

Acknowledgements

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We very much hope that this resource book will help facilitate the learning and teaching of Section 12.8 “Structure determination of organic compound” of the revised Advanced Level Chemistry Curriculum and be a handy guide for students and teachers in secondary schools in Hong Kong.

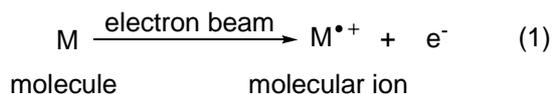
Introduction

Identifying the structures of organic compounds is very important in organic chemistry. Only when the structure of a compound becomes known, chemists can design efficient ways to synthesise it and perform detailed studies of its chemical, physical or biological properties.

Traditionally, the structures of organic compounds were identified by determining their empirical formulae by “elemental analysis” and studying their physical and chemical properties by a series of tests. These methods are impractical if the amount of sample is limited or when the compound has a very complicated structure.

Modern technology has led to the development of many advanced instrumental techniques which can provide a lot more detailed information about the structure of a compound than simple chemical tests do. **Mass spectrometry** is one of the most widely used instrumental techniques. It enables us to determine the molecular mass and molecular formula of a compound, as well as certain structural features of the compound.

To obtain a **mass spectrum**, a tiny amount of the sample is introduced into a **mass spectrometer**, where the sample is vapourised by heating under reduced pressure. The molecules in the gas phase are then bombarded by an energetic beam of electrons causing an electron to be removed from the molecule. The **molecular ion** formed is basically a radical cation with an unpaired electron (eq. 1).



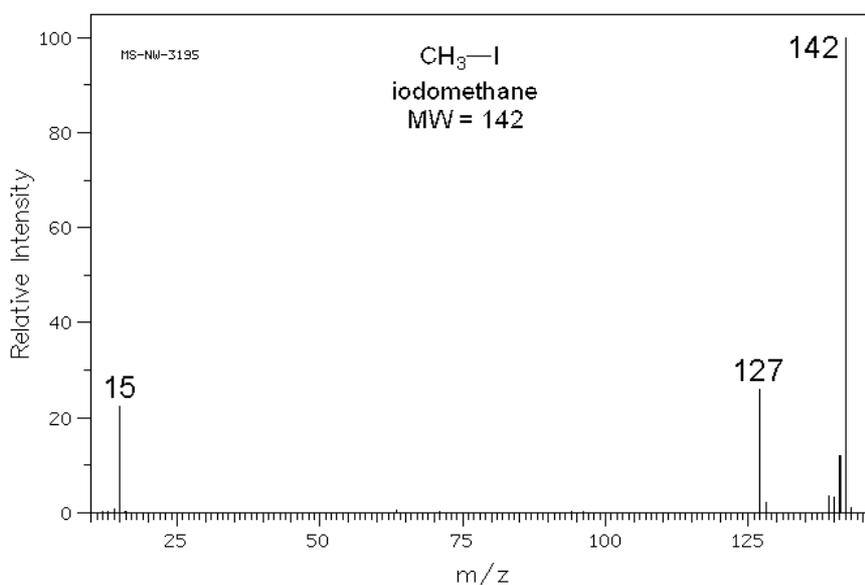
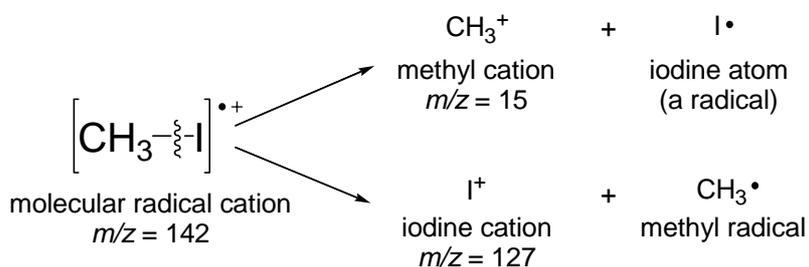
The molecular ion so formed will undergo fragmentation. The fragments generated can be cations, radicals, neutral molecules or radical cations.

The **mass-to-charge ratios** (m/z) and the intensities of the molecular and fragment ions are recorded on the mass spectrum. Since most of the ions recorded on the mass spectrum possess a +1 charge, the m/z values correspond to the masses of the species, compared to $^{12}\text{C} = 12.00$.

Certain bonds adjacent to a functional group are more readily to be cleaved. The intensities of the fragment peaks depend on the strength of the chemical bonds involved and the stability of the fragment ions. Ions with a higher stability will usually give a more intense signal as a large number of these ions are generated and detected in the recorder. Thus fragmentation provides invaluable information about the structure of the molecule.

The peak for the molecular radical cation is known as the **molecular ion peak**. Peaks with smaller m/z values are due to the fragment ions. The peak that has the highest intensity is called the **base peak**, which corresponds to the species which has the highest stability.

The mass spectrum of iodomethane is given below as an example. The spectrum shows the base peak at $m/z = 142$, which is also the molecular ion peak. This peak corresponds to the radical cation of iodomethane. The C—I bond in the molecular ion breaks preferentially to give a methyl cation (CH_3^+ , $m/z = 15$) and an iodine atom, or an iodine cation (I^+ , $m/z = 127$) and a methyl radical. By comparing the peak intensities, it suggests that the molecular radical cation has a higher stability than the two fragment ions.

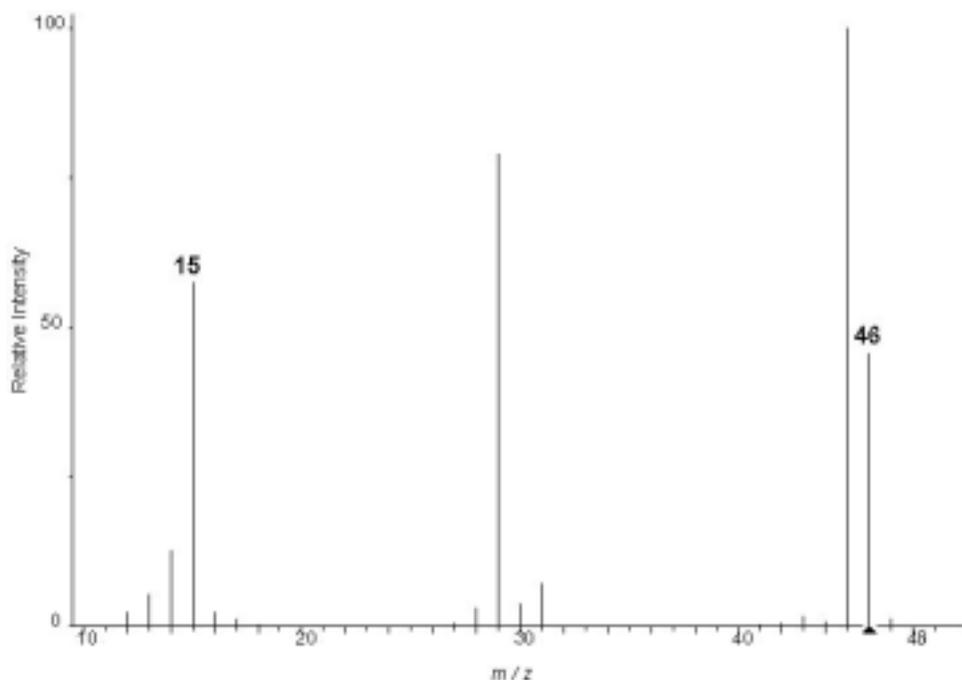


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Exercise and Suggested Solutions

1. Compound A has the following composition by mass: 52.1% of C, 13.2% of H, and 34.7% of O. It does not react with active metals such as sodium and potassium. The mass spectrum of compound A is shown below.

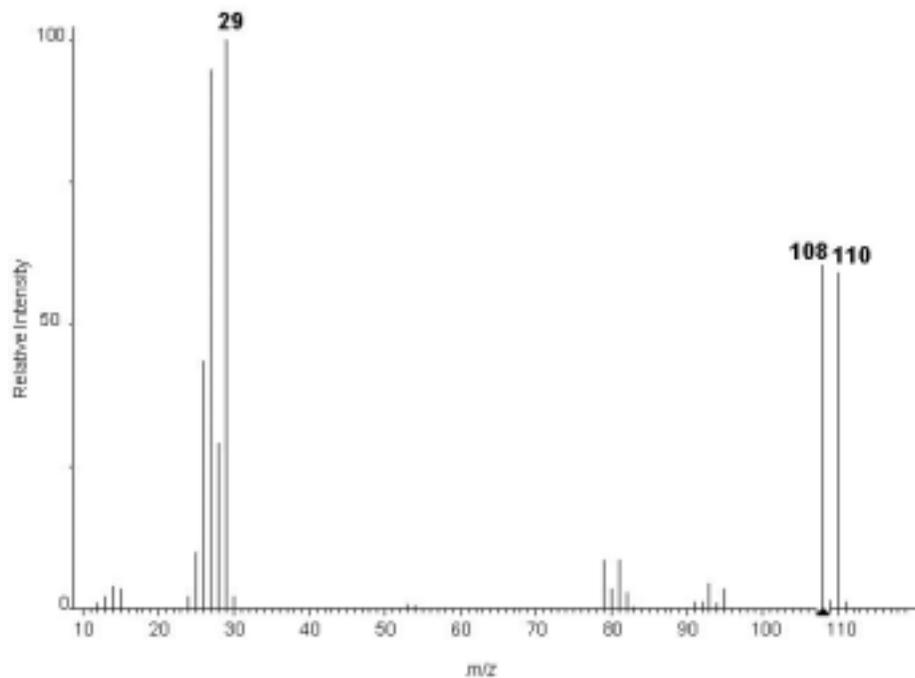
(Relative atomic masses: $C = 12.0$, $H = 1.0$, $O = 16.0$)



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- Determine the empirical formula of compound A.
- Using the information in the mass spectrum, determine the molecular formula of compound A.
- Draw all possible structures of compound A.
- What fragment is responsible for the peak at $m/z = 15$?
- Identify compound A.

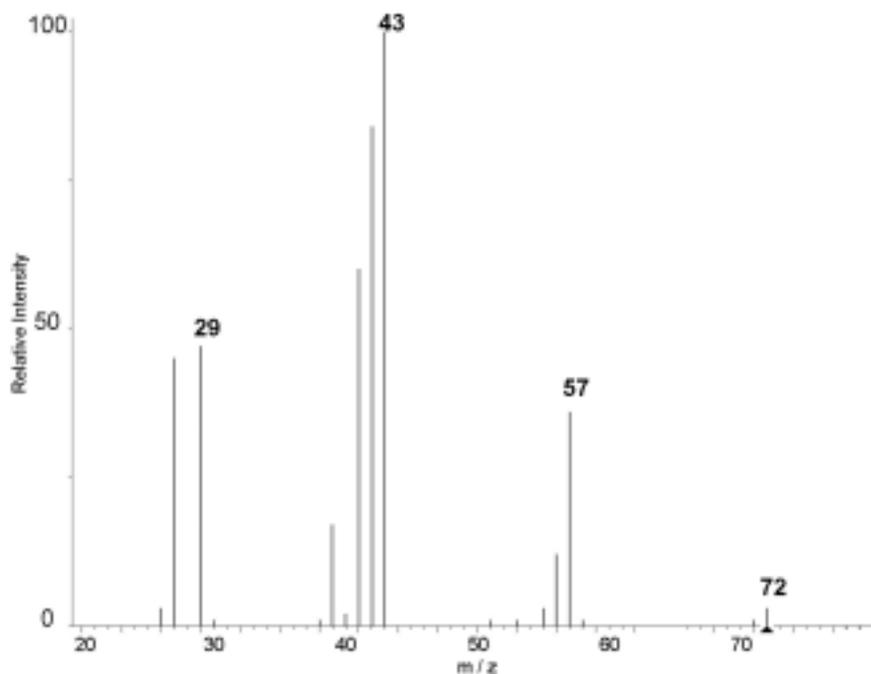
2. Shown below is the mass spectrum of a haloalkane B.
- What is the fragment for the base peak at $m/z = 29$?
 - Deduce and explain the halogen present in the compound. Hence, identify compound B.
 - Suggest why the two peaks at $m/z = 108$ and 110 have almost the same intensity?



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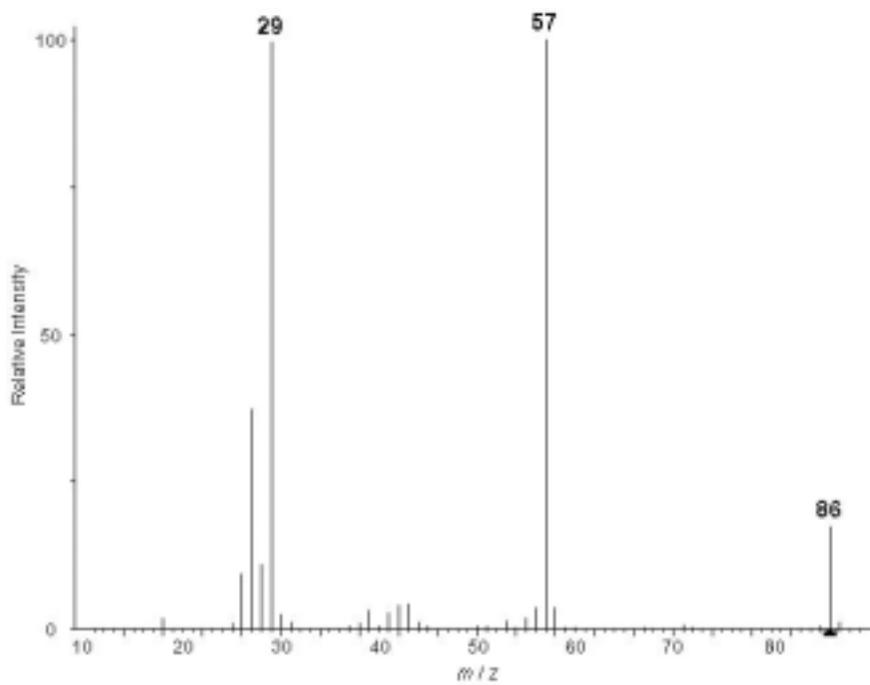
(Relative atomic masses: $F = 19.0$, $Cl = 35.5$, $Br = 79.9$, $I = 126.9$)

3. The following figure shows the mass spectrum of a hydrocarbon.
- Propose a molecular formula for this compound assuming that the molecular ion can be detected.
 - Draw the structural formulae of all possible isomers of this hydrocarbon.
 - By considering the relative intensity of the labelled peaks, suggest the most plausible structure for this hydrocarbon.



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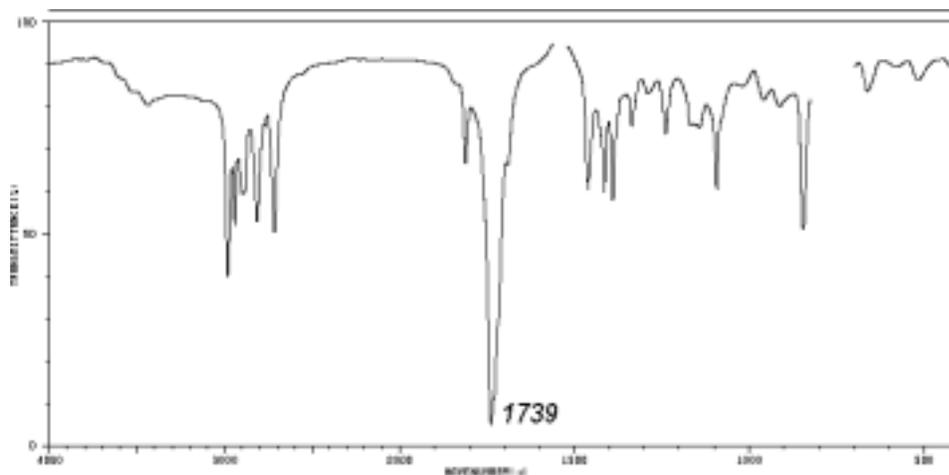
4. Shown below is the mass spectrum of an unknown acyclic compound C. This compound reacts with 2,4-dinitrophenylhydrazine to give an orange precipitate, and gives no observable change when treated with acidified potassium dichromate(VI).



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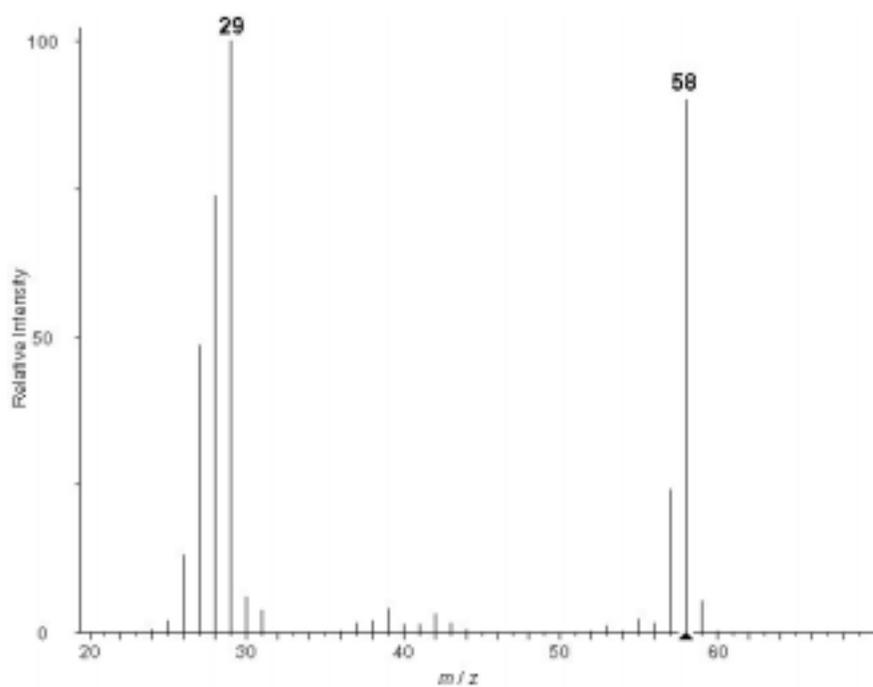
- Based on the results of chemical tests, deduce the functional group of compound C?
- Deduce the molecular formula of compound C.
- What are the fragments for the peaks at $m/z = 29$ and 57 ?
- With the above information, identify compound C.

5. The infrared and mass spectra of an unknown compound D are given below. Deduce the structure of this compound from these spectra.



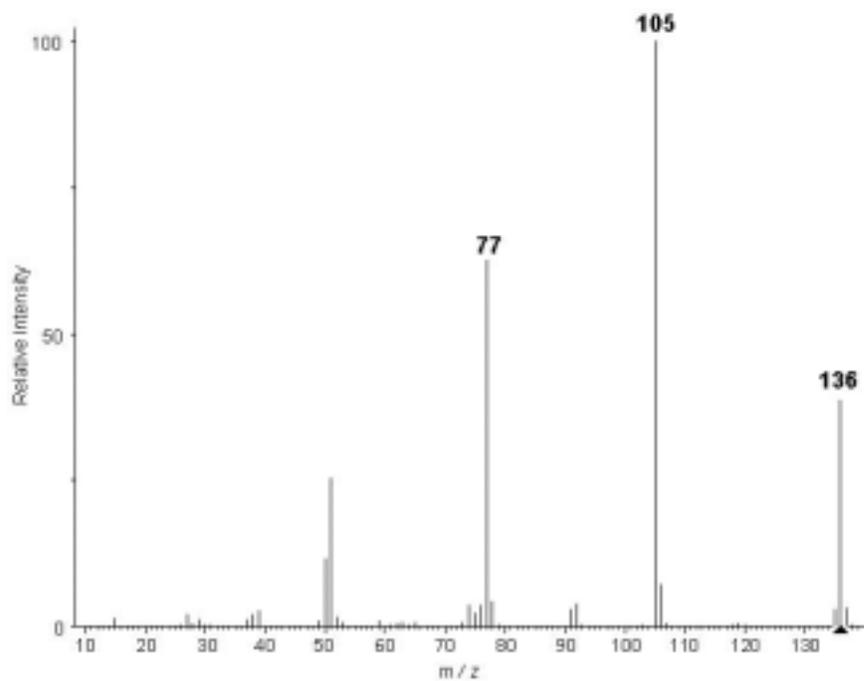
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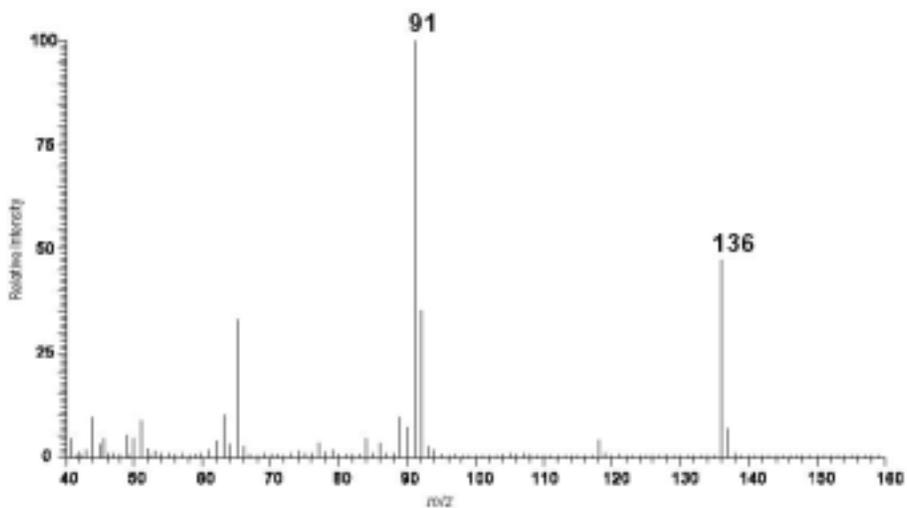
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6. Compound E is a volatile organic liquid with a fruity smell. Its mass spectrum is given below. Identify the fragments at $m/z = 77$ and 105, then propose a structure for this compound.



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7. Compound F is a mono-substituted aromatic compound which dissolves readily in aqueous sodium carbonate solution. Its mass spectrum is given below. Identify the base peak at $m/z = 91$, then propose a structure for this compound.



References

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