Q1 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 .....

.....

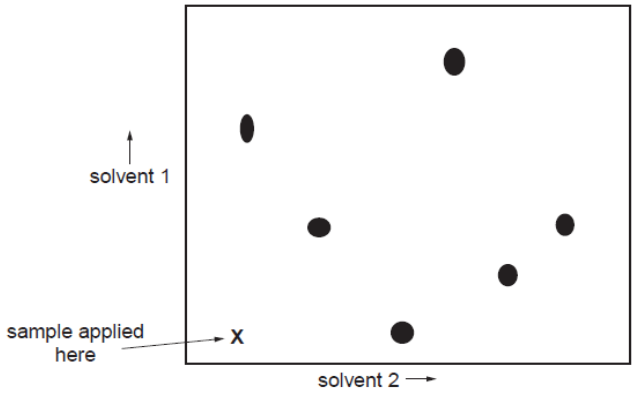
.....

(ii) adsorption .....

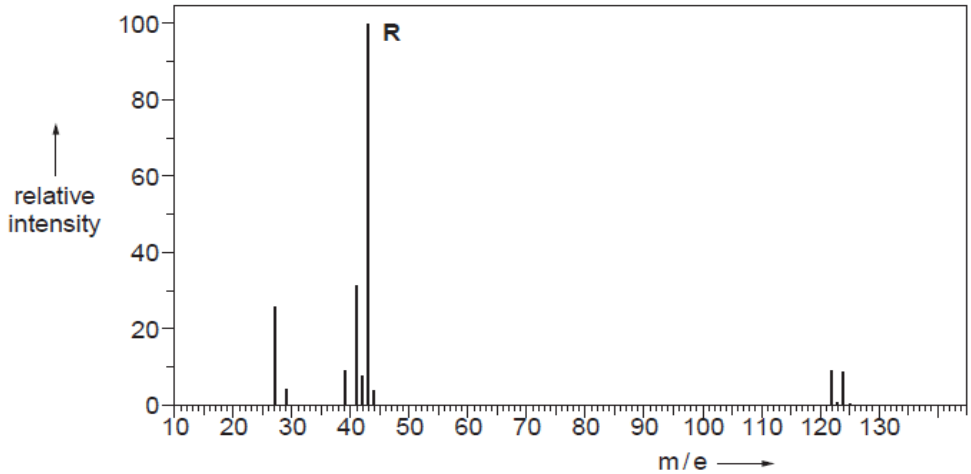
.....

..... [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.
(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 labeled **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]

(June 2011 P41 Q8)

Q2 The technique of DNA fingerprinting has been one of the most important developments in biochemical analysis in recent times. It has enabled enormous advances to be made in forensic science, medicine and archaeology.

(a) The table shows different stages in the production of a genetic fingerprint. Use the numbers 1 to 6 to put the stages in the correct sequence in the blank column.

stages	process	correct sequence (numbers)
A	place samples on agarose gel	
B	use polymerase chain reaction	
C	label with radioactive isotope	
D	extract DNA	
E	use restriction enzyme	
F	carry out electrophoresis	

(b) One of the stages above uses a radioactive isotope.

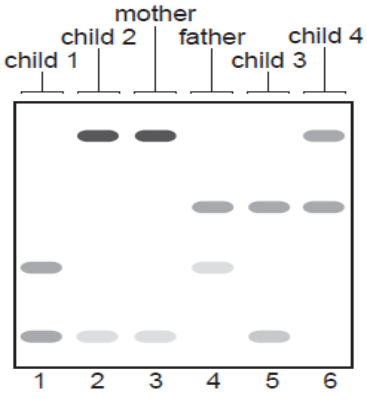
(i) What isotope is used? .....

(ii) Why is this isotope chosen?

.....

.....[2]

(c) The following DNA fingerprints were taken from a family of mother, father and four children.



(i) Are all of the children related to the mother? State the evidence for your answer.

.....

.....

(ii) Which child is unlikely to be related to the father? State the evidence for your answer.

.....

.....

(d) DNA fingerprinting has been successfully used in archaeological investigations.
(i) Ancient writings were often made on goatskins. Over the centuries these have often become broken into fragments, making reconstruction of the writings almost impossible. Suggest how the use of DNA fingerprinting might be able to identify which fragments came from a particular skin.

.....

.....

.....

(ii) Apart from the examples of human remains and goatskins, state one other material that could be investigated using this technique.

.....

.....

(June 2011 P42 Q7)

Q3 One of the key areas of investigation in understanding the structures of polypeptides and proteins is the sequence of amino acids that make up the polypeptide chains.
(a) One of the methods used to determine the amino acids present in a polypeptide chain is electrophoresis. Sketch and label the apparatus used to carry out electrophoresis.
(b) In electrophoresis, different amino acids move in different directions and at different speeds.
(i) What factors determine the *direction of travel* of an amino acid?

.....

.....

(ii) What factors determine the *speed of movement* of an amino acid?

.....

.....

(c) Another important technique used to examine the structure of proteins is X-ray crystallography. In this technique the position of individual atoms can be determined, and the distances between them measured.
(i) Hydrogen atoms never produce images using X-ray crystallography. Explain why this is the case.

.....

.....

(ii) Suggest and explain which one of the atoms in a molecule of cysteine, $H_2NCH(CH_2SH)CO_2H$, would show up most clearly using X-ray crystallography.

.....

.....

(Nov 2011 P41 Q7)

Q4 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	

(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

.....

.....

.....

(ii) thin-layer chromatography

.....

.....

.....

(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**.

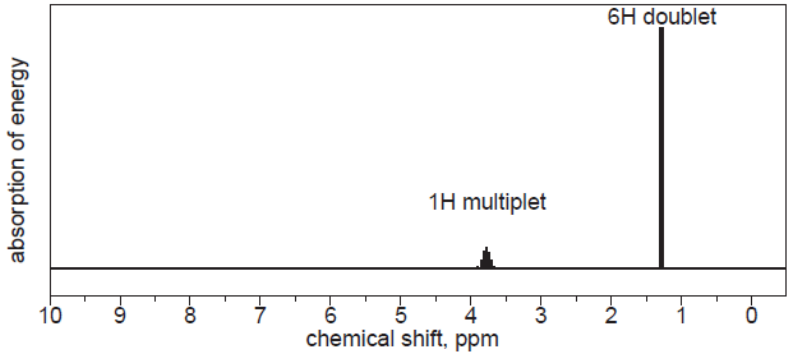
.....

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

.....

.....

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.

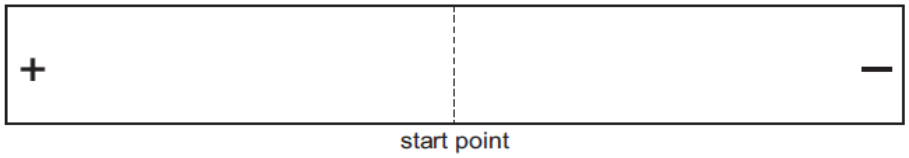
(Nov 2011 P43 Q7)

Q5 The analysis of a protein may be carried out by breaking it down into its amino acids. These can then be separated by a process called electrophoresis.

(a) The structures of glycine, lysine and glutamic acid at pH 7 are shown.

glycine	$H_3N^+CH_2CO_2^-$
lysine	$H_3N^+CH(CH_2CH_2CH_2CH_2NH_3^+)CO_2^-$
glutamic acid	$H_3N^+CH(CH_2CH_2CO_2^-)CO_2^-$

Draw and label three circles on the chart below to indicate the likely position of each of these amino acids after electrophoresis of solution containing these amino acids in buffer at pH 7.



(b) Some organic compounds have very different solubilities in water and in organic solvents such as hexane. They may be extracted from an aqueous reaction mixture by shaking the mixture with portions of hexane and separating the two layers.

The process of distribution of a compound between two solvents is called *partition*.

(i) State what is meant by the term *partition coefficient*.

.....

.....

.....

(ii) One of the concerns about organic pollutants, such as pesticide residues, is that they can enter the food chain and become concentrated in human breast milk. Explain how this can happen.

.....

.....

.....

(c) Propene was treated with bromine in the presence of chloride ions and the product analysed using mass spectrometry.
A group of peaks was found in the range *m*/*e* 156–160 with the following relative heights.

m/*e*	relative height
156	3
158	4
160	1

(i) Identify the species responsible for each of these peaks.

156 .....

158 .....

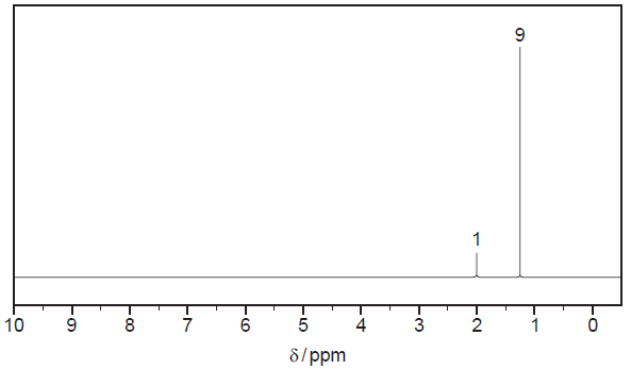
160 .....
A large peak was present in the spectrum with a *m*/*e* value of less than 20.
(ii) Suggest the *m*/*e* value for the peak and the species that produced it.

m/*e* ..... species .....
(June 2012 P41 Q7)

Q6 NMR and X-ray crystallography are two important analytical techniques which can be used to study the structure and function of molecules.
(a) Nuclear magnetic resonance, NMR, arises because protons possess spin which generates a small magnetic moment. When an external magnetic field is applied the protons can align with or against the external field. If they are given a small amount of energy in the radio frequency range each can be 'promoted' so that their magnetic moment opposes the external field.
Two factors can influence the energy required for this promotion. What are they?

(i) .....

(ii) .....[2]
(b) A compound, **J**, has the formula $C_4H_{10}O$. The NMR spectrum of **J** is shown.



(i) Indicate the groups responsible for each peak and hence deduce the structure of **J**.
peak at 1.26 δ ..... peak at 2.0 δ .....
structure of **J**

(ii) There are three other isomers of **J** containing the same functional group as **J**.
Draw the structures of two of these three isomers and indicate how many different chemical shifts each would show in its NMR spectrum.

isomer 1 isomer 2

number of groups of peaks ..... number of groups of peaks .....[6]

(c) X-ray crystallography can be useful in gathering information about the structure of large organic molecules, such as nucleic acids.

(i) Which element will show up most strongly in the X-ray crystallography of a nucleic acid? Explain your answer.

.....

.....

(ii) X-ray crystallography will **not** detect hydrogen atoms. Explain why this is so.

.....

.....

(June 2012 P42 Q7)

Q7 DNA fingerprinting has become an important analytical technique, largely due to its use in 'screening' crime suspects. It also has a range of applications in modern analysis including determining family links, medicine and archaeology.

(a) (i) DNA fingerprinting uses an analytical technique you have studied. What is the name of that technique?

.....

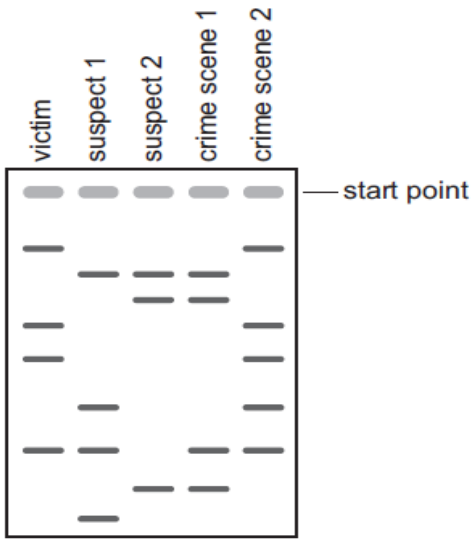
(ii) In order to carry out DNA fingerprinting, the DNA must first be broken down into shorter lengths of polynucleotides. How is this accomplished?

.....

(iii) What part of the DNA fragments enables them to move in an electric field?

.....[3]

(b) The DNA fingerprints shown were obtained from a crime scene. DNA samples were recovered from two rooms in the house where the crime took place. The victim's DNA and that of two possible suspects were included in the analysis.

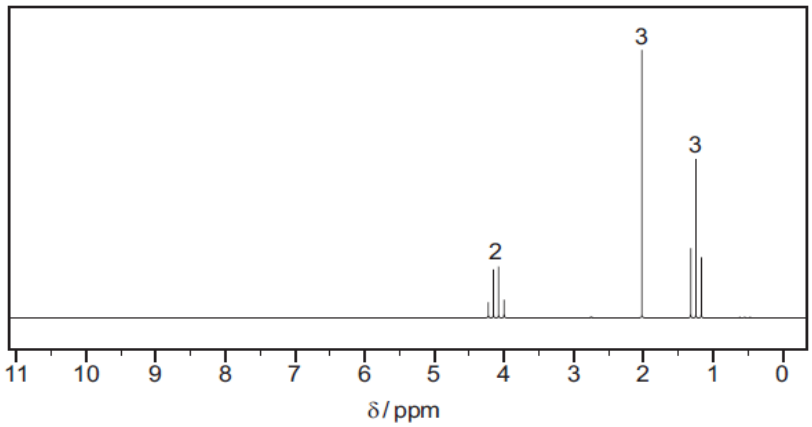


(i) Indicate with an **X** on the diagram, which lines from suspect 1 and from suspect 2 **cannot** distinguish which of them was present in the house.
(ii) Based on this evidence one suspect was arrested. Which suspect would you expect this to be? Explain your reasoning.

.....

.....

(c) A sample of a liquid, **P**, was found at the scene of the crime and was analysed using mass spectrometry and NMR spectroscopy.
The mass spectrum has M and M+1 peaks in the ratio of 5.1: 0.22 with the M peak at *m/e* = 88. The NMR spectrum is shown



Use the data to suggest a structure for **P**, explaining your answer.

.....

.....

.....

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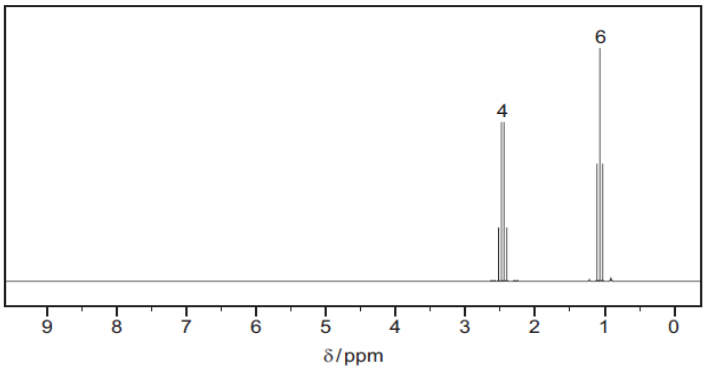
.....

.....

structure of **P**

(Nov 2012 P41 Q7)

Q8 Although the chemical reactions of compounds remain important pointers to their functional groups, instrumental techniques such as mass spectrometry and NMR spectroscopy are increasingly used to determine molecular structures.
(a) Compound **J** was analysed using these two techniques with the following results.
The mass spectrum showed that
● the M peak was at *m/e* 86,
● the ratio of heights of the M and M+1 peaks was 23.5 : 1.3.
The NMR spectrum is shown below.



(i) Use the data to determine the number of carbon and hydrogen atoms present in **J**, showing your working.

(ii) Use the information given above and your answer to **(i)** to identify the other element present in **J**.

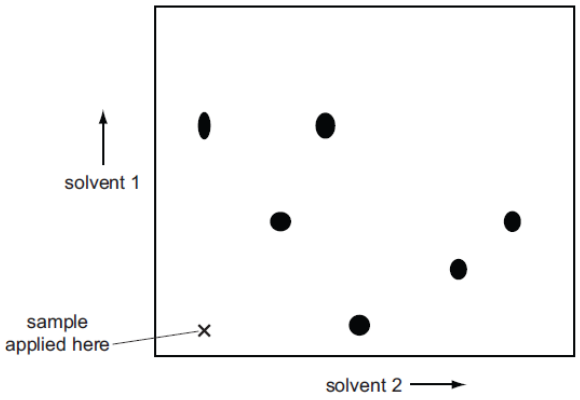
.....
(iii) Determine the structure of **J**, explaining how you reach your conclusion.
structure of **J**

explanation .....

.....
(b) Chromatography is another important analytical technique used in chemistry.
(i) Paper, thin-layer and gas-liquid chromatography rely on different physical methods to separate the components in a mixture. Complete the table indicating the appropriate method on which the technique is based.

technique	physical method
paper chromatography	
thin-layer chromatography	
gas-liquid chromatography	

In paper 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.



(ii) How many spots were visible **before** solvent 2 was used?.....
(iii) Ring the spot that did **not** move in solvent 2.
(iv) How many spots travelled further in solvent 2 than they did in solvent 1?.....
(Nov 2012 P43 Q7)

Q9 Modern methods of analysis have had far-reaching effects on a number of branches of science including medicine, forensic science, environmental monitoring and archaeology.
(a) Outline, in simple terms, the technique of DNA fingerprinting.

.....

.....

.....

.....

.....[4]
(b) Complete the table by indicating whether the items can be used for DNA fingerprinting. Use a tick for items which can be used for DNA fingerprinting and a cross (**x**) for items which cannot.

item for testing	suitable for DNA fingerprinting
human hair	
piece of a flint tool	
piece of Iron Age pot	
piece of Roman leather	

(c) Various forms of chromatography can be used to separate and analyse mixtures. HPLC (high performance liquid chromatography) can be used to separate each of the following mixtures. State another method of chromatography which would separate each mixture.
insecticides in a sample of water .....

dyes present in a foodstuff .....

drug residue in an athlete's urine .....
(June 2013 P41 Q7)

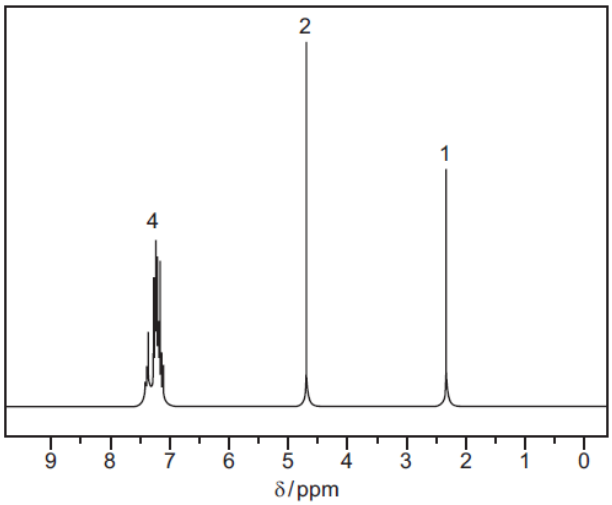
Q10 The techniques of mass spectrometry and NMR spectroscopy are useful in determining the structures of organic compounds.
(a) The three peaks of highest mass in the mass spectrum of organic compound **L** correspond to masses of 142, 143 and 144.
The ratio of the heights of the M : M+1 peaks is 43.3 : 3.35, and the ratio of heights of the M : M+2 peaks is 43.3 : 14.1.
(i) Use the data to calculate the number of carbon atoms present in **L**.

(ii) Explain what element is indicated by the M+2 peak.

.....

.....

Compound **L** reacts with sodium metal. The NMR spectrum of compound **L** is given below.



(iii) What does the NMR spectrum tell you about the number of protons in **L** and their chemical environments?

.....

.....

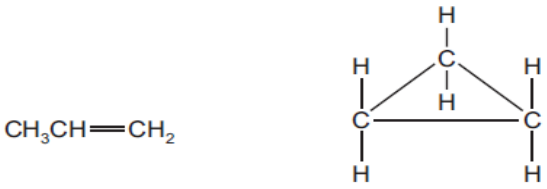
(iv) Use the information given and your answers to **(i)**, **(ii)** and **(iii)** to deduce a structure for **L**. **Explain** how you arrive at your answer.

structure of **L**

Explanation.....

.....

(b) The molecular formula C_3H_6 represents the compounds propene and cyclopropane.



propene cyclopropane

(i) Suggest **one** difference in the fragmentation patterns of the mass spectra of these compounds.

.....

.....

(ii) Suggest **two** differences in the NMR spectra of these compounds.

.....

.....

.....

(June 2013 P42 Q7)

Q11 Electrophoresis is a technique which can be used to separate amino acids or peptide fragments present in a mixture.

(a) Draw a diagram to show the apparatus used to carry out electrophoresis. You should label each of the relevant parts of the apparatus.

(b) How far an amino acid will travel during electrophoresis depends on the pH of the solution.

For a given potential difference, state **two other** factors that will affect how far a given amino acid travels in a fixed time during electrophoresis.

1. .....

.....

2. .....

.....

(c) A number of analytical and separation techniques rely on substances having different partition coefficients.

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

.....

.....

.....

(d) The partition coefficient of **X** between ethoxyethane and water is 40.0.
A solution contains 4.00 g of **X** dissolved in 0.500 dm^3 of water.
Calculate the mass of **X** that can be extracted from this aqueous solution by shaking it with
(i) 0.050 dm^3 of ethoxyethane,

(ii) two successive portions of 0.025 dm^3 of ethoxyethane.

(Nov 2013 P42 Q7)

Q12 Instrumental analysis plays an increasingly important role in modern chemistry. Two important techniques are NMR spectroscopy and X-ray crystallography.
(a) Both techniques use part of the electromagnetic spectrum.
Which technique uses radiation with the longer wavelength, and in which part of the spectrum is it found?

.....

(b) NMR spectroscopy provides detailed information about protons, but X-ray crystallography is unable to detect them. Explain these facts.

.....

.....

.....

.....

(c) The protein found in hair contains the amino acid cysteine, $C_3H_7SNO_2$. Crystalline cysteine was examined using X-ray crystallography. State which atom produced the strongest reflection, explaining your answer.

.....

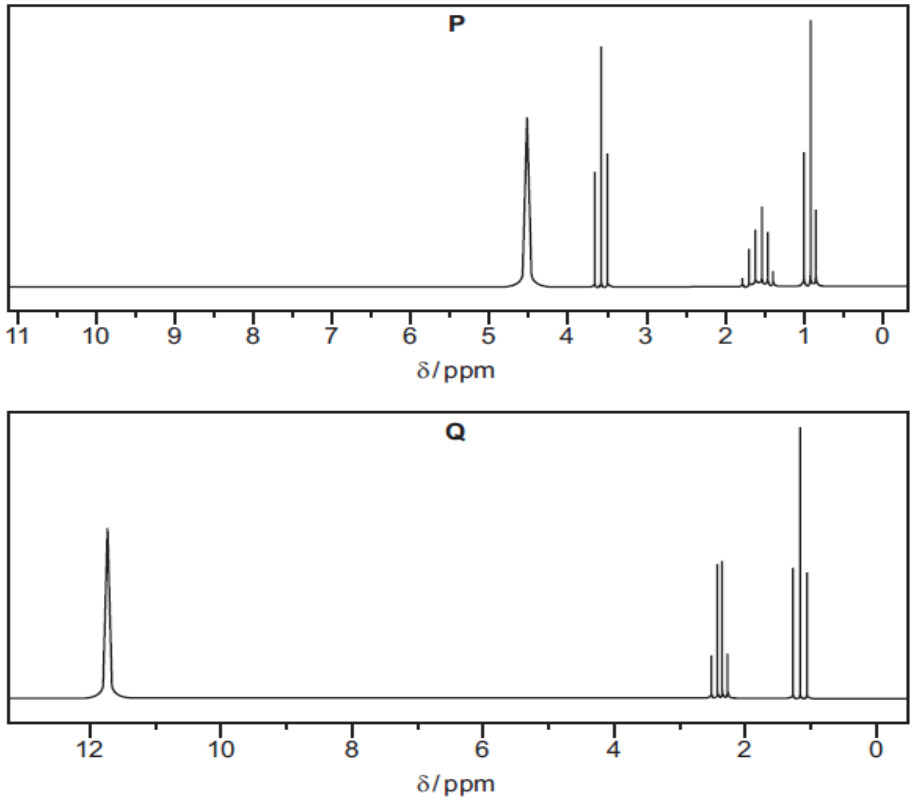
.....

(d) Compound **P** is an alcohol that can be converted into compound **Q** in the following reaction sequence.

$$\mathbf{P} \rightarrow C_xH_6O \rightarrow \mathbf{Q}$$

Spectral analyses of **P** and **Q** were carried out.
(i) The mass spectrum of **P** shows an M : M+1 peak ratio of 4.5 : 0.15.
Calculate the number of carbon atoms in **P**.

The NMR spectra of **P** and **Q** are shown below.



(ii) In the spectrum of **P**, clearly label the peak due to the –OH group with an **X**.

(iii) State how many different proton environments are present in compound **Q**.

.....

(iv) What evidence is there in these spectra that **P** is a primary rather than a secondary alcohol?

.....

.....

.....

.....

(v) Draw a structure for **Q**.

(Nov 2013 P43 Q8)