# F324: Rings, Polymers & Analysis
# 4.3.2 – Spectroscopy MARK SCHEME

**1.** (a) **infrared – 1 mark only**

shows (very broad) peak between 2500–3300 ($cm^{-1}$)
(due to O–H bond) ✓

> ***ALLOW** (very broad) peak around 3000 (cm$^{-1}$) **OR** any stated value between 2500 and 3300 (cm$^{-1}$) for O–H*
>
> ***DO NOT ALLOW** peak in range 3200–3550 (cm$^{-1}$)*
>
> ***IGNORE** any reference to C=O or C–O as both are also present in an ester **OR** to fingerprint region*

**$^{13}$C NMR – 2 marks**

$(CH_3)_2CHCH_2COOH$ has 4 peaks (due to 4 different C environments) ✓
$(CH_3)_3CCOOH$ has 3 peaks (due to 3 different C environments) ✓

> ***ALLOW** '$^{13}$C NMR detects the number of/different C environments' for 1 ✓, suitable example for the 2nd mark 3*

**3**

(b) **splitting pattern**
explains any two in terms of '*n* + 1 rule' for two marks ✓✓
Explains any one peak for 1 mark ✓

> ***1 mark** for correct ester*
>
> *if two splitting patterns are correctly analysed **ignore** the third*

- *singlet* therefore adjacent C (if any) has no Hs

> ***ALLOW** singlet because next or bonded to an O*

- *multiplet* **OR** split into 7 therefore adjacent Cs have lots of/6 Hs

> ***ALLOW** multiplet/heptet because next to 2 CH$_3$s*

- *doublet* therefore adjacent C is bonded to 1H

> ***ALLOW** doublet because next to a CH*

*must spell **one** of multiplet / heptet, singlet, doublet correctly*

**max = 2 marks**

**chemical shifts**
two marks if any two absorptions are identified correctly ✓✓
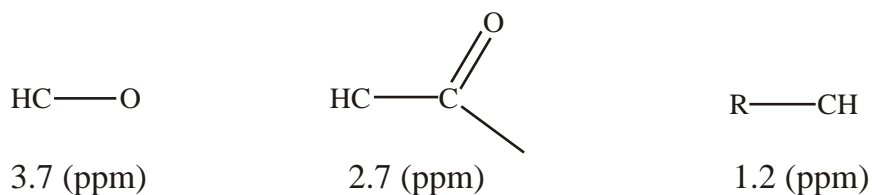one mark if any one absorption is identified correctly ✓

> *ALLOW tolerance on δ values; 3.6–3.8, 2.6–2.8 and 1.1–1.3 (ppm)*

- peak ~3.7 (ppm) – bonded to an O

- peak ~2.7 (ppm) – indicates it is next to a C=O

- peak ~1.2 (ppm) – bonded to other Cs **OR** part of a chain

**max = 2 marks**

> *ALLOW any two gets 2 marks, any one scores 1 mark*

$$HC\!-\!O \qquad HC\!-\!C\!\!\overset{\displaystyle O}{\diagup}\diagdown \qquad R\!-\!CH$$

3.7 (ppm)           2.7 (ppm)           1.2 (ppm)

> *ALLOW peaks labelled on the spectrum*
> *ALLOW singlet must be bonded to O, multiplet to C=O and doublet to CH or R for both chemical shift marks*
>
> *if two chemical shifts are correctly identified **IGNORE** the third*

compound identified as $(CH_3)_2CHCOOCH_3$ ✓✓
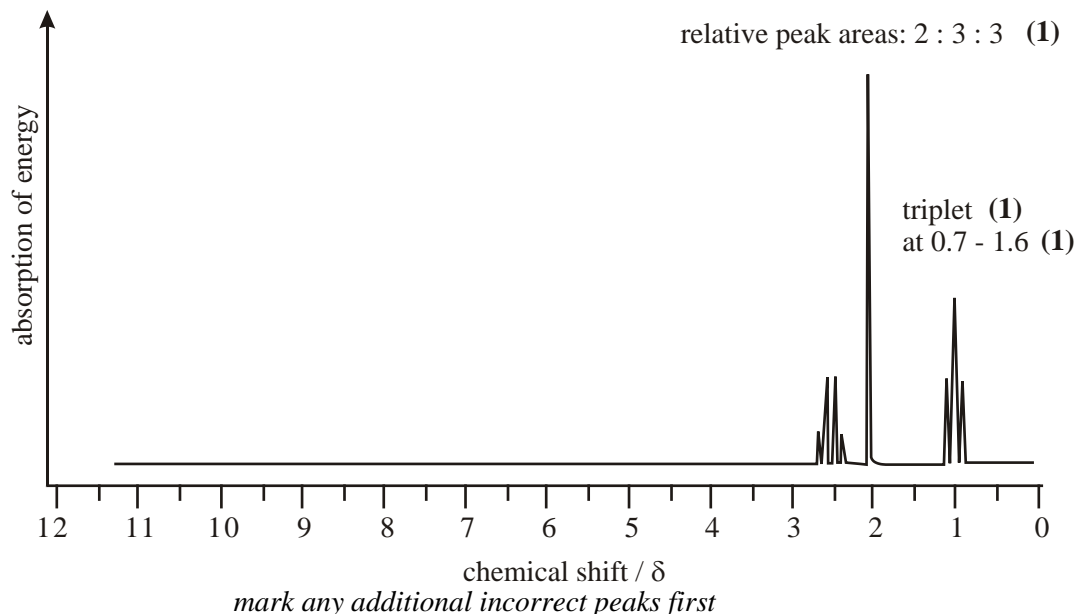
compound identified as $CH_3COOCH(CH_3)_2$ ✓

**6**

**[9]**

**2.** (i) the peak is due to the $CH_3CO-$ group **(1)**

not split, so next to a C with no protons / has no neighbouring proton / δ value is in the range 2.0 – 2.9 **(1)**     2

(ii) adjacent to a C with three protons / to a $CH_3$ **(1)**     1

(iii) and (iv)                                                         3

relative peak areas: 2 : 3 : 3 **(1)**

triplet **(1)**
at 0.7 - 1.6 **(1)**

*(graph: y-axis labelled "absorption of energy", x-axis labelled "chemical shift / δ" with values 12 11 10 9 8 7 6 5 4 3 2 1 0)*

chemical shift / δ
*mark any additional incorrect peaks first*

**[6]**

**3.**   IR

**Similarities**
**Any 2 of the following three peaks (must give the quoted range)**
peak corresponding to OH in all three ($3230 – 3550$ cm$^{-1}$) **(1)**
peak corresponding to NH in all three ($3100 – 3500$ cm$^{-1}$) **(1)**
peak corresponding to CO in all three ($1000 – 1300$ cm$^{-1}$) **(1)**           2 max

**Differences**
only shown in the fingerprint region **(1)**           1

**Mass Spec**

**similarities**
$M_r$ (75)/ base peak will be the same **(1)**           1
M + 1 peak same **(1)**           1

**Differences**
Fragmentation pattern may show differences between isomers
/ specific example, eg $CH_3+$ at m/e 15 **(1)**           1
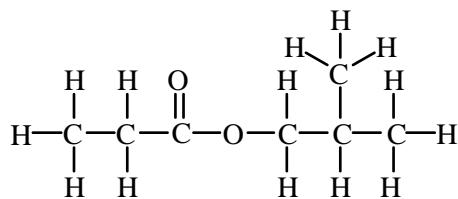
                            (MAX 5)

**QWC**
Use of any two terms from: functional group / amino group /
hydroxy group / fingerprint / fragmentation / fragment ion(s) /
base peak or molecular ion / M + 1 peak / m/e           1

**[6]**

**4.** (a)



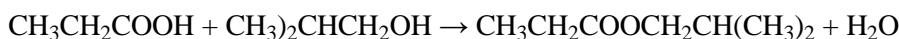propanoate and ester group **(1)**          2-methyl propyl **(1)**                    2

(b)     propanoic acid **(1)**
        (2-)methylpropan-1-ol **(1)**

        heat **(1)**
        conc. $H_2SO_4$ **(1)**
        *(allow ecf from part (a) for the equation)*

        $CH_3CH_2COOH + (CH_3)_2CHCH_2OH \rightarrow CH_3CH_2COOCH_2CH(CH_3)_2 + H_2O$
                    reactants **(1)**                              products **(1)**              6

(c)     mass spectrum / spectrometry **(1)**

        molecular ion peak /
        *m/e* or mass of the peak furthest right **(1) AW**                    2

                                                                                      **[10]**


**5.**     **$\delta$ value / chemical shift** gives the 'type' of proton /
        chemical environment **(1) AW**
        example quoted from data sheet **(1)**

        **number of peaks** gives the number of different types of proton /
        chemical environments **(1)**

        relative / ratio of **(1)**
        **peak areas** gives the number of protons (of each type) **(1)**

        **splitting** gives number of neighbouring / adjacent protons **(1)**

        description of *n* + 1 rule / example of doublet, triplet or quadruplet
        showing 1, 2 and 3 protons neighbouring (carbon) atom **(1) AW**

        **$D_2O$** can be used to identify OH groups **(1)**
        *ANY 7 marks out of 8*                                                        7
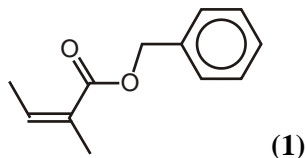
        **Quality of written communication** mark for correct use and
        organisation of at least two of the following technical terms:
        proton, environment, singlet (doublet *etc*.), ppm, equivalent,
        chemical shift, splitting, labile, integration                              1

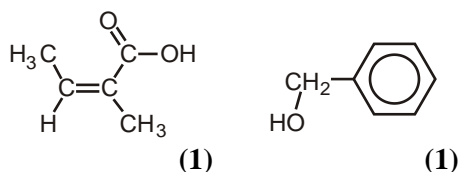                                                                                      **[8]**

**6.** (a) (i) alkene **(1)**
ester **(1)**            2
*allow "C=C double bond"*

          i.



                                         **(1)**      1

          ii.      $C_{12}H_{14}O_2$ **(1)**      1

(b) same structural formula/order of bonds,
different spacial arrangement **AW (1)**

description or diagram showing **B** and how it is different from **A (1)**☐      2

(c)



                **(1)**                     **(1)**      2

(d) (i) peak at 1680-1750 (cm$^{-1}$) due to C=O **(1)**

           peak at 1000-1300 (cm$^{-1}$) due to C-O / **(1)**      2

     (ii) 2500-3300 / 3230-3550 (cm$^{-1}$)    **(1)**

           O-H /carboxylic acid/alcohol is **not** present in **A (1)**

           allow 1 mark for ~500-1500 (cm$^{-1}$) which is a unique
           fingerprint region etc      2

                                                                       **[12]**


**7.** (a) low boiling point / easily turns to a gas **AW (1)**      1

(b) 2,4-dinitrophenylhydrozine / 2,4-DNP(H) / Brady's reagent **(1)**

purify/recrystallise the product/solid (derivative) **(1)**

measure the melting point /mp **(1)**

compare the result with data book/known values **(1)**      4

                                                                         **[5]**

**8.** (a) (i) Molecular ion peak: the peak caused by the unfragmented molecule / the peak with the highest m/e value / the peak that tells you the Mr.      1

Base peak : peak with the greatest (relative) intensity / peak representing most stable/abundant fragment
**NOT** the tallest / biggest / most common peak      1

(ii) The molecular ion is too unstable / will have been <u>completely</u> fragmented / may not carry a positive charge      1
**NOT** peak too small to be seen / too little ion present

(b) IR spectrum:
C=O peak at approx 1650 $cm^{-1}$ (1680-1750 $cm^{-1}$)      1
broad O-H peak at value(s) between 2500-3300 $cm^{-1}$      1
**ignore** any references to C-O peak at 1000 – 1300 $cm^{-1}$

mass spectrum:
Fragment with m/e = 31 is $CH_2OH^+$      1
Fragment at m/e = 45 is $COOH^+$      1

penalise missing + sign once only

(c) 2 proton peak at $\delta$ = 3.3-4.3 – singlet (-CH$_2$-)      1
1 proton peak at $\delta$ = 3.5-5.5 – singlet (-OH)      1
1 proton peak at $\delta$ = 11.0-11.7 – singlet (-COOH)      1
(ranges of chemical shift ($\delta$) values taken from data sheet)
•   penalise each error once only
•   ignore peak areas/heights unless incorrectly labelled

Labelled diagram of the structure of G proposed by the student may be used to provide evidence for the positioning of peaks on the sketched spectrum.

**Both** OH and COOH protons disappear on shaking with $D_2O$      1

**[11]**

**9.** (i)
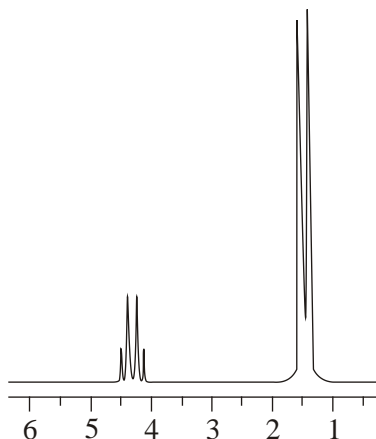


**splitting:**
doublet **(1)**
quartet **(1)**
    *ignore any other peaks*

**position:**
doublet peak is at ~1.4 and
quartet peak is at ~4.3 **(1)**
    *allow ecf from **one** incorrect splitting pattern*

**areas:**
1 and 3 on the correct peaks
(or either way round as ecf if any errors above) **(1)**                4


(ii)    4 **(1)**
OH/labile protons now visible AW **(1)**                2

                                                                                            **[6]**


**10.**  (a)  (i)   Find the m /e of …. **(1)**
                ... the peak furthest to the right / with highest m /e or mass **(1)**        2
                    *allow attempts to cater for the $^{13}C$ peak*

                $C_2H_3O_2$ /empirical formula has $M_r$ = 59 **(1)**
                so $M_r$ of molecular formula is $^{118}/_{59}$ = 2 /twice the empirical formula **(1)**    2


      (b)  (i)   OH <u>peak</u> disappears (with $D_2O$ / on the second spectrum)        1

(ii)　no of peaks: one **(1)**

splitting: none **(1)**

all four protons equivalent / in the same environment **(1)**　　　　3
　　　*if the wrong structure is chosen allow ecf for:*
　　　*two peaks (1),*
　　　*splitting (1)(1) (as last 2 marks for part (ii))*

**[8]**


**11.**　(i)　　**A** $C_3H_6$ **(1)**　　　**B** $C_4H_8$ **(1)**　　　　　　　　　　2

(ii)　**A** $CH_3CH=CH_2$ (or displayed) ('sticks' penalised once)　　　1


(iii)　$C_3H_5^+$ **(1)** for formula and **(1)** for charge　　　　　　2

**[5]**