Student guide: Time of flight mass spectrometry – example questions and answers

01.1 One of the methods of ionising samples in time of flight mass spectrometry is by electron impact. How is this ionisation done? [4 marks]

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01.2 A second method of ionising samples in time of flight mass spectrometry is by electrospray ionisation. How is this ionisation done? [4 marks]

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01.3 Which method is most likely to lead to the break up of the ions into fragments? [1 mark]

01.4 Ionisation by electron impact causes removal of one electron from each particle. Write an equation for the ionisation of each of the following species by loss of one electron. [2 marks]

Ca  
C₂H₆  

01.5 Electrospray ionisation creates an ion by protonation of a molecule. Write an equation for the formation of a positive ion by electrospray ionisation of lactic acid (C₃H₆O₂). [1 mark]

02 The 1+ ions are accelerated using a negatively charged electric plate.

02.1 Why is a negatively charged plate used? [2 marks]

02.2 Complete this sentence: The ions are accelerated by an electric field so that they each have the same ___________________________________________________________________________ [1 mark]

03 The 1+ ions enter the flight tube through a hole in the negatively charged plate.

03.1 Explain why different ions take different times to travel through the flight tube. [2 marks]

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03.2 Which of these ions will reach the detector first? Explain your answer in each case.

[2 marks]

$^{79}\text{Br}^+$ or $^{81}\text{Br}^+$

$^{12}\text{C}^1\text{H}_4^+$ or $^{13}\text{C}^1\text{H}_4^+$

04 The mass spectrum of a sample of gallium is shown.

04.1 What isotopes are present in this element? [1 mark]

04.2 Calculate the relative atomic mass of this element. Give your answer to the appropriate number of significant figures. Show your working. [2 marks]
05 The mass spectrum of the element chlorine (Cl_2) is shown.

Identify the ion responsible for the peak at:

\( m/z \) 70 ______________
\( m/z \) 72 ______________
\( m/z \) 74 ______________

[2 marks]

06 The mass spectrum shown is of a hydrocarbon that has been produced via electron impact ionisation.

06.1 What is the relative molecular mass of this compound? [1 mark]

06.2 Why are there peaks with much lower \( m/z \) ratios? [1 mark]
06.3 Why is there a peak / peaks with higher m/z ratios?


07 The mass spectrum shown is of a protein that has been produced by electrospray ionisation.

![Mass Spectrum]

What is the relative molecular mass of this protein?


08 The kinetic energy of the ions in a TOF mass spectrometer is given as: $$KE = \frac{1}{2}mv^2$$

and the time to travel through the flight tube as: $$t = \frac{d}{v}$$

where:

- $$t$$ = time of flight (s)
- $$KE$$ = kinetic energy of particle (J)
- $$m$$ = mass of the particle (kg)
- $$v$$ = velocity of the particle (m s\(^{-1}\))
- $$d$$ = length of flight tube (m)
08.1 Show how these expressions can be used to show the time of flight as: \[ t = \frac{d}{\sqrt{\frac{m}{2KE}}} \] [2 marks]

08.2 A sample of copper was analysed and found to contain two isotopes, $^{63}$Cu and $^{65}$Cu. All the ions were accelerated to have $1.000 \times 10^{-16}$ J of kinetic energy and travelled through a flight tube that was 0.8000 m long. $^{63}$Cu$^+$ ions took $1.829 \times 10^{-5}$ s.

How long would $^{65}$Cu$^+$ ions of mass $1.079 \times 10^{-25}$ kg take to travel along the same flight tube?
Give your answer to the appropriate number of significant figures.
Show your working. [2 marks]
Example answers

01.1 ✓ high energy electrons
✓ from hot cathode / electron gun
✓ fired at sample
✓ knocks off one electron

01.2 ✓ sample dissolved in volatile solvent
✓ injected through a fine hypodermic needle giving a fine mist / aerosol
✓ tip of needle has high voltage
✓ each gains a proton as it leaves the needle

01.3 ✓ electron impact / electron ionisation

01.4 ✓ Ca(g) → Ca⁺(g) + e⁻
✓ C₂H₆(g) → C₂H₆⁺(g) + e⁻

01.5 ✓ C₃H₆O₂ + H⁺ → C₃H₇O₂⁺

02.1 ✓ as the positively charged ions are attracted to the negative plate

02.2 ✓ same kinetic energy

03.1 ✓ time of flight depends on mass of ions
✓ lighter particles travel faster

03.2 ✓ ⁷⁹Br⁺ as it is lighter
✓ ¹²C¹H₄⁺ as it is lighter

04.1 ✓ ⁶⁹Ga and ⁷¹Ga

04.2 ✓ \[ \frac{(69.0 \times 60.1) + (71.0 \times 39.9)}{60.1 + 39.9} \]
✓ = 69.8 (3sf)

05 ³⁵Cl⁺, ³⁵Cl⁻, ³⁷Cl⁺, ³⁷Cl₂⁺
✓ for correct isotopes
✓ for + charge in each case

06.1 ✓ 56

06.2 ✓ due to fragmentation

06.3 ✓ due to some molecules containing ²H or ¹³C
07  \( \checkmark  \) 484.1

08.1  \( \checkmark v^2 = \frac{2KE}{m} \)  \( \therefore v = \sqrt{\frac{2KE}{m}} \)

\( \checkmark t = \frac{d}{v} \)  \( \therefore t = \frac{d}{\sqrt{\frac{2KE}{m}}} \)  \( \therefore t = d \sqrt{\frac{m}{2KE}} \)

08.2  \( \checkmark t = 0.8000 \sqrt{\frac{1.079 \times 10^{-24}}{2 \times 1 \times 10^{-16}}} \)

\( \checkmark 1.858 \times 10^{-5} \text{ s (4sf)} \)