Loughborough University

MASS SPECTROMETRY AND ASSOCIATED TECHNIQUES

22CMP058

Semester 1 2022/23 In-Person Exam paper

This examination is to take place in-person at a central University venue under exam conditions. The standard length of time for this paper is **2 hours**.

You will not be able to leave the exam hall for the first 30 or final 15 minutes of your exam. Your invigilator will collect your exam paper when you have finished.

Help during the exam

Invigilators are not able to answer queries about the content of your exam paper. Instead, please make a note of your query in your answer script to be considered during the marking process.

If you feel unwell, please raise your hand so that an invigilator can assist you.

You may use a calculator for this exam. It must comply with the University's Calculator Policy for In-Person exams, in particular that it must not be able to transmit or receive information (e.g. mobile devices and smart watches are **not** allowed).

Answer all **THREE** questions. Use a **SEPARATE ANSWER BOOK** for **EACH QUESTION**.

1. Answer **ALL** parts

(a) Butylisopropylamine has a molecular formula of $C_7H_{17}N$. Using the structure and the Electron Ionisation (EI) spectrum provided in Figure 1, propose a fragmentation scheme for the ions at m/z 115, 114, 100, 72, 58, 44, and 30.

[18 marks]

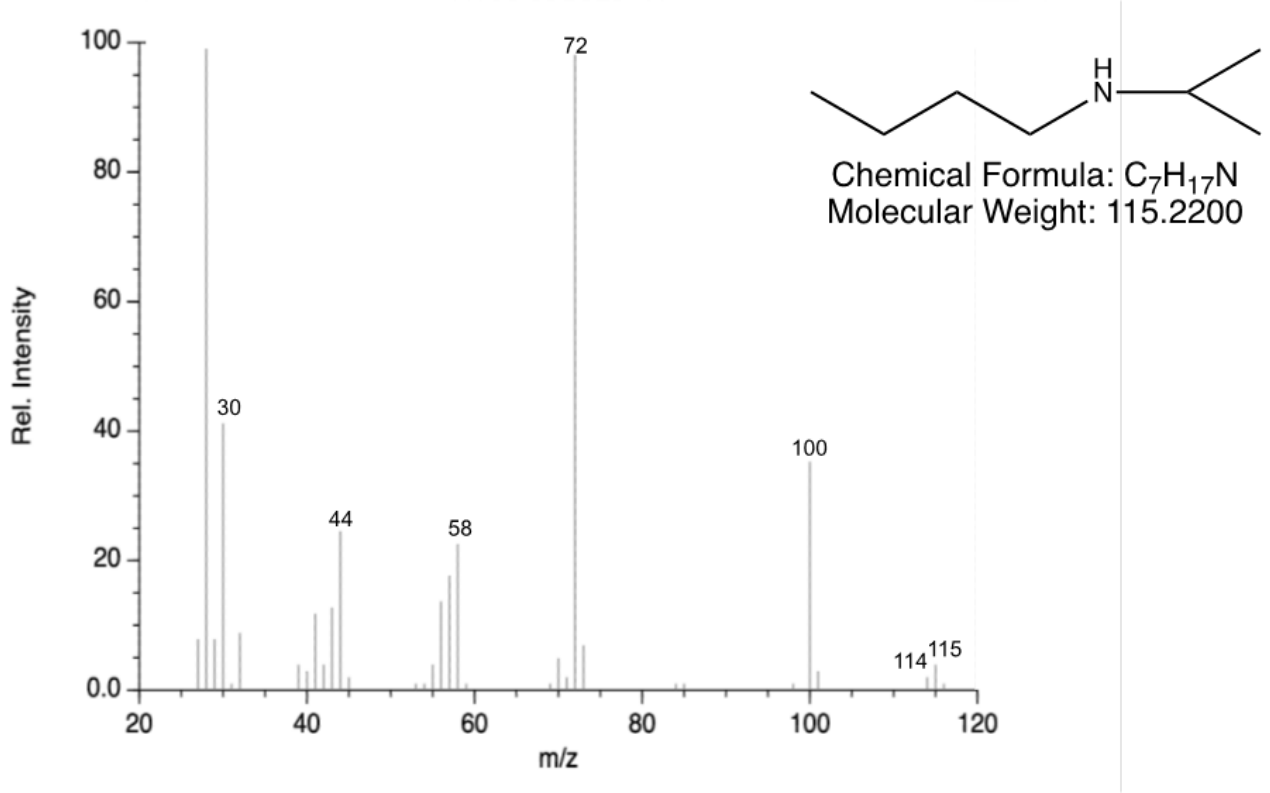


Figure 1. Electron Ionisation (EI) spectrum and structure of Butylisopropylamine

(b) Explain why 70eV is the default ionisation voltage used in an Electron Ionisation source.

[7 marks]

2. Answer **ALL** parts

(a) A magnetic sector mass spectrometer has a fixed accelerating voltage of 8 kV and a radius of 0.25 m. What magnetic field strength range would need to be applied in order to scan across a m/z range from 5 to 250 Da?

[charge on an electron = 1.60×10^{-19} C, mass of a Dalton = 1.66×10^{-27} kg]

[8 marks]

continued.....

(b) Explain why mass spectrometers containing a magnetic analyser are often fitted with a second mass analyser to create a double focussing instrument.

[5 marks]

(c) Name one configuration of double-focussing mass spectrometer and sketch a labelled diagram of it.

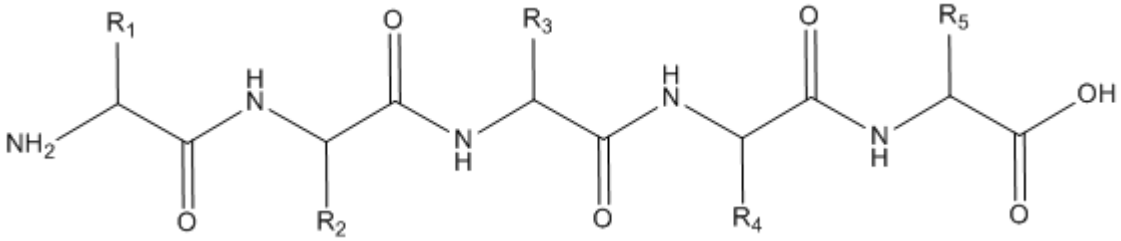
[6 marks]

(d) Explain why magnetic sector instruments are now less common, compared to quadrupole instruments. Your answer should also indicate any scenarios where magnetic sector instruments might still be favoured.

[6 marks]

3. Answer **ALL** parts

(a) Peptide ions can be fragmented using tandem mass spectrometry to give a range of diagnostic fragment ions that can be used to determine the identity of their parent protein. Sketch out the structure of the model pentapeptide below and indicate on the structure where the b_3, y_2, a_4 and y_4 ions originate from, making sure to indicate where the charge is retained.



[7 marks]

(b) Sketch out the structure of the ion formed from subsequent a_4 and y_4 fragmentations making sure to indicate where the charge is located. What is this type of ion called and what information can it give you?

[3 marks]

continued...

(c) Explain why b and y type fragment ions are the main fragment ions observed in low energy collision induced dissociation spectra obtained from peptide ions.

[3 marks]

(d) Explain the role of a nebuliser and a spray chamber in inductively coupled plasma – mass spectrometry (ICP-MS).

[4 marks]

(e) Figure 2 shows time resolved data for the analysis of a copper solution, measured by four different analysts using ICP-MS. Discuss the four graphs and suggest reasons for the trends observed. Would you advise any of the analysts to repeat the experiment using an adjusted method?

[8 marks]

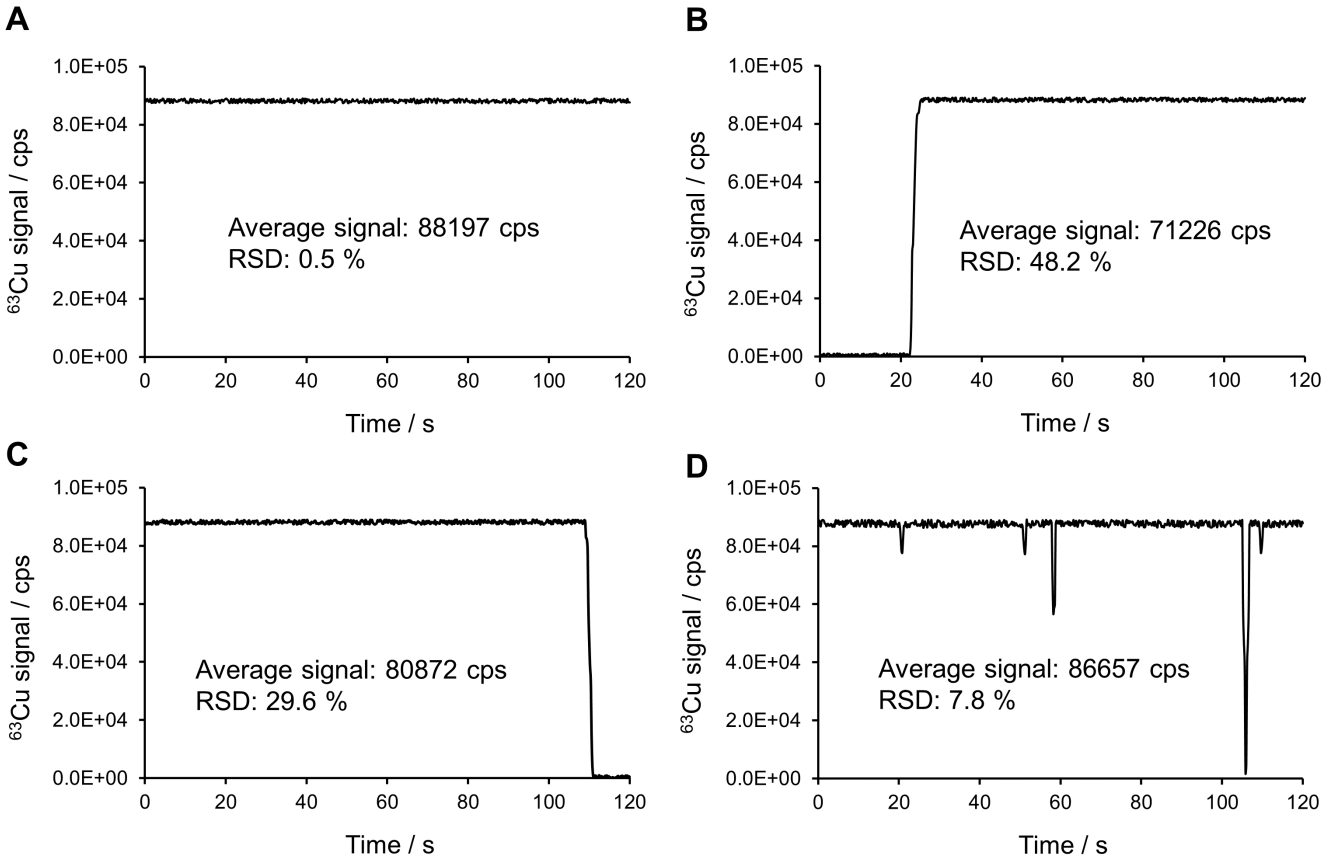


Figure 2. Graphs showing the signal obtained over a 2-minute analysis window for the analysis of copper in a sample by ICP-MS. Data collected by four different analysts is shown, labelled A-D, along with the average signal and percent relative standard deviation across each analysis.

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