \times 12.23 \times 10^{-3}$ [1]

Mole of excess $Cr_2O_7^{2-}$

$= \dfrac{1}{6} \times 0.118 \times 12.23 \times 10^{-3} = 2.405 \times 10^{-4}$ [1]

Mole of $Cr_2O_7^{2-}$ added $= 0.156 \times 25 \times 10^{-3} = 3.9 \times 10^{-3}$

Mole of $Cr_2O_7^{2-}$ that react with CH_3CH_2OH

$= 3.9 \times 10^{-3} - 2.405 \times 10^{-4} = 3.659 \times 10^{-3}$ [1]

Concentration of ethanol in the brand of spirit

$= \dfrac{3.659 \times 10^{-3} \times 10}{10 \times 10^{-3}} \times \dfrac{3}{2} = 5.49 \text{ mol dm}^{-3}$ [1]

DSE12PP_03b

(i) Wash the precipitate thoroughly with deionized water. [1]

Dry the precipitate in an oven / ensure that the precipitate is dried before it is weighed. [1]

(ii) $Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$

no. moles of Ba^{2+} present $= \dfrac{0.291}{(137.3 + 32.1 + 16 \times 4)} = 1.25 \times 10^{-3}$ [1]

mass of Ba in the sample $= 1.25 \times 10^{-3} \times 137.3 = 0.171$ [1]

% by mass of Ba in the sample $= \dfrac{0.171}{0.305} = 56.1$ [1]

(acceptable range : 56.0 to 56.4)

(c) Any TWO of the following: [2]

- The reaction must be significantly complete, i.e. the precipitate is practically insoluble.
- The product (precipitate) should have definite chemical composition.
- The rate of reaction must be fast enough to be practical.

DSE12_03c

(i) (acidified) $AgNO_3(aq)$ and $NH_3(aq)$ [2]

(ii) Step 1: Add excess $AgNO_3(aq)$ to the solution to form AgCl(s) and AgI(s). [1]

Step 2: Filter the mixture, wash with deionized water and dry the residue. [1]

Step 3: Determine / Weigh the total mass of AgCl(s) and AgI(s) collected. [1]

Step 4: Wash the solid residue with excess ammonia solution to dissolve / remove AgCl(s), filter and dry the residue, and determine the mass of AgI(s) remains. [1]

(iii) Subtracting the total mass of AgCl(s) and AgI(s) determined in Step 3 by the mass of AgI(s) determined in Step 4 to get the mass of AgCl(s). [1]

Number of mole of AgCl and AgI can be obtained by dividing their respective mass by the corresponding molar mass. Mole ratio of $Cl^-(aq)$ to $I^-(aq)$ can then be determined. [1]

DSE13_03b

(i) Any ONE of the following: [1]

- A significant observable change can easily be detected with the complete consumption of the reagent in the conical flask, i.e. availability of suitable indicator

- The reaction must be significantly complete / it is not a reversible reaction
- The rate of reaction must be fast enough to be practical

(ii) SO_2 easily escapes from solution / I_2 is volatile. [1]

(iii) From colorless to blue-black / blue / dark blue [1]

(iv) Mole of I_2 used $= 0.00412 \times 10.50 \times 10^{-3} = 4.33 \times 10^{-5}$ [1]

Mole of SO_2= no. of mole of $I_2 = 4.33 \times 10^{-5}$ [1]

Mass of $SO_2 = 4.33 \times 10^{-5} \times 64.1 = 2.77 \times 10^{-3}$ g $= 2.77$ mg [1]

$[SO_2]$in the wine sample $= \dfrac{2.77}{0.025} = 111 \text{ mg dm}^{-3}$ (Range: 110 – 112) [1]

(v) This method cannot be used as the intense red color of red wine may mask the color of iodine / iodine-starch complex which leads to a difficulty in the end-point detection. [1]

OR This method can be used if the color of red wine can be removed.

DSE14_03b

(i) To ensure the reaction go to completion / To increase the reaction rate. [1]

(ii) (1) No more gas is given out / All solids are dissolved. [1]

(2) Brown precipitate formed. [1]

(iii) Mole of CaC_2O_4 formed in step 6 $= \dfrac{2.374}{128.1} = 0.01853$ [1]

Mass of $CaCO_3$ in the limestone sample $= 0.01853 \times 100.1 = 1.855$ g [1]

% mass of $CaCO_3 = \dfrac{1.855}{2.025} = 91.60\%$ (*Range*: 91.3 – 91.9) [1] ✓

(iv) Gravimetric analysis [1]

DSE15_03

(i) (1) $NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$ [1]

OR $(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3 + Na_2SO_4 + 2H_2O$

(2) $NH_3 + H^+ \longrightarrow NH_4^+$ [1]

OR $NH_3 + HCl \longrightarrow NH_4Cl$

(ii) From red to orange [1]

(iii) Moles of KOH used in the titration $= 0.100 \times 13.55 \times 10^{-3}$ [1]

$= 1.355 \times 10^{-3}$

Moles of H^+ ions remained after Step 2 $= 1.355 \times 10^{-3} \times 10 = 0.01355$ [1]

Moles of H^+ ions used in Step 2 $= 1.00 \times 50 \times 10^{-3} = 0.05$ [1]

Moles of NH_3 liberated $= 0.05 - 0.01355 = 0.03645$

Mass of N in the sample $= 0.03645 \times 14 = 0.5103$ g

% by mass of N in the sample $= \dfrac{0.5103}{3} \times 100 = 17.01\ \%$ [1]

(iv) The amount of nitrogen determined may come from other nitrogen-containing substances present in milk powder. [1]

DSE16_03a

Any ONE of the following answers: [1]

- Sodium hydroxide (solid) is deliquescent / hygroscopic / can absorb H_2O / can dissolve in H_2O.
- Sodium hydroxide (solid) absorbs / reacts with carbon dioxide (gas from air). (accept any reasonable acidic gas e.g. SO_2 / NO_2 …)

DSE16_03b

(i) (1) $Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(l)$ [1]

(2) Moles of $Fe^{2+} = 0.0642 \times 26.88 \times 10^{-3} = 0.0017257$ [1]

$[Cr_2O_7^{2-}(aq)] \times 25.00 \times 10^{-3} \times 6 = 0.0017257$

$[Cr_2O_7^{2-}(aq)] = 0.0115$ mol dm^{-3} [1]

(0.011505 mol dm^{-3} / 0.0120 mol dm^{-3} / wrong unit 0 mark)

(ii) (1) (Blue filter allows blue light to pass through and the) orange $Na_2Cr_2O_7(aq)$ solution absorbs blue light to a large extent. [1]

(2) The absorbance is directly proportional to / ∝ the concentration of $Cr_2O_7^{2-}$ (aq). / linear relationship / shows a straight line [1]

(3) Absorbance = 0.26,

$[Cr_2O_7^{2-}(aq)]$ found from the graph is 7.0×10^{-4} (mol dm^{-3}) [1]

$[Cr_2O_7^{2-}(aq)]$ in sample B = $7.0 \times 10^{-4} \times (100) = 0.07$ mol dm^{-3} [1]

Range : 0.0685 to 0.0705 mol dm^{-3})

(iii) Colorimetry is more appropriate. / Volumetric analysis is less appropriate. [1]

The low color intensity of the solution can still be determined by colorimetry. [1]

DSE17_03b

(i) From (yellowish) green to pale pink. [1]

(ii) (1) $(37.62 + 37.58 + 37.60) \div 3 = 37.60\ cm^3$ [1]

[Not accept 37.6] Must show step and unit

(2) Moles of Fe^{2+} ions formed in Step (1)

$= 0.0282 \times 37.6 \times 10^{-3} \times 5 \times 10 = 0.0530$ [1]

Moles of Fe^{3+} ions reacted in Step (1) = 0.0530 [1]

[Accept 37.785 / 37.79 / 37.6 for 37.60, Range 0.0530 – 0.0533]

Mole of $HONH_2$ reacted = $0.875 \div 33.0 = 0.0265$ [1]

Mole ratio of $HONH_2 : Fe^{3+} = 1 : 2$ [1]

(3) The oxidation number of iron changes from +3 to +2 and the oxidation number of N in $HONH_2$ is −1.

Since the mole ratio of $HONH_2 : Fe^{3+} = 1 : 2$, [1]

the oxidation number of N in this oxide = −1 + 2 = +1 [1]

(iii) N_2O [1]

DSE18_03b

(i) Place the dissolved sample into a (250.0 cm^3) volumetric flask. [1]

(Deionised) water should be added to the mark of the volumetric flask (until the bottom of the meniscus reach the graduation mark) [1]

(ii) $ClO_3^-(aq) + 6I^-(aq) + 6H^+(aq) \longrightarrow Cl^-(aq) + 3I_2(aq) + 3H_2O(l)$ [1]

(iii) The solution turns from blue to colourless. [1]

(iv) $I^-(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

moles of $I_2(aq) = 0.112 \times 0.02788 \times \frac{1}{2} = 0.001561$ [1]

moles of $NaClO_3$ in the sample $= \frac{0.001561}{3} \times \frac{250.0}{10.0} = 0.01301$ [1]

% by mass of $NaClO_3 = \frac{0.01301 \times 106.5}{1.63} \times 100\%$ [1]

= 85.0% [Range: 84 – 86]

DSE19_03b

(b) (i) It is to prevent the formation of solid Ag_2CO_3 etc. 1

(ii) 1

Correct labelling :
Burette, conical flask, KSCN(aq), acidified bacon sample with $AgNO_3(aq)$ 1

(iii) No. of mole of KSCN(aq) = No. of mole of $Ag^+(aq)$ left in the mixture = No. of mole of $Ag^+(aq)$ reacted with KSCN(aq) = 0.1 × 0.00942 4
No. of mole of AgCl formed
= 1.0 × 0.0025 – 0.1 × 0.00942 = 0.001558
Percentage by mass of sodium = (0.001558 × 23.0 / 2.0) × 100%
= 1.79%

DSE20_03c

3. (c) (i) (1) orange to green 1
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ 1

(2) Driver **B** has a higher ethanol intake because the breath can also change the colour of the gel in position c while Driver **A** cannot. 1
(A comparative sense and similar meaning)

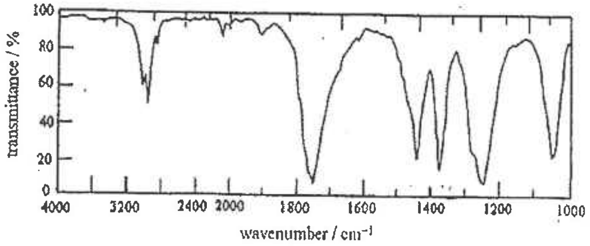
(3) (Exhale the) same amount / volume / strength of breath (into the tube). 1

(ii) No. of mole of ethanol = 0.025 × 4.38 × 10^{-3} × 3 = 0.0003285 mol (0.00033 / 0.000329) 1*
Mass of the ethanol = 0.0003285 × 46 (× 46) 1*
= 0.01511 g = 15.11 mg
The mass of ethanol in 100 cm^3 of serum sample = 15.11 mg ÷10 × 100 (÷10 × 100) 1*
= 151.1 mg
(The mass is) 151.1 mg (which exceeds 55 mg. The driver would be found) guilty. 1
(Range of answer: 150 – 152, max. 3 dec. places)

Instrumental Analysis

AL97(II)_06

Compound **H**, $C_3H_6O_2$, does not react with $NaBH_4$ and displays the following infra-red spectrum. Deduce all possible structures of **H**.



(4 marks)

AL98(I)_08a

Show how you would distinguish between propan-2-ol and propanone using spectroscopy

(1 mark)

AL98(II)_04

Sketch the expected mass spectrum for a gas sample having the composition: N_2 78%, O_2 21% and CO_2 1%.

(You only need to consider the major isotope of each elements)

(3 marks)

AL99(II)_01

Rubidium occurs naturally in two isotopic forms. The table below lists the mass and the relative abundance of each isotope.

Isotope	Mass / a.m.u.	Relative abundance
^{85}Rb	84.939	72.15%
^{87}Rb	86.937	27.85%

(a) Suggest an experimental method to detect the isotopes of rubidium and state how the relative abundance of each isotope can be obtained.

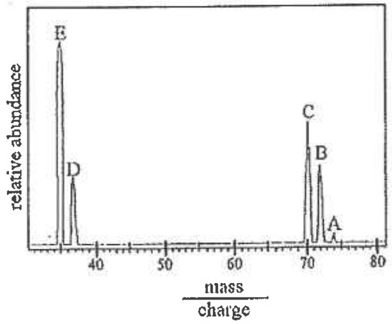
(2 marks)

(b) Calculation the relative atomic mass of rubidium.

(2 marks)

AL00(II)_01

Consider the mass spectrum of chlorine gas:



(A, B, C, D and E represent five different ionic species.)

(a) Explain why there are five peaks in the mass spectrum.

(3 marks)

(b) The ratio of relative abundance of D to E is 1 : 3.

(i) Calculate the relative atomic mass of chlorine.

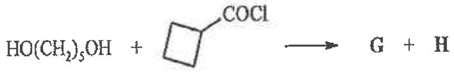
(2 marks)

(ii) Calculate the ratio of relative abundance of A to B to C.

(2 marks)

AL00(II)_05

A mixture of two organic products, G and H, was obtained in the reaction:



The mixture was separated by paper chromatography using a mixture of hexane and ether as solvent. The R_f values of G and H were found to be 0.84 and 0.55 respectively.

(a) Deduce the structures of G and H.

(4 marks)

(b) Suggest a chemical test to distinguish between G and H.

(2 marks)

(c) State how the use of infra-red spectroscopy can provide further proof for the structures of G and H.

(2 marks)

AL01(II)_01

Briefly describe the principle of mass spectrometry and its use to determine the relative atomic mass of a noble gas.

(8 marks)

AL01(II)_07

Study the following information:

Aromatic compound **T** and **U** have the same molecular formula $C_{10}H_{12}O$.

T gives positive result in iodoform test.

U reacts with hydrogen in the presence of a palladium catalyst to give compound **V** ($C_{10}H_{14}O$).

V can also be obtained from the reaction of **T** with $LiAlH_4$.

(a) Deduce the structures of **T**, **U** and **V**. For each compound, give all possible stereoisomers.

(7 marks)

(b) Suggest how infra-red spectroscopy can be used to distinguish between **T** and **U**.

(2 marks)

AL02(I)_05

Two acyclic structural isomeric compounds have the molecular formula $C_3H_6O_3$. Both are optically active and have infrared absorptions at 3400 and 1700 cm^{-1}. Neither possesses an alkoxy group.

(a) Draw the structure of each of the compounds. Label one of these structures 'A' and the other 'B'.

(2 marks)

(b) Suggest a chemical test, giving the expected observation, to distinguish between the compounds represented by 'A' and 'B'.

(2 marks)

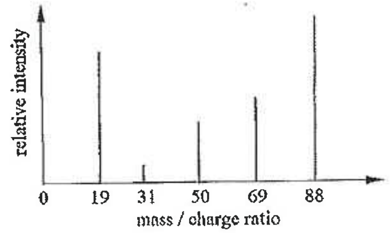
(c) Give the structure of the major organic product formed when the two compounds are treated separately with excess $LiAlH_4$.

Product from the compound represented by 'A'	Product from the compound represented by 'B'

(2 marks)

AL02(II)_01b

Elements **A** and **B** form a compound with molecular formula AB_3. A sample of the compound was injected into a mass spectrometer and the mass spectrum shown below was obtained.



(i) A molecular ion AB_3^+ was formed in the mass spectrometer. Suggest how AB_3^+ was formed.

(2 marks)

(ii) The peaks at mass/charge ratios 69 and 50 are due to cations formed from detaching one and two atoms of **B** from AB_3^+ respectively.

Account for the presence of the peaks at mass/charge ratios 19 and 31.

(2 marks)

(iii) Suggest what compound AB_3 is.

(1 mark)

AL03(II)_05

(a) Hardening of vegetable oils can be done by hydrogenation. Explain.

(2 marks)

(b) The fumes from the two processes below were collected and analyzed using infra-red (IR) spectroscopy. The table below lists the wavenumbers of the major absorption peaks.

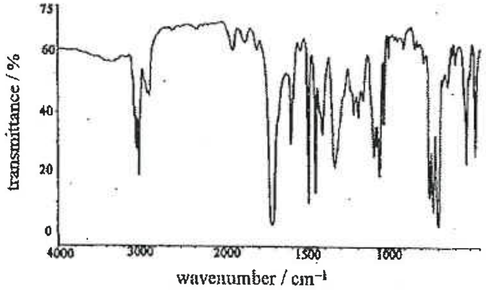
Process	Wavenumbers of major IR absorption peaks / cm^{-1}
Heating molten margarine	2950 and 1750
Frying potatoes with margarine	3100 (broad peak), 2959 and 1740

With the help of equation(s), suggest why the fumes from the two processes resulted in different IR absorptions.

(3 marks)

AL03(II)_07

Compound **E** ($C_{15}H_{14}O$) is a white solid with a melting point of 32 °C and displays the following infra-red spectrum.



E gives a negative result when treated with Tollens' reagent but reacts readily with $LiAlH_4$ to give a achiral compound **F**. Drastic oxidation of **F** with potassium manganate(VII) gives an aromatic compound **G** ($C_7H_6O_2$) with pK_a value of 4.2 as the major product.

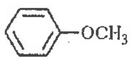
Deduce the structure of **E**, **F** and **G**.

(6 marks)

AL05(II)_05

Consider the isomeric compounds J and K below:

J 

K 

(a) Name the type of isomerism involved.

(1 mark)

(b) Suggest, with explanation, how J and K can be distinguished from each other by

(i) A physical method

(2 marks)

(ii) A chemical method, and

(2 marks)

(iii) A spectroscopic method.

(2 marks)

AL05(II)_06a

Formaldehyde (methanal) is one of the commonly found organic indoor air pollutants.

(i) Suggest a source of household formaldehyde.

(1 mark)

(ii) Some indoor purifiers remove formaldehyde by chemical means. Suggest one chemical for the removal of formaldehyde with the formation of less harmful products.

(1 mark)

(iii) Name one other organic indoor air pollutant and suggest its source.

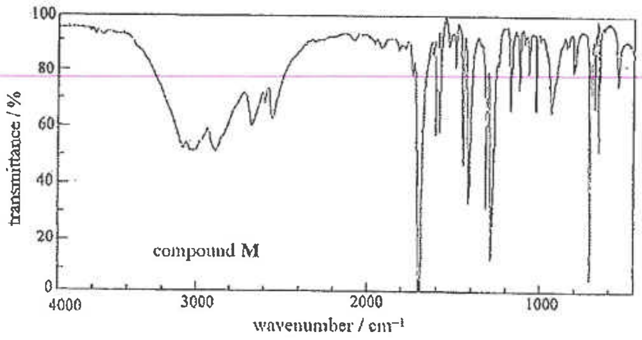
(2 marks)

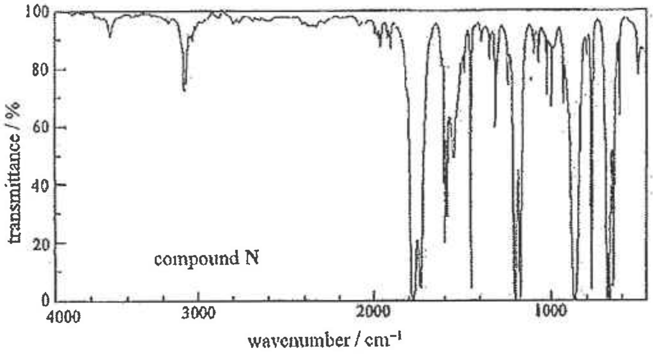
AL05(II)_07

Compound L, with a relative molecular mass of 108, has the following composition by mass:

C 77.8%, H 7.4 % and O 14.8%

L does not react with bromine, but undergoes oxidation with acidified $Na_2Cr_2O_7(aq)$ to give compound M. M reacts with PCl_5 to yield compound N. The infra-red spectra of M and N are shown below:





(a) Calculate the molecular formula of L.

(3 marks)

(b) Based on the above information, deduce the structures of L, M and N.

(5 marks)

AL06(II)_05

Deduce the structure of compound D on the basis of the information given below:

(1) Elemental analysis data show that D has the following composition by mass: C 40 %, H 6.7 % and O 53.3 %.

(2) The relative molecular mass of D is estimated to be in the range of 172 to 182.

(3) The infra-red spectrum of D shows, apart from the absorption of C–H stretching near 2900 cm^{-1}, a strong and broad absorption around 3400 cm^{-1}, and no appreciable absorption around 1700 cm^{-1}.

(4) All carbon atoms of D have the same bonding environment.

(5) D is highly soluble in water, and the solution does not decolorize bromine water.

(8 marks)

AL06(II)_06

Organic compounds in waste water can be degraded by oxidation with ozone. In a typical process, phenol is oxidized to give acyclic compound E ($C_6H_6O_4$). The infra-red spectrum of E shows a broad absorption band around 3300 cm^{-1} and a strong absorption at about 1700 cm^{-1}. Hydrogenation of E in the presence of 10% Pd on charcoal produces an acidic compound F ($C_6H_{10}O_4$).

(a) Suggest one structure for E and one for F, and explain your answer.

(5 marks)

(b) Suggest two advantages of using ozone to degrade organic compounds.

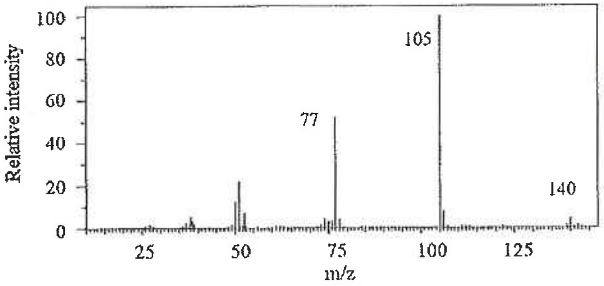
(2 marks)

AL07(II)_07

Compound **M** has the following composition by mass:

C, 59.8%; H, 3.6%; Cl, 25.2%; O, 11.4%

M displays the mass spectrum as shown below:



(a) Calculate the empirical formula of M.

(2 marks)

(b) Deduce the structure of M.

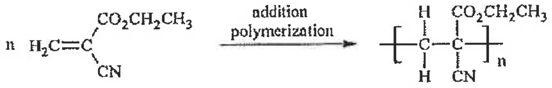
(3 marks)

(c) Suggest a chemical method to confirm the identity of a sample of M.

(2 marks)

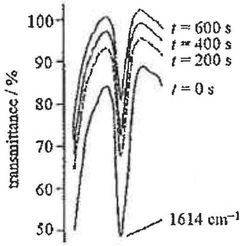
AL08(I)_08a

Super glue works as an adhesive by addition polymerization as shown below:



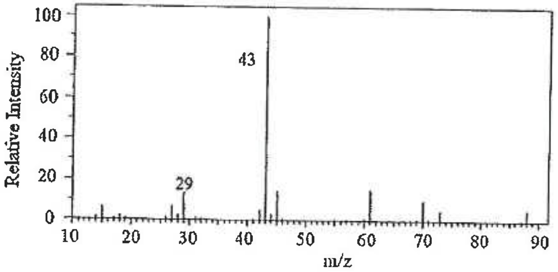
The progress of this polymerization was monitored by infra-red spectroscopy. Figure shows the change of transmittance with time (t) for the reaction system. Assign the functional group corresponding to the absorption at 1614 cm^{-1}. Account for the change of transmittance of this peak with time.

(2 marks)

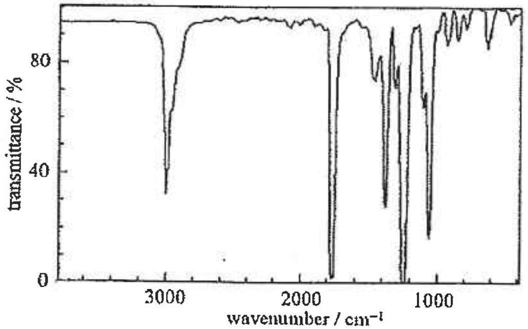


AL08(II)_06

Figures below respectively show the mass spectrum and infra-red spectrum of compound **A** ($C_4H_8O_2$). Based on the information in the figures, deduce ONE possible structure of **A**.



Mass spectrum of A

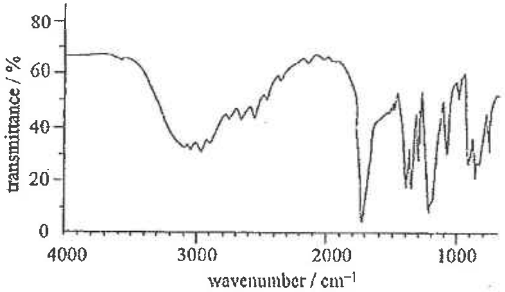


Infra-red spectrum of A

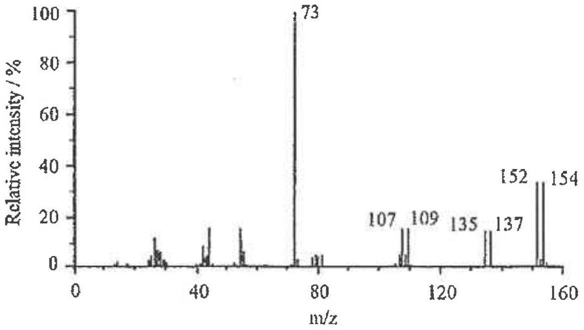
(6 marks)

AL09(II)_05

Below respectively show the infra-red spectrum and mass spectrum of compound **P** ($C_3H_5O_2Br$). Based on the information in the figures, deduce ONE possible structure of **P**.



Infra-red spectrum of **P**



Mass spectrum of **P**

(7 marks)

AL10(II)_03b

Mass spectrometry is often used in the determination of relative molecular mass, which is numerically equal to molar mass. Suggest TWO reasons why mass spectrometry is superior to the traditional method.

(2 marks)

AL10(II)_05

Compound **L** has the following composition by mass:

C, 70.6% ; H, 5.9%; O, 23.5%

Figures 5.1 and 5.2 respectively show the infra-red spectrum and mass spectrum of **L**.

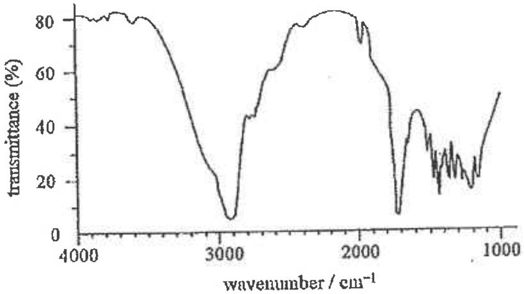


Figure 5.1 Infra-red spectrum of **L**

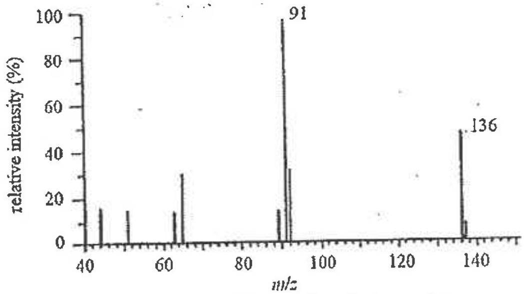


Figure 5.2 Mass spectrum of **L**

(a) Calculate the empirical formula of **L**.

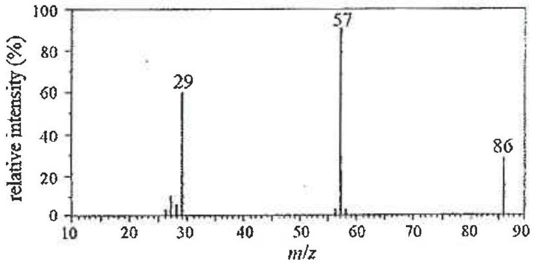
(2 marks)

(b) Deduce ONE possible structure of **L**.

(6 marks)

AL11(II)_10

Compound A contains carbon, hydrogen and oxygen only. It reacts with 2,4-dintrophenylhydrazine to give a yellow precipitate, but shows negative results when treated with acidified $K_2Cr_2O_7(aq)$. The mass spectrum of A is shown below. Deduce ONE possible structure of A.



(5 marks)

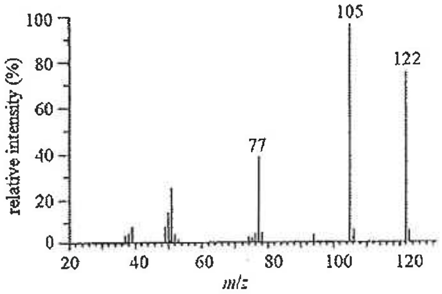
AL12(I)_05

Based on the information given below, deduce the possible structures of compound F, G and J:

(1) F ($C_9H_{10}O_2$) is optically active aromatic compound.

(2) F reacts with acidified $K_2Cr_2O_7(aq)$ to give an optically inactive compound G. When treated with excess $NaHCO_3(aq)$, 1 mole of G gives 2 mole of $CO_2(g)$.

(3) F reacts with hot acidified $KMnO_4(aq)$ to give another optically inactive compound J. J has the following mass spectrum.



(7 marks)

AL13(I)_15

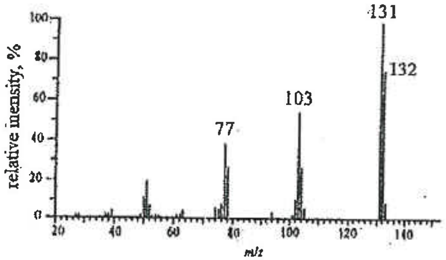
Form in information given below, deduce ONE possible structure for compound D.

(1) D has the following composition by mass:

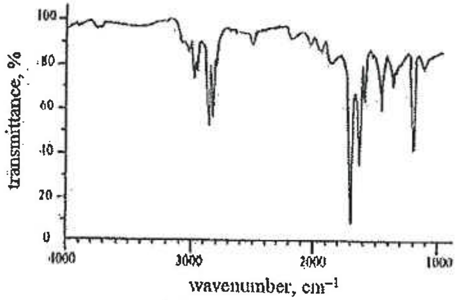
C, 81.8% H, 6.1% O, 12.2%

(2) D can turn acidified $K_2Cr_2O_7(aq)$ from orange to green.

(3) D displays the following mass spectrum and infra-red spectrum.



mass spectrum of D

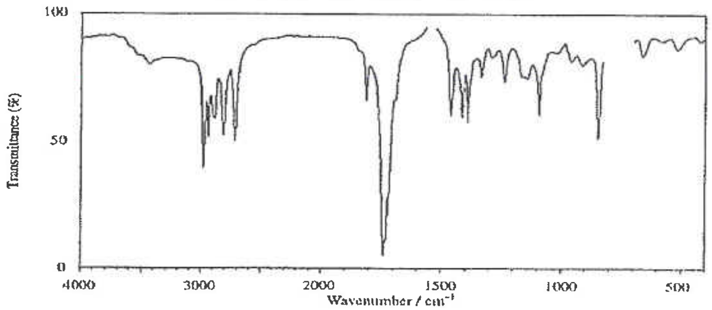


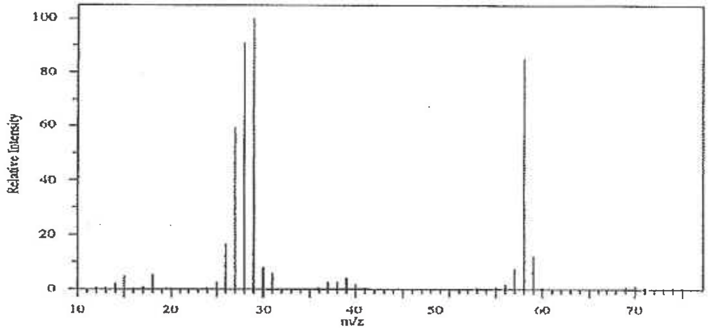
infra-red spectrum of D

DSE11SP_03a

Compound **G**, with relative molecular mass of 58, has the following composition by mass:

C: 62.1% H: 10.3% O: 27.6%





(i) Deduce the molecular formula of compound **G**.

(2 marks)

(ii) From the given spectral information and the molecular formula obtained in (i), deduce the structural formula of compound **G**.

(4 marks)

(iii) Suggest an experiment, with detailed procedures, to support the structure of compound **G** you have deduced in (ii).

(4 marks)

DSE12PP_03a

A colorless compound **X** ($C_9H_8O_2$) is obtainable from cinnamon. **X** has a melting point of 134 °C and is insoluble in water.

An experiment to extract **X** from an impure sample, which contains non-polar organic impurities, involves the following five steps:

Step 1:	Dissolve the sample in excess NaOH(aq).
Step 2:	Shake the solution from Step 1 with hexane and discard the organic layer.
Step 3:	Add HCl(aq) to the aqueous layer obtained until a white precipitate forms and the solution becomes acidic.
Step 4:	Collect the white precipitate by filtration.
Step 5:	Using ethanol as solvent, recrystallize the precipitate collected to obtain **X**.

(i) From the above experimental steps, suggest ONE functional group present in **X**.

(1 mark)

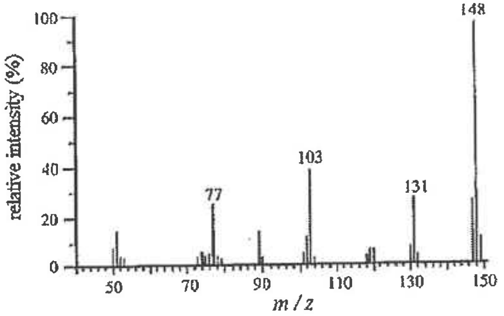
(ii) Name the apparatus used in Step 2.

(1 mark)

(iii) Briefly explain the purpose of carrying out Steps 1, 2 and 3 respectively.

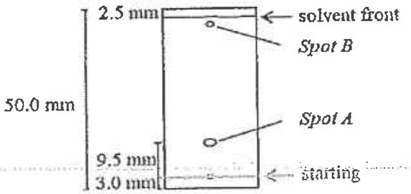
(3 marks)

(iv) **X** can decolorize Br_2 in CH_3CCl_3. It displays the following mass spectrum. Deduce ONE possible structure of **X**.



(5 marks)

(v) Another sample of **X** is contaminated with a colorless organic compound. The sample is analyzed by thin-layer chromatography (TLC), and the result is shown below:



(1) Suggest ONE method that can be used to make the two spots on the chromatographic plate become visible.

(1 mark)

(2) Given that *Spot A* corresponds to X, calculate the R_f of X.

(1 mark)

(3) Based on the TLC results, suggest ONE method to separate X from the contaminated sample.

(1 mark)

DSE12_03a

Compound X (molar mass < 118 g) contains a $-C_6H_5$ group. Two chemical tests are performed on X and the results are as follows:

Test (1) : X turns acidified potassium dichromate solution green.

Test (2) : X gives a negative result when tested with 2,4-dinitrophenylhydrazine.

(i) With reference to the result of Test (1) only, suggest TWO functional groups that X may have.

(2 marks)

(ii) (1) What is the purpose of using 2,4-dinitrophenylhydrazine in Test (2)?

(1 mark)

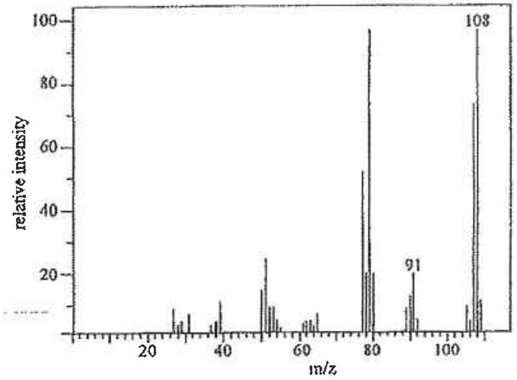
(2) State the expected observation if X gives a positive result in Test (2).

(1 mark)

(iii) With reference to the results of both Test (1) and Test (2), suggest one functional group that may be present in X.

(1 mark)

(iv) The mass spectrum of X is shown below:



Suggest one chemical species corresponding to each of the signals at m/z = 91 and 108.

(2 marks)

(v) Draw a possible structure of X.

(1 mark)

DSE12_03b

The dioxin levels in air are generally measured through instrumental analysis but not gravimetric analysis or volumetric analysis.

(i) Suggest a source of dioxin in air.

(1 mark)

(ii) Explain why there is a need to measure the dioxin levels in air.

(1 mark)

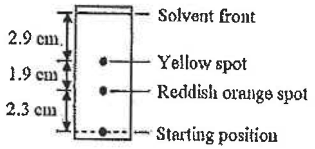
(iii) Suggest an instrumental analytical method for measuring the dioxin levels in air, and state why this method, rather than methods based on gravimetric analysis or volumetric analysis, is to be used.

(2 marks)

DSE13_03c

The main pigments in a certain brand of tomato paste are lycopene (reddish orange) and β-carotene (yellow). In order to isolate lycopene from the tomato paste, and experiment involving solvent extraction, thin-layer chromatography (TLC) and column chromatography was performed.

(i) The result of TLC is shown below:



Calculate the R_f value for the lycopene spot.

(1 mark)

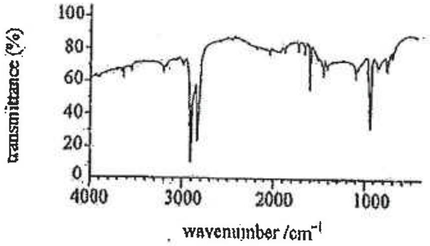
(ii) With reference to the result of TLC, explain whether the first-collected colored fraction in the column chromatography is lycopene or β-carotene, if the same stationary phase and mobile phase are used.

(1 mark)

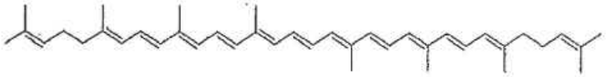
(iii) Suggest an instrumental method that can be used to determine the concentration of lycopene in the collected lycopene fraction. State the physical property of the lycopene fraction that needs to be measured.

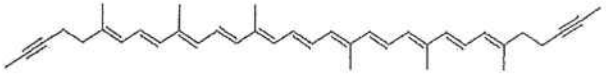
(2 marks)

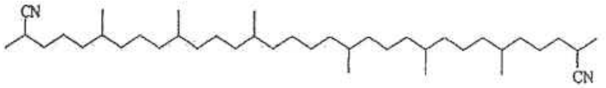
(iv) The infra-red spectrum of lycopene is shown below:

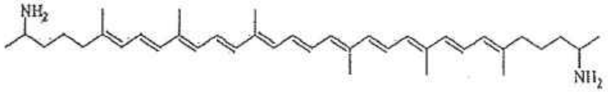


By referring to the Characteristic Infra-red Absorption Wavenumber Ranges (Stretching modes) given in the table below, suggest which of the following structure (W, X, Y or Z) may be the structure of lycopene. Explain your answer.

W:


X:


Y:


Z:


(4 marks)

DSE14_03c

Under room temperature, T ($C_xH_yO_z$) is a colorless oily liquid and is immiscible with water. Moreover, T does not react with $NaHCO_3(aq)$.

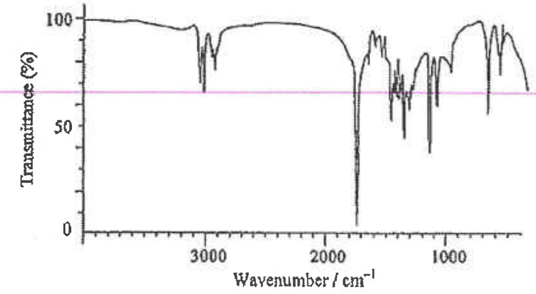
(i) A sample of T contains an organic acid as impurity. Outline the experimental steps for purifying the sample by using $NaHCO_3(aq)$ and pentane.

(2 marks)

(ii) With reference to the information given below, deduce the functional group(s) that T may have.

(I) T is NOT an ester, and it gives negative result with Tollen's reagent.

(II) T gives the following infra-red spectrum:



(2 marks)

(iii) The mass spectrum of T shows a parent peak at m/z = 134, and a strong peak at each of m/z = 43 and 91. Suggest one chemical species corresponding to each of the signals at m/z = 43 and 134.

(2 marks)

(iv) Draw one possible structure of T.

(1 mark)

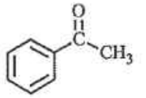
DSE15_03a

Suggest an instrumental method for determining the content of octane in a petrol sample.

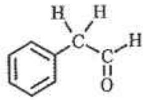
(1 mark)

DSE15_03b

Compounds X and Y shown below are isomers with relative molecular mass 120.



X



Y

(i) Each of X and Y can react with 2,4-dinitrophenylhydrazine solution to give a similar observation. State the observation.

(1 mark)

(ii) Suggest a chemical test to distinguish between X and Y.

(2 marks)

(iii) Illustrate how X and Y can be distinguished from their mass spectra.

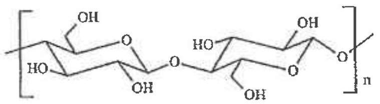
(2 marks)

(iv) With reference to the information given in the table below, suggest whether infra-red spectroscopy can be used to distinguish between X and Y.

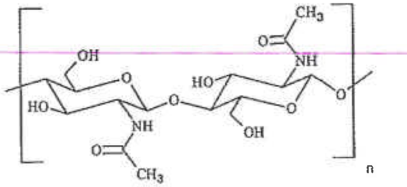
(2 marks)

DSE16_03a

Both cellulose and chitin are natural polymers. Their structures are shown below:



cellulose



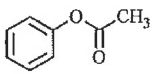
chitin

By referring to the data given in the table below, suggest one similarity and one difference between the infra-red spectra of cellulose and chitin.

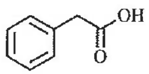
(2 marks)

DSE16_03c

X and Y are isomeric compounds with their structures shown below:



X



Y

(i) Suggest, with explanation, how X and Y can be differentiated from their respective mass spectra.

(2 marks)

(ii) The melting point of X is 50 °C while that of Y is 77 °C. Both of them are insoluble in water but soluble in dichloromethane. When treated with dilute $Na_2CO_3(aq)$, no reaction occurs for X but reaction occurs for Y to form a soluble salt.

(1) You are provided with dilute $Na_2CO_3(aq)$ and dilute $H_2SO_4(aq)$. Outline an experimental procedure, based on solvent extraction, to separate solid Y from a solution of X and Y in dichloromethane.

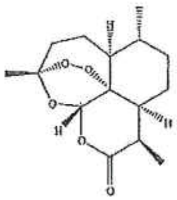
(4 marks)

(2) Suggest how you can identify that the solid obtained in (1) is pure compound Y.

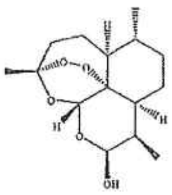
(1 mark)

DSE17_03c

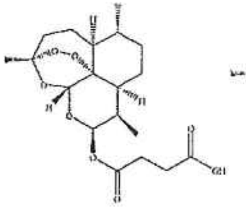
Artemisinin is an organic compound obtained from a certain plant. Artemisinin cannot react with $NaHCO_3(aq)$. Its infra-red spectrum shows a strong absorption peak at around 1700 cm^{-1}. Suggest which one of W, X, Y and Z below would be a possible structure of artemisinin. Explain your answer.



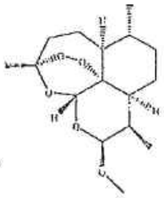
W



X



Y



Z

(3 marks)

DSE18_03c

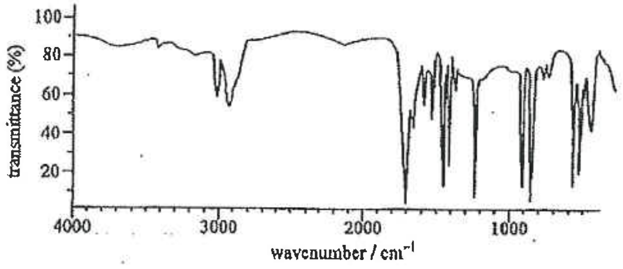
A liquid mixture consists of two organic compounds X and Y:

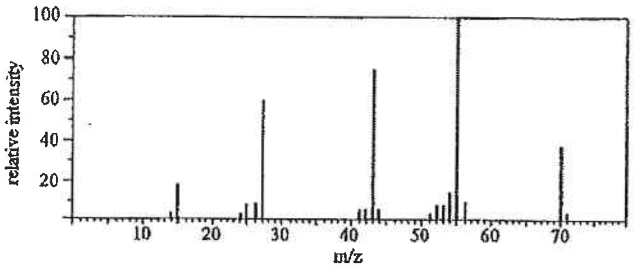
	X	Y
Molecular formula	C_4H_6O	C_4H_8O
Boiling point / °C	81.4	79.6

(i) Explain why fractional distillation is NOT a suitable method to separate X from the mixture.

(1 mark)

(ii) X gives the following infra-red spectrum and mass spectrum:





(1) By referring to the infra-red spectrum and the information given in the table below, deduce one functional group that may be present in X.

(1 mark)

(2) By referring to the mass spectrum, suggest one chemical species corresponding to each of the signals at m/z = 43 and 55.

(2 marks)

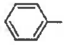
(3) According to (1) and (2) above, draw a possible structure of X.

(2 marks)

(iii) Compound Y shows a positive result in 2,4-dinitrophenylhydrazine test, and a negative result in Tollens' reagent test. Deduce what Y may be.

(3 marks)

DSE19_03cii

3. (c) Chlorine reacted with ethylbenzene ( $-CH_2CH_3$) under sunlight to give a mixture of different chlorinated compounds.

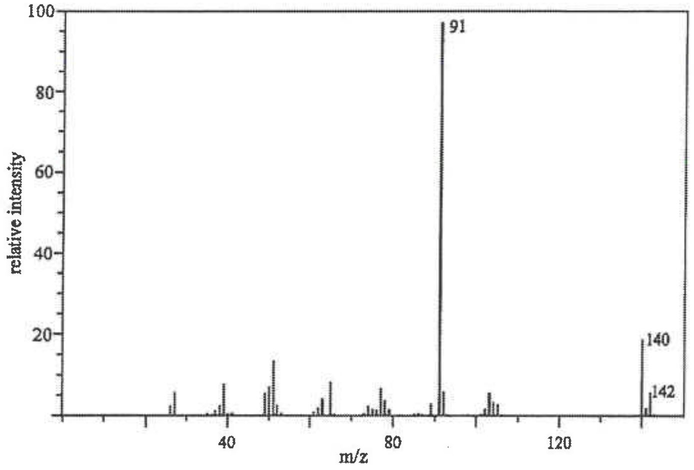
(i) Thin layer chromatography (TLC) was used to separate a small amount of the mixture.

(1) Explain briefly why chromatography can be used to separate a mixture.

(2) Based on the result in TLC, suggest a method to separate a large amount of the mixture.

(3 marks)

(ii) A monochlorinated compound was isolated from the mixture. It is known that chlorine has two isotopes, ^{35}Cl and ^{37}Cl. The mass spectrum of the compound is shown below :

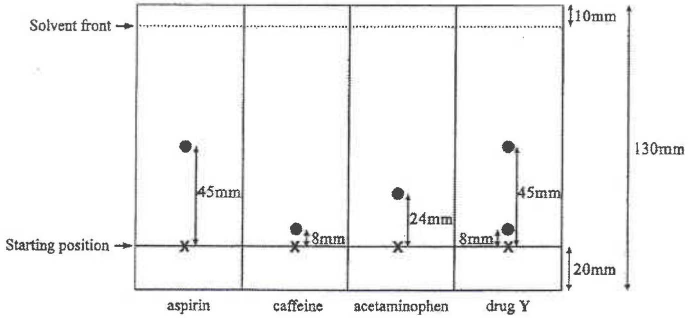


By referring to the labelled peaks, deduce a possible structure of the compound.

(3 marks)

DSE20_03 iv

(b) The chromatograms from thin-layer chromatography (TLC) of aspirin, caffeine, acetaminophen and a drug Y are shown below.



(i) Draw a labelled diagram for the set-up in performing a TLC experiment.

(2 marks)

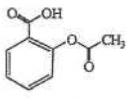
(ii) Calculate the R_f value for aspirin.

(1 mark)

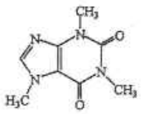
(iii) Based on the chromatograms provided, suggest whether drug Y would contain aspirin, caffeine or acetaminophen.

(1 mark)

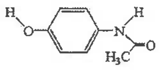
(iv) Consider the following structures :



aspirin



caffeine



acetaminophen

3. (b) (iv) (1) With reference to the table below, suggest how aspirin and caffeine can be distinguished from their infra-red spectra.

Characteristic Infra-red Absorption Wavenumber Ranges
(Stretching modes)

Bond	Compound type	Wavenumber range / cm^{-1}
C=C	Alkenes	1610 to 1680
C=O	Aldehydes, ketones, carboxylic acids and derivatives	1680 to 1800
C≡C	Alkynes	2070 to 2250
C≡N	Nitriles	2200 to 2280
O–H	Acids (hydrogen-bonded)	2500 to 3300
C–H	Alkanes, alkenes, arenes	2840 to 3095
O–H	Alcohols (hydrogen-bonded)	3230 to 3670
N–H	Amines	3350 to 3500

(2) A pure sample may be aspirin, caffeine or acetaminophen. There is a major peak at m/z = 43 in the mass spectrum of the sample. Explain whether this information can confirm that the sample is aspirin, caffeine or acetaminophen.

(3 marks)

Marking Scheme

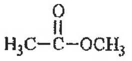
AL97(II)_06

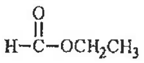
IR peat at ~1750 cm^{-1} indicates the presence of a C=O, carbonyl group. [1]

No broad OH band at 2500 – 3400 cm^{-1} implies that **H** is not a carboxylic acid.

No reaction with $NaBH_4$ implies **H** is not ketone or aldehyde / may be an ester.

Possible structures of **H**: [2]


$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3$


$H-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_2CH_3$

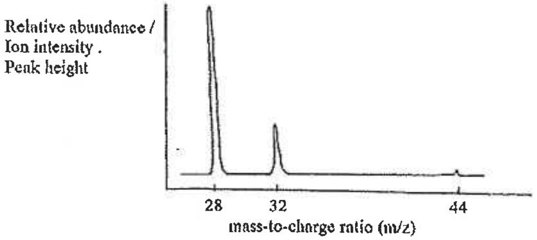
(deduce 1 mark for each extra structure).

AL98(I)_08a

One of the following: [1]

- Infra-red spectroscopy, only propan-2-ol shows absorption (OH stretch) from 3230 – 3670 cm^{-1}.
- Infra-red spectroscopy, only propanone shows strong C=O stretching absorption at about 1680 – 1750 cm^{-1}.
- Mass spectroscopy, propan-2-ol has a m/z peak of 60 and propanone of 58.

AL98(II)_04



[3]

(½ marks for each axis; ½ marks for showing the correct position of each peak;
½ marks for showing the correct relative abundance)

AL99(II)_01

(a) Mass spectrometry [1]

The abundance of an isotope is proportional to the height of the peak (current intensity) of its cation. [1]

OR, $$\frac{\text{Abundance of } {}^{85}\text{Rb}}{\text{Abundance of } {}^{87}\text{Rb}} = \frac{\text{height of peak at } m/z = 85}{\text{height of peak at } m/z = 87}$$

(b) Relative atomic mass of Rb

$= 84.939 \times 72.15\% + 86.937 \times 27.85\%$ [1]

$= 85.495$ [1]

AL00(II)_01

(a) Chlorine has two isotopes ^{35}Cl and ^{37}Cl. [1]

Bombardment of electron on chlorine produces atomic ion Cl^+ and molecular ion $[Cl–Cl]^+$. [1]

The five peaks correspond to the species: $^{35}Cl^+$, $^{37}Cl^+$, $[^{35}Cl–^{35}Cl]^+$, $[^{35}Cl–^{37}Cl]^+$ and $[^{37}Cl–^{37}Cl]^+$. [1]

(b) (i) $$\text{relative atomic mass of } Cl_2 = \frac{35 \times 3 + 37 \times 1}{4} = 35.5$$ [2]

(ii) $\text{Abundance of A} \propto \frac{1}{4} \times \frac{1}{4}$ [½]

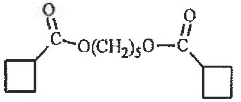
$\text{Abundance of B} \propto 2 \times \frac{1}{4} \times \frac{3}{4}$ [½]

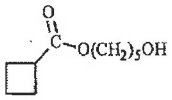
$\text{Abundance of C} \propto \frac{3}{4} \times \frac{3}{4}$ [½]

$\text{Ratio of relative abundance of A : B : C} = \frac{1}{16} : \frac{6}{16} : \frac{9}{16} = 1 : 6 : 9$ [½]

AL00(II)_05

(a) [2]

G


H


G is less polar than H (or H has a polar OH group) and is therefore less tightly [1] bound to the stationary phase and hence moves faster. [1]

(b) Reagent: PCl_5 / PCl_3 / $SOCl_2$ [1]

Only H will give misty fumes of HCl [1]

OR, Regent: Na

Only H will react with Na to give gas bubbles (H_2).

(c) Compound H shows a IR absorption at 3200 – 3700 cm^{-1} but G does not because [1] H has an OH functionality whereas G does not. [1]

AL01(II)_01

The sample is vaporized in the mass spectrometer and is bombarded by fast moving electrons to give positive ions. [1]

The ions are accelerated by an electric field. [1]

The accelerated ions are then deflected by a magnetic field. [1]

The mass spectrometer is operated at low pressure to prevent ions from colliding with other particles. [1]

The lighter the positive ion, the greater is the deflection. [1]

By varying the strength of the deflecting magnetic field, ions of a particular mass / charge (m/e) ratio are brought to the ion detector. [1]

Determination of the relative atomic mass of a noble gas:

The current intensity produced by cations formed from an isotope is proportional to the [1]

relative abundance of the isotope.
Relative atomic mass of the noble gas = $\sum(isotopic\ mass \times relative\ abundance)$ [1]

AL01 II_(7)

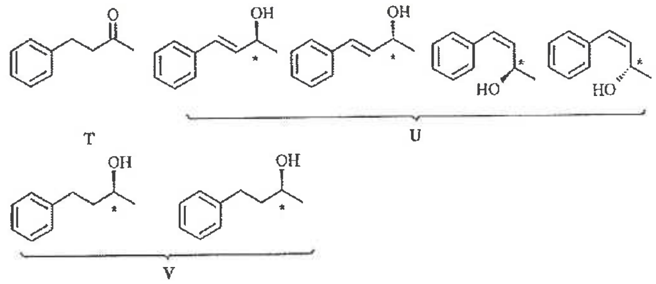
(a) T gives positive result in the iodoform test and has the structural characteristic [1]

$$-\overset{O}{\overset{\|}{C}}-CH_3 \qquad -\overset{OH}{\overset{|}{C}H}-CH_3$$

[½]

U reacts with H₂ Pd ∴ U is an alkene / has a C=C group. [½]

T can be reduced by LiAlH₄ ∴ T is a ketone / has a C=O group



[4]

T: 1 mark; U: 2 marks for 4 structures; V: 1 mark for 2 structures

(b) T has a sharp absorption peak in the wavenumber range from 1680 to 1750 cm^{-1} but [½]
U has not. [½]
U has a broad absorption peak in the wavenumber range from 3230 to 3670 cm^{-1} but [½]
T has not. [½]

AL02(I)_05

(a)

$$\text{A}\quad CH_3-\underset{OH}{\underset{|}{C}H}-COOH \qquad \text{B}\quad \underset{OH}{\underset{|}{C}H_2}-\underset{OH}{\underset{|}{C}H}-CHO$$

[2]

(b) Treat compounds with Na₂CO₃(aq) [1]
Only the carboxylic acid (A) will give CO₂(g) [1]
OR, Treat compounds with 2,4-dinitrophenylhydrazine / Fehling's reagent
Only the aldehyde (B) will give a yellow precipitate / red precipitate.
(Accept other test for the carbonyl group and the corresponding expected observations)

(c) [2]

product from the carboxylic acid (A)	product from the aldehyde (B)
$CH_3-\underset{OH}{\underset{|}{C}H}-CH_2OH$	$\underset{OH}{\underset{|}{C}H_2}-\underset{OH}{\underset{|}{C}H}-CH_2OH$

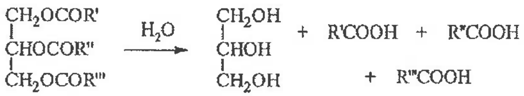
AL02(II)_01b

(i) In the ionization chamber, AB₃ molecules were bombarded by fast moving electrons. [1]
Knocking out an electron from AB₃(g) give AB₃⁺(g). [1]
(ii) The peak at m/z ration = 31 is due to A⁺ (P⁺) ions. [1]
The peak at m/z ration = 19 is due to B⁺ (F⁺) ions. [1]
(iii) PF₃ [1]

AL03(II)_05

(a) **Degree of unsaturation of oil decreases upon hydrogenation.** [½]
Vegetable oil contains C=C bonds which are rigid. [1]
The C=C bonds **prevent molecules of oil from packing close together.** In hardened oils, interlocking of hydrocarbon chains restricts the relative motion of the fat molecules. ∴ Vegetable oils become hardened upon hydrogenation. [½]

(b) The fumes from heating molten margarine consist mainly of triglycerides. The IR absorption wavenumbers at 2950 cm^{-1} and 1750 cm^{-1} are due to the stretching of C–H bond and C=O bond respectively. [½] [1]
Potatoes contain water which causes margarine to undergo hydrolysis to give free carboxylic acids and glycerine.



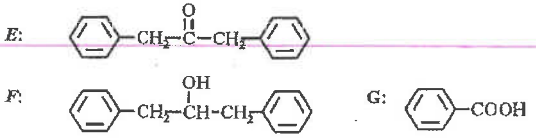
$$\begin{array}{l} CH_2OCOR' \\ | \\ CHOCOR'' \\ | \\ CH_2OCOR''' \end{array} \xrightarrow{H_2O} \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + R'COOH + R''COOH + R'''COOH$$

[1]

The IR absorption at is due to O–H bonds in glycerine and in carboxylic acids. [½]

AL03(II)_07

G ($C_7H_6O_2$) is an aromatic compound with pK$_a$ value 4.2. It is benzoic acid. [½]
E has an IR absorption peak at 1720 cm^{-1}. It possesses a carbonyl group. [½]
E can be reduced by LiAlH₄ but cannot oxidized by Tollens' reagent
∴ E is a ketone. [½]
F is formed from the reduction of a ketone. It is a secondary alcohol. [½]
Structure of E, F and G.



[4]

(3 marks for the three structure; 1 mark for optical inactive / achiral)

AL05(II)_05

(a) Functional group isomerism [1]
(b) (i) Compare their boiling points / melting points. [1]
J has a higher boiling point / melting points.

OR, J is a solid while K is liquid.
Intermolecular force between J molecules is hydrogen bond, while that between K molecules is van der Waals' force. [1]

(ii) Any ONE of the following: [2]

1. Suspend compounds in a little water, and add NaOH(aq). Only J dissolves.
2. Treat compounds with neutral $FeCl_3(aq)$. Only J gives a purple solution. (Out of syllabus)
3. Dissolve compounds in a little NaOH(aq), then add $C_6H_5N_2^+(aq)$. Only J gives a bright red precipitate / an azo dye.

(iii) Run IR spectrum of J and of K [1]
Only J gives a broad and strong absorption from 3230 to 3670 cm^{-1} / stretching of O–H in alcohol. [1]

AL05(II)_06a

(i) Foam for insulation / furniture stuffing / carpet / plywood [1]

(ii) $KMnO_4$ on Al_2O_3 [1]
HCHO is oxidized to less harmful and less volatile product (HCOOH).

(iii) [2]

Pollutant	Source
Benzene / toluene	Paint / thinner / gasoline
Chlorinated hydrocarbons	Garments after dry cleaning
Chloroform	Chlorine-treated water

AL05(II)_07

(a)
$$\text{mole ratio of C : H : O} = \frac{77.8}{12} : \frac{7.4}{1} : \frac{14.8}{16} = 7 : 8 : 2$$ [1]

Empirical formula: C_7H_8O [1]
Molecular formula: $(C_7H_8O)_n$
Relative molecular mass of L is 108
n = 1
∴ molecular formula: C_7H_8O [1]

(b) Each point 1 mark, maximum 5 marks: [5]

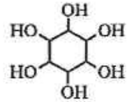
- ✧ L does not react with Br_2 ∴ L does not possess C=C bond.
- ✧ L has a double bond equivalence of 4. It is likely to be an aromatic compound. L is likely to be $C_6H_5CH_2OH$
- ✧ M has a broad IR absorption in the wavenumber range of 3300 – 2500 cm^{-1} which is resulted from the stretching of O–H bond.
- ✧ M is obtained from the oxidation of L. M is likely to be benzoic acid C_6H_5COOH.
- ✧ The other absorption at 1700 cm^{-1} is due to the stretching of C=O bond.
- ✧ N is also a carbonyl compound (IR) absorption at 1750 cm^{-1}). It is benzoyl chloride C_6H_5COCl. The absorption at 3000 cm^{-1} is due to the stretching of C–H bond.

AL06(II)_05

$$\text{mole ratio of C : H : O} = \frac{40.0}{12} : \frac{6.7}{1} : \frac{53.3}{16} = 3.3 : 6.7 : 3.33 = 1 : 2 : 1$$ [1]

Empirical formula: CH_2O
Molecular formula: $(C\ CH_2O)_n$ [1]
Relative molecular mass of D is 108
$172 < (12 + 2 + 16)n < 182$
n = 6
molecular formula of D is $C_6H_{12}O_6$ [1]
Infra-red spectrum:

- ✧ Strong and broad absorption near 3400 cm^{-1}. ∴ D has O–H groups. [1]
- ✧ No absorption around 1700 cm^{-1}. D does not possess carbonyl groups. [1]
- ✧ D does not decolorize bromine ∴ D does not have C=C bond. [1]
- ✧ All carbon atoms of D have the same bonding environment, i.e. they are in same hybridization state, bonded to the same groups, and have the same configuration. [1]

D:


[1]

AL06(II)_06

(a) From IR spectrum

- ✧ E possesses a O–H group (broad absorption peat at 3300 cm^{-1}) [1]
- ✧ And carbonyl group (absorption peak at 1700 cm^{-1}) [1]

$$\underset{\textbf{E}}{C_6H_6O_4} \xrightarrow{H_2 / Pd} \underset{\textbf{F}}{C_6H_{10}O_4}$$

- ✧ E has two C=C bonds or one C≡C bond. [1]
- ✧ F is acidic. F has the structure $HOOC(CH_2)_4COOH$ [1]
- ✧ E is an acyclic compound with formula $C_6H_6O_4$. It has the structure HOOCCH=CH–CH=CH–COOH [1]

(b) Upon reduction, ozone gives H_2O which is harmless. [1]
Ozone has short lifetime. The residual O_3 will not remain in the atmosphere for a long time. [1]

AL07(II)_07

(a) mole ratio of C : H : Cl : O $= \frac{59.8}{12} : \frac{3.6}{1} : \frac{25.2}{35.5} : \frac{11.4}{16} = 4.98 : 3.6 : 0.71 : 0.71$ [1]

mole ratio of C : H : Cl : O = 7 : 5 : 1 : 1

Empirical formula: C_7H_5ClO [1]

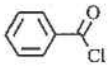
(b) The molecular-ion of M has m/z = 140 [½]

∴ molecular formula of M is C_7H_5ClO [½]

The peak at m/z = 105 is likely to be due to the stripping off of a Cl atom from the molecular-ion, e.g. $C_7H_5O^+$ [½]

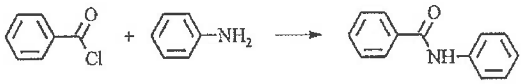
The peak at m/z = 77 is due to $C_6H_5^+$ [½]

M is



[1]

(c) M can be identified by preparing a solid derivative of M, such as [1]



and compare the m.p. of the derivative with that of an authentic sample. [1]

OR,

- ✧ Add water to M. The white fume HCl will be given.
- ✧ Add $AgNO_3$(aq). White precipitate will be given.

AL08(I)_08a

The absorption at 1614 cm^{-1} is due to the stretching of the C=C bond. [1]

As polymerization proceeds, the concentration of the monomers decreases. Thus, the intensity of C=C absorption reduces. [1]

AL08(II)_06

The IR spectrum of A shows a strong absorption at around 1750 cm^{-1}. A is likely to possess a carbonyl group. [1]

A does not have a broad absorption peak in the region of 2500 to 3500 cm^{-1}. A does not possess a hydroxyl group. [1]

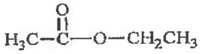
A can be an ester or an alkoxyl carbonyl compound. [1]

In the mass spectrum, the peak at m/z = 88 is that of the molecular-ion. [½]

Peak at m/z = 43 is that of the $CH_3C{\equiv}O^+$ ion. ∴ A is not an aldehyde. [1]

Peak at m/z = 29 is likely to be due to the $CH_3CH_2^+$ ion. ∴ A carries an ethyl group. [½]

A possible structure of A is $CH_3COOCH_2CH_3$ [1]



$H_3C-\overset{\overset{O}{||}}{C}-O-CH_2CH_3$

AL09(II)_05

The IR spectrum of P shows a broad absorption from around 2500 to 3300 cm^{-1}. P is likely to possess an OH group. [1]

P shows a strong absorption at 1710 cm^{-1} (1680 – 1800 cm^{-1}). It is likely to possess a carbonyl group. [1]

The peaks at m/z = 152 and 154 are due to the two molecular ions as Br has two isotopes with mass numbers 79 and 81, and they have almost the same relative abundance. [1]

The peaks at m/z = 135 and 137 are formed from the molecular ions by stripping off the OH group. [1]

The peaks at m/z=107 and 109 are formed by further stripping off the C=O group. P is likely to be a carboxylic acid. [1]

The peaks at m/z = 73 is formed from the molecular ions by stripping off the Br atom. P is a bromopropanoic acid. [1]

Possible structure of P:

$BrCH_2CH_2COOH$ or $CH_3CHBrCOOH$ [1]

AL10(II)_03b

Any TWO of the following: [2]

- Relative molecular mass can be determined to very high accuracy.
- Only a very small amount of the compound is required.
- The time for the experiment is short.
- It can also be used to determine the relative molecular mass of non-volatile compounds.

AL10(II)_05

(a) mole ratio of C : H : O $= \frac{70.6}{12} : \frac{5.9}{1} : \frac{23.5}{16}$ [1]

= 5.88 : 5.9 : 1.47 = 4 : 4 : 1

Empirical formula: C_4H_4O [1]

(b) Molecular formula: $(C_4H_4O)_n$

m/z of molecular ion is 136

$(12\times4 + 4 + 16\times1)n = 136$, n=2

Molecular formula: $C_8H_8O_2$ [1]

In the IR spectrum, the broad peak in the wavenumber range of 2500 to 3300 cm^{-1} shows the presence of an –OH group. [1]

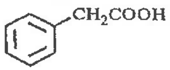
The absorption at 1680 to 1800 cm^{-1} shows the presence of C=O group. [1]

L is likely to have the structure of $C_7H_7(CO)(OH)$. It is an aromatic compound. [1]

The peak at m/z = 91 is likely to be due to the stable tropylium ion ($C_6H_5CH_2^+$). [1]

The tropylium ion is likely to be formed from L^+ by stripping off a –COOH group. (136 – 45 = 91)

L is likely to be



[1]

AL11(II)_10

A gives yellow precipitate with 2,4-dinitrophenylhydrazine. ∴ it is an aldehyde or ketone. [½]

A does not react with acidified $K_2Cr_2O_7(aq)$. It is a ketone. [½]

The molecular ion at m/z = 86 suggests the molecular mass of A to be 86. [½]

86 – 28 (formula mass of C=O) = 58. A is likely to have the formula $(C_4H_{10})CO^+$ as the formula mass of C_4H_8 is 58. [½]

Molecular ions of ketone $(RCOR')^+$ tend to usually undergo fragmentation to give RCO^+ and $R'CO^+$. The peak at m/z = 57 is likely to be due to $C_2H_5CO^+$. [1]

The peak at m/z = 29 is likely to be due to $C_2H_5^+$ which is formed from $C_2H_5CO^+$ by stripping off the CO. [1]

A does not show other prominent m/z peak. It is likely to be $C_2H_5COC_2H_5$. [1]

AL12(I)_05

F has a double bond equivalence of 5

F is an aromatic compound. ∴ F has a benzene ring and a double bond.

Treating F with hot MnO_4^-/H^+ oxidized the alkyl side chain to carboxylic acid. [½]

J is an aromatic monocarboxylic acid.

From the mass spectrum, the molecular ion of J has m/z = 122. It is due to $[C_6H_5COOH]^+$. [½]

J can only be C_6H_5COOH [1]

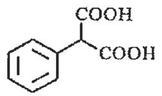
The peak at m/z = 105 (122 – 17) is due to $[C_6H_5CO]^+$. [½]

The peak at m/z = 77 (105 – 28) is due to $[C_6H_5]^+$ [½]

As J is benzoic acid, F can only be a mono-substituted aromatic compound.

G reacts with excess $NaHCO_3(aq)$ to give 2 mole of $CO_2(g)$. G is a dicarboxylic acid. [½]

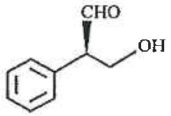
G is

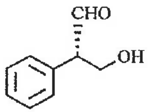


[1]

$Cr_2O_7^{2-}/H^+$ can only oxidize –CHO or –CH_2OH to carboxylic acid. [½]

F is optically active. It can be [½]





[1]

AL13(I)_15

mole ratio of C : H : O $= \dfrac{81.8}{12} : \dfrac{6.1}{1} : \dfrac{12.1}{16} = 6.82 : 6.1 : 0.76 = 9 : 8 : 1$ [1]

Empirical formula: C_9H_8O [1]

D react with acidified $K_2Cr_2O_7(aq)$. It is either a primary alkanol, secondary alkanol or aldehyde. [½] [½]

From the mass spectrum, the molecular ion of D has m/z = 132. It is due to $[C_9H_8O]^+$. [½]

Molecular formula of D is C_9H_8O. [½]

D has a double bond equivalence of 6

The peak at m/z = 77 is due to $[C_6H_5]^+$. ∴ D has a benzene ring. [1]

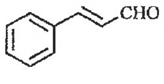
The absorption at ~1680 cm^{-1} shows the presence of C=O group. [1]

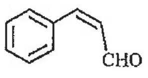
D does not have a broad absorption peak in the region of 2500 to 3670 cm^{-1}. D does not possess –OH / a hydroxyl group. [1]

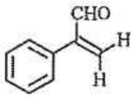
D can be an aldehyde because the peak at m/z = 103 (132 – 29 = 103) is likely formed from $C_9H_8O^+$ by stripping off the –CHO. [1]

OR D can be an aldehyde because the peak at m/z = 131 (132 – 1 = 131) is likely formed from $C_9H_8O^+$ by stripping off the H.

D







[1]

DSE11SP_03a

(i) mole of carbon atom $= \dfrac{58 \times 0.621}{12} = 3$ [2]

mole of hydrogen atom $= \dfrac{58 \times 0.103}{1} = 6$

mole of oxygen atom $= \dfrac{58 \times 0.276}{16} = 1$

Molecular formula of G is C_3H_6O

(ii) From the IR spectrum, the presence of a sharp absorption peak at 1740 cm^{-1} indicates the presence of a carbonyl group. [1]

From the mass spectrum, the peaks at m/e 29 corresponds to $C_2H_5^+$ and [1]

the peak at m/e 58 corresponds to $CH_3CH_2CHO^+$. [1]

The structural formula of G should be CH_3CH_2CHO. [1]

(iii) Add 2,4-dinitrophenylhydrazine to G to prepare the corresponding 2,4-dinitrophenylhydrazone. [1]

Recrystallize the 2,4-dinitrophenylhydrazone. [1]

Measure its melting point using a melting point apparatus. [1]

A sharp melting point, which is the same as that quoted in the literature, will support the deduction of G. [1]

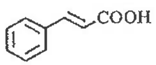
DSE12PP_03a

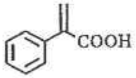
(i) Carboxylic acid / carboxyl group (because **X** is soluble in NaOH(aq)) [1]
(Also accept phenol).

(ii) Separating funnel [1]

(iii) Step 1: Allow **X** to dissolve in NaOH(aq) to give (carboxylate) anions / a salt. [1]
Step 2: Allow the non-polar impurities to dissolve in hexane while the (carboxylate) anions / salt to stay in the aqueous layer. [1]
OR, Separate the non-polar impurities (in hexane) from the salt of **X**.
Step 3: Regenerate the (carboxylic) acid (which is insoluble in water) by adding acid. [1]

(iv) **X** possesses a C=C bond because it decolorizes Br_2 in CH_3Cl_3. [1]
In the mass spectrum, the peak at m/z = 148 is due to the molecular ion. [1]
Any TWO of the following: [2]
The peak at m/z = 131 is due to the cation formed from the molecular ion by stripping off a –OH.
The peak at m/z = 103 is due to the cation formed from the molecular ion by stripping off a $-CO_2H$.
The peak at m/z = 77 shows that **X** carries a benzene ring (m/z for $C_6H_5^+$ ion = 77).
Possible structures of **X**:





[1]

(v) (1) **Put the chromatographic plate into a jar that is saturated with iodine vapor.** The spot will appear brown. [1]
OR, **Irradiate the plate with UV.** The stationary phase is fluorescent while the two spots are not.

(2) $$R_f = \frac{\text{distance travelled by X}}{\text{distance travelled by solvent}} = \frac{9.5}{(50-3-2.5)} = 0.21$$ [1]

(3) Column chromatography (using the same moving phase and stationary phase [1]

DSE12_03a

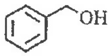
(i) hydroxyl (group) / –OH / alcohol [1]
aldehyde (group)/ –CHO / aldehyde [1]

(ii) (1) Test for aldehyde (group) or ketone (group)/ carbonyl (group)/ aldehyde (group)and ketone (group). [1]
(2) 2,4-dinitrophenylhydrazine reacts with aldehyde or ketone to give yellow, orange or red precipitate. [1]

(iii) hydroxyl (group)/ –OH [1]

(iv) m/z = 91 suggested the presence of $C_7H_7^+$ / $C_6H_5CH_2^+$. [1]
m/z = 108 suggested the presence of $C_7H_8O^+$ / $C_7H_7OH^+$ $C_6H_5CH_2OH^+$. [1]

(v)



[1]

DSE12_03b

(i) Any ONE of the following: [1]
Combustion of materials containing chlorine / PVC
Incineration of materials containing chlorine
Emission from incinerators
Burning / combustion of plastic waste

(ii) Dioxin is carcinogenic / can cause cancer. [1]

(iii) Gas chromatogra DSE12_03b phy-mass spectrometry / GCMS [1]
It can measure more accurately the low level of dioxin than using gravimetric analysis or volumetric analysis.

DSE13_03c

(i) $$\frac{2.3}{2.3+1.9+2.9} = \frac{2.3}{7.1} = 0.32$$ [1]
(Accept also 0.324 and 0.3239 BUT NOT 0.3)

(ii) β–Carotene
Lycopene has a smaller Rf value / lycopene moves slower [1]
Lycopene takes a longer time to reach the bottom of the column.

(iii) Method: colorimetry / use of colorimeter / use of spectrophotometer [1]
Measurement: absorbance / color intensity / light intensity / transmittance [1]

(iv) Compound **W** is lycopene [1]
The absence of (absorption) peaks at around 2070 – 2250 cm^{-1} suggesting it does not contain C=C groups / ruling out the possibility of compound **X**. [1]
The absence of (absorption) peaks at around 2220 – 2280 cm^{-1} suggesting it does not contain C≡N groups / ruling out the possibility of compound **Y**. [1]
OR The presence of (absorption) peaks at around 1630 cm^{-1} (1600 – 1680 cm^{-1}) (shows the presence of C=C / C–C double bonds) ruling out the possibility of compound **Y**.

(Note: 2 marks for the absence of (absorption) peaks at around 2070 – 2280 cm^{-1} suggesting it does not contain C≡C and C≡N groups / ruling out (the possibility of compounds **X** and **Y**.)

The absence of sharp (absorption) peaks at around 3350 – 3500 cm^{-1} suggesting it does not contain $-NH_2$ group / ruling out the possibility of compound **Z**. [1]

Compound **W** is a hydrocarbon which contains only C–H, C–C and C=C bonds. This agrees with the feature of the spectrum as there are small peaks at around 1630 cm^{-1}, showing the presence of C=C double bonds.

DSE14_03c

(i) Dissolve the sample in pentane and shake the solution with **$NaHCO_3$(aq)** in a **separating funnel.** [1]

Collect the organic layer and carry out **fractional distillation / distillation.** [1]

[Only fractional distillation / distillation: 0 mark]

(ii) The spectrum does not show strong absorption at about **3230 – 3670** cm^{-1}, **ruling** out the presence of a **hydroxyl** group (the possibility of being an alcohol) [1]

OR, The absence of absorption at **2070 – 2250** cm^{-1} ruled out the presence of C≡C group.

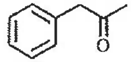
OR, The absence of absorption at **1610 – 1680** cm^{-1} ruled out the presence of C=C group.

The spectrum has a strong absorption at 1730 (1700 to 1750) cm^{-1}, **which corresponds to C=O** stretching. The compound may contain an aldehyde group or a ketone group. [1]

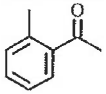
(iii) m/z = 43: $[CH_3CO]^+$ [1]

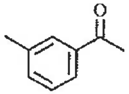
m/z = 134 $[C_7H_7COCH_3]+$ *OR* $[C_6H_5C_3H_5O]^+$ [1]

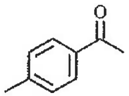
NOT accept: $[C_2H_3O]^+$ / $[C_9H_{10}O]^+$

(iv)  [1]

Other possible structures:







DSE15_03a

Chromatography / GC / GCMS / HPLC [1]

DSE15_03b

(i) yellow / orange / red precipitate (solid/ppt) [1]

(ii) Add acidified $K_2Cr_2O_7$(aq). [1]

Only Y turns the solution from orange to green. [1]

OR Only Y turns MnO_4^-/H^+ from purple to colorless.

OR Only Y gives a silver mirror in Tollens' test.

OR Only X gives a yellow precipitate with I_2/NaOH(aq).

(iii) A significant peak appears at m/z 105 ($C_6H_5CO^+$) / 43 (CH_3CO^+) / 15 (CH_3^+) in mass spectrum of X only. [1]

A significant peak appears at m/z 91 ($C_6H_5CH_2^+$) or 29 (HCO^+) in mass spectrum of Y only. [1]

(iv) Both compounds show a characteristic absorption in the wavenumber range (1680 to 1800 cm^{-1}) which is characteristic of carbonyl group (>C=O bond). [1]

As the two compounds do not possess other different functional groups, they cannot be differentiated from each other using the given information. [1]

DSE16_03a

Similarity: Both show an absorption peak at 3230 – 3670 (cm^{-1}) (O–H groups) [1]

Difference: Only chitin shows an absorption peak at 1680 – 1800 (cm^{-1}) (C=O groups) [1]

(comparison must be shown)

DSE16_03c

(i) The mass spectra of X and Y are recorded respectively.

In the mass spectrum of X, a significant peak at m/z = 43 appears for CH_3CO^+ ions which does not appear in the mass spectrum of Y. [1]

In the mass spectrum of Y, a significant peak at m/z = 119 appears for $C_6H_5CH_2CO^+$ ions which does not appear in the mass spectrum of X. [1]

OR

Mass spectrum of X	Mass spectrum of Y
CH_3^+ or m/z 15	
CH_3CO^+ or m/z 43	
$C_6H_5O^+$ or m/z 93	
$C_6H_5OCO^+$ or m/z 121	
	OH^+ or m/z 17
	$COOH^+$ or m/z 45
	$C_6H_5CH_2^+$ or $C_7H_7^+$ or m/z 91
	$C_6H_5CH_2CO^+$ or $C_7H_7CO^+$ or m/z 119

(any 2 answers each with comparisons: 1 mark each)

(ii) (1)
- Na_2CO_3(aq) is added to the dichloromethane solution of X and Y. [1]
- The mixture is shaken in a **separating funnel.** [1]
- The mixture in the separating funnel is allowed to settle, and the aqueous layer was then separated from the organic layer.
- Dilute H_2SO_4(aq) is added to the **aqueous layer** / upper layer / lower **aqueous layer** / (until no more precipitate is formed.) / (the solution becomes acidic). [1]
- Solid Y can be obtained by **filtration.** [1]

(2) Measure the melting point of the solid obtained.

If the melting point of the solid is 77°C /a sharp m.p measured / a narrow melting point range, it may be pure compound Y. [1]

(mixed melting point technique → sharp melting point / m.p. 77 °C;

OR compare the IR spectrum / mass spectrum / NMR spectrum of the solid obtained with that of authentic sample, if they are identical → pure

OR run a TLC / paper chromatography for the sample; if only one spot is detected on the chromatogram → pure)

DSE17_03c

W [1]

It has >C=O / carbonyl group as it has a strong absorption (peak) at around 1700 cm^{-1} in its IR spectrum. [Y OR W; NOT X and Z] [1]

It has no –COOH / carboxyl group as it does not react with $NaHCO_3(aq)$. [NOT Y] [1]

[NOT accept $NaHCO_3(s)$]

Accept: From the given information in IR spectrum, it has >C=O group
From the given information on the reaction with $NaHCO_3$, it has no –COOH group.

NOT accept: From the given information, it has >C=O / no COOH group (i.e. without further elaboration)]

DSE18_03c

(i) Boiling points of X and Y are too close. [1]

(ii) (1) Absorption peak at wavenumber about 1700 cm^{-1} corresponds to a C=O group. [1]
OR, Absorption peak at wavenumber about 1650 cm^{-1} corresponds to a C=C group.
[Range: C=O, 1680 – 1800; C=C, 1610 – 1680 one number: C=O: 1680 – 1720; C=C: 1630 – 1670]

(2) At m/z = 43: CH_3CO^+ / $C_2H_3O^+$ [CH_2CHO^+ not accepted] [1]
At m/z = 55: CH_2CHCO^+ / $C_3H_3O^+$ [1]

(3) CH_2=$CHCOCH_3$ [1]
[Must show C=C]

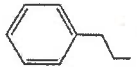
(iii)
- positive result for 2,4-dinitrophenylhydrazine test: presence of carbonyl group [1]
- negative result for Tollens' reagent test: not an aldehyde [1]
- [Note: If just have the conclusion: it is a ketone : 1 mark]
- Y may be $CH_3CH_2COCH_3$ / butanone. [1]

DSE19_03c

(c) (i) (1)
- Different substances have different adsorptivity to the stationary phase. 1
- They have different solubility in mobile phase. 1

(2) column chromatography 1

(ii) The chemical species for the peak at m/z = 91 may be $C_6H_5CH_2^+$. 1
The chemical species for the peak at m/z = 140 may be $C_6H_5CH_2CH_2{}^{35}Cl^+$. 1
(or m/z = 142 may be $C_6H_5CH_2CH_2{}^{37}Cl^+$)
Possible structure :



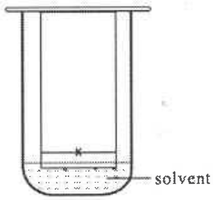
1

(iii) (1) High levels of dioxins may cause cancer. 1

(2) Modern instrumentation is accurate and sensitive enough to measure very low levels of dioxins. 1

DSE20_03b

(b) (i) 2



(1 mark for labelling: solvent
1 mark for the drawing: pencil line above solvent, spot of mixture, TLC plate and a container)

(ii) R_f = 45 / (130–10–20) = 0.45 1
(Only mark the answer.)

(iii) Aspirin and Caffeine 1

(iv) (1) IR spectrum of Aspirin shows (strong absorption) peak at 2500 (cm^{-1}) to 3300 (cm^{-1}) / corresponding to O–H group of carboxylic acid while that of caffeine does not. 1
(A comparative sense)

(2) m/z = 43 corresponds to a CH_3CO^+ ion. 1
(Accept $CH_3CO\bullet^+$
Not accept $CH_3CO—^+$, CH_3CO)
Both aspirin and acetaminophen have this fragment, only this information cannot help confirm which one of the three chemicals the sample is. 1

Contribution of Analytical Chemistry to Our Society

DSE19_03c ii

(iii) **Pollutants, such as dioxins, can be formed in the manufacturing process of certain chlorine-containing products.**

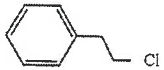
(1) **Explain why there is a need to measure dioxin levels.**

(2) **Suggest why dioxin levels are generally measured using modern instrumentation.**

(2 marks)

Marking Scheme

DSE19_03c

(c) (i) (1)	• Different substances have different adsorptivity to the stationary phase.	1
	• They have different solubility in mobile phase.	1
(2)	column chromatography	1
(ii)	The chemical species for the peak at m/z = 91 may be $C_6H_5CH_2^+$.	1
	The chemical species for the peak at m/z = 140 may be $C_6H_5CH_2CH_2{}^{35}Cl^+$. (or m/z = 142 may be $C_6H_5CH_2CH_2{}^{37}Cl^+$) Possible structure :	1
		1
(iii) (1)	High levels of dioxins may cause cancer.	1
(2)	Modern instrumentation is accurate and sensitive enough to measure very low levels of dioxins.	1