Answer all the questions below then check your answers.

1. Name the 4 steps key stages in a TOF mass spectrometer.

2. What are the two distinct methods used to ionise a sample in a TOF mass spectrometer?

a. Explain how electron impact ionisation works.

b. Explain how electro-spray ionisation works.

c. What advantages does electro-spray ionization have over electron impact ionisation?

3. The following two substances were ionised by electron impact ionisation. Write an equation to show the ionisation of each substance in the spectrometer.

a. Na

b. CH_4

4. Why are the acceleration plates in a mass spectrometer given a negative charge?

5. When the ions are accelerated in the mass spectrometer what do they have the same amount of?

a. Explain why different ions take different times to travel through the flight tube.

6. Which of the following ions will reach the detector first? Explain your choice.

a. $^{35}Cl^{+}$ or $^{37}Cl^{+}$ b. $^{12}CCl_4^{+}$ or $^{13}CCl_4^{+}$

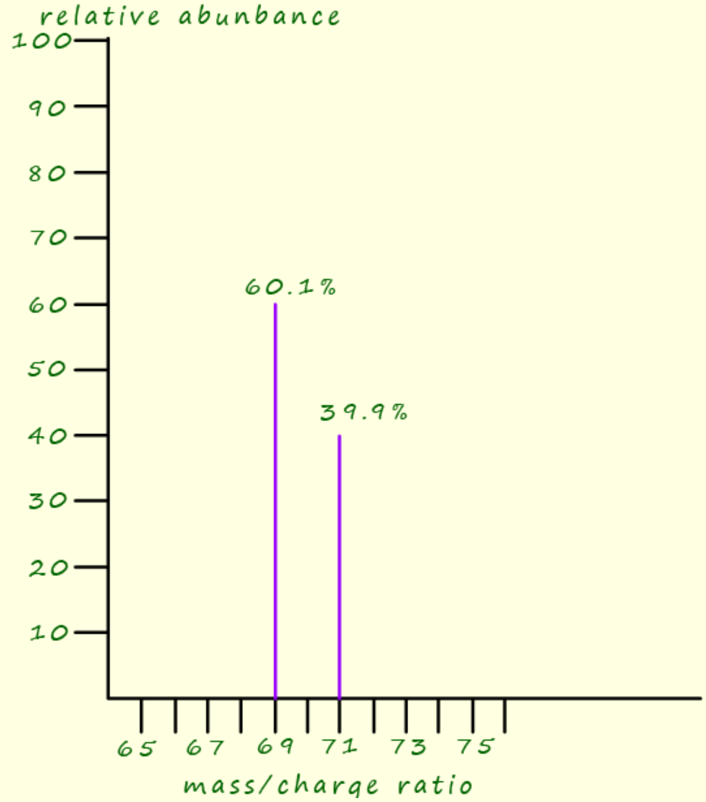
7. The mass spectrum for a sample of the element gallium is shown opposite.

a. How many isotopes does gallium have?

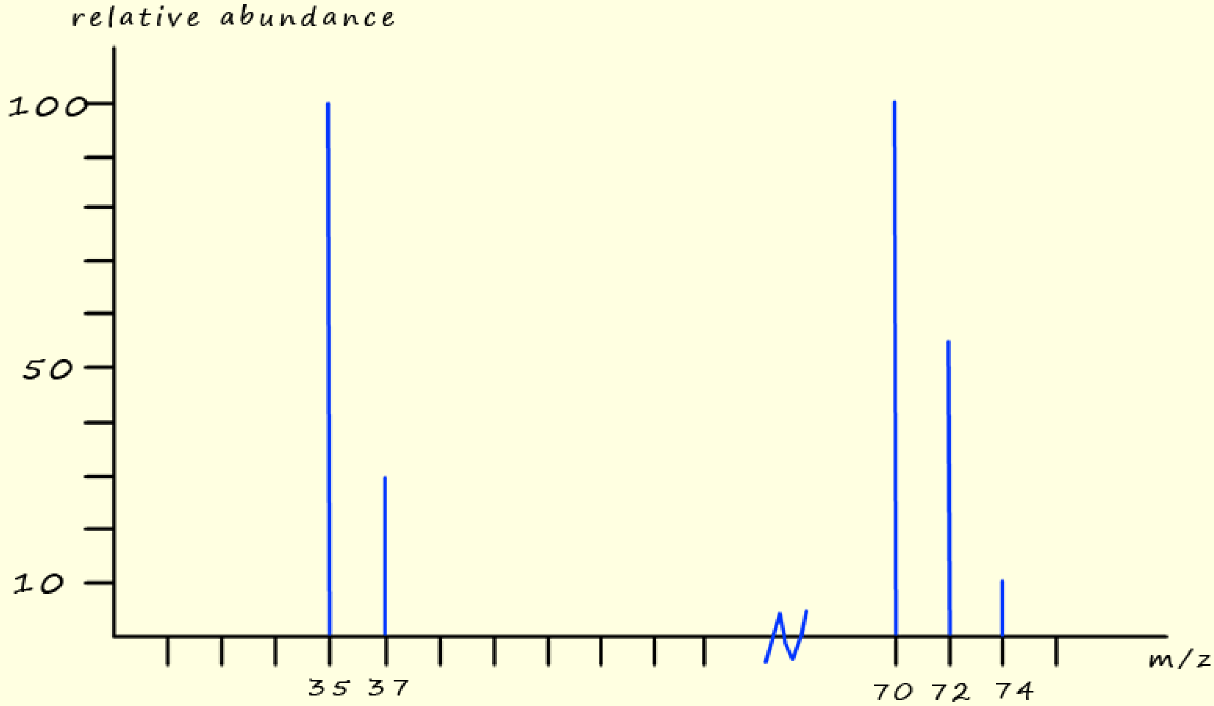
b. What is an isotope?

c. Write the chemical symbol for the two isotopes of gallium shown.

d. Calculate the relative atomic mass of gallium using the information in the mass spectrum.

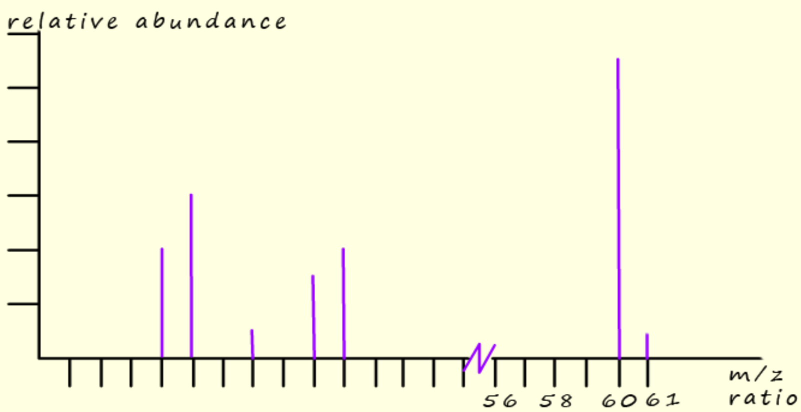


8. Chlorine is a diatomic gas. Chlorine has 2 isotopes; these are ^{35}Cl and ^{37}Cl. The mass spectrum for a sample of chlorine gas is shown below.



a. Identify the species responsible for each of the peaks in the spectrum and give its chemical symbol.

9. The mass spectrum of an unknown compound X is shown below. The mass spectrum was produced by electron impact ionisation.



a. What is the relative molecular mass of compound X?

b. Why are there peaks with lower m/z?

c. Why are there peaks with higher m/z ratios than the M_r of the compound?

10. Complete the table below to show the correct units for each of the variable:

variable	units
Time (t)	
Kinetic energy (KE)	
Mass (m)	
Velocity (v)	
Length of flight tube (d)	

11. Calculate the mass in kilograms of a single ion for each of the following elements:

The Avogadro constant = 6.022×10^{23}

a. $^{65}Cu^{+}$ b. $^{65}Cu^{2+}$ c. $^{23}Na^{+}$ d. $^{16}O^{2-}$ e. $^{35}Cl^{-}$

b. How long would a $^{65}Cu^{+}$ ion with KE of 1.000×10^{-16}J take to travel along a flight tube of length 0.8000m?

12. A sample of the metal titanium was analysed in a TOF mass spectrometer. The abundances of the isotopes of Ti is shown below:

m/z ratio	46	47	48	49
%abundance	9.1	7.8	74.6	8.5

a. Write the symbol for one isotope of titanium and explain in terms of sub-atomic particles what an isotope is.

b. Calculate the relative atomic mass of titanium.

c. The sample of titanium was ionised by electron impact ionisation. Write an equation to show the ionisation of the ion that would reach the detector last.

d. Calculate the mass in Kg of one atom of ^{48}Ti.

e. The TOF spectrometer used gives each ion 1.013 x 10^{-13}J of KE. The flight time of a $^{49}Ti^{+}$ ion is 8.56 x 10^{-7} s. Calculate the flight time of the $^{47}Ti^{+}$ ion.

13. A sample of copper was analysed in a TOF mass spectrometer. The most common isotopes of copper are copper-63 (^{63}Cu) and copper-65 (^{65}Cu). The TOF mass spectrometer has a flight tube of length is 1.8 meters. The copper ions enter the flight tube with a kinetic energy of 3.204 x 10^{-15}J. Assume the copper ions are formed with a single positive charge (+1).

a. What is the mass of the copper-63 ion formed in the mass spectrometer in kilograms? (The Avogadro constant = 6.022 x 10^{23})

b. Calculate the Velocity of the $^{63}Cu^{+}$ ion in the flight tube:

c. Calculate Flight Time:

Answers

1. Name the 4 steps key stages in a TOF mass spectrometer.

- Ionisation
- Acceleration
- Ion-drift
- detection

2. What are the two distinct methods used to ionise a sample in a TOF mass spectrometer?

- Impact ionisation using an electron gun
- Electro-spray ionisation where sample is dissolved in volatile polar solvent.

a. Explain how electron impact ionisation works.

- Sample is dissolved in volatile polar solvent.
- Sample injected using a fine needle which has a large voltage across it, this produces a mist or fine aerosol.#
- On needle tip the sample gains a hydrogen ion, H^+ from the solvent: we can show this as:

$$M_{(g)} + H^+ \longrightarrow MH^+_{(g)}$$

<u>This results in the sample gaining 1 unit of mass (hydrogen added to it!)</u>

b. Explain how electro-spray ionization works.

See answer to part a above

c. What advantages does electro-spray ionization have over electron impact ionisation?

Difficult to manage the energy of the electrons from the electron gun, this means larger molecules with weaker bonds are likely to be broken up, so the Mr of the parent molecule will not be revealed by the mass spectra. However electro-spray ionisation uses less harsh conditions and larger molecules are likely to stay intact and not be smashed to pieces!

3. The following two substances were ionised by electron impact ionisation. Write an equation to show the ionisation of each substance in the spectrometer.

a. Na

$Na_{(g)} + H^+ \longrightarrow NaH^+_{(g)}$

b. CH_4

$CH_{4\,(g)} + H^+ \longrightarrow CH^+_{5\,(g)}$

4. Why are the acceleration plates in a mass spectrometer given a negative charge?

The spectrometer produces positively charged ions during the ionisation stage, to be accelerated we need oppositely charged negative plates.

5. When the ions are accelerated in the mass spectrometer what do they have the same amount of?

Kinetic energy. The smaller lighter ions are moving faster than the larger slow moving ones, but all ions have the small kinetic energy.

a. Explain why different ions take different times to travel through the flight tube.

Flight time depends on mass/charge ratio. Lighter ions are travelling faster than the heavier ions, so they arrive at the detector first.

6. Which of the following ions will reach the detector first? Explain your choice.

a. $^{35}Cl^+$ or $^{37}Cl^+$

Workout mass/charge (m/z) ratio for each ion. Simply 35/1 and 37/1. The lighter ion with mass/charge of 35 will reach the detector first

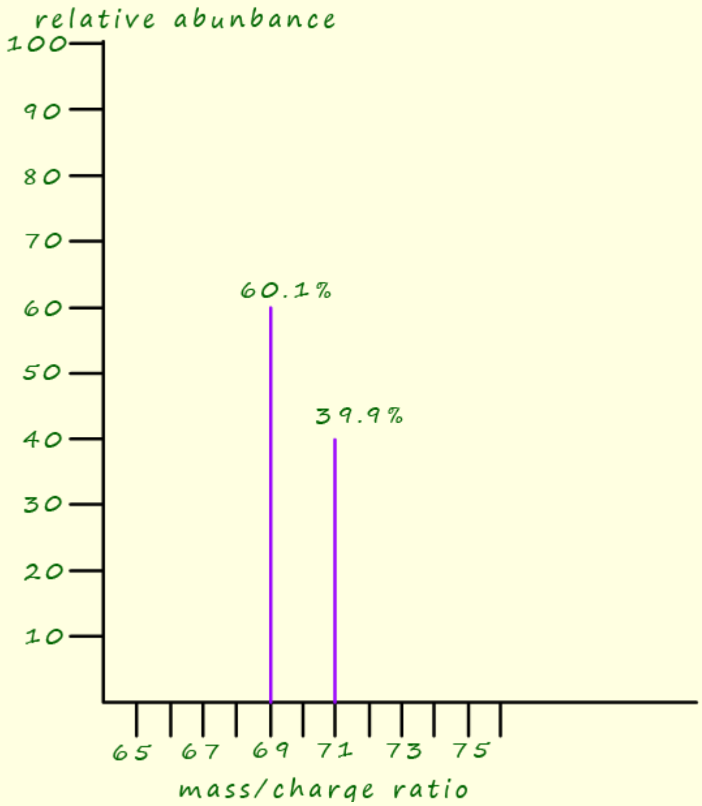
b. $^{12}CCl_4^+$ or $^{13}CCl_4^+$

The first ion has a smaller m/z ratio so will reach the detector first.

7. The mass spectrum for a sample of the element gallium is shown opposite.

a. How many isotopes does gallium have?

2 peaks so 2 isotopes



b. What is an isotope?

Same atomic number different mass number due to extra neutrons

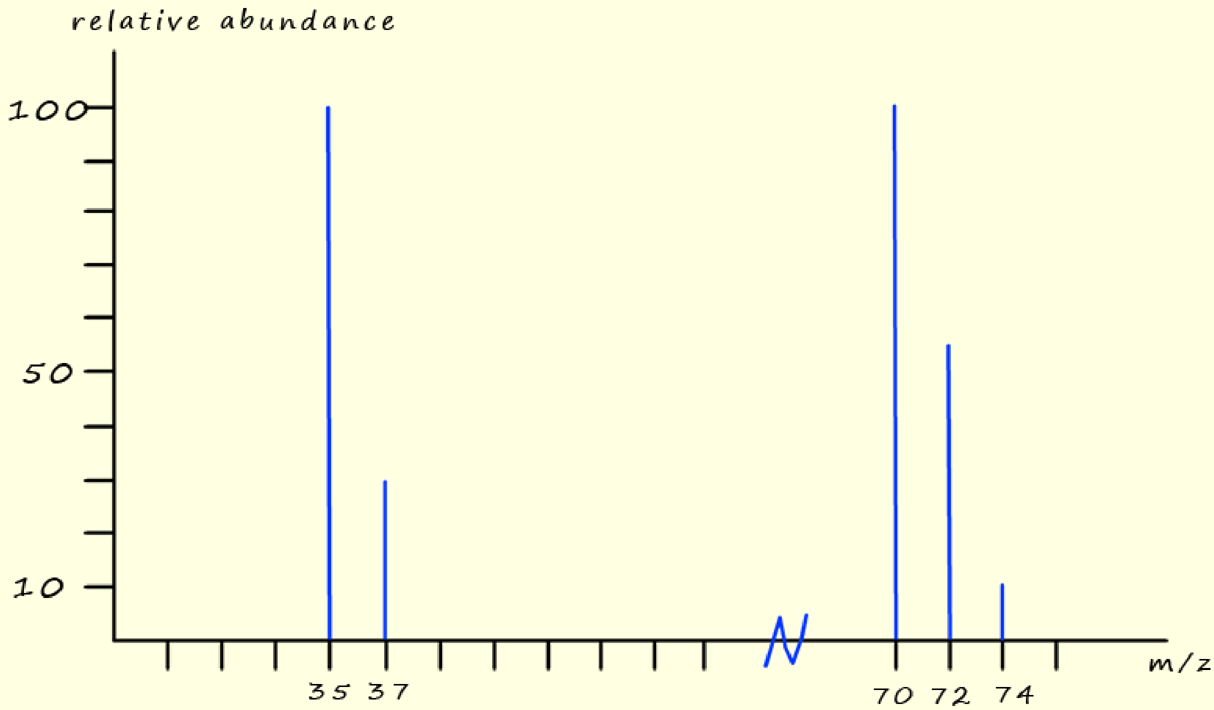
c. Write the chemical symbol for the two isotopes of gallium shown.

$^{69}Ga^+$ $^{71}Ga^+$

d. Calculate the relative atomic mass of gallium using the information in the mass spectrum.

$$Ar = \frac{(69 \times 60.1) + (71 \times 39.9)}{100} = \frac{(4146.1) + (2832.9)}{100} = 69.79$$

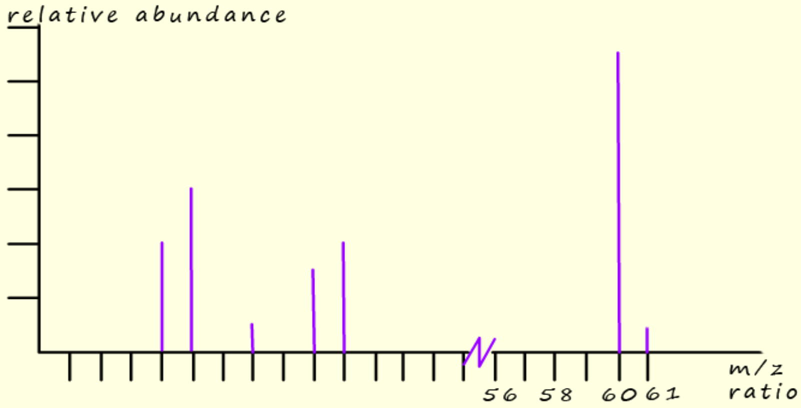
8. Chlorine is a diatomic gas. Chlorine has 2 isotopes; these are ^{35}Cl and ^{37}Cl. The mass spectrum for a sample of chlorine gas is shown below.



a. Identify the species responsible for each of the peaks in the spectrum and give its chemical symbol.

Mass/charge ratio	Ion responsible for peak
35	$^{35}Cl^+$
37	$^{37}Cl^+$
70	$^{35}Cl_2{}^+$
72	$^{35}Cl-^{37}Cl^+$
74	$^{37}Cl_2{}^+$

9. The mass spectrum of an unknown organic (contains carbon) compound X is shown below. The mass spectrum was produced by electron impact ionisation.



a. What is the relative molecular mass of compound X?

Mr of X is 59. Largest peak is at 60, and this will be the parent ion as electro-spray ionisation tends not to cause the parent molecule to break up, however during electro- spray ionisation a hydrogen ion is added, this will add one unit of mass to the parent molecule, so you need to remember to subtract this.

b. Why are there peaks with lower m/z?

Some fragmentation of the parent ion has occurred.

c. Why are there peaks with higher m/z ratios than the M_r of the compound?

Presence of isotopes of carbon are likely to be responsible for the peak at 61, isotope of carbon will be ^{13}C

10. Complete the table below to show the correct units for each of the variable:

variable	units
Time (t)	Seconds (s)
Kinetic energy (KE)	J (joules)
Mass (m)	Kilogram (Kg)
Velocity (v)	Metres per second (ms^{-1})
Length of flight tube (d)	metres

11. Calculate the mass in kilograms of a single ion for each of the following elements:

a. $^{65}Cu^{+}$ b. $^{65}Cu^{2+}$ c. $^{23}Na^{+}$ d. $^{16}O^{2-}$ e. $^{35}Cl^{-}$

Simply divide the Ar for each element by Avogadro number, divide by 1000 to covert to Kg.

a. $65/(6.022 \times 10^{23} \times 1000) = 1.079 \times 10^{-25}$ Kg , do the same calculation for each ion above!

b. How long would a $^{65}Cu^{+}$ ion with KE of 1.000×10^{-16}J take to travel along a flight tube of length 0.8000m?

Use the formula for flight time opposite:

d = 0.8m

m=1.097×10^{-25}kg from part a above

KE = 1×10^{-16}J

Substitute values into equation:

$t = 0.8 / \sqrt{(1.097 \times 10^{-25}\text{kg}/ 2(1 \times 10^{-16}\text{J})}$

$= 1.87 \times 10^{-5}$ s

$\text{time} = \frac{\text{distance}}{\text{velocity}}$ or $t = \frac{d}{v}$ in m, in ms^{-1}

We already have an equation for v, the velocity.

$$v = \sqrt{\frac{2KE}{m}}$$

now substitute this into the t=d/v equation and this will give:

$$t = \frac{d}{\sqrt{\frac{2KE}{m}}}$$

or by rearranging we get:

$$t = d\sqrt{\frac{m}{2KE}}$$

12. A sample of the metal titanium was analysed in a TOF mass spectrometer. The abundances of the isotopes of Ti is shown below:

m/z ratio	46	47	48	49
% abundance	9.1	7.8	74.6	8.5

a. -atomic partic

Atomic number is 22, mass for first isotope is 46.

$^{46}_{22}Ti$ 22 protons, electrons, 46-22 = 24 neutrons

b. Calculate the relative atomic mass of titanium.

$Ar = (46 \times 0.091) + (47 \times 0.078) + (48 \times 0.746) + (49 \times 0.085) = 47.82$

c. The sample of titanium was ionised by electron impact ionisation. Write an equation to show the ionisation of the ion that would reach the detector last.

Last to reach the detector will be the heaviest isotope.

$^{49}Ti + H^{+} \longrightarrow TiH^{+}$

d. Calculate the mass in Kg of one atom of ^{48}Ti.

$48/(6.022 \times 10^{23} \times 1000) = 7.97 \times 10^{-26} kg$

e. The TOF spectrometer used gives each ion 1.013×10^{-13}J of KE. The flight time of a $^{49}Ti^{+}$ ion is 8.56×10^{-7} s. Calculate the flight time of the $^{47}Ti^{+}$ ion.

Simply use t=d/v where d is length of flight tube, v is velocity.

To find v we use the $KE=1/2mv^2$, rearrange to find v

- Mass of 1 atom of $^{49}Ti^{+}$ = $49/(6.022 \times 10^{23} \times 1000) = 8.136 \times 10^{-26}$Kg.
- Velocity = $\sqrt{(2KE/m)}$ = 1578026 ms^{-1}
- So length of flight tube = v x t= 1.35m

So use t=d/v to calculate the flight time of the $^{47}Ti^{+}$ ion. Rearrange the KE formula to calculate the velocity as we did for the $^{49}Ti^{+}$ ion and use the length of flight tube calculated above!

13. A sample of copper was analysed in a TOF mass spectrometer. The most common isotopes of copper are copper-63 (^{63}Cu) and copper-65 (^{65}Cu). The TOF mass spectrometer has a flight tube of length is 1.8 meters. The copper ions enter the flight tube with a kinetic energy of 3.204×10^{-15}J. Assume the copper ions are formed with a single positive charge (+1).

a. What is the mass of the copper-63 ion formed in the mass spectrometer in kilograms? (The Avogadro constant = 6.022×10^{23})

Mass = $(63/1000)/(6.022 \times 10^{23}) = 1.046 \times 10 x^{-25}$ kg

(Note 63 is divided by 1000 to covert grams into kilograms)

b. Calculate the Velocity of the $^{63}Cu^{+}$ ion in the flight tube:

$v = \sqrt{[(2KE) / m]}$

$v = \sqrt{[(2 \times 3.204 \times 10 \times ^{-15} J) / (1.046 \times 10^{-25} kg)]}$

$v = \sqrt{[6.13 \times 10^{10}]}$

$v = 247511$ m/s

c. Calculate Flight Time:

The flight time is calculated from the equation:

$T = d\sqrt{(m/2kE)}$

$= 1.8 \times \sqrt{((1.046 \times 10^{-25})/(2 \times 3.204 \times 10^{-15}))}$

$= 7.27 \times 10^{-6} s$