Using spectroscopy to determine purity

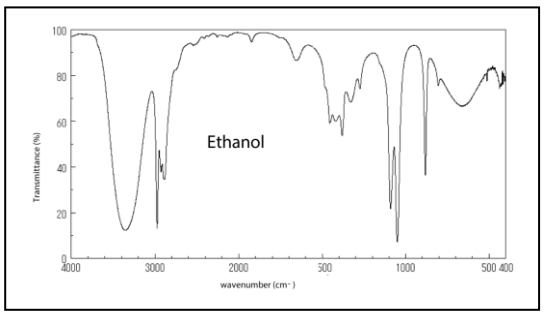
Worksheet – Use of spectroscopy in qualitative and quantitative analysis.

Steps for verifying purity using IR spectroscopy:

1. **Obtain the reference spectrum:**
    - Obtain the IR spectrum of the pure substance from the literature.
2. **Identify characteristic troughs:**
    - Note the specific absorption troughs and their corresponding wavenumbers in the reference spectrum that are characteristic of the pure substance.
3. **Analyze the sample's IR spectrum:**
    - Obtain the IR spectrum of the sample in question.
4. **Compare Spectra:**
    - Compare the sample's IR spectrum with the reference spectrum.
    - Check if all the characteristic troughs of the pure substance are present in the sample's spectrum at the same wavenumbers.
5. **Look for additional troughs:**
    - Identify any additional troughs in the sample's IR spectrum that are not present in the reference spectrum, use the 2024-2027 data booklet.
    - Unexpected troughs may indicate the presence of impurities.
6. **Interpret the troughs:**
    - Analyze the unexpected troughs to identify possible impurities by comparing them with known IR spectra of other compounds.
7. **Draw Conclusions:**
    - Determine if the sample's spectrum matches the reference spectrum, indicating purity.
    - If there are additional troughs, assess their intensity and nature to estimate the extent and type of impurities.

Example 1.

Analyse the purity of a sample of ethanol.



1. **Obtain the reference spectrum:**

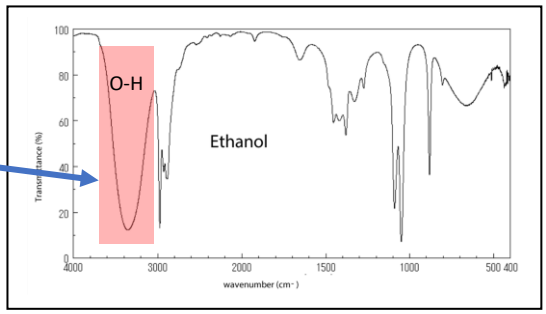
2. **Identify characteristic troughs:**

   Note the specific absorption troughs and their corresponding wavenumbers in the reference spectrum that are characteristic of the pure substance. Use the 2024-2027 data booklet.

Characteristic ranges for infrared absorption

Bond	Wave number (cm^{-1})	Bond	Wave number (cm^{-1})
C=O (amides)	1630–1680	C–H (alkanes, alkenes, arenes)	2850–3090
C=O (aldehydes)	1660–1745	O–H (acids)	2500–3500
C=O (acids)	1680–1740	O–H (alcohols)	3200–3600
C=O (ketones)	1680–1850	N–H (amines and amides)	3300–3500
C=O (esters)	1720–1840		

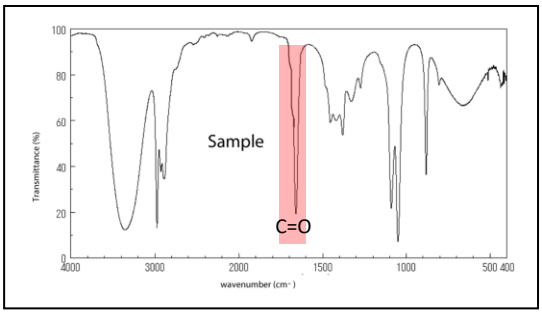
IR from the 2024-2027 data booklet



   O-H bond at 3200-3600

3. **Analyze the sample's IR spectrum:**

   Obtain the IR spectrum of the sample in question.



4. **Compare spectra:**

   All the characteristic signals of ethanol are present in the sample IR.

5. **Look for additional troughs and interpret the signals:**

   An unexpected trough at 1660 indicates the presence of an aldehyde C=O according to the data booklet.

6. **Draw conclusions:**

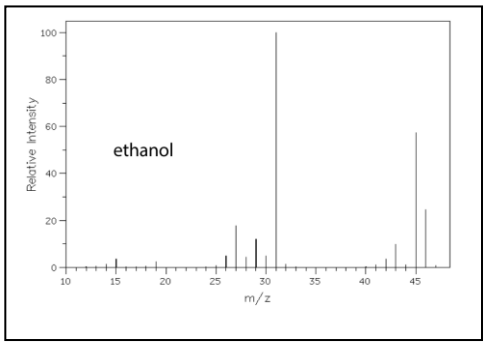
   Using the information provided and the references from the data booklet it is likely that the sample of ethanol is contaminated with an aldehyde.

Steps for verifying purity using mass spectroscopy:

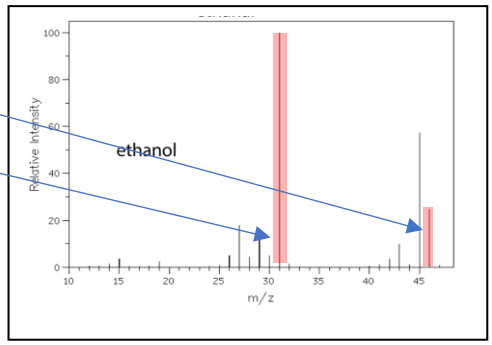
1. **Obtain the reference mass spectrum:**
    - Find and study the mass spectrum of the pure substance from the literature.
2. **Identify key peaks:**
    - Note the key peaks m/z values) and their relative abundances in the reference spectrum that are characteristic of the pure substance.
3. **Analyse the sample's mass spectrum:**
    - Obtain the mass spectrum of the sample in question.
4. **Compare Spectra:**
    - Compare the sample's mass spectrum with the reference spectrum.
    - Check if all the key peaks of the pure substance are present in the sample's spectrum at the same m/z values.
5. **Look for Additional peaks:**
    - Identify any additional peaks in the sample's mass spectrum that are not present in the reference spectrum.
    - Unexpected peaks may indicate the presence of impurities.
6. **Interpret the peaks:**
    - Analyse the unexpected peaks to identify possible impurities by comparing them with known mass spectra of other compounds.
    - Look for fragment ions and their patterns to gain more information about possible impurities.

Example 2 – Ethanol was produced via a chemical pathway where the feedstock was ethene. The final product was analysed for impurities and extent of reaction using mass spectroscopy. Analyse the purity of a sample of the ethanol, whose MS is given to you, and comment on whether this pathway yields 100% ethanol. The MS of pure ethanol is also given provided.

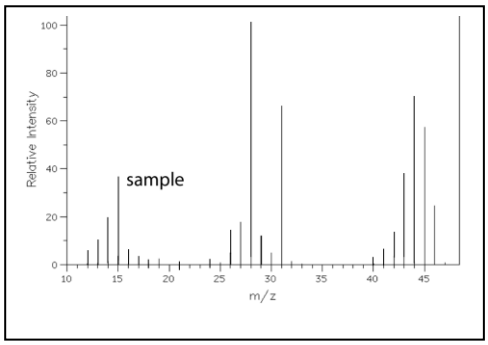
1. **Obtain the reference mass spectrum:**



2. **Identify key peaks:**
   - m/z 46 molecular ion $[CH_3CH_2OH]^+$
   - base peak at m/z 31 $[CH_3OH]^+$



3. **Analyse the sample's mass spectrum:**
   - peaks at m/z 46 and 31 are still there indicating ethanol is present.
   - new peaks at m/z 44
   - peak at m/z 15 possibly a $[CH_3]^+$, has increased in size indicating the presence of a CH_3 in the impurity.
   - peak at m/z 28 is now the base peak indicating the presence of a stable fragment in the impurity, such as $[CH_3CH]^+$
   - m/z 44 now shows a strong signal most likely the parent ion of the impurity such as $[CH_3CHO]^+$



4. Possible impurity might be ethanal (CH_3CHO)
   Obviously ethanal is the precursor to the formation of ethanol and makes sense that we have identified an unused amount of ethanal still in the final product mix.
   The reaction does not produce a 100% yield.

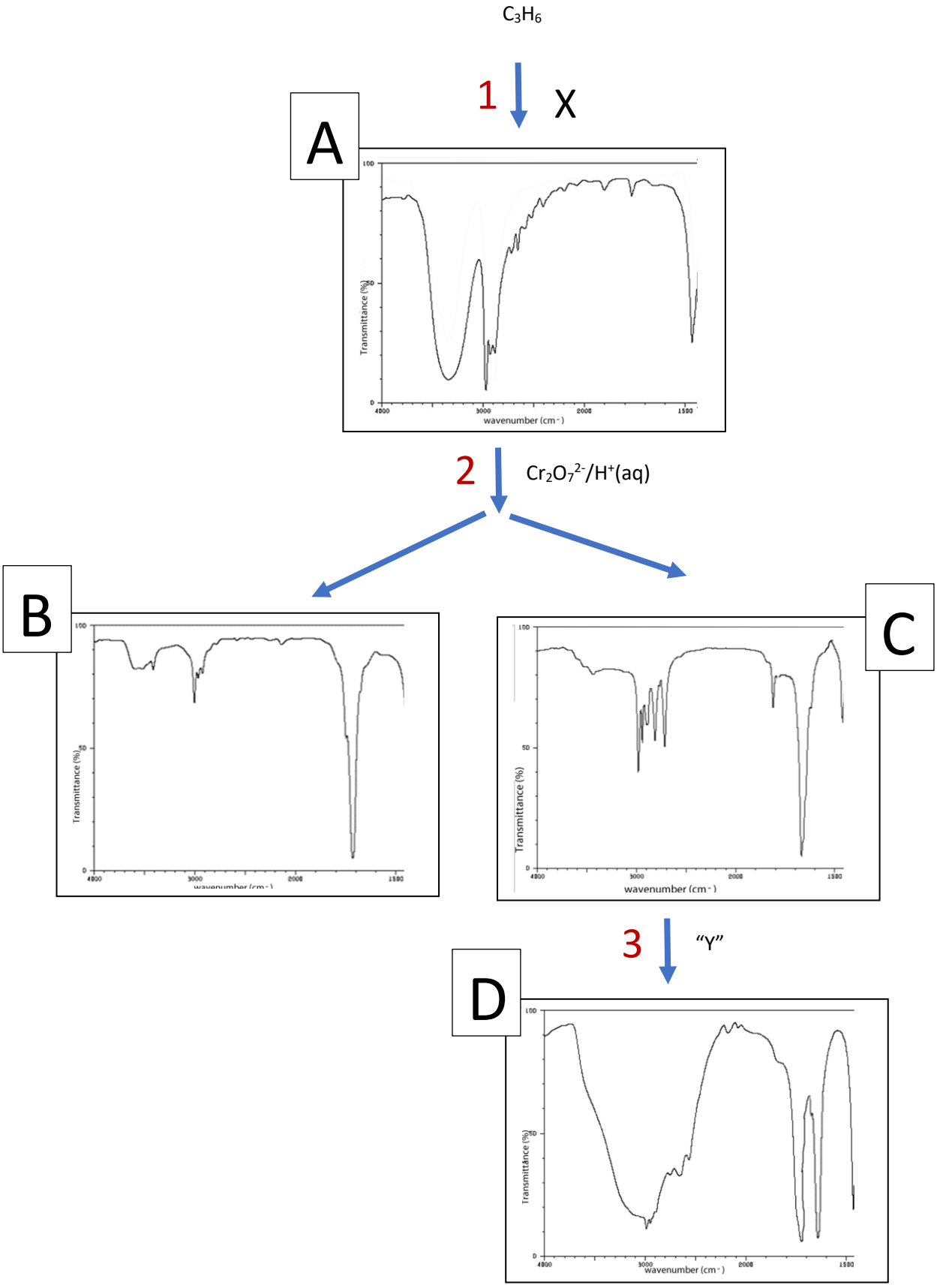


Figure 1 – Reaction pathway of propene.

1. Consider the reaction pathway shown in figure 1. The IR spectra of the different products formed are shown for wave numbers between 1500 cm^- to 4000 cm^-. Samples of each substance A, B, C and D were analysed after each step with IR spectroscopy. Substances A, B, C and D can be mixtures or pure substances.

   a. What are the reagents and conditions represented by "X"?
   _____*$H_2O(g)$ $H_3PO_4(s)$ catalyst at 300^oC*. _____
   _____

   b. Consider substance "A".
      i. To what class of compounds does "A'" belong to?
      ____*Alcohols*____

      ii. Justify your answer with reference to the IR spectrum to question i. above..
      A broad absorption between wave numbers 3200 and 3600 cm^- indicates an alcohol O-H.
      _____

      iii. Is "A" a pure substance? ____*NO*_____
      iv. Justify your answer to question iii. above, with reference to the reaction pathway shown.
      It is a mixture of a primary and secondary alcohols. Oxidation of mixture A yields a ketone and an aldehyde. IR evidence that "B" is ketone is in the absorption between 1680 – 1850 cm^-. This is obtained from the data booklet. C is most likely an aldehyde as it absorbs strongly between 1660 – 1745 cm^-, once again derived from data booklet. We can also accept that C is an aldehyde because it oxidized into an organic acid the IR spectrum of D indicates with a strong absorption between 2500 – 3500cm^-indicating an acidic O-H bond.
      _____
      _____

   c. What are the reagents and conditions represented by "Y"?
   ____*any oxidant in an acidic solution such as $Cr_2O_7^{2-}$ and MnO_4^-*_____
   _____

   d. Name (IUPAC) the compound formed during reaction "3".
   _____*propanoic acid*_____

   e. Consider substance "D".

      i. Is substance "D" a pure substance or a mixture? _____*mixture*_____

      ii. Justify your answer to question i. above with reference to the IR spectrum of substance "D".
      A strong absorption at 1660 – 1745 cm^- (from data booklet) indicates the presence of an aldehyde indicating incomplete oxidation has taken place causing the presence of the aldehyde in the acid sample as an impurity.

2. Propan-1-ol is synthesized via an addition reaction using propene as a feedstock water at 300°C in the presence of an acid catalyst. A sample of the final product was taken and analysed for purity. The MS of pure propan-1-ol is shown in fig. 2. Figure 3 shows the MS of a product sample.

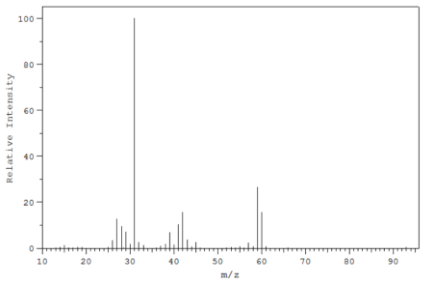


Figure 2 -MS of pure propan-1-ol

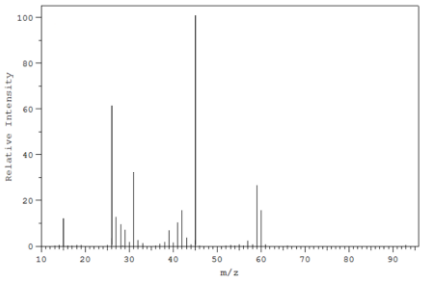


Figure 3 – MS of sample

Analyse the spectra provided and build a case for the purity of the product and a likely contaminant. Provide direct evidence from the spectra for your conclusions.

1-Propanol or propan-1-ol

1-Propanol ($CH_3CH_2CH_2OH$) typically shows the following key features in its mass spectrum:

- ***Molecular Ion Peak (M^+)**: The molecular ion peak will appear at m/z 60.*
- ***Base Peak (m/z 31)**: This is a major fragment peak corresponding to the CH_2OH^+ fragment.*
  Fragmentation: $CH_3CH_2CH_2OH + e \rightarrow CH_2OH^+ + CH_3CH_2\cdot + 2e$
- ***Peak at m/z 43**: represents the $[CH_3CH_2CH_2]^+$*

2-Propanol or propan-2-ol

2-Propanol ($CH_3CHOHCH_3$) shows different fragmentation patterns in its mass spectrum:

- ***Molecular Ion Peak (M^+)**: The molecular ion peak will also appear at m/z 60.*
- ***Base Peak (m/z 45)**: This is a major fragment peak corresponding to the $[CH_3CHOH]^+$.*
  Fragmentation: $CH_3CHOHCH_3 + e \rightarrow CH_3CHOH^+ + CH3\cdot$
- ***Peak at m/z 43**: Similar to 1-propanol, but this represents the $[CH_3CHCH_3]^+$ fragment*

Key Differences

- ***Base Peak**: The base peak for 1-propanol is at m/z 31, while for 2-propanol, it is at m/z 45.*
- ***Peak at m/z 31**: This peak is prominent in 1-propanol but much less significant or absent in 2-propanol.*
- ***Peak at m/z 45**: This peak is prominent in 2-propanol but much less significant or absent in 1-propanol.*

Hence we can conclude that the sample contains a mixture of primary (propan-1-ol) and secondary(propan-2-ol) alcohols.

3. You are provided with the IR spectrum of an unknown ethanol solution in fig 4. The absorbance (measured as trough height) of the O-H stretch band around 3400 cm^{-1} for the ethanol sample is 0.75 cm. A calibration curve is to be created using solutions of ethanol, and the following transmittance (trough heights) data was obtained, table 1, for the O-H stretch

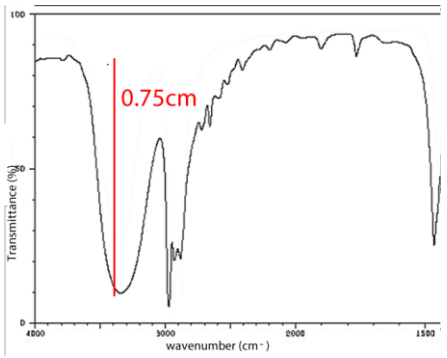


Figure 4 – IR transmittance of ethanol

Concentration (mg/L)	Trough height at (3400 cm^{-1}) in cm
10	0.2
20	0.4
30	0.6
40	0.8
50	1.0

Table 1 – concentration vs trough height

a. Using the data in table 1 plot a calibration curve on the graph paper provided on the next page and draw the line of best-fit.

b. Using the calibration curve, give the concentration of ethanol in the sample in:

i. mg/L = *37.5 mg/L*

ii. mol/L

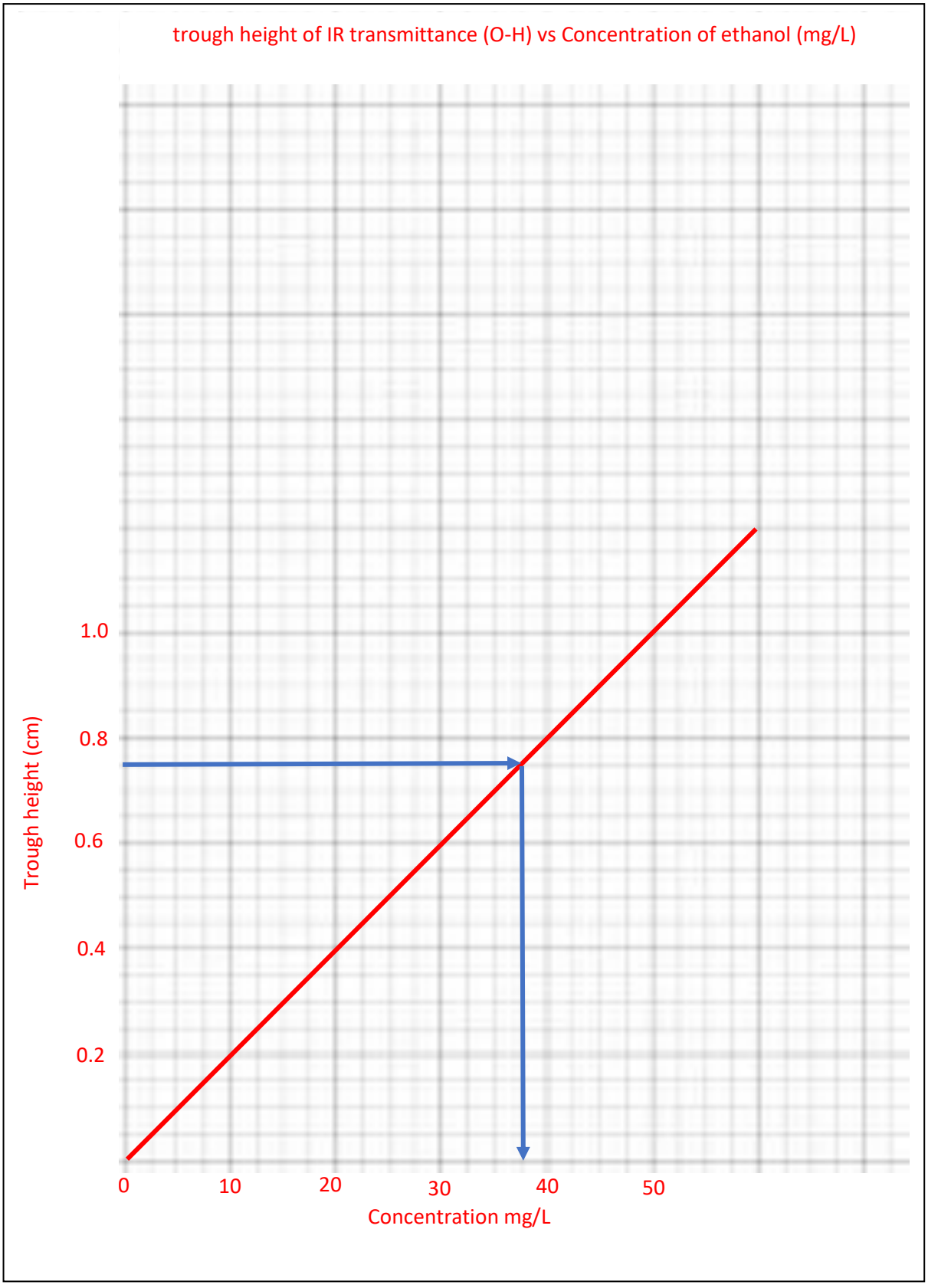
/ 1000 / Fm

=> 37.5 mg → *8.15 X 10^{-4}M*

iii. ppm *= 37.5 ppm*

iv. % v/v (density of ethanol 0.789 g/mL)

=> Find volume 37.5mg or 0.0375 g of ethanol.
=> (0.0375 g) / 0.789 g/mL = 0.0475 mL
=> (0.0475 / 1000 mL) X 100 = 4.75 X 10^{-3} %v/v


trough height of IR transmittance (O-H) vs Concentration of ethanol (mg/L)
Trough height (cm)
1.0
0.8
0.6
0.4
0.2
0
10
20
30
40
50
Concentration mg/L

4. You are provided with a mass spectrum of an unknown ethanol sample. A calibration curve was previously created using known ethanol concentrations and the absolute, rather than the relative heights, were measured. The following data was obtained using peak height for the m/z 31 ion:

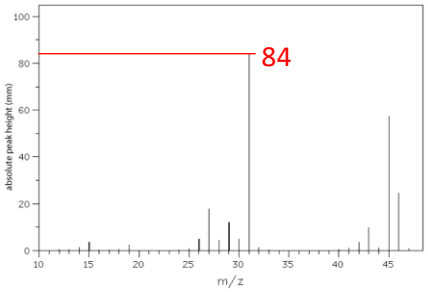


Figure 5 – MS of ethanol absolute values.

Concentration (mg/L)	absolute intensity at m/z 45 (mm)
10	**24**
20	**51**
30	74
40	**102**
50	1.26

Table 2 – concentration vs absolute value of peak.

a. Using the data in table 1 plot a calibration curve on the graph paper provided on the next page and draw the line of best-fit.

b. What fragment formed the peak at 45 m/z? _____ $[CH_3CH_2O]^+$ _____

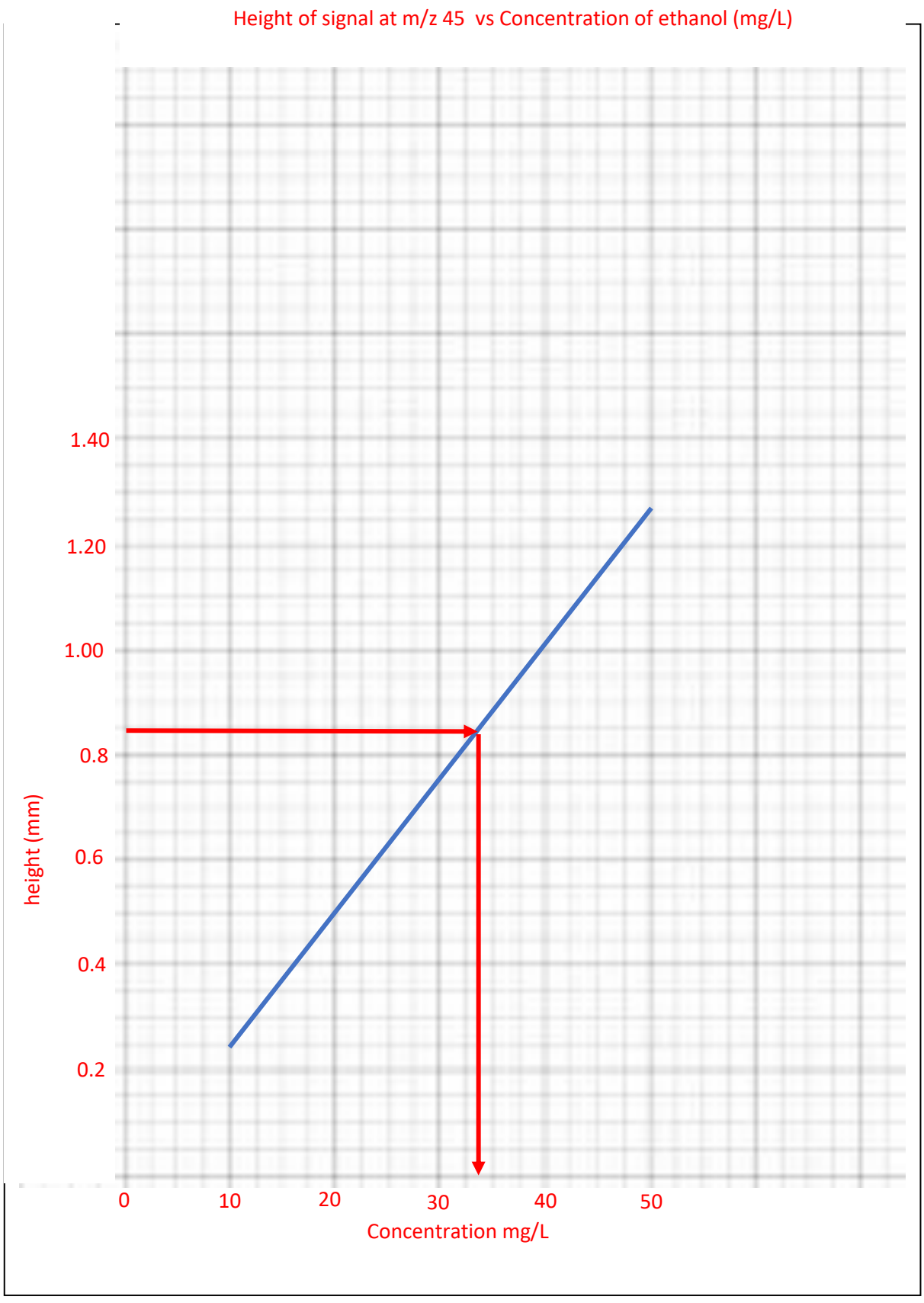
c. Using the calibration curve, give the concentration of ethanol in the sample in:

i. mg/L = *33.5 mg/L*

ii. mol/L = (33.5 / 1000) / 46.0 = *7.28 X 10^{-4} M.*

iii. ppm = *33.5 ppm*

iv. % v/v (density of ethanol 0.789 gmL)
=> Convert mass of ethanol into volume using density (be careful with units)
=> 0.0335 / 0.789 = 0.0425 g
=> (0.0425 mL/1000mL) X 100 = 0.425 % v/v


Height of signal at m/z 45 vs Concentration of ethanol (mg/L)
1.40
1.20
1.00
0.8
0.6
0.4
0.2
height (mm)
0
10
20
30
40
50
Concentration mg/L

5. Acetaldehyde (C_2H_4O) is formed via an oxidation reaction with ethanol. Consider the mass spectra of pure ethanol and a product sample of ethanal.

a. Consider the sample MS. identify the fragments that formed peaks at the following m/z values from the simple splitting of the parent ion eg just one bond break

- 15 _____$[CH_3]^+$_____
- 29 ___$[CHO]^+$ from ethanal or $[CH_3CH_2]^+$ from ethanol
- 44 ___$[CH_3CHO]^+$ ethanal parent ion
- 45 ___$[\ ^{13}CH_3{}^{12}CHO]^+$ ethanal parent ion
- 43 ____$[CH_3CO]^+$ from ethanal or $[CH_3CH_2]^+$ from ethanol
- 46 ___$[CH_3CH_2OH]^+$_____
- 31 ___$[CH_2OH]^+$ from ethanol

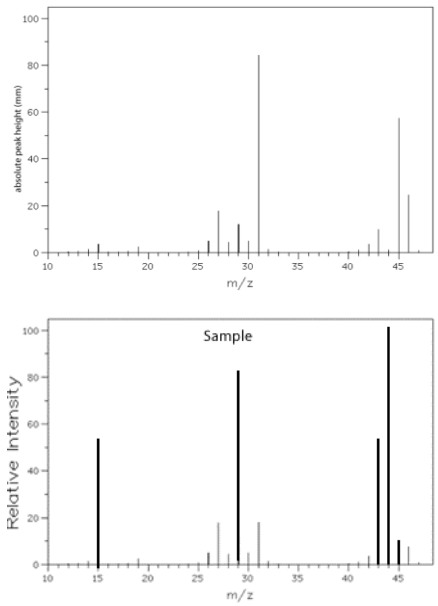


Figure 6 – mass spectra of pure ethanol and sample.

b. Has the reaction to convert ethanol into ethanal resulted in a 100% yield? Explain with evidence from the spectra given in figure 6.

Consider the simple splitting of the sample.

*at **m/z = 31** $[CH_2OH]^+$: This fragment is characteristic of ethanol*

*at **m/z = 46** $[CH_3CH_2OH]^+$ is unique to ethanol. The fragment at m/z 46 represents the parent ion for ethanol.*

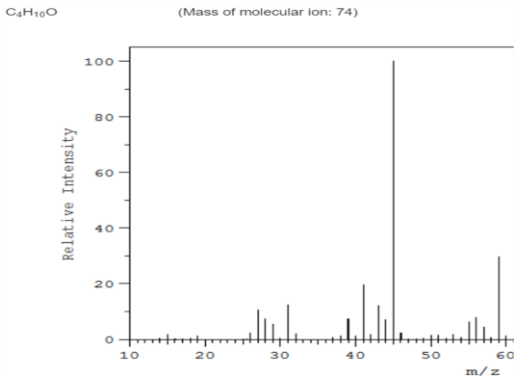
This indicates the presence of unreacted ethanol and hence not 100% yield.

c. Why would the fragment at m/z 15 not be an accurate indicator of contamination?

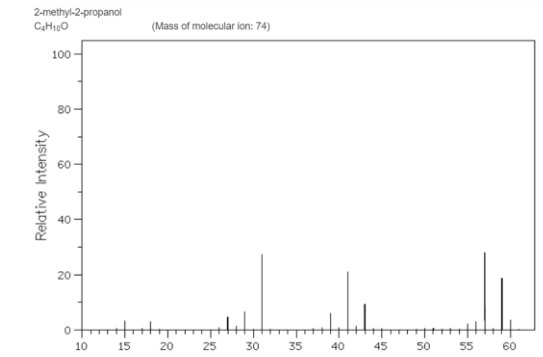
m/z 15 is a common fragment $[CH_3]^+$ for both ethanol and ethanal mass spectra. Its presence would not conclusively prove presence of an ethanol contaminant.

6. Consider the three MS of three organic molecules (alcohols) with the molecular formula $C_4H_{10}O$.
a. Identify compounds A, B and C . Justify each choice with reference to the MS of each compound by completing table 1 below.

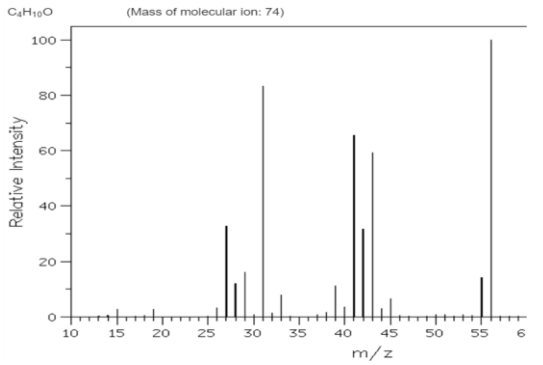
A



B



C



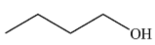
Molecule (IUPAC)	*Skeletal structure*	*Identifying m/z signal/s due to simple, one-bond-break, splitting.*	*Fragment/s.*
A – butan-2-ol		*45, 43*	*$[CH_3CHOH]^+$ $[CH_3CH_2CH_2]^+$*
B – 2-methylpropan-2-ol		*57*	*$[C_4H_9]^+$*
C – Butan-1-ol		*31, 56*	*$[CH_2OH]^+$ $[C_4H_8]^+$*

Table 1