Mass Spectrometry

Question Paper 3

Level	International A Level
Subject	Chemistry
Exam Board	CIE
Topic	Analytical techniques
Sub-Topic	Mass Spectrometry
Paper Type	Theory
Booklet	Question Paper 3

Time Allowed:	**60 minutes**
Score:	**/50**
Percentage:	**/100**

Grade Boundaries:

A*	A	B	C	D	E	U
>85%	777.5%	70%	62.5%	57.5%	45%	<45%

1 Chromatography is an important analytical technique in chemistry. There is a number of techniques under the general heading of chromatography.

(a) Paper and gas chromatography rely on partition to separate the components in a mixture, whereas thin-layer chromatography uses adsorption.

Explain what is meant by **(i)** *partition* and **(ii)** *adsorption*, in the context of chromatography.

(i) partition .....

.....

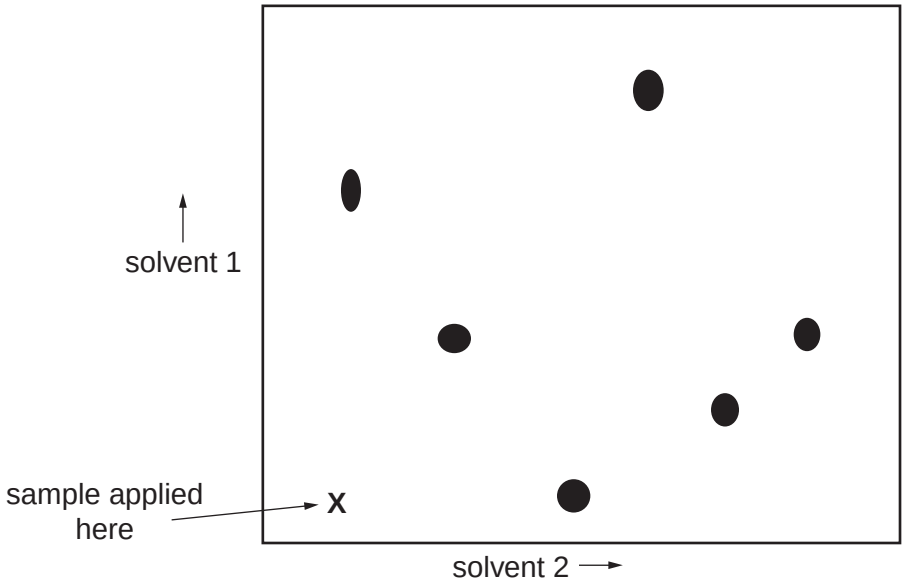
.....

(ii) adsorption .....

.....

.....[2]

(b) In paper or thin-layer chromatography, better separation may be achieved by running the chromatogram in one solvent, then turning the paper at right angles and running it in a second solvent. The chromatogram below was produced in this way.

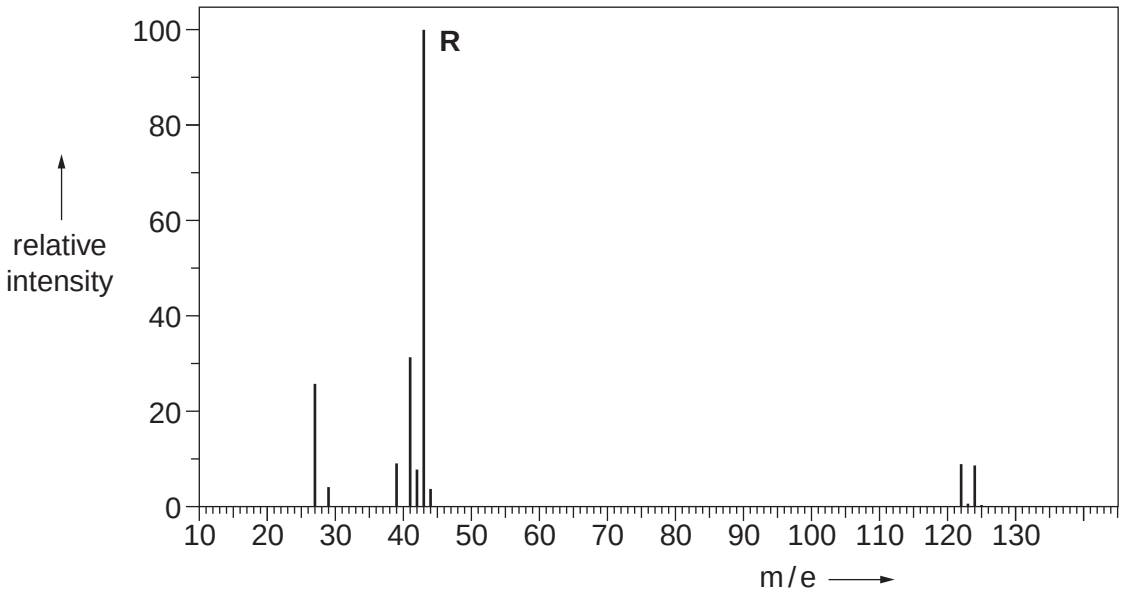


(i) Ring the spot which was insoluble in solvent 1.

(ii) Label as **A** and **B** the spots which were **not** resolved using solvent 1.

[2]

(c) The mass spectrum shown was obtained from a compound of formula C_pH_qX, where *X* represents a halogen atom.



(i) Deduce the identity of *X*, giving a reason.

X is .....

.....

(ii) If the relative heights of the M and M+1 peaks are 9 and 0.3 respectively, calculate the value of *p*. Use this value and the m / e value of the molecular ion to calculate the value of *q*, and hence the molecular formula of the compound. Show your working.

(iii) Suggest a formula for the ion responsible for the peak labelled **R**.

..... [4]

(d) In the fragmentation of alcohols which occurs in a mass spectrometer, small stable, neutral molecules are sometimes produced. Suggest the identity of **two** such molecules, each with an M_r less than 30.

(i) ..... **(ii)** ..... [2]

[Total: 10]

2 Different analytical techniques are used to build up a picture of complex molecules. Each technique on its own provides different information about complex molecules but together the techniques can give valuable structural information.

(a) Complete the table, identifying the technique which can provide the appropriate structural information.

structural information	analytical technique
three-dimensional arrangement of atoms and bonds in a molecule	
chemical environment of protons in a molecule	
identity of amino acids present in a polypeptide	

[3]

(b) One general method of separating organic molecules is chromatography. Briefly explain the chemical principles involved in each of the following techniques.

(i) paper chromatography

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.....

.....

(ii) thin-layer chromatography

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.....

.....

[2]

(c) A combination of mass spectrometry and NMR spectroscopy is often enough to determine the structure of a simple organic compound.
The organic compound **N** produced a mass spectrum in which the ratio of the M:M+1 peaks was 5.9:0.20, and which had an M+2 peak of similar height to the M peak.

(i) Calculate how many carbon atoms are present in one molecule of **N**.

(ii) Deduce which element, other than carbon and hydrogen, is present in **N**.

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(iii) Explain how many atoms of this element are present in one molecule of **N**.

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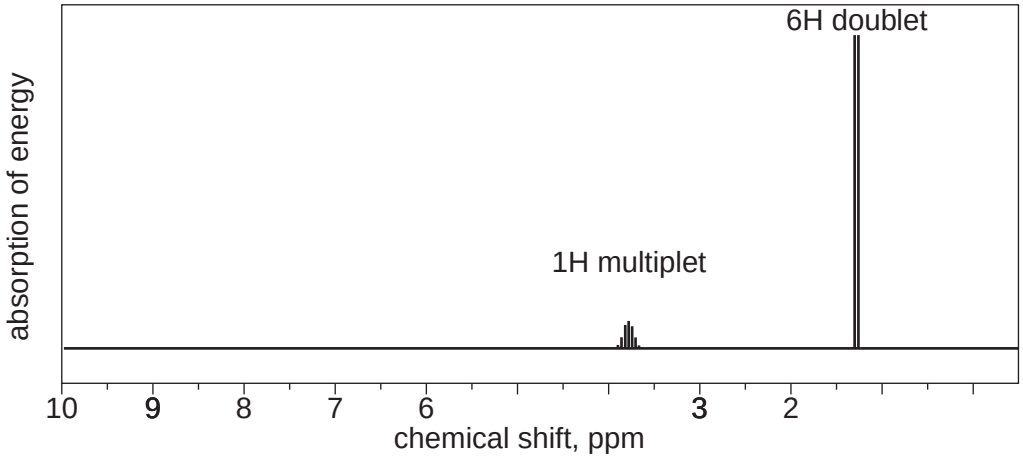
The NMR spectrum of **N** is shown.



(iv) State the empirical formula of **N** and, using the NMR data, suggest the structural formula of **N**, explaining your reasons.

[6]

[Total: 11]

3 Instrumental methods of analysis have become increasingly important in recent years. The use of chromatography to separate substances, and NMR spectroscopy to identify them, has become routine in many laboratories.

(a) Chromatography relies on either partition or adsorption to help separate substances.

(i) Briefly explain how each method brings about separation.

partition .....

.....

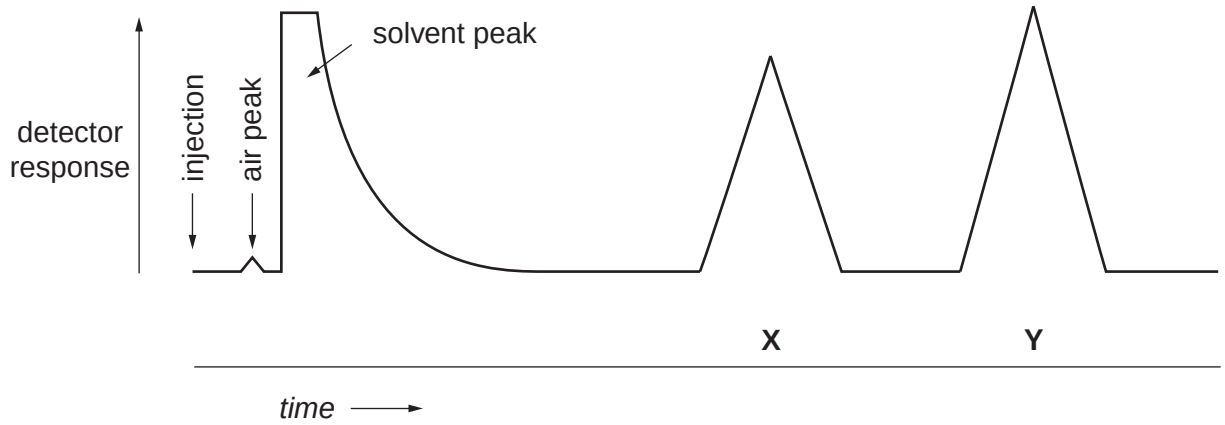
adsorption .....

.....

(ii) The table shows three different techniques of chromatography. Identify which separation method, *partition or adsorption*, applies to each.

technique	separation method
paper chromatography	
thin-layer chromatography	
gas/liquid chromatography	

(iii) The diagram represents the output from gas/liquid chromatography carried out on a mixture.



Determine the percentage of each of the two components **X** and **Y** in the mixture.

[5]

(b) NMR spectroscopy is a very important analytical technique for use with organic compounds.

(i) Why is NMR spectroscopy particularly useful for organic compounds?

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(ii) Two molecules, propanal and propanone, have the same molecular formula, C_3H_6O. Draw the displayed formula of each compound and explain briefly how NMR spectroscopy can distinguish between the two structures.

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[4]

[Total: 9]

4 The residues from organohalogen pesticides are known to be a major cause of the decline in numbers of different birds of prey in many countries. These residues are concentrated in birds at the top of food chains.

(a) Analysis of the bodies of birds of prey show that the pesticide residues accumulate in the fatty tissues of the birds. This is because of the high partition coefficient between the fat in the tissues and water found in blood.

Explain what is meant by the term *partition coefficient*.

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.....[2]

(b) A particular pesticide has a partition coefficient of 8.0 between the solvent hexane and water. If a 25 cm^3 sample of water containing 0.0050 g of the pesticide is shaken with a 25 cm^3 sample of hexane, calculate the mass of pesticide that will dissolve in the hexane layer.

[2]

(c) Compounds used as pesticides may contain bromine or chlorine.

(i) What would be the difference in the ratio of the M: M+2 peaks if the pesticide contained one chlorine rather than one bromine atom?

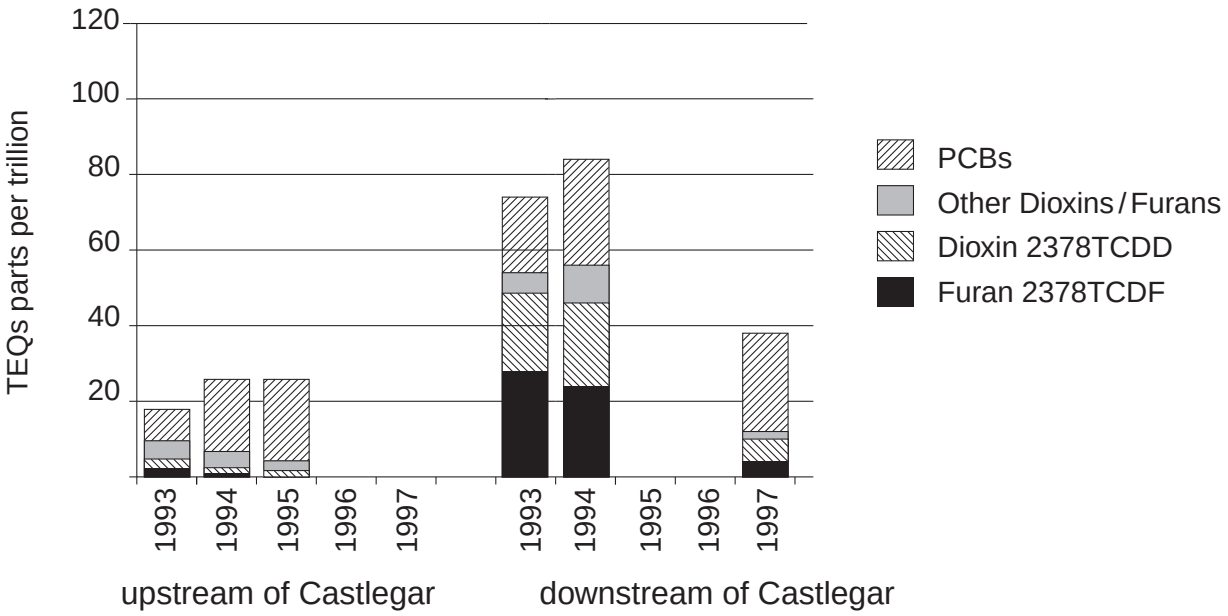
.....

(ii) If a given pesticide contains **two** chlorine atoms per molecule, deduce the relative heights of the M, M+2 and M+4 peaks.

[3]

(d) The following graph shows the occurrence of pesticide residues in the eggs of fish-eating birds of prey upstream and downstream of a paper mill at Castlegar on the Columbia River in Canada.

Columbia River Basin



PCBs, the dioxin 2378TCDD, and the furan 2378TCDF all come from chemicals containing chlorine.

(i) Suggest which compounds are present directly as a result of the paper mill.

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(ii) By studying the data for 1994, suggest which chemical(s) come from sources other than the paper mill.

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(iii) Compare the downstream data for 1994 with that for 1997. Suggest what might be responsible for the change.

.....

(iv) A molecule of 2378TCDD contains four chlorine atoms. How many molecular ion peaks would this compound show in its mass spectrum?

.....

[4]

[Total:11]

5 Much of the preparation of evidence to solve crimes now relies on instrumental analysis. This question deals with some of the techniques used.

(a) Electrophoresis can be used to separate amino acids produced by hydrolysing proteins. The amino acids are placed in a buffered solution in an electric field. In a solution of given pH, what **two** factors affect the movement of a given amino acid?

(i) .....

(ii) .....

[2]

(b) Nuclear magnetic resonance (NMR) spectroscopy and mass spectrometry are also used in the detection of certain molecules, particularly those containing hydrogen atoms.

(i) Explain how and why the NMR spectrum of propanal, CH_3CH_2CHO, would be different from that of propanone, CH_3COCH_3, which contains the same atoms.

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(ii) Explain how and why the mass spectrum of the two compounds in **(i)** would be different.

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[4]

(c) At one time, bromomethane, CH_3Br, was widely used to control insect pests in agricultural crops and timber. It is now known to break down in the stratosphere and contribute to the destruction of the ozone layer.

Samples can be screened for traces of bromomethane by subjecting them to mass spectrometry.

(i) Which peak(s) would show the presence of bromine in the compound?

.....

(ii) How could you tell by studying the M and M+2 peaks that the compound contained bromine rather than chlorine?

.....

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[3]

[Total: 9]

6 **(a)** Define *an isotope* in terms of its sub-atomic particles.

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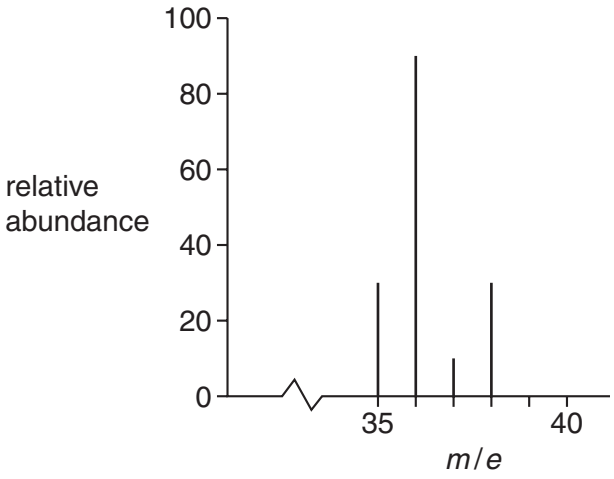
[1]

(b) In a mass spectrometer some hydrogen chloride molecules will split into atoms. The mass spectrum of H*Cl* is given. Chlorine has two isotopes. The hydrogen involved here is the isotope $^{1}_{1}H$ only.



(i) What particle is responsible for the peak at mass 35? .....

(ii) What particle is responsible for the peak at mass 38? .....

[2]

(c) Use the relative heights of the peaks to determine the proportions of the two isotopes of chlorine. Explain simply how you obtained your answer.

[2]

(d) Use your answer to **(c)** to explain why chlorine has a relative atomic mass of 35.5.

[1]

[Total : 6]