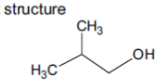
Question 1

8	(a)	M:M+1 = 100/(1.1 x n) 20.4/0.9 = 100/(1.1 x n) x =4	1 1	
	(ii)	$C_4H_{10}O$	1	[3]
	(b) (i)	2-methylpropan-1-ol **OR** correct structure 	1	
	(ii)	0.9-1.0 is (2 x)$CH_3R/CH_3/RCH$ multiplet/1.8 is CHR/R_3CH singlet/2.5 is OH 3.4 is CH_2O/CH_3O	1 1 1 1	
	(iii)	doublet 1H/one proton on adjacent carbon	1 1	
	(iv)	OH peak or one peak disappears OH proton is labile ***or*** exchanges for D of D_2O ***or*** as an equation e.g. $D_2O + OH \rightarrow DOH + OD$ as a minimum	1 1	[9]
Total				**12**

Question 2

8 (a) NMR **and** radiowaves (*or* VHF / UHF *or* 40 – 800 MHz) [1]
[1]

(b) NMR: protons have (nuclear) spin
or (spinning) proton produces magnetic moment / field *or* two spin states
or protons can align with or against an applied magnetic field [1]

there is insufficient electron density / cloud around H atoms for X-ray crystallography [1]
[2]

(c) Sulfur, because it has the highest electron density [1]
[1]

(d) (i) $\frac{4.5}{1.5} = \frac{100}{1.1} \times n$

$n = \frac{100 \times 0.15}{4.5 \times 1.1} = 3.03 = \mathbf{3}$ (calculation must be shown) [1]

(ii) the –OH peak (broad singlet) at δ 4.6 [1]

(iii) 3 (three) [1]

(iv) **Q** has peak at 11.7δ. [1]
which is due to $-CO_2H$ [1]
(This can only be formed by oxidising a *primary* alcohol.)

or **P** has 4 peaks in its NMR spectrum, not 3 [1]
in a secondary alcohol with 3 carbons, two (methyl) groups will be in the same chemical environment (or wtte) [1]

or analysis of the splitting pattern in **P**: the peaks at δ 0.9 and 3.6 are triplets, [1]
so each must be adjacent to a $-CH_2-$ group. (hence $-CH_2-CH_2-CH_3$) [1]

(v) $CH_3CH_2CO_2H$ (**structure** needed, not name) [1]
[6]

[Total: 10]

Question 3

7 (a) Expression: $n = \frac{100 \times 2.5}{1.1 \times 74}$ or equivalent [1]
n = 3.1 hence **G** has three carbon atoms [1]

(b) (i) (δ 1.1) RCH_3 *or* RCH_2R *or* methyl *or* CH_3

(δ 2.2) $(R)CH_2CO(R)$ *or* $CH_3CO(R)$

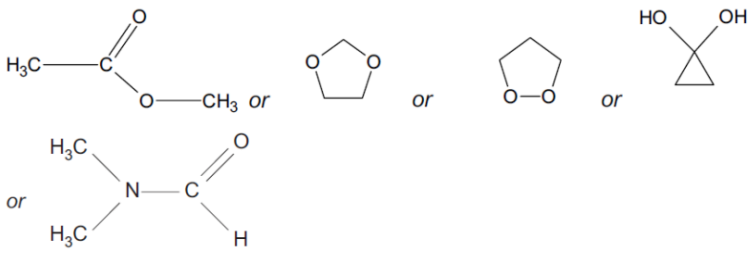
(δ 11.8) (R)COOH or (R)CONH(R) 3 × [1]

(ii) The (–OH) peak at δ 11.8 (disappears) [1]

because of (O)H-D exchange *or* equation showing this
(e.g. R-OH + D_2O ⇌ R-OD + HOD) [1]

(iii) $CH_3CH_2CO_2H$ [1]

(c) (i)



[1]

(ii) If methyl ethanoate: δ 2.0–2.1 [1]
δ 3.3–4.0 [1]

Or if 1, 3-dioxolane: δ 3.3–4.0 [1]
δ 3.3–5.0 [1]

Or if 1, 2-dioxolane: δ 0.9–1.4 [1]
δ 3.3–4.0 [1]

Or if dihydroxycyclopropane: δ 0.9–1.4 [1]
δ 0.5–6.0 [1]

[Total: 11]

Question 4

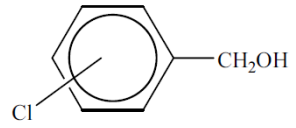
7. (a) (i) $\frac{43.3}{3.35} = \frac{100}{1.1 \times n}$

$n = \frac{100 \times 3.35}{43.3 \times 1.1}$ = 7.03 = 7 (calculation must be shown) [1]

(ii) The M and M+2 peaks are in the ratio 3 : 1 hence the halogen is chlorine/C*l* [1]

(iii) **L** contains 7 hydrogen atoms *or* there are 3 types/environments of proton/H [1]

(iv) The multiplet with 4 hydrogens *or* peaks at δ 7.3 suggests a benzene ring
The singlet with 2 hydrogens *or* peak at δ 4.7 suggests a $–CH_2–$ group
The singlet with 1 hydrogen *or* peak at δ 2.3 suggests an –OH group
or reaction with Na suggests an OH group
OH must be an alcohol, not a phenol (due to its δ value)
Since **L** also contains 7 carbon atoms and chlorine, this accounts for 126 of the 142 mass, the remaining atom must be oxygen
Thus **L** is



(allow the 2-, 3- or 4- isomer)

[6]
[9 max 7]

(b) (i) we expect propene to have a CH_3 peak *or* a peak at m/e 15
or cyclopropane would have fewer peaks

[1]

(ii) cyclopropane would have 1 peak (ignore splitting)
propene would have 2 (*or* 3, *or* 4) peaks (ignore splitting)
or propene would have peaks in the δ 4.5-6.0 (alkene) region
no splitting of cyclopropane peak
(any two points) [2]
[3]
[Total: 10]

Question 5

(c) **P** is $CH_3CO_2CH_2CH_3$ [1]

any <u>four</u> of:

- 3 different (proton) environments
- (M and M+1 data shows no of carbons present is) $(100 \times 0.22)/(1.1 \times 5.1) =$ **4 carbons**
- the NMR spectrum shows 8 hydrogens leaving 32 mass unit or 2 oxygen ***or*** $M_r = 88$ **and** (molecular formula is) $C_4H_8O_2$
- 4 peaks/quartet (at 4.1) shows an adjacent $3H/CH_3$
- 3 peaks/triplet (at 1.3) shows an adjacent $2H/CH_2$
- (peak at) 2.0/singlet shows CH_3CO (group)
- (peak at) 4.1/quartet **and** 1.3/triplet shows presence of ethyl/CH_3CH_2 (group)

4 × [1]

[5]

Question 6

7 **(a)**

structural information	analytical technique
three-dimensional arrangement of atoms and bonds in a molecule	X-ray crystallography/diffraction
chemical environment of protons in a molecule	NMR (spectroscopy) **only**
identity of amino acids present in a polypeptide	Electrophoresis / chromatography / mass spectrometry

[1] + [1] + [1]
[3]

(b) **(i)** **paper chromatography;**
The components **partition** between the solvent/moving phase and the water/liquid stationary phase *or* separation relies on different solubilities (of components) in the moving solvent and the stationary water phase. [1]

(ii) **thin-layer chromatography.**
Separation depends on the differential **adsorption** of the components onto the solid particles/phase *or* Al_2O_3 *or* SiO_2. [1]
[2]

(c) **(i)** No. of carbon atoms present = $\frac{0.2 \times 100}{5.9 \times 1.1}$ = 3.08 hence 3 carbons [1]

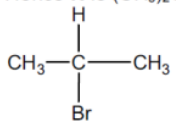
(ii) Bromine [1]

(iii) **One** bromine is present as there is only an M+2 peak / no M+4 peak *or* the M and M+2 peaks are of similar height [1]

(iv) *NMR spectrum shows a single hydrogen split by many adjacent protons and 6 protons in an identical chemical environment. This suggests...*
two $-CH_3$ groups and a lone proton attached to the central carbon atom [1]

Empirical formula of **N** is C_3H_7Br [1]

Hence **N** is $(CH_3)_2CHBr$ *or*



[1]
[6]

[Total: 11]

Question 7

(c) **(i)** They have insufficient electron density / only one electron [1]

(ii) Sulfur [1]
because it has the greatest atomic number / number of electrons [1]
[3]

Question 8

(b) **(i)** They are largely composed of (carbon and) hydrogen which are active in the NMR (owtte) *or* protons/H^+/H exist in <u>different chemical environments</u> (with characteristic absorptions) (1)

(ii) 2 correct displayed formulae (1)

In propanone all the protons are in a similar chemical environment (and hence there will be one proton peak.) (1)

In propanal there are (three) <u>different chemical environments</u> and hence there will be (three) <u>proton peaks</u> *or* three different chemical environments *or* three proton peaks (1)
[4]

Question 9

8 **(a)** Protons (1)
in NMR, energy is absorbed due to the two spin states (1)
Electrons (1)
in X-ray crystallography, X-rays are diffracted (by regions of high electron density) (1) **[4]**

(b) **(i)** 1 – no mark
The spectrum of alcohol / **Y** contains different peaks
Alcohol / **Y** contains different chemical environments
Spectrum 2 contains only one peak (1)

(ii) Spectrum 2 only shows 1 peak so **Z** must be a ketone (1)

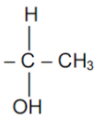
Hence **Y** must be a 2° alcohol (1)

Number of carbon atoms present $= \frac{0.6 \times 100}{17.6 \times 1.1} = 3$ (1)

Thus **Z** must be CH_3COCH_3 (1)

Hence **Y** must be propan-2-ol, $CH_3CH(OH)CH_3$ (1)

(iii)

Y is  (1)

(iv) All of the protons in **Z** are in the same chemical environment (1) **[8] max [7]**

Question 10

(c) **(i)** Ratio would be 3 : 1 [1]

(ii) Each chlorine at could be ^{35}Cl or ^{37}Cl
Only way of getting M+4 is for both chlorines to be ^{37}Cl (1 in 9 chance) [1]
Ratio of peaks M M+2 M+4
9 6 1 [1]
[3]

(d) **(i)** Accept dioxins and furans (without specifying) [1]

(ii) PCBs (but don't penalise non-specified dioxins and furans) [1]

(iii) Allow : pollution control / environmental legislation / removal of dioxins and furans / mill closed down (owtte) [1]

(iv) Five [1]
[4]

Question 11

7 (a) (i) Positions of atomic nuclei / atoms (1)

(ii) Insufficient electrons / electron density / electron cloud (around H atom) (1) [2]

(b) X-ray crystallography can show the geometry of the arrangement of atoms / bonding between atoms / shape of atoms (1)

This can help explain how e.g. enzymes work (any reasonable example) (1) [2]

(c) (i) Nuclear spin (1)

(ii) (If M : M+1 gives a ratio 15 : 2)

Then $x = \frac{100 \times 2}{1.1 \times 25} = 7$ (1)

Single peak at 3.7 δ due to $-O-CH_3$ (1)

Single peak at 5.6 δ due to phenol / OH (1)

1,2,1 peak at 6.8 δ due to hydrogens on benzene ring (1)

Pattern suggests 1,4 subsitution (1)

(x = 7,) y = 8, z = 2 (1)

Compound is 4-methoxylphenol (1)
Max 5 [6]

Question 12

(b) (i) NMR can be done in solution / in *vivo* / shows labile protons / shows positions of protons and/or carbon atoms [1]
X-ray crystallography shows the positions of most atoms in structure / allows measurement of bond length [1]

(ii) different types of tissue have protons in different chemical environments / tumour and healthy tissue absorb differently / allow at different frequencies [1]

(c) (i) M : M+1 = 48 : 1.7

$x = \frac{100 \times 1.7}{1.1 \times 48} = 3.2$ hence there are 3 carbon atoms in the compound [1]
NB if calculation shown 1.1 divisor MUST be present

since the compound has an *m/e* of 73 and contains 3 carbon atoms, 1 nitrogen atom and 1 oxygen atom, *y* = 73–(36 +14+16) = 7 [1]

(ii) the NMR spectrum shows a quartet, triplet pattern characteristic of an ethyl group [1]
the other broad peak must be due to N–H protons [1]

thus the structure of the compound is likely to be
$CH_3CH_2CONH_2$ [1]

Question 13

1 (a) (i) 162 ($^{81}Br^-$ $^{81}Br^+$) for molecular species [1]
160 ($^{81}Br^-$ $^{79}Br^+$) for atomic species [1]
158 ($^{79}Br^-$ $^{79}Br^+$) *ignore missing charges* for 5 masses [1]
81 ($^{81}Br^+$)
79 ($^{79}Br^+$)

(ii) 158:160:162 =1:2:1 [1]
79:81 =1:1 [1]

(b) (i) *either* $BrCH_2CHBr\text{-}CHO$ *or* $CH_2{=}CH\text{-}CH_2OH$ (double bond needed) [1]

(ii) reaction I: Br_2(aq or in CCl_4 etc.), light negates – *solvent not needed* [1]
reaction II: $NaBH_4$ *or* H_2/Ni etc. (but not if **A** is $CH_2{=}CH\text{-}CH_2OH$)
allow $LiAlH_4$ or Na/ethanol [1]
(*reactions can be reversed*)

(c) (i) $C_3H_6OBr_2$ = 216, 218 and 220 (any one) [1]

(ii) 31 is CH_2OH^+/CH_3O^+
106 is $C_2H_3{}^{79}Br^+$
108 is $C_2H_3{}^{81}Br^+$
185 is $C_2H_3{}^{79}Br_2{}^+$ *ignore missing charges*
187 is $C_2H_3{}^{79}Br^{81}Br^+$ 6 correct [4]
189 is $C_2H_3{}^{81}Br_2{}^+$ 5 correct [3] etc

if no mass numbers given – [1] only [4]

[Total: 13 max 12]

Question 14

9 (a) Suitable diagram showing origin of two energy states/or description [1]
Needs to mention applied magnetic field/electron transfer negates
Indication that energy difference is in the radio frequency range [1]
Indication that frequency of absorption *or* gap between the 2 energy states depends on the nature of nearby atoms *or* the chemical environment of the ^1H [1]
[3]

(b) They do not damage tissues/X-rays harmful/NMR of lower energy [1]
They are not obscured by bones/skeleton [1]
They can be tuned to examine particular tissues/tumours/*organs*/protons [1]
[max 2]

(c) (i) M : M+1 = 100/(1.1n)

$$n = \frac{0.66 \times 200}{14.5 \times 1.1} = \frac{66}{15.95} = 4.14 = 4 \text{ carbon atoms}$$ [1]

Check for 1.1 in divisor, if missing, penalise

(ii) Singlet at δ 2 suggests methyl adjacent to C=O [1]
Quartet at δ 4 suggests a $-CH_2-$ group *(*adjacent to a –methyl group*)* [1]
(allow $-OCH_2-$)
Triplet at δ 1.2 suggests a methyl group *(*adjacent to a $-CH_2-$*)* [1]
G is ethyl ethanoate (or structure)/if methyl propanoate given here cannot score first marking point [1]
[5]

[Total: 10]

Question 15

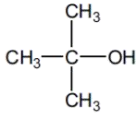
7 (a) (i) + (ii) any two from:

- The nature/electronegativity of the atom the proton is attached to *or* is near *or* the electronic/chemical environment of the proton
- The number/spin states of adjacent protons *or* protons attached to adjacent atoms
- The (strength of) the applied/external magnetic field [1] + [1]

[2]

(b) (i) Peak at 1.26δ = (3 ×) CH_3 *or* methyl **and** Peak at 2.0δ = –O–H *or* alcohol [1]

Structure: [1]



(ii)

Isomer	Isomer	Isomer
$CH_3CH_2CH_2CH_2OH$	$(CH_3)_2CHCH_2OH$	$CH_3CH_2CH(CH_3)OH$
5 groups of peaks	4 groups of peaks	5 groups of peaks

structures of any two isomers (Also allow both stereoisomers of butan-2-ol) [1] + [1]
correct assignation of no. of peaks [1] + [1]

[6]

(c) (i) Phosphorus – it has more electrons *or* high electron density (NOT phosphate) [1]

(ii) H atoms don't have enough electron density to show up *or* they only contain one e^- [1]

[2]

[Total: 10]

Question 16

(c) (i) 156 = $C_3H_6{}^{35}Cl^{79}Br^+$ [1]
158 = $C_3H_6{}^{37}Cl^{79}Br^+$ [1]
158 = $C_3H_6{}^{35}Cl^{81}Br^+$ [1]
160 = $C_3H_6{}^{37}Cl^{81}Br^+$ [1]

(ii) *m/e* = 15 Species = CH_3^+ [1]

[5 max 4]

Question 17

(c) (i) **X** is bromine – M and (M+2) peaks almost same height [1]

(ii) $\frac{M}{M+1} = \frac{100}{1.1} \times \frac{9}{n} = \frac{100}{0.3}$ 1.1 × n

Hence $n = \frac{100 \times 0.3}{1.1 \times 9} = 3.03$ p = 3

(answer + working) [1]

(If the mass peak is at 122 and the compound contains Br and 3 C atoms then Q = (122 – 79 – 36)) thus **Q = 7** ecf from **(ii)** [1]

(The compound is C_3H_7Br)

(iii) *(R is at m/e 43)*, hence **$C_3H_7^+$** [1]

(d) Any **two** from H_2, H_2O, CO, C_2H_4, C_2H_2, CH_4 2 × [1]

Question 18

(d) (i) $Si_3Cl_8O_2$ (this has M_r = 84 + 280 + 32 = 396) *or* $Si4Cl_4O_9$ *or* $Si_8Cl_4O_2$ (1)

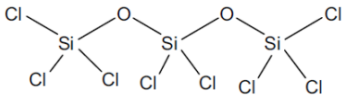
(ii)

mass number	structure
133	Cl_3Si
247	$Cl_3Si\text{-}O\text{-}SiCl_2$
263	$Cl_3Si\text{-}O\text{-}SiCl_2\text{-}O$

(3)

(if correct structures are **not** given for last 2 rows, you can award (1) mark for ***two*** correct molecular formulae:
either $Si_2Cl_5O + Si_2Cl_5O_2$ *or* $Si_3ClO_8 + Si_3ClO_9$ *or* $Si_7ClO + Si_7ClO_2$)

(iii)



allow ecf on the structure drawn in the third row of the table in **(ii)**
but any credited structure must show correct valencies for Si, Cl and O. (1) [5]

Question 19

9 **(a)** spinning proton produces two spin states / magnetic moments (1)
these can align with or against an applied magnetic field (1) [2]

(b) field experienced by protons is influenced by adjacent atoms / protons are in two different chemical environments (1)
peaks are in the area ratio 3 : 1 (methyl to –OH protons)
or are at 0.5 – 6.0δ and 3.3 – 4.0δ (1) [2]

(c) **(i)**

$CH_3CH_2CO_2H$	$CH_3CO_2CH_3$	$HCO_2CH_2CH_3$
propanoic acid	methyl ethanoate	ethyl methanoate

all for (2) two for (1)

(ii) compound is $CH_3CO_2CH_3$ *or* methyl ethanoate (1)
the other two compounds each have 3 different proton environments, but the spectrum shows only 2 peaks. (1)

A is OCH_3, B is CH_3CO (1)

(iii) compound – propanoic acid *or* ethyl methanoate
the –OH proton *or* the H–CO proton (1) [6]

(d) **(i)** distance between atoms / bond lengths / bond angles (1)

(ii) hydrogen atoms (1) [2]
[Total: 12 max 10]

Question 20

(b) **(i)** CH_3COCH_3 would show
a single peak/no splitting since all the Hs are in the same chemical environment
or a peak at δ = 2.1 due to CH_3CO group [1]

CH_3CH_2CHO would show 3 (sets of) peaks since there are 3 different proton environments
or there would be a peak at δ = 9.5 – 10.0 due to the –CHO group
or a peak at δ = 0.9 due to CH_3
or a peak at δ1.3 due to CH_2 [1]

(reasons needed for the marks. Salvage: if reasons are not given, but candidate states that propanone will have one peak and propanal three, then award [1] mark)

(ii) different fragments:

- CH_3COCH_3 would form **fewer** fragments (must be stated in words)
- CH_3COCH_3 would form a fragment of CH_3CO^+ *or* at (m/e) 43
- CH_3CH_2CHO would form a fragment of $CH_3CH_2^+$ *or* CHO^+ at (m/e) 29
- CH_3CH_2CHO would form a fragment of $CH_3CH_2CO^+$ *or* at (m/e) 57

[charges on fragments not required for mark]
any 3 points [3] **[5]**

(c) **(i)** peaks at (m/e) 79 **and** 81 *or* at (m/e) 94 **and** 96 [1]

(ii) in chlorine the M and M+2 peaks are the ratio 3:1 [1]
whereas in bromine they are approx. 1:1 [1] **[3]**

Question 21

(c) **(i)** $16 = O^+$ $17 = OH^+$ $18 = H_2O^+$ *(ignore charges)* all 3 [1]
$14 = N^+$ $16 = O^+$ $28 = N_2^+$ $30 = NO^+$ $44 = N_2O^+$ all 5 [3]
any 4 *[2]*
(ignore charges) *any 3* *[1]*
∴ **A** = H_2O **and** **B** = N_2O (or in equation below) [1]

(ii) $NH_4NO_3 \longrightarrow N_2O + 2H_2O$ [1] **[6]**