3.6 Organic analysis

Functional group tests
- Through the study of organic chemistry, there are a few reactions that are unique to a particular functional group.

<table>
<thead>
<tr>
<th>Test</th>
<th>Functional groups</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromine water</td>
<td>Alkene C=C</td>
<td>Orange $\rightarrow$ colourless</td>
</tr>
<tr>
<td>Hydrolysis of halogenoalkane with AgNO$_3$</td>
<td>Halogenoalkane</td>
<td>AgX precipitate (white, cream, yellow)</td>
</tr>
<tr>
<td>Oxidation with K$_2$Cr$_2$O$_7$ / H$_2$SO$_4$</td>
<td>1° 2° alcohols / aldehydes / Not 3° alcohols</td>
<td>Orange $\rightarrow$ green</td>
</tr>
<tr>
<td>Fehlings / Benedicts solution</td>
<td>Aldehydes</td>
<td>Red precipitate</td>
</tr>
<tr>
<td>Tollens reagent</td>
<td>Aldehydes</td>
<td>Silver mirror</td>
</tr>
<tr>
<td>Sodium carbonate solution / Limewater</td>
<td>Carboxylic acids</td>
<td>Fizzing / limewater goes cloudy</td>
</tr>
</tbody>
</table>

- These, along with a few other reactions, can be used as chemical tests for these functional groups:
Organic Functional group tests

1) Test for Alkenes – Unsaturation – C=C

\[
\begin{align*}
\text{H} & \quad \text{C} \quad \text{H} \\
\text{H} & \quad \text{C} \quad \text{C} \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{Br} & \quad \text{Br} \\
& \quad \rightarrow \quad \text{H} & \quad \text{C} & \quad \text{C} & \quad \text{H} \\
& & \quad \text{Br} & \quad \text{Br} \\
\end{align*}
\]

Orange \quad \text{Colourless}

**Chemical test for alkene - C=C / unsaturation:**
- Add bromine water, Br\(_2\)
- Orange to clear and colourless

2) Test for Halogenoalkanes RX (X is a halogen)

\[
\begin{align*}
\text{RCH}_2\text{X} & \quad + \quad \text{OH}^- & \rightarrow & \quad \text{RCH}_2\text{OH} & \quad + \quad \text{X}^- \\
\text{Ag}^+_{(aq)} & \quad + \quad \text{X}^-_{(aq)} & \rightarrow & \quad \text{AgX}_{(s)} \\
\end{align*}
\]

**Precipitate** (white / cream / yellow)

**Chemical test for halogenoalkane:**
- Add sodium hydroxide, NaOH / warm
- Acidify with Nitric acid, HNO\(_3\)
- Add silver nitrate, AgNO\(_3\)
- Precipitate white / cream / yellow
3) Test for carboxylic acid, RCOOH

a) Carboxylic acids react with sodium metal, Na (all alcohols do too):

\[ \text{RCOOH} \ + \ \text{Na} \ \rightarrow \ \text{RCOONa} \ + \ \frac{1}{2}\text{H}_2 \]

b) Only Carboxylic acids react with sodium carbonate, Na$_2$CO$_3$

\[ \text{RCOOH} \ + \ \text{Na}_2\text{CO}_3 \ \rightarrow \ \text{RCOONa} \ + \ \text{H}_2\text{O} \ + \ \text{CO}_2 \]

\[ \text{CO}_2(\text{g}) \ + \ \text{Ca(OH)}_2(\text{aq}) \ \rightarrow \ \text{CaCO}_3(\text{s}) \ + \ \text{H}_2\text{O}(\text{l}) \]

White Precipitate

**Chemical test for carboxylic acids:**

- Add sodium carbonate, Na$_2$CO$_3$
- Collect CO$_2$ with a pipette
- Bubble through limewater – white precipitate (goes cloudy)
4) Test for alcohols, ROH

c) All alcohols and carboxylic acids react with sodium metal:

\[
RCH_2OH + Na \rightarrow RCH_2ONa + \frac{1}{2}H_2
\]

d) Only 1°, 2° alcohols can be oxidised

The oxidising agent – Potassium dichromate (VI) / sulphuric acid

\[
\text{Cr}_2\text{O}_7^{2-} (aq) + 14H^+ (aq) + 6e^- \rightarrow 2\text{Cr}^{3+} (aq) + 7H_2O
\]

Orange  \rightarrow  Green

- This is orange in colour and is a mixture of Sulphuric acid, H\text{}_2\text{SO}_4 (H^+) and K\text{}_2\text{Cr}_2\text{O}_7.

Summary of alcohol oxidation

**1° Alcohol**

- Ethanol

**2° Alcohol**

- Propan-2-ol

**3° Alcohol**

- 2 – methyl Propan – 2 – ol

Chemical test for alcohols:

- Add sodium, Na – fizzing with all alcohols, 1°, 2° and 3°
- Add potassium dichromate, K\text{}_2\text{Cr}_2\text{O}_7 / sulphuric acid, H\text{}_2\text{SO}_4 and warm
- 1° and 2° alcohols orange \rightarrow green
5) Test for aldehydes

- Remember aldehydes can oxidise further to carboxylic acids.
- Ketones cannot.

![Chemical reaction diagram](image)

**Organic reaction / oxidation**

\[ \text{RCHO} + [\text{O}] \rightarrow \text{RCOOH} \]

**a)** Add potassium dichromate, \( \text{K}_2\text{Cr}_2\text{O}_7 \) and sulphuric acid, \( \text{H}_2\text{SO}_4 \) and warm.

\[
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}
\]

- Orange \( \rightarrow \) Green

**b)** Add Tollens’ reagent, \( \text{AgNO}_3 \) dissolved in ammonia – Silver mirror test.

\[
\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}(s)
\]

- Colourless \( \rightarrow \) Silver ppt

**c)** Fehling’s solution – \( \text{CuSO}_4 \) / \( \text{NaOH} \) / Warm.

\[
2\text{Cu}^{2+} + 2\text{OH}^- + 2\text{e}^- \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O}
\]

- Blue \( \rightarrow \) Red

**Chemical test for aldehydes:**

- **a)** Add potassium dichromate, \( \text{K}_2\text{Cr}_2\text{O}_7 \) and sulphuric acid, \( \text{H}_2\text{SO}_4 \) and warm
  - Orange \( \rightarrow \) green

- **b)** Add Tollens’ reagent, \( \text{AgNO}_3 \) dissolved in ammonia – Silver mirror test
  - Silver precipitate / mirror

- **c)** Add Fehling’s solution – \( \text{CuSO}_4 \) / \( \text{NaOH} \) / Warm
  - Blue \( \rightarrow \) red
The following tests were carried out and the results recorded below:

<table>
<thead>
<tr>
<th>Organic compound</th>
<th>Na added</th>
<th>Br₂ water added</th>
<th>Tollens’ reagent</th>
<th>K₂Cr₂O₇ / H₂SO₄</th>
<th>Na₂CO₃ added</th>
<th>NaOH / HNO₃ / AgNO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-</td>
<td>-</td>
<td>Silver mirror</td>
<td>Orange → green</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>-</td>
<td>Orange → colourless</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>Fizzing</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D</td>
<td>Fizzing</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Fizzing</td>
<td>-</td>
</tr>
<tr>
<td>E</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>F</td>
<td>Fizzing</td>
<td>-</td>
<td>Orange → green</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>G</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>White precipitate</td>
</tr>
</tbody>
</table>

Compounds A – F are one of the following: Add the letter next to the compound

- Carboxylic acid
- Ketone
- Alkene
- Halogenoalkane

- Aldehyde
- 1° Alcohol
- 3° Alcohol
Questions:

1) 2 organic compounds that are functional group isomers of each other have the molecular formula C₃H₆O. When Tollen's reagent was added, only one of them gave a silver precipitate. Identify and draw the structure of the 2 organic compounds. Explain your answer.

2) 3 organic liquids A,B and C are unknown. Upon chemical analysis the following results were obtained:
   
   A: Turned K₂Cr₂O₇ / H₂SO₄ orange → green and fizzed with Na
   B: Turned K₂Cr₂O₇ / H₂SO₄ orange → green and produced a silver precipitate with Tollens' reagent
   C: No change with K₂Cr₂O₇ / H₂SO₄. Fizzed with Na₂CO₃

Identify with reasons the functional groups present in A,B and C.

3) 2 organic liquids X and Y are unknown. Upon chemical analysis the following results were obtained:

   A: Did not fizz with Na but turned K₂Cr₂O₇ / H₂SO₄ orange → green
   B: Turned bromine water orange → colourless and fizzed with Na₂CO₃

Identify with reasons the functional groups present in X and Y.
4) An organic compound was found to have the following composition by mass. Its mass spectra had a molecular ion peak of 74.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>% by mass</td>
<td>64.86</td>
<td>13.51</td>
<td>21.62</td>
</tr>
</tbody>
</table>

a. Calculate the molecular formula of the organic compound.

b. The organic compound was found to fizz when Na was added. What functional group must the compound have?

c. Draw the 4 possible isomers that include the functional group identified in (b) and classify them.

d. The organic compound was then refluxed with K₂Cr₂O₇ / H₂SO₄ and the oxidising mixture turned orange → green. What does the colour change tell you about the organic compound?

e. The oxidation product was tested with Na₂CO₃ and there was no fizzing observed. What functional group is in the oxidation product? Draw and name the oxidation product.

f. What does (e) tell you about the structure of the original organic compound? Draw and name the original organic compound.
Infrared spectroscopy

Infrared radiation and molecules:

- All molecules absorb IR light.
- The IR light makes the bonds in a molecule vibrate (like the engine of a bus making the windows vibrate).

Every bond vibrates at its own unique frequency depending on:

1) Bond strength
2) Bond length
3) Mass of atom at either end of the bond

How it works:

- The full IR spectrum is passed through a sample.
- Specific bonds vibrate at specific frequencies (unique to that bond).
- When a bond vibrates it absorbs energy from the IR light at that specific frequency.
- This means less IR light at that specific frequency gets through the sample to the detector.
- Each ‘peak’ is characteristic of a particular bond / atoms vibrating.
- A trace which we call a spectrum is produced.
- The frequencies are measured as wavenumbers.
- The amount of IR light at that frequency reaching the detector is measured in transmittance.
Specific bonds and their unique IR wavenumbers:

<table>
<thead>
<tr>
<th>Bond</th>
<th>Wavenumber /cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>N—H (amines)</td>
<td>3300 – 3500</td>
</tr>
<tr>
<td>O—H (alcohols)</td>
<td>3230 – 3550</td>
</tr>
<tr>
<td>C—H (acids)</td>
<td>2850 – 3300</td>
</tr>
<tr>
<td>O—H (acids)</td>
<td>2500 – 3000</td>
</tr>
<tr>
<td>C≡N</td>
<td>2220 – 2260</td>
</tr>
<tr>
<td>C＝O</td>
<td>1680 – 1750</td>
</tr>
<tr>
<td>C＝C</td>
<td>1620 – 1680</td>
</tr>
<tr>
<td>C—O</td>
<td>1000 – 1300</td>
</tr>
<tr>
<td>C—C</td>
<td>750 – 1100</td>
</tr>
</tbody>
</table>

- The peak at 3000 represents an O - H group in a carboxylic acid.
- The peak at 1680 - 1750 represents a C=O group.
- This would represent a Carboxylic acid functional group - COOH

**Fingerprint region**

- Between 1000 – 1500 cm⁻¹ is called the fingerprint region.
- These are unique to a particular molecule.
- This means that this region can be compared with a database to identify a specific compound.
The identification of functional groups by looking at IR spectra:

- By looking at the **peaks present**
- By looking at **peaks that are absent** – this removes certain functional groups and are as important as peaks that are present

**Carbonyl peak, C=O:**

- The peak at 1700 cm\(^{-1}\) would represent a C=O.
- It does not have a peak between 2500 – 3000 cm\(^{-1}\).
- Or any other key peaks – Suggests that the molecule is an **aldehyde** or **ketone**.

**Alcohols, OH:**

- The peak at 3400 cm\(^{-1}\) would represent a O–H in alcohols
- The peak at 1000 cm\(^{-1}\) would represent a C–O
- The absence of any other key peaks – Suggests that the molecule is an **alcohol**
Questions

1) List the key absorptions and wavenumbers you would expect to find in the following molecules:

\[
\begin{array}{c}
\text{H} \quad \text{C} \quad \text{H} \\
\text{H} \quad \text{C} \quad \text{OH} \\
\text{H} \quad \text{H} \quad \text{H} \\
\hline
\text{H} \quad \text{C} \quad \text{C} \\
\text{H} \quad \text{C} \quad \text{O} \\
\text{H} \quad \text{H} \\
\hline
\text{H} \quad \text{C} \quad \text{C} \\
\text{H} \quad \text{C} \quad \text{O} \quad \text{H} \\
\text{H} \quad \text{H} \\
\hline
\text{H} \quad \text{C} \quad \text{C} \\
\end{array}
\]

2) Draw and name the bonds you would expect at the following wavenumbers:

<table>
<thead>
<tr>
<th>Wavenumber cm(^{-1})</th>
<th>1100</th>
<th>1650</th>
<th>1700</th>
<th>2900</th>
<th>3300</th>
</tr>
</thead>
<tbody>
<tr>
<td>Possible bonds (maybe more than one)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3) This molecule is cyclic and contains 6 carbon atoms. Use this information and the IR spectra below to suggest a structure:

SDBSWeb: http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, 23/03/2016)

Structure:
4) This organic compound has the following % by mass and the mass spectra gave a molecular ion peak of 60.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>% by mass</td>
<td>62.07</td>
<td>13.80</td>
<td>27.59</td>
</tr>
</tbody>
</table>

a. Calculate and write the molecular formula of the organic compound.

b. Use the IR spectra below to identify the functional group(s) present in the compound.

![IR Spectra Image](http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, 08/03/2016))

Draw and name the possible structures

c. How would you use the above spectra to identify which of the above structures the organic compound is?

d. What chemical test could you carry out to confirm the identity of the organic compound. Explain your answer.
IR radiation, CO₂ and global warming:

- Radiation from the sun reaches the planet.
- The radiation is absorbed by the Earth and re-emitted as IR radiation.
- Most of this IR radiation goes back into space but some is absorbed by gases in the atmosphere.
- These gas molecules absorb the IR radiation then re-emit it as energy, this energy warms up the atmosphere.
- These gases are: water, methane and carbon dioxide.

How do gases absorb radiation?

- Just like IR spectroscopy, the bonds in these greenhouse gases absorb IR radiation in their bonds.
- The bonds vibrate absorbing the IR radiation.
- Different gases will absorb different amounts of IR radiation.
- 3 factors determine the impact a gas has on Global warming:
  1. Its concentration in the atmosphere
  2. Its ability to absorb IR radiation
  3. Its lifetime in the atmosphere

- These 3 factors make up the GWP (Global Warming Potential)
- The term Climate Change explains that although the average temperature of the planet is rising, different areas around the planet will suffer from extreme weather patterns.
The mass spectrometer – a recap:

Summary of how a mass spectrometer works:

<table>
<thead>
<tr>
<th>Process</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vaporised</td>
<td>Dissolved in a volatile solvent and fed through a fine needle producing droplets.</td>
</tr>
<tr>
<td>Electrospray ionisation</td>
<td>Passed through a high voltage positive terminal / removes electrons from the sample / solvent and producing a fine ‘spray’ of positive droplets. The solvent evaporates leaving positive ions.</td>
</tr>
<tr>
<td>Acceleration</td>
<td>The ions are accelerated towards a highly negatively charged plate with a hole in. They are all given the same kinetic energy. The speed at which the ion will travel will depend upon the mass of the ion, ( m/z )</td>
</tr>
<tr>
<td>Ion drift</td>
<td>The ions pass through the hole and pass along the flight tube to the detector.</td>
</tr>
<tr>
<td>Detector</td>
<td>The ions with a smaller mass reach the detector first. The ion picks up an electron from the detector to complete the circuit.</td>
</tr>
<tr>
<td>Data analysis</td>
<td>A computer generates a spectrum (shown below).</td>
</tr>
</tbody>
</table>

Summary

A short time of flight = small mass / charge \( m/z \)

A long time of flight = large mass / charge \( m/z \)

The time taken to reach the detector determine the mass / charge of the ion. As the mass of electrons are negligible, this is the Ar of that isotope.
Mass Spectrometry of compounds:

- Works in exactly the same way but you also get fragments of that molecule / compound:

- This fragments are caused by the molecule breaking apart under the conditions in the spectrometer.
- Highest $m/z = \text{Mr}$ of the molecule. This is called the molecular ion peak

High resolution mass spectroscopy:

- High resolution mass spectroscopy measures the masses of atoms / molecules to many decimal places.
- This means that molecules with the same Mr’s as a whole number now have several decimal places

Precise Ar values:

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.0078</td>
<td>N</td>
</tr>
<tr>
<td>C</td>
<td>12.0000</td>
<td>O</td>
</tr>
</tbody>
</table>

Look at the following molecules:

$\text{C}_3\text{H}_6\text{O}$  $\text{C}_4\text{H}_{10}$  $\text{C}_3\text{H}_8\text{N}$

- Using conventional mass spectroscopy, they would all have an $m/z = 58$, Mr = 58
- Using high resolution mass spectroscopy, $m/z = \textbf{58.0408}$
- Calculating the Mr using the precise atomic masses:

$\text{C}_3\text{H}_6\text{O} = \textbf{58.0406}$  $\text{C}_4\text{H}_{10} = 58.0780$  $\text{C}_3\text{H}_8\text{N} = 58.0655$

- This allows you to identify the molecule as $\text{C}_3\text{H}_6\text{O}$
Combustion analysis:

- This is basically empirical formula calculations:
- A recap:

A sample of hydrocarbon was found to have 1.20g of carbon and 0.25g of hydrogen. Calculate the Empirical formula of this compound. Then find out the molecular formula if the Mr = 58

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Masses</td>
<td>1.20</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>1.20 / 12</td>
<td>0.25 / 1</td>
</tr>
<tr>
<td>Moles</td>
<td>0.10</td>
<td>:</td>
</tr>
<tr>
<td></td>
<td>0.10 / 0.10</td>
<td>:</td>
</tr>
<tr>
<td>Ratio</td>
<td>1</td>
<td>:</td>
</tr>
<tr>
<td>Whole No Ratio</td>
<td>2</td>
<td>:</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C₂H₅</td>
<td>(29 x 2 = 58)</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C₄H₁₀</td>
<td></td>
</tr>
</tbody>
</table>

- Combustion analysis uses the combustion products to calculate the mass of carbon and hydrogen in a hydrocarbon:

  \[
  \text{H} \quad \rightarrow \quad \text{H}_2\text{O} - \frac{2}{18} \text{ths of the mass of water is the mass of H} \\
  \text{C} \quad \rightarrow \quad \text{CO}_2 - \frac{12}{44} \text{ths of the mass of carbon dioxide is the mass of C} \\
  \]

- Any mass left over is oxygen.
Example:

1) 1.50 g sample of hydrocarbon undergoes complete combustion to produce 4.40 g of CO$_2$ and 2.70 g of H$_2$O. What is the empirical formula of this compound?

<table>
<thead>
<tr>
<th>Element</th>
<th>CO$_2$ → C</th>
<th>H$_2$O → H</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Masses CO$_2$ / H$_2$O</td>
<td>4.40</td>
<td>2.70</td>
<td></td>
</tr>
<tr>
<td>4.40 x 12/44</td>
<td>2.70 x 2/18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Masses of C / H</td>
<td>1.20 :</td>
<td>0.30 :</td>
<td>Check for O: 1.20 + 0.30 = 1.50</td>
</tr>
<tr>
<td>1.20 / 12 :</td>
<td>0.302/ 1 :</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moles of C / H</td>
<td>0.1 :</td>
<td>0.30 :</td>
<td></td>
</tr>
<tr>
<td>( / smallest)</td>
<td>0.1 / 0.1 :</td>
<td>0.30 / 0.1 :</td>
<td></td>
</tr>
<tr>
<td>Whole No Ratio</td>
<td>1 :</td>
<td>3 :</td>
<td></td>
</tr>
<tr>
<td>Empirical formula</td>
<td>CH$_3$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2) A 0.2500 g sample of a compound known to contain carbon, hydrogen and oxygen undergoes complete combustion to produce 0.3664 g of CO$_2$ and 0.1500 g of H$_2$O. What is the empirical formula of this compound?

<table>
<thead>
<tr>
<th>Element</th>
<th>CO$_2$ → C</th>
<th>H$_2$O → H</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Masses CO$_2$ / H$_2$O</td>
<td>0.3664</td>
<td>0.1500</td>
<td></td>
</tr>
<tr>
<td>0.3664 x 12/44</td>
<td>0.1500 x 2/18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Masses of C / H / O</td>
<td>0.0999 :</td>
<td>0.0166 :</td>
<td>0.2500 – (0.0999 + 0.0166) = 0.1335</td>
</tr>
<tr>
<td>0.0999 / 12 :</td>
<td>0.0166 / 1 :</td>
<td>0.1335 / 16</td>
<td></td>
</tr>
<tr>
<td>Moles of C / H / O</td>
<td>0.00833 :</td>
<td>0.0166 :</td>
<td>0.00834</td>
</tr>
<tr>
<td>( / smallest)</td>
<td>0.0833 / 0.0833 :</td>
<td>0.0166 / 0.0833 :</td>
<td>0.00834 / 0.0833</td>
</tr>
<tr>
<td>Whole No Ratio</td>
<td>1 :</td>
<td>2 :</td>
<td>1</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>CH$_2$O</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Tip: You may not be told that the other element is oxygen so always add the carbon and hydrogen masses together to see if it equals the sample mass.
- If it doesn’t, the difference is always oxygen, O.
Questions:

1) 0.105 g organic compound containing only C, H, and O. When burned completely it gave 0.257 g of CO$_2$ and 0.0350 g of H$_2$O. Given an m/z value from mass spectra of 108, what is its molecular formula?

2) 1.000 g sample of a compound is combusted in excess oxygen and the products are 2.492 g of CO$_2$ and 0.6495 g of H$_2$O. Given an m/z value from mass spectra of 388, what is its molecular formula?