ORGANIC ANALYSIS

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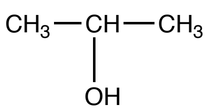
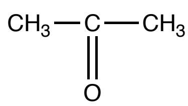
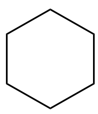
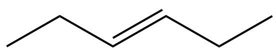
CHEMICAL ANALYSIS

Functional group	Test	Positive result	Negative result
C=C alkene			
O-H in primary & secondary alcohol (also works with aldehyde)			
-CHO aldehyde			
-COOH carboxylic acid			
-Cl / -Br / -I halogenoalkane			

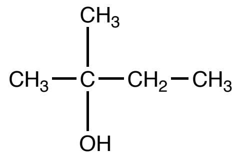
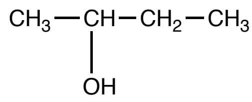
TASK 1 – Chemical tests

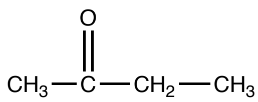
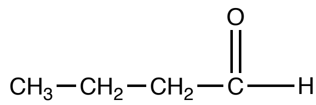
For each pair of compounds, state reagent(s) that could be used to distinguish the compounds and give the result for each compound.

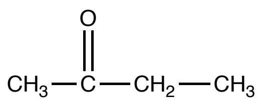
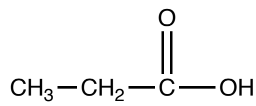
PAIR 1 Compound		
Test		
Result		

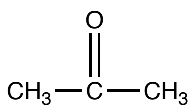
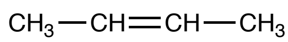
PAIR 2 Compound		

Test		
Result		

PAIR 3 Compound		
Test		
Result		

PAIR 4 Compound		
Test		
Result		

PAIR 5 Compound		
Test		
Result		

PAIR 6 Compound		
Test		
Result		

INFRARED SPECTROSCOPY

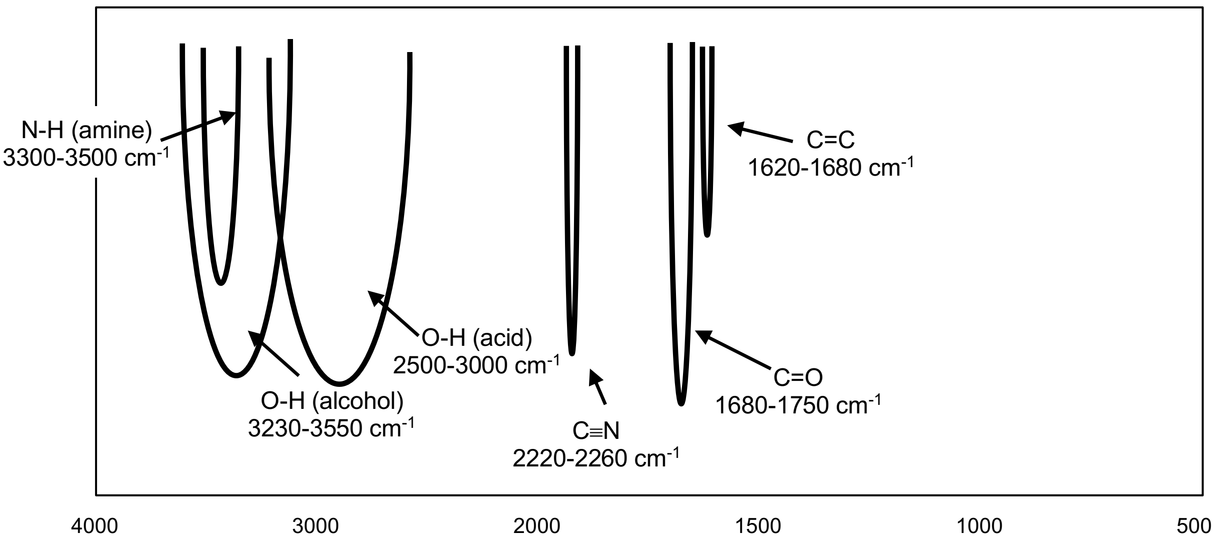
- Infrared spectroscopy is a very important technique that can be used to analyse organic compounds.
- All covalent bonds vibrate at a characteristic frequency (stretching and contracting as well as bending vibrations are the commonest types).

- The frequency depends on the mass of the atoms in the bond, the bond strength, and the type of vibration.
- The frequencies at which they vibrate are in the infrared region of the electromagnetic spectrum.
- If infrared light is passed through the compound, it will absorb some or all of the light at the frequencies at which its bonds vibrate.
- Rather than using the actual values of the wavelength or frequency, the IR light is measured in wavenumbers [1/frequency (in cm)] because it gives convenient numbers in the range 4000 – 400 cm^{-1}
- There are two main things you need to be able to do with infra-red spectra:
    1) identify functional group signals (above 1500 cm^{-1}) – to identify functional groups
    2) use the "fingerprint" region (below 1500 cm^{-1}) – to identify specific compounds

1) Identifying functional group signals (above 1500 cm^{-1})

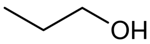
- This part of the spectrum is used to spot characteristic signals for functional groups (there are some below 1500 cm^{-1} but they are usually difficult to identify due to the high number of signals in that region of the spectrum).
- The table gives the wavenumber of some common bonds.
- It is also useful to remember that C-H bonds are all around 3000 cm^{-1}, but are C-H bonds on saturated C atoms are below 3000 cm^{-1} and those on unsaturated C atoms are above 3000 cm^{-1}
- However, there are some useful signals to look out for.

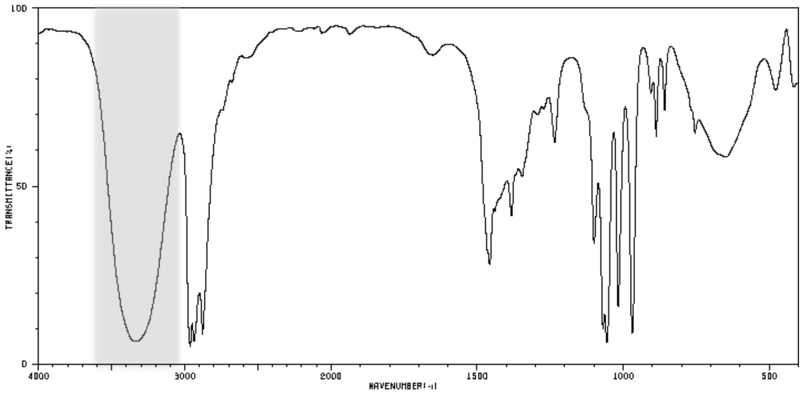
Bond	Wavenumber / cm^{-1}
N–H (amines)	3300 – 3500
O–H (alcohols)	3230 – 3550
C–H	2850 – 3300
O–H (acids)	2500 – 3000
C≡N	2220 – 2260
C=O	1680 – 1750
C=C	1620 – 1680
C–O	1000 – 1300
C–C	850 – 1100



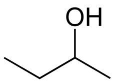
O–H alcohol	3230 – 3550 cm^{-1}	these are often very broad and obvious

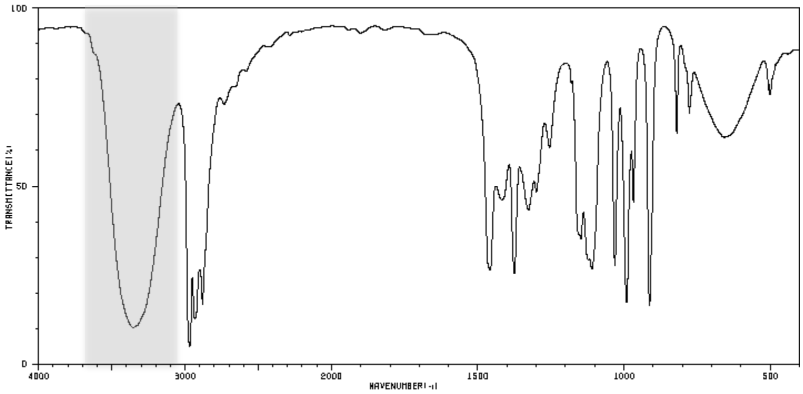
e.g. propan-1-ol





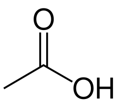
e.g. butan-2-ol

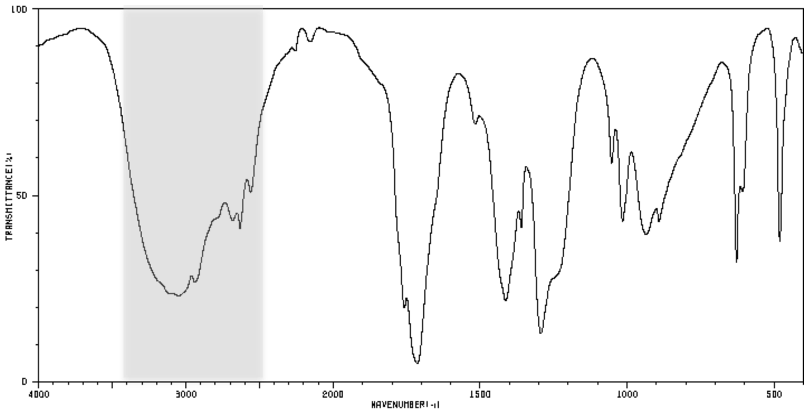




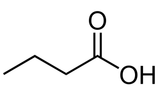
O–H acid	2500 – 3000 cm^{-1}	these are often very broad and obvious, but with C-H signals overlapping as well so making them "bumpy"

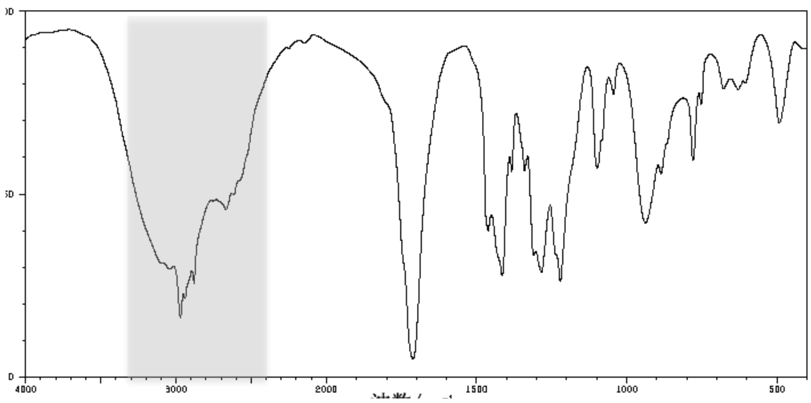
e.g. ethanoic acid





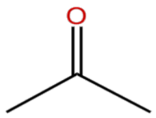
e.g. butanoic acid

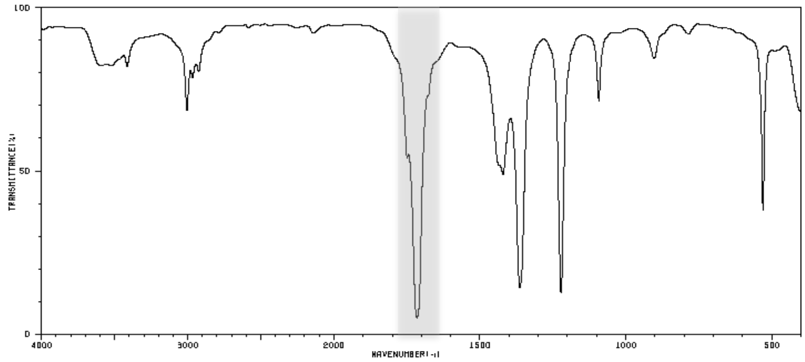




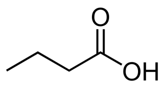
C=O	1680 – 1750 cm^{-1}	these are often narrow but very strong; they are found in aldehydes, ketones, acids, ester, amides, etc

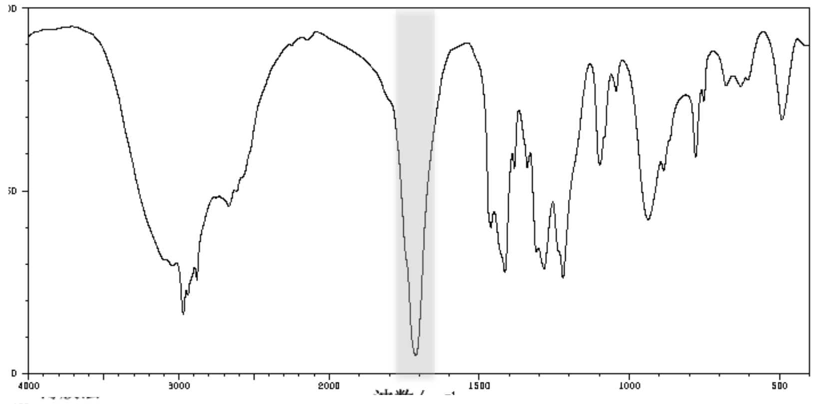
e.g. propanone



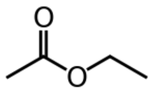


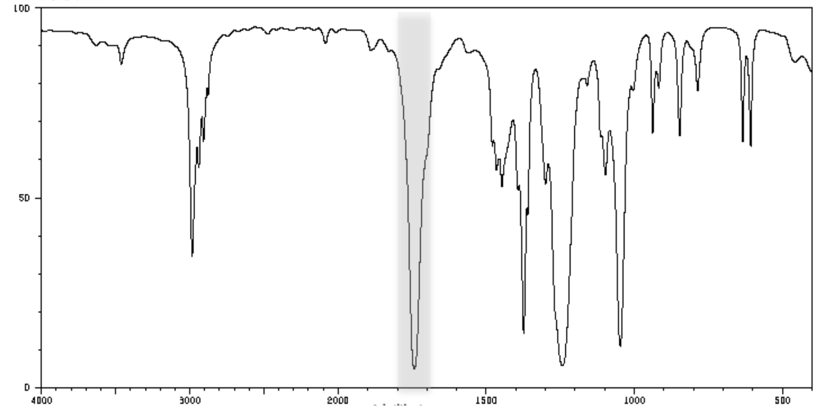
e.g. butanoic acid



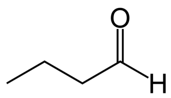


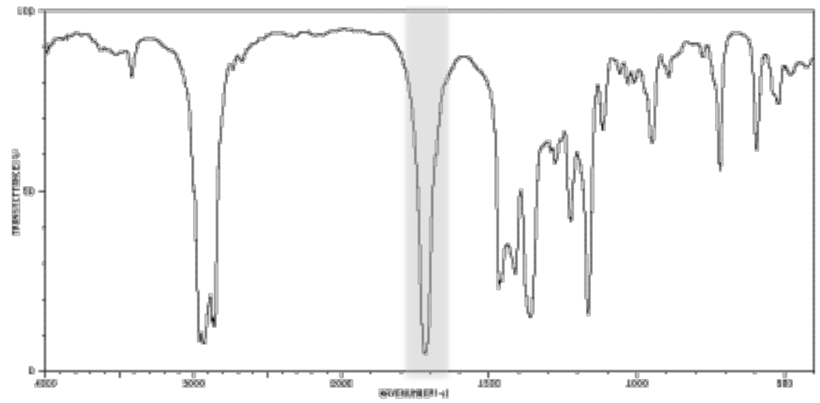
e.g. ethyl ethanoate





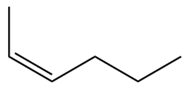
e.g. butanal

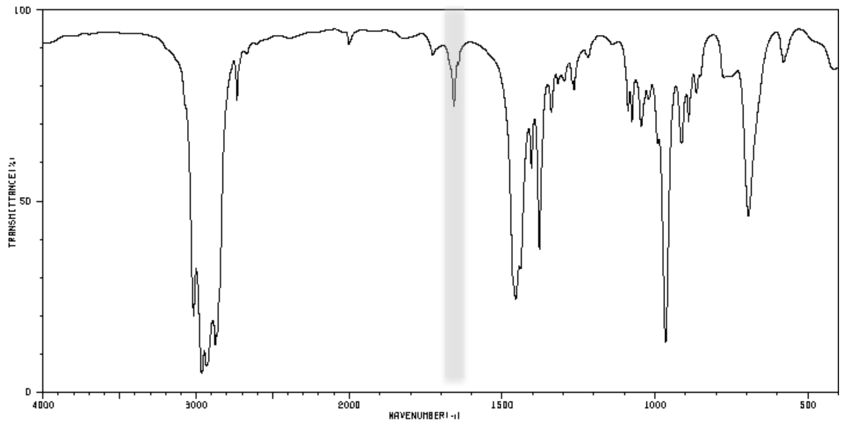




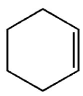
C=C	1620 – 1680 cm^{-1}	these are often narrow but relatively weak absorption

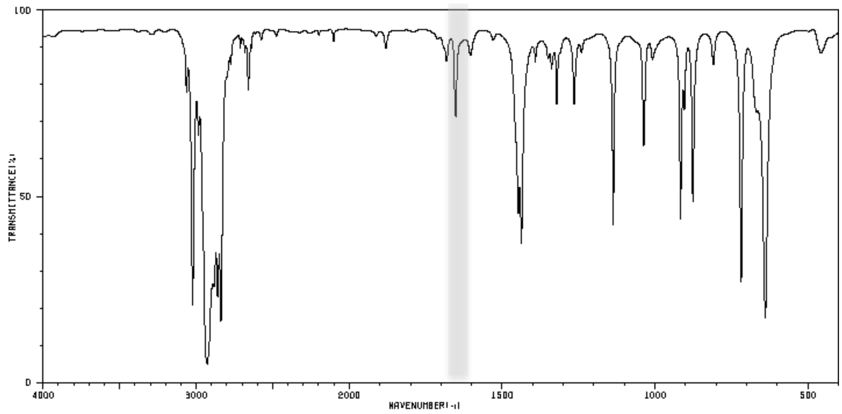
e.g. hex-2-ene





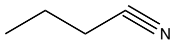
e.g. cyclohexene

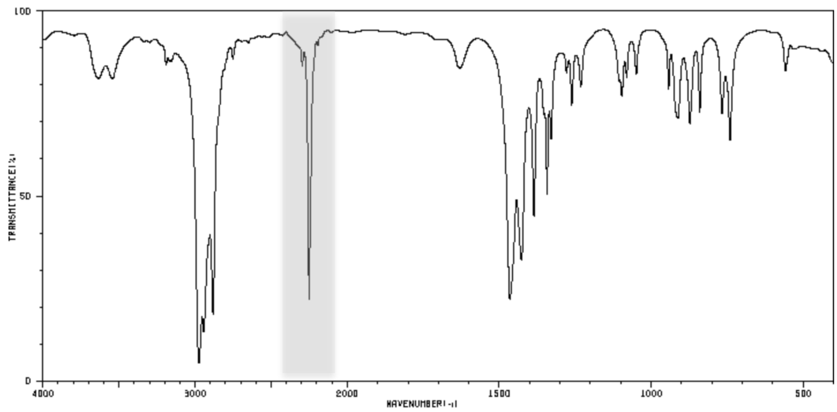




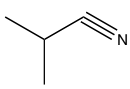
C≡N	2220– 2260 cm^{-1}	these are often narrow and strong

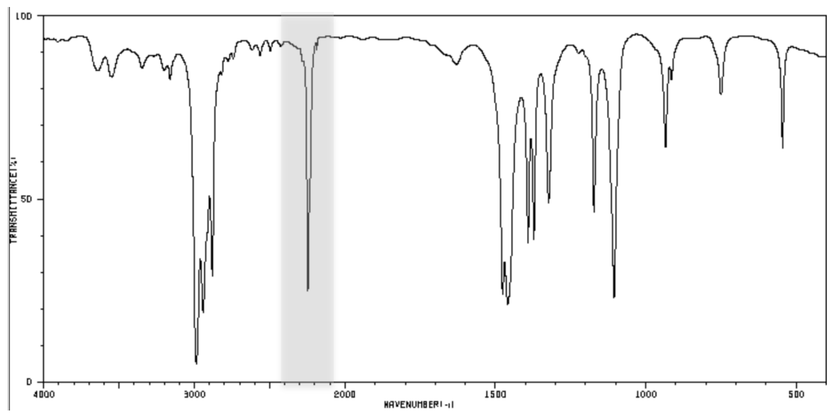
e.g. butanenitrile





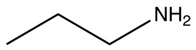
e.g. methylpropanenitrile

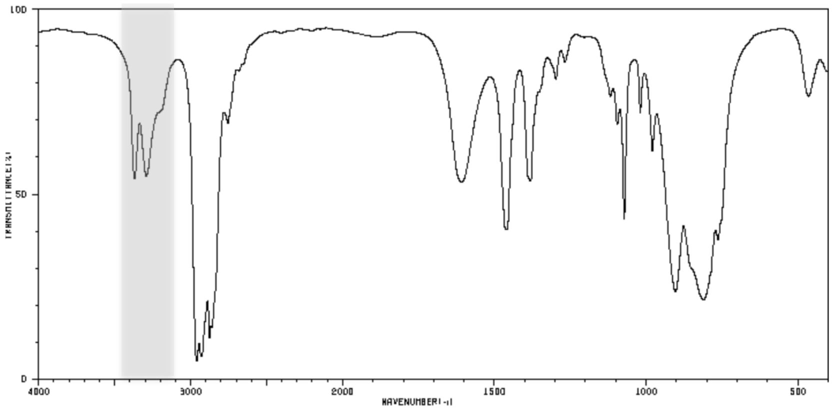




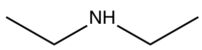
N–H (amines)	3300 – 3500 cm^{-1}	these are very obvious, large peaks; for primary amines (with NH_2 group) there are two peaks

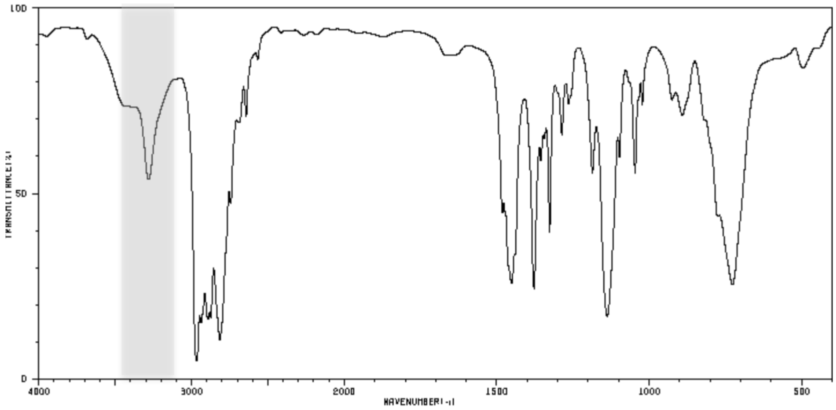
e.g. propylamine





e.g. diethylamine

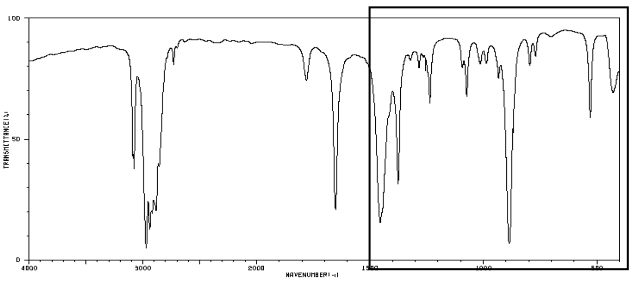


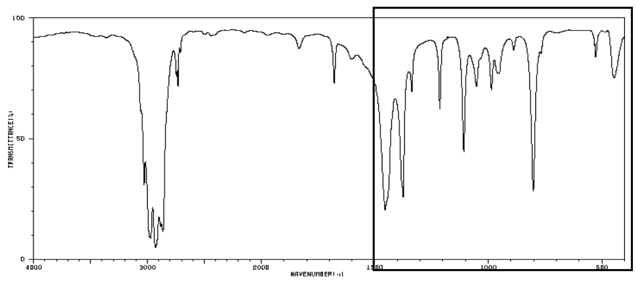


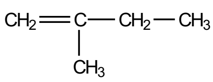
2) Using the “finger-print” region (below 1500 cm^{-1})

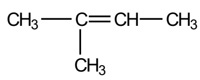
- This part of the spectrum is more complicated and contains many signals which means that we do not use it to identify functional groups.
- However, this part of the spectrum is unique for every compound, and so can be used as a "fingerprint". Comparison of the spectrum to that of known compounds can identify it.

e.g. these two IR spectra are for 2-methylbut-1-ene and 2-methylbut-2-ene – these are very similar compounds but the fingerprint region of their IR spectra are very different







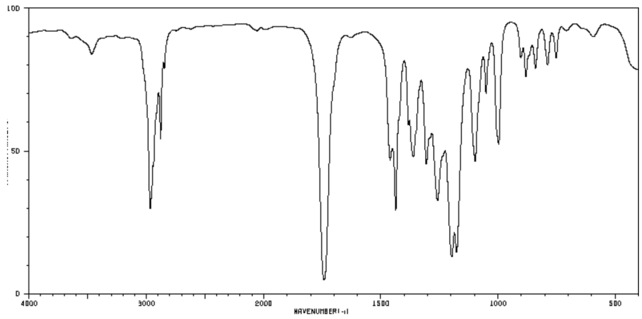


- This region can also be used to check if a compound is pure. If a comparison of the spectrum of a sample is made to the spectrum of the pure compound, they should be identical. If there are any extra peaks in the fingerprint region, they must be due to an impurity.

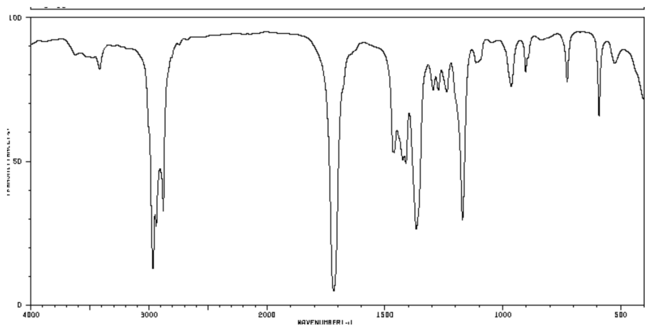
TASK 2 – IR Problems A

Which of these compounds contain a C=O bond?

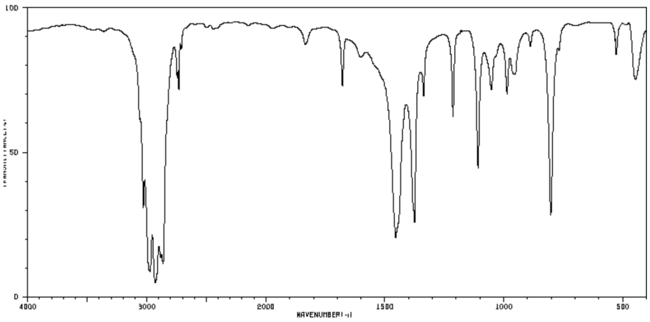
A1



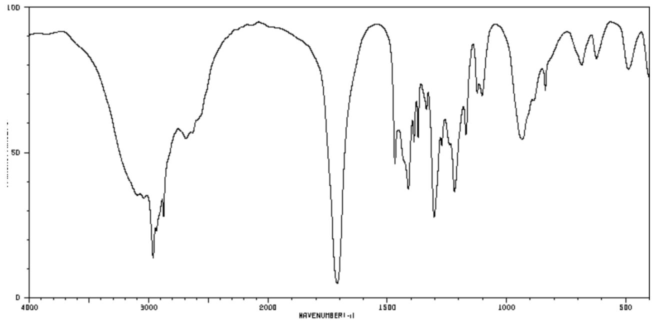
A2



A3

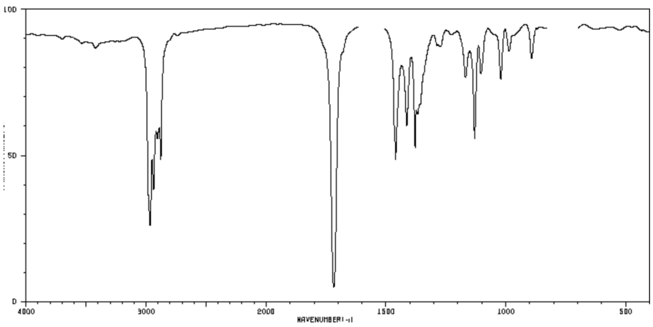


A4

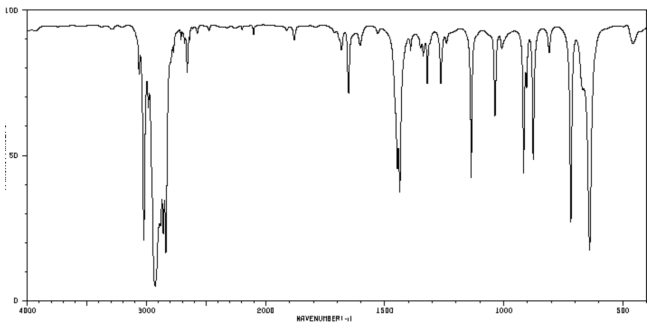


Which of these compounds contain a C=C bond?

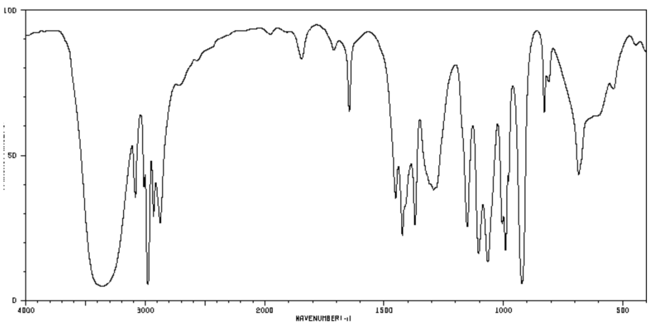
B1



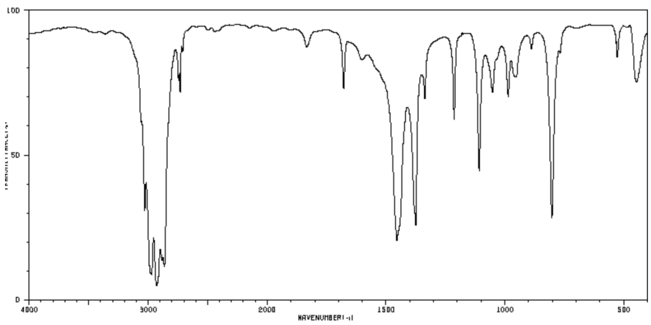
B2



B3

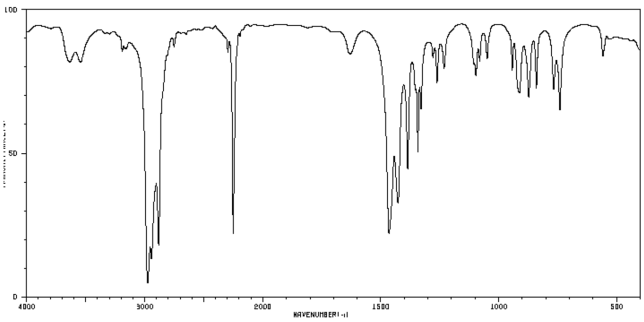


B4

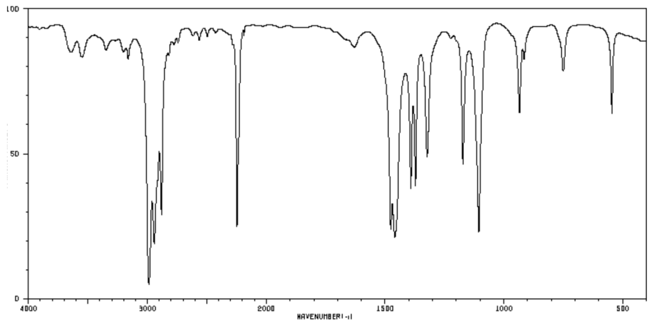


Which of these compounds contain a C≡N bond?

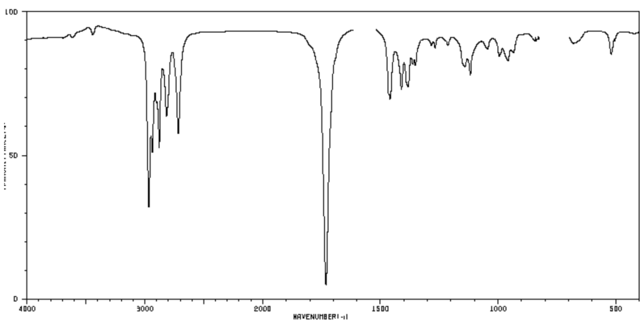
C1



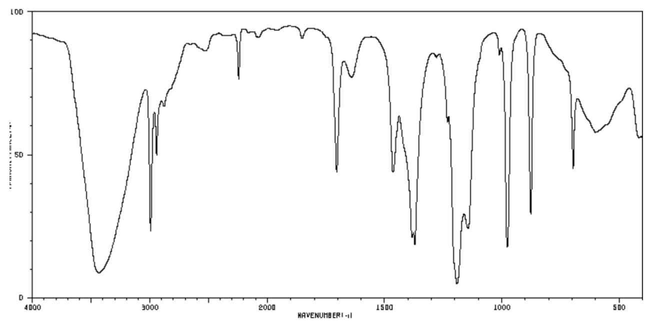
C2



C3

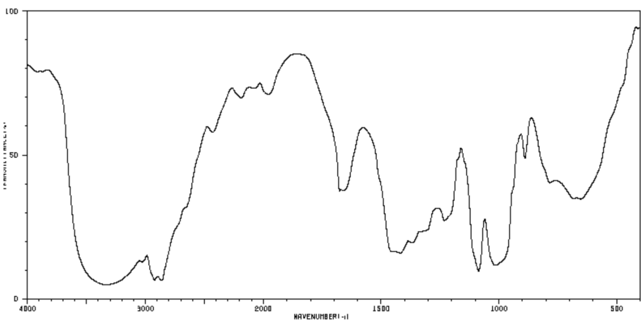


C4

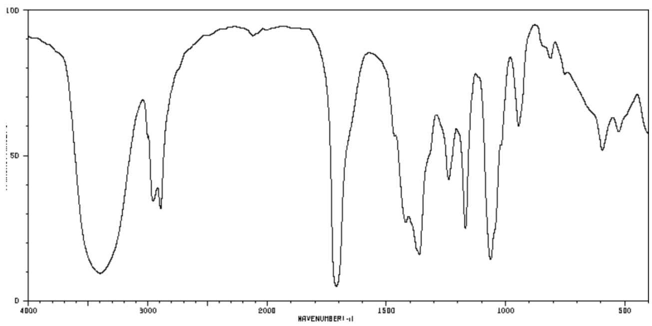


Which of these compounds contain an O–H (acid) bond?

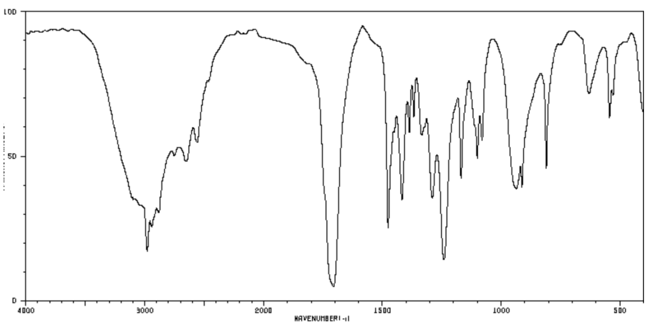
D1



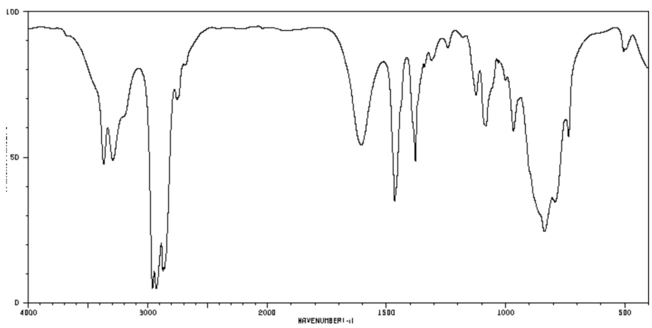
D2



D3

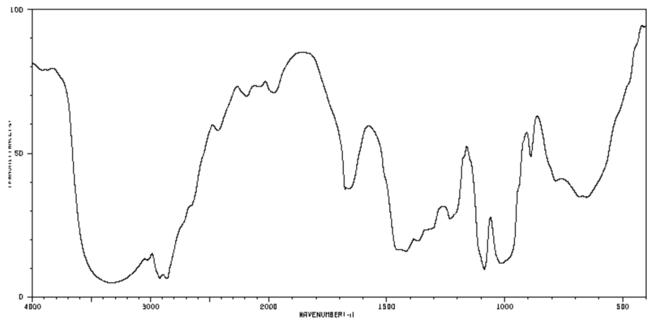


D4

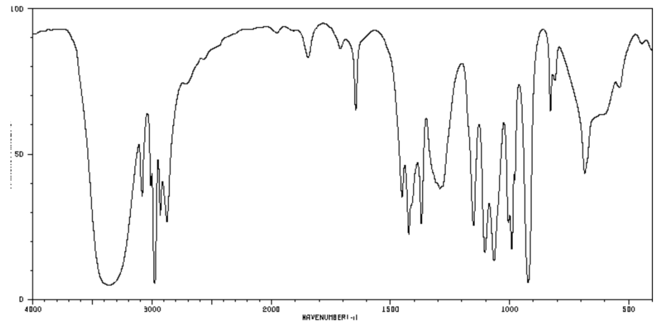


Which of these compounds contain an O–H (alcohol) bond?

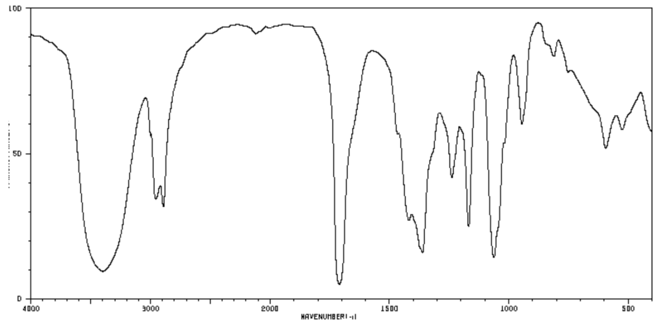
E1



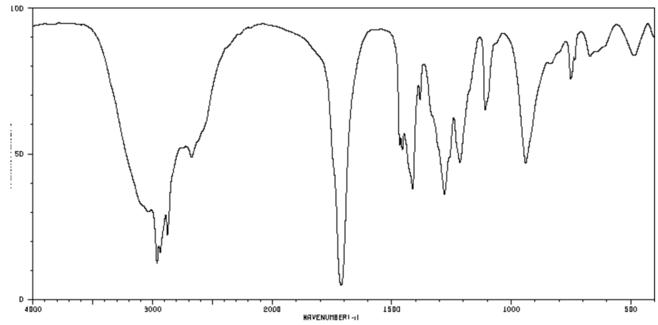
E2



E3

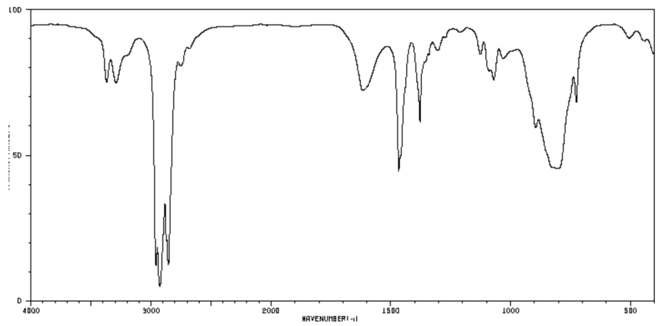


E4

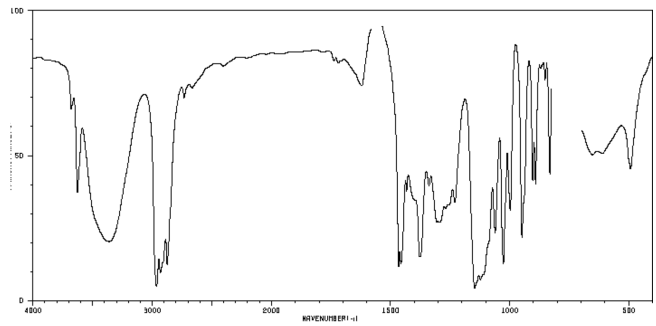


Which of these compounds contain an N–H (amine) bond?

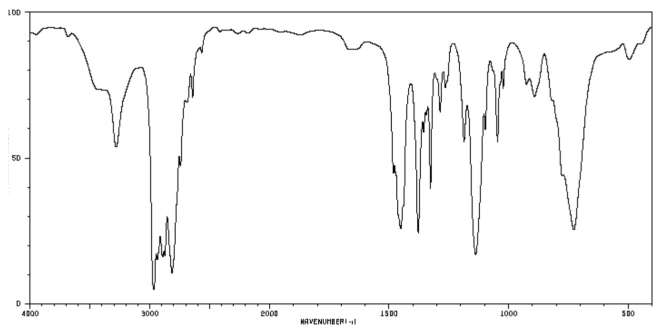
F1



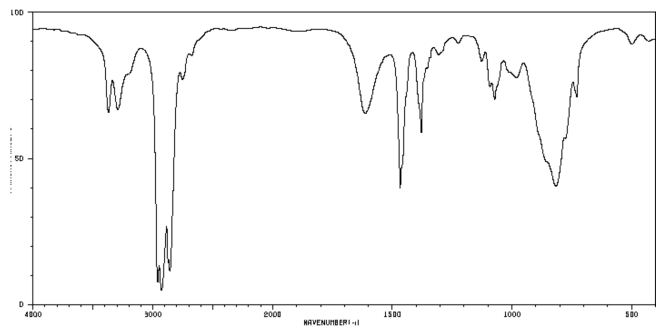
F2



F3

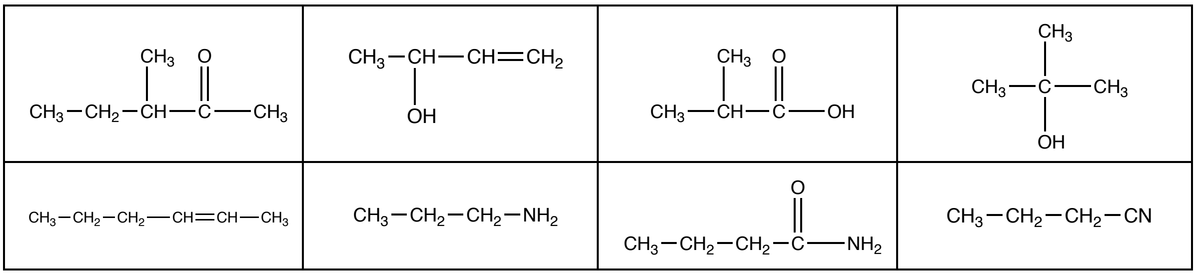


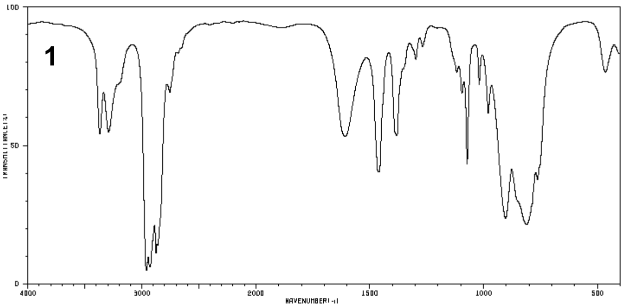
F4

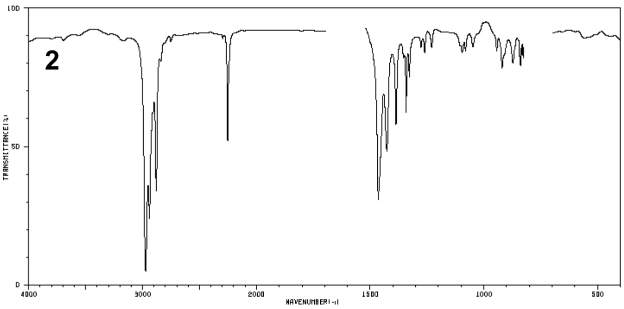


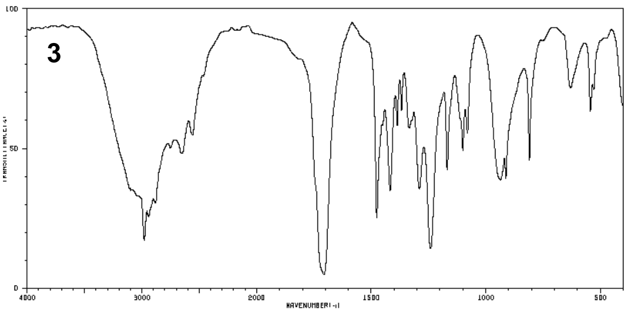
TASK 3 – IR Problems B

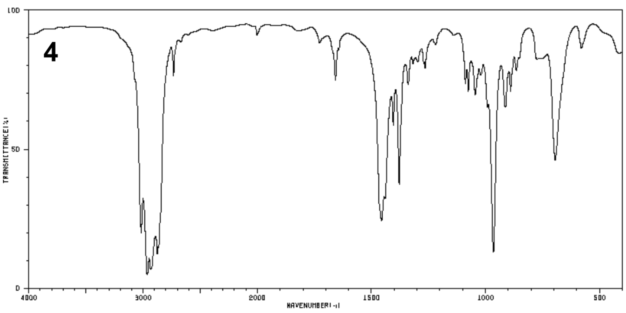
- The IR spectra of the following eight compounds are shown. Deduce which spectrum is for which compound.
- Write the number of the correct spectrum in the box.
- Mark the key bonds on the IR spectra.

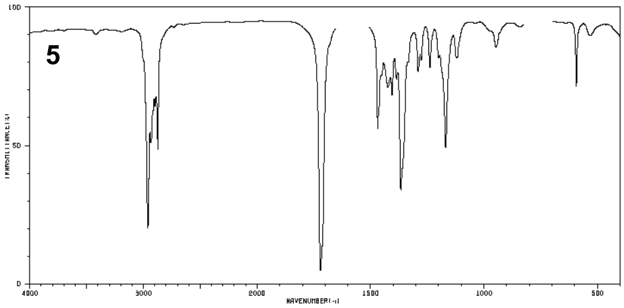


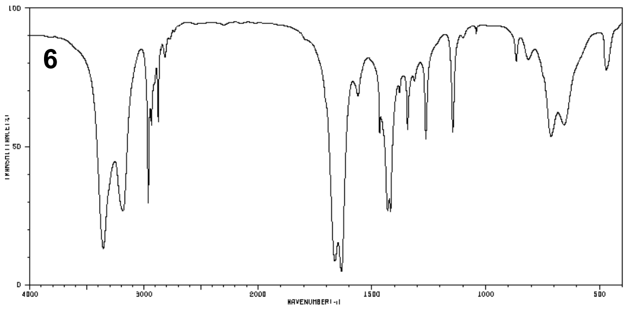


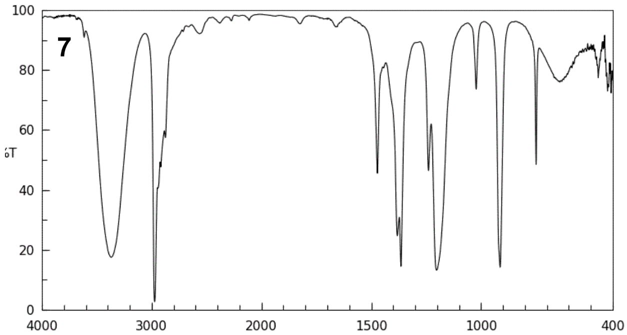


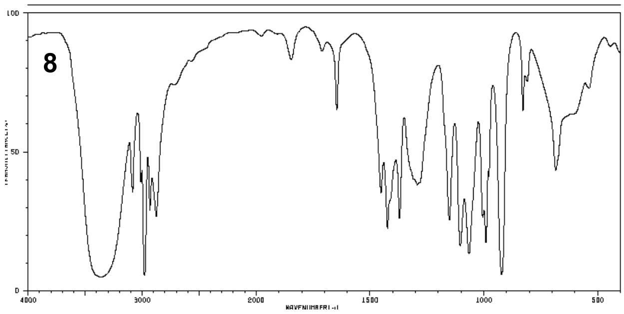








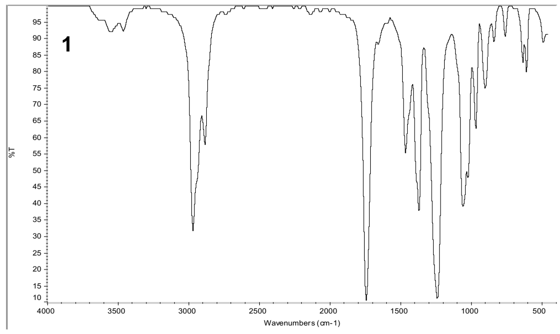


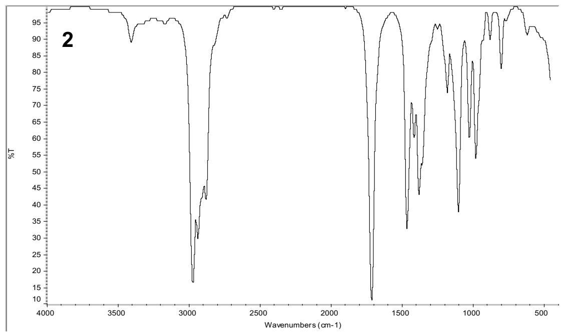


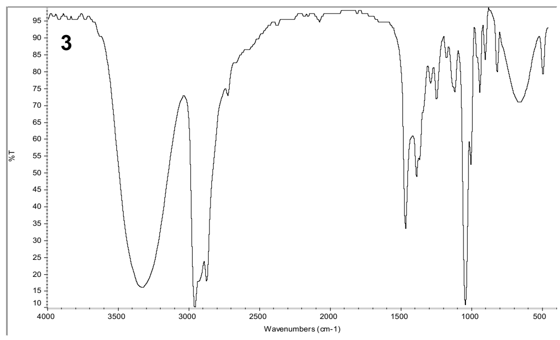
TASK 4 – IR Problems C

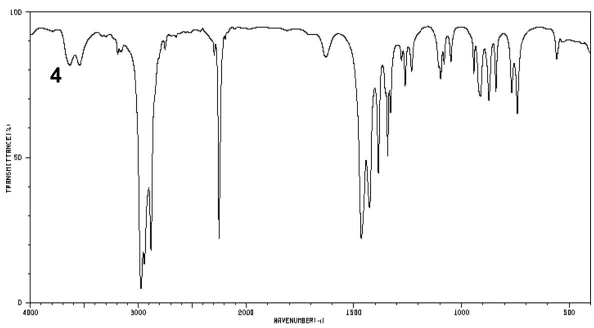
The infra-red spectra of the following eight compounds are shown. Draw the structure of each compound below in the box and then work out which spectrum is which (you may not be able to distinguish all of them). Write the spectrum number in the box.

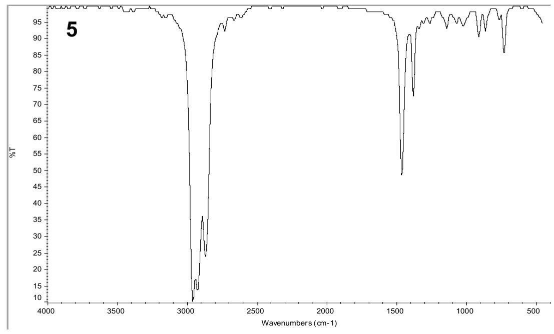
hex-2-ene	pentane	methylpropan-1-ol	2-methylpentan-3-one
butanal	butanoic acid	propyl ethanoate $CH_3-C(=O)-O-CH_2-CH_2-CH_3$	butanenitrile

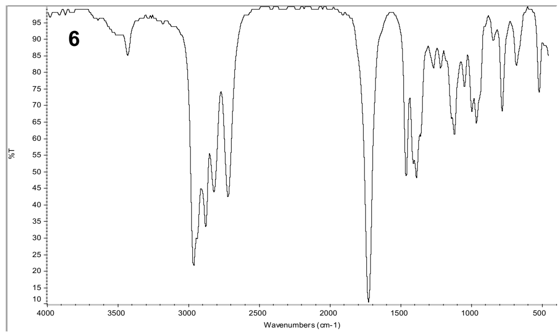


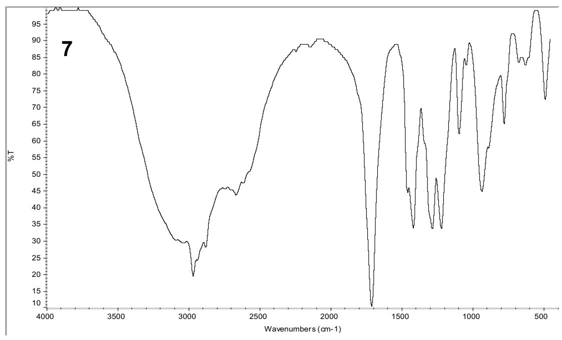


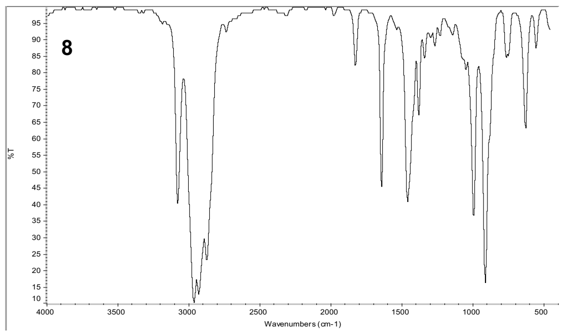








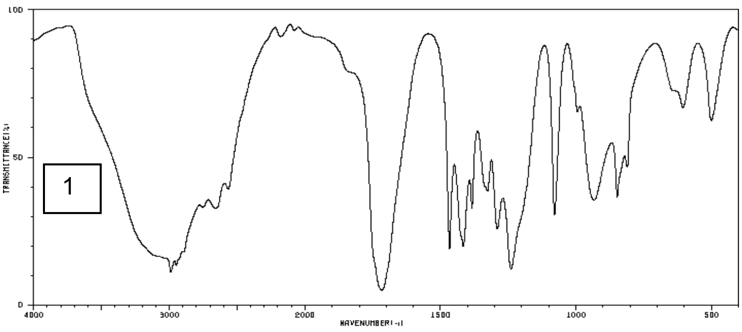




TASK 5 – IR Problems D

The IR spectra of five compounds are shown. Next to its IR spectrum, draw the structure of the compound and identify by wavenumber and bond the key signals that helped you identify that compound.

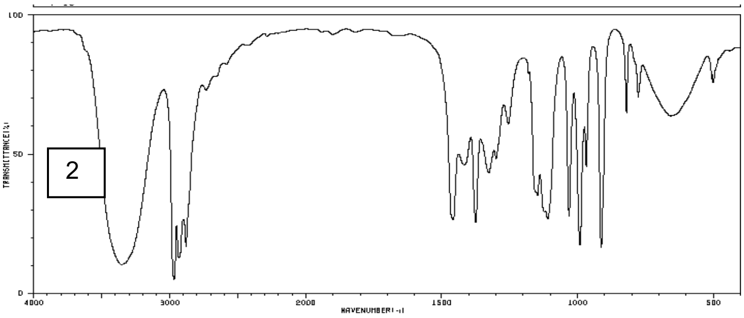
propanoic acid, butanone, 2-methylbut-2-ene, 1-hydroxypropanone, butan-2-ol



Compound ……………………………..……………

Bond & range (cm^{-1}) …………………………………

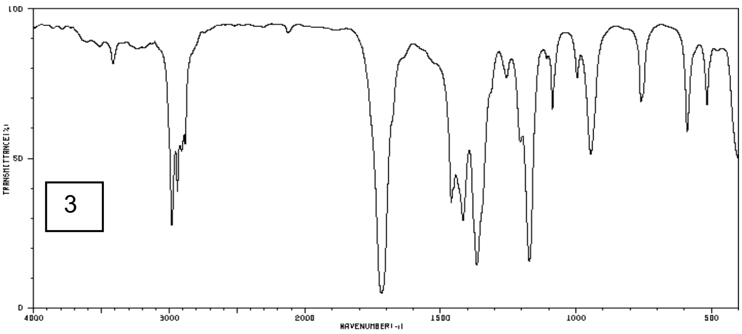
Bond & range (cm^{-1}) …………………………………



Compound ……………………………..……………

Bond & range (cm^{-1}) …………………………………

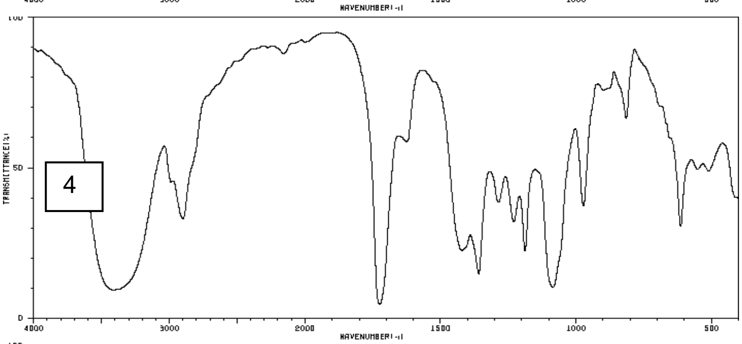
Bond & range (cm^{-1}) …………………………………



Compound ……………………………..……………

Bond & range (cm^{-1}) …………………………………

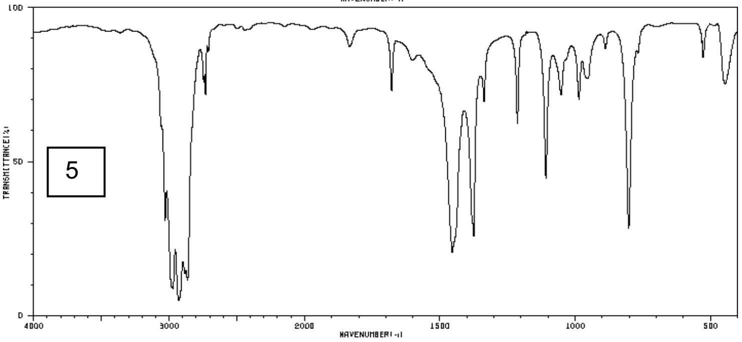
Bond & range (cm^{-1}) …………………………………



Compound ……………………………..……………

Bond & range (cm^{-1}) …………………………………

Bond & range (cm^{-1}) …………………………………



Compound ……………………………..……………

Bond & range (cm^{-1}) …………………………………

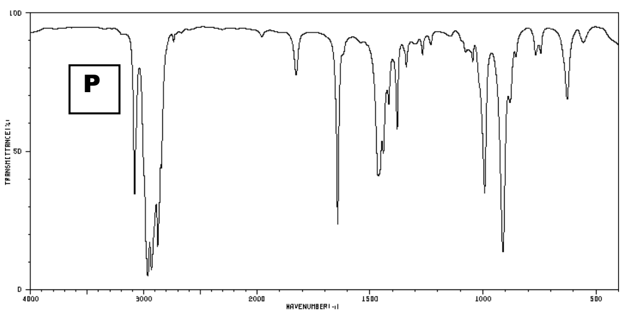
Bond & range (cm^{-1}) …………………………………

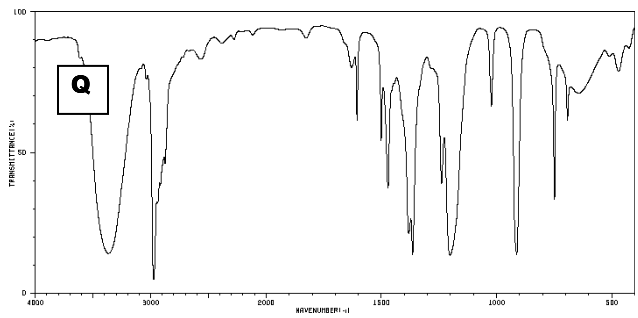
TASK 6 – IR Problems E

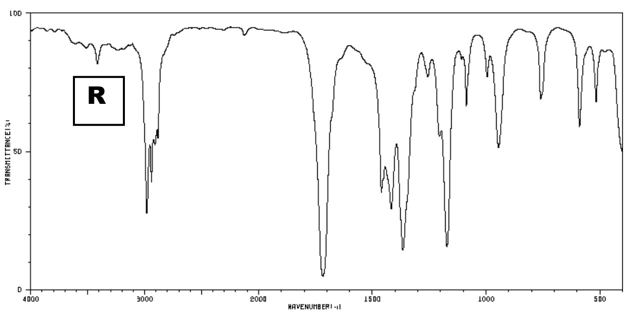
The IR spectra of six compounds are shown. Complete the table to match the spectra to the compounds. Identify any key signals you used to identify each compound. You may not be able to decide between two of the compounds.

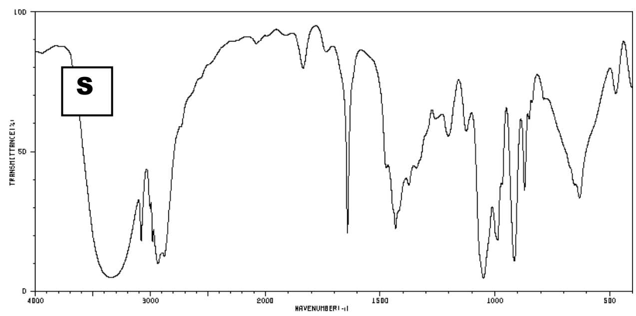
	butanoic acid	butanone	but-3-en-1-ol
Structure			
Spectrum			
Bond(s)			
Wavenumber range (cm^{-1})			

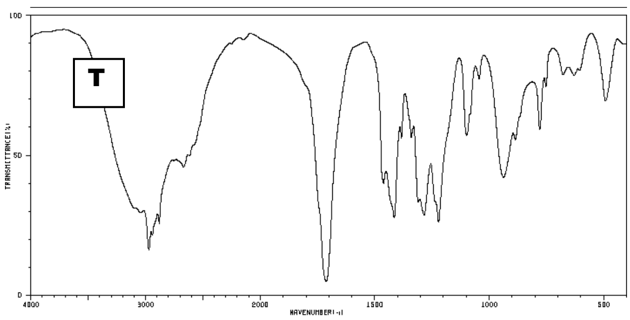
	2-methylpropan-2-ol	2-ethylbutan-1-ol	pent-1-ene
Structure			
Spectrum			
Bond(s)			
Wavenumber range (cm^{-1})			

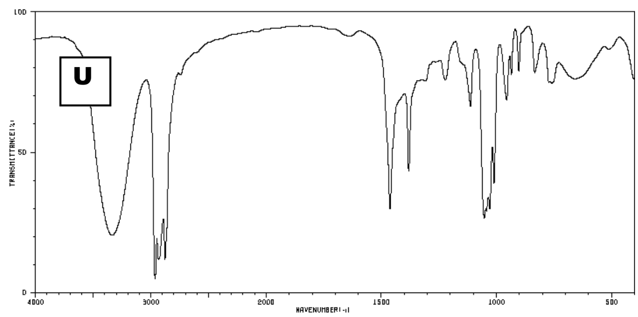






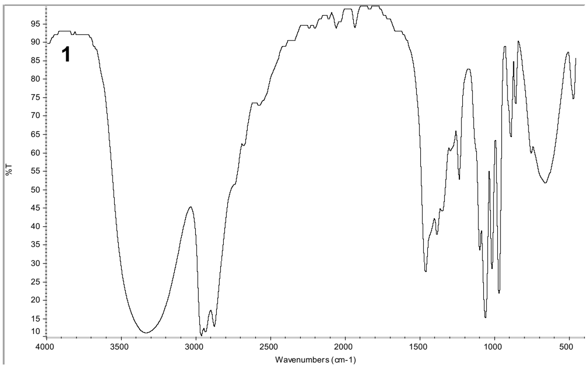


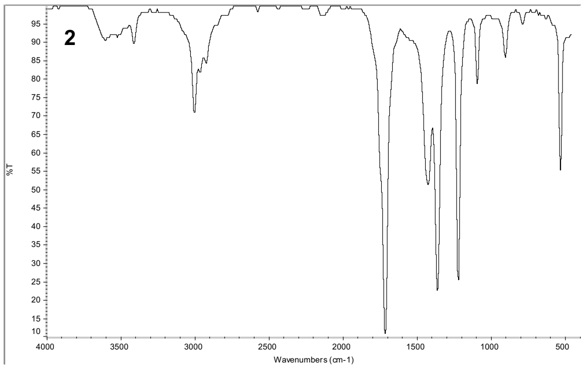


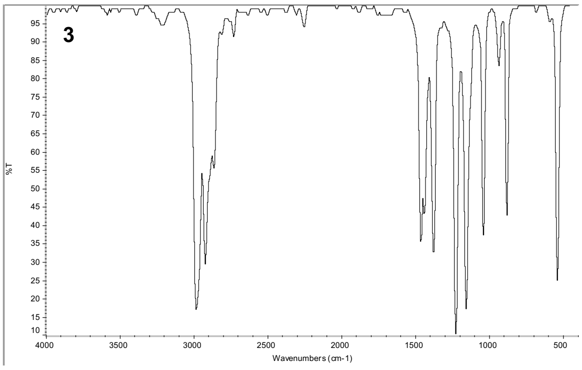


TASK 7 – IR Problems F

1) Propene reacts with HBr to form **H**. **H** reacts with sodium hydroxide to form **I**, and **I** reacts with warm acidified potassium dichromate (VI) to form **J**. The infra-red spectra of **H**, **I** and **J** are given below, but it does indicate which is which. Identify the three compounds **H**, **I** and **J**, using the infra-red spectra below, and decide which spectrum belongs to which compound.

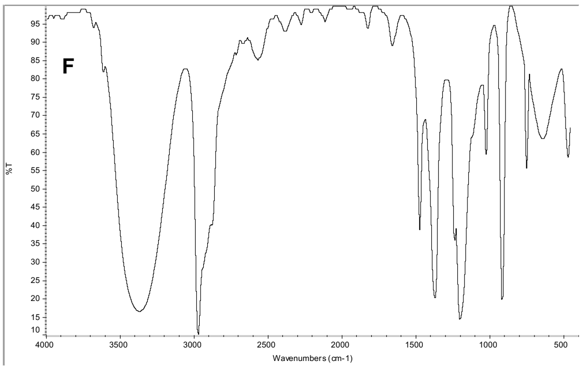


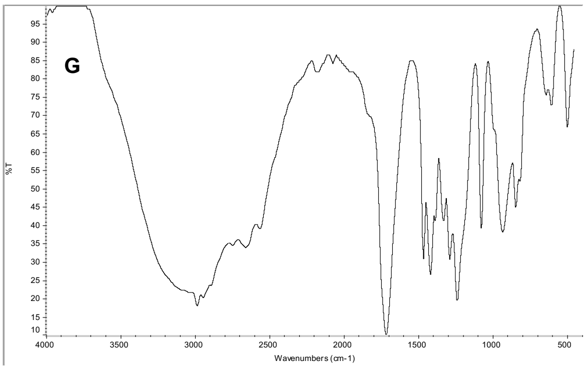




2) Compound **E**, which is a branched chain haloalkane, was found to have the composition by mass of 39.8% C, 7.3% H, and 52.9% Br. There were two peaks for the molecular ions in the spectrum at 150 and 152, of approximately equal intensity. **E** reacts with sodium hydroxide to form **F**, whose infra-red spectrum is shown. **F** does not undergo dehydration with concentrated sulphuric acid.

F reacts further with acidified potassium dichromate (VI) to form **G**, whose infra red spectrum is also shown. Draw the structures and name **E**, **F** and **G**. Identify the species responsible for the peaks at 150 and 152 in the mass spectrum of **E**.





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MASS SPECTROMETRY

- Mass spectrometry is used to find the relative molecular mass (M_r) of compounds.
- Compounds are converted into 1+ ions (often called the molecular ion)

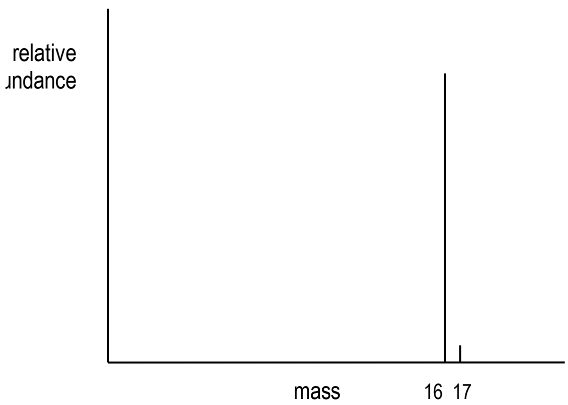
	Electron impact	Electrospray ionisation
What it does	removes one electron to form M^+ ion $M(g) \rightarrow M^+(g) + e^-$	Adds one proton to form MH^+ ion $M(g) + H^+(g) \rightarrow MH^+(g)$
Which compounds	Compounds with low M_r	Compound with high M_r (e.g. proteins)
How is it done	High energy electrons (from an "electron gun" are fired at the sample).	The compound is dissolved in a volatile solvent and sprayed out into a fine mist via a hypodermic needle whose tip is connected to the positive terminal of a high voltage power supply.

- Note that electron impact often breaks the molecular ion into smaller fragments. In this work we are ignoring (and not showing) any fragments.

The impact of ^{13}C and ^{2}H isotopes on signals for the molecular ion

- Spectra measure the mass of individual ions that hit the detector. Therefore whether an ion contains a ^{13}C rather than a ^{12}C atom, or ^{2}H instead of ^{1}H, affects the mass detected.
- The more C and H atoms there are in an organic molecule, the more chance of there being one ^{13}C (1.1% of C atoms) or one ^{2}H atom (0.015% of H atoms). There is often a small peak with a value that is 1 greater than that for the molecular ion.

e.g. CH_4



Isotopes of Cl and Br

- Chlorine contains 75% ^{35}Cl and 25% ^{37}Cl (and so ¾ of Cl atoms have mass 35 and ¼ of Cl atoms have mass 37)
- Bromine contains 50% ^{79}Br and 50% ^{81}Br (and so ½ of Br atoms have mass 79 and ½ of Br atoms have mass 81)
- Molecular ions in compounds containing chlorine or bromine are impacted significantly by these isotopes.

<table>
<tr><th>Compound</th><th>Molecule</th><th>Mass</th><th colspan="2">Probability</th><th>Mass spectrum peaks</th></tr>
<tr><td rowspan="2">CH_3Cl</td><td>$CH_3{}^{35}Cl$</td><td>50</td><td colspan="2">$\frac{3}{4}$</td><td rowspan="2">2 signals @ 50, 52 in ratio 3:1</td></tr>
<tr><td>$CH_3{}^{37}Cl$</td><td>52</td><td colspan="2">$\frac{3}{4}$</td></tr>
<tr><td rowspan="4">CH_2Cl_2</td><td>$CH_2{}^{35}Cl_2$</td><td>84</td><td colspan="2">$\frac{3}{4} x \frac{3}{4} = \frac{9}{16}$</td><td rowspan="4">3 signals @ 84, 86, 88 in ratio 9:6:1</td></tr>
<tr><td>$CH_2{}^{35}Cl{}^{37}Cl$</td><td>86</td><td>$\frac{3}{4} x \frac{1}{4} = \frac{3}{16}$</td><td rowspan="2">$\frac{6}{16}$</td></tr>
<tr><td>$CH_2{}^{37}Cl{}^{35}Cl$</td><td>86</td><td>$\frac{1}{4} x \frac{3}{4} = \frac{3}{16}$</td></tr>
<tr><td>$CH_2{}^{37}Cl_2$</td><td>88</td><td colspan="2">$\frac{1}{4} x \frac{1}{4} = \frac{1}{16}$</td></tr>
</table>

TASK 8 – Molecular ion peaks

- For the compounds shown, determine the mass of each molecular ion and their relative abundance.
- Assume that all C atoms are ^{12}C and all H atoms are ^{1}H
- Bromine atoms are 50% ^{79}Br and 50% ^{81}Br
- Chlorine atoms are 75% ^{35}Cl and 25% ^{37}Cl

1) CH_3Br

2) CH_2Br_2

3) CHBrCl

4) CCl_4

HIGH-RESOLUTION MASS SPECTROMETRY

- Most mass spectrometers record masses to the nearest 1 or 0.1, but high-resolution mass spectrometers record masses to a much higher resolution (e.g. 0.0001).
- The M_r given by a high-resolution mass spectrometer allows the **molecular formula** of a compound to be determined.

type of mass spectrometer	low-resolution	high-resolution
resolution of M_r	nearest unit (e.g. 60)	0.0001 or better (e.g. 60.0211)
what it tell us	M_r to nearest unit	M_r to to high resolution molecular formula

- High-resolution mass spectrometry does not identify a compound, but it does give the **molecular formula**.
- For example:
  - if a low-resolution mass spectrometer gives M_r = 60, then there are many compounds it could be with several different molecular formulas (e.g. propan-1-ol, propan-2-ol, methoxyethane, ethanoic acid, methyl methanoate, urea)
  - if a high-resolution mass spectrometer gives M_r = 60.0211 then it indicates that the molecular formula mass be $C_2H_4O_2$ narrowing down what the compound could be (ethanoic acid or methyl methanoate)

Low resolution M_r	High resolution M_r	Molecular formula	Possible compounds	
60	60.0211	$C_2H_4O_2$	CH_3COOH $HCOOCH_3$	ethanoic acid methyl methanoate
60	60.0575	C_3H_8O	$CH_3CH_2CH_2OH$ $CH_3CH(OH)CH_3$ $CH_3OCH_2CH_3$	propan-1-ol propan-1-ol methoxethane
60	60.0324	CH_4N_2O	H_2NCONH_2	urea

TASK 9 – High-resolution mass spectrometry problems

In this task, assume that the H, C, N and O atoms are ^{1}H, ^{12}C, ^{14}N and ^{16}O

Accurate masses of atoms:

^{1}H	^{12}C	^{14}N	^{16}O	^{35}Cl	^{37}Cl
1.0078	12.0000	14.0031	15.9949	34.9689	36.9659

1) How could high-resolution mass spectroscopy be used to distinguish propane and ethenol?

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2) A compound is found to have an accurate relative formula mass of 46.0417. It is thought to be either CH_3CH_2OH or $H_2NCH_2NH_2$. Calculate the M_r of each compound to 4 decimal places to work out which one it is.

CH_3CH_2OH ………..

$H_2NCH_2NH_2$ ………..

Molecular formula of compound = …………………………………...

3) High-resolution mass spectroscopy showed the M_r of difluoromethane to be 52.0124. The only stable isotope of fluorine is ^{19}F. Calculate the mass of one atom of ^{19}F to 4 decimal places.

…….

…….

…….

4) Calculate the accurate mass to 4 decimal places of the two molecular ion peaks in the high-resolution mass spectrum of chloroethane.

peak 1 ……..…….

peak 2 ……..…….

5) Analysis of an organic compound showed that its relative formula mass is 102. High resolution mass spectroscopy showed it to be 102.0678.

a) Calculate the M_r to 4 decimal places of each of these molecular formulas (which have M_r = 102) and then determine the correct molecular formula.

$C_5H_{14}N_2$ ……..

$C_5H_{10}O_2$ ……..

$C_3H_6N_2O_2$ ……..

Molecular formula = ……………………………………………….

b) Draw and name two possible compounds that have M_r = 102.0678

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