

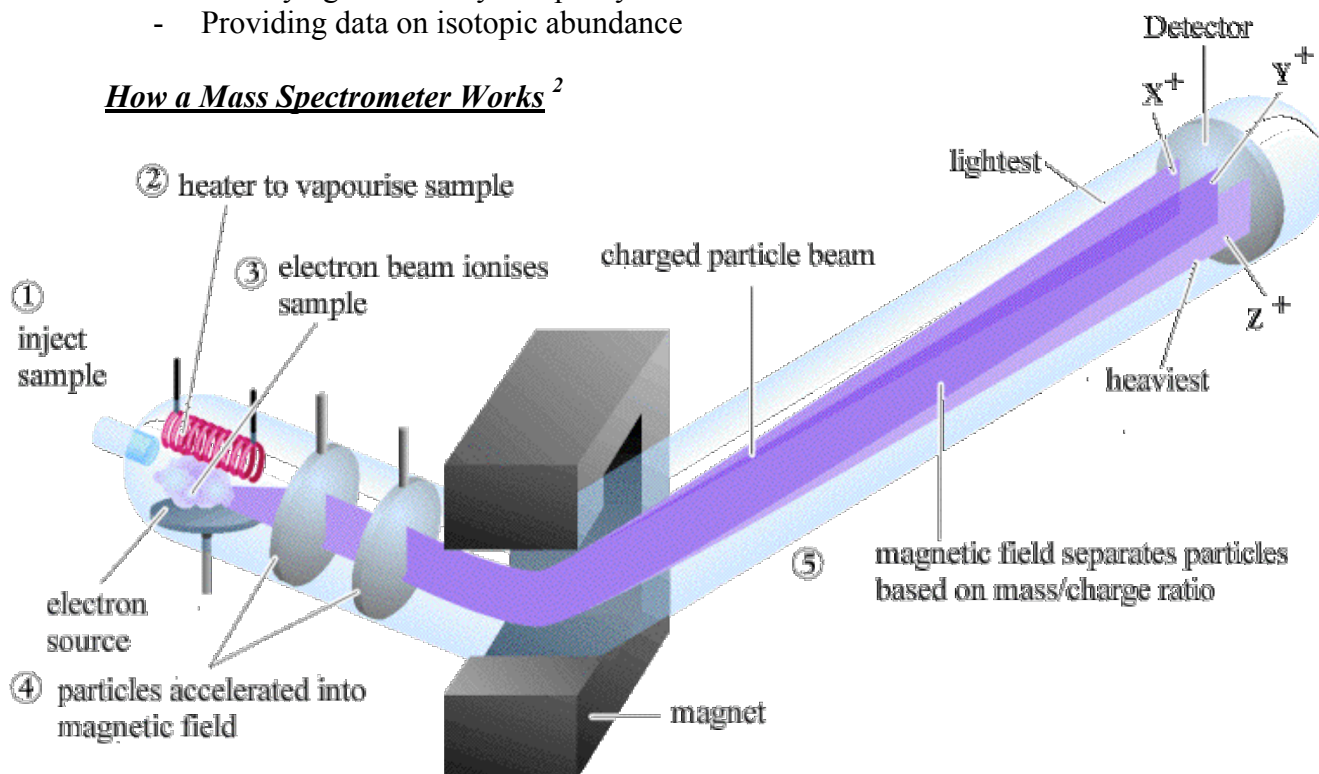
Mass Spectrometry

Overview

Mass Spectrometry is an analytic technique that utilizes the degree of deflection of charged particles by a magnetic field to find the relative masses of molecular ions and fragments.² It is a powerful method because it provides a great deal of information and can be conducted on tiny samples. Mass spectrometry has a number of applications in organic chemistry, including:

- Determining molecular mass
- Finding out the structure of an unknown substance
- “Verifying the identity and purity of a known substance”¹
- Providing data on isotopic abundance

How a Mass Spectrometer Works²



* Figure A³

Step 1: The sample is vaporized, and then ionized by being bombarded by a beam of high-energy electrons (usually at 70 eV). The electron beam knocks out an electron from the molecule of the injected sample, creating a **molecular ion** (which is also a **radical cation** because it has an unpaired electron and a positive charge). Losing an electron weakens the bond, while the collision gives it extra kinetic energy. These factors make it more likely for the molecular ion to break into fragments as it travels through the mass spectrometer.

Step 2: There is a pair of oppositely charged plates in the ionization chamber. The positively charged one causes the positively charged radical cation to accelerate into an analyzer tube.

¹ Chem 14C Course Thinkbook by Professor Steven Hardinger, Summer 2006 Version, Pg. 41

² Bibliographical source: Pg. 702 of Atkins and Jones, Chemical Principles, 3rd Edition and Pg. 484 of Bruice, Organic Chemistry, 4th Edition

³ Figure A from <http://www.chem.ucalgary.ca/courses/351/Carey/Ch13/1334.gif> (Site visited on 8/23/06)

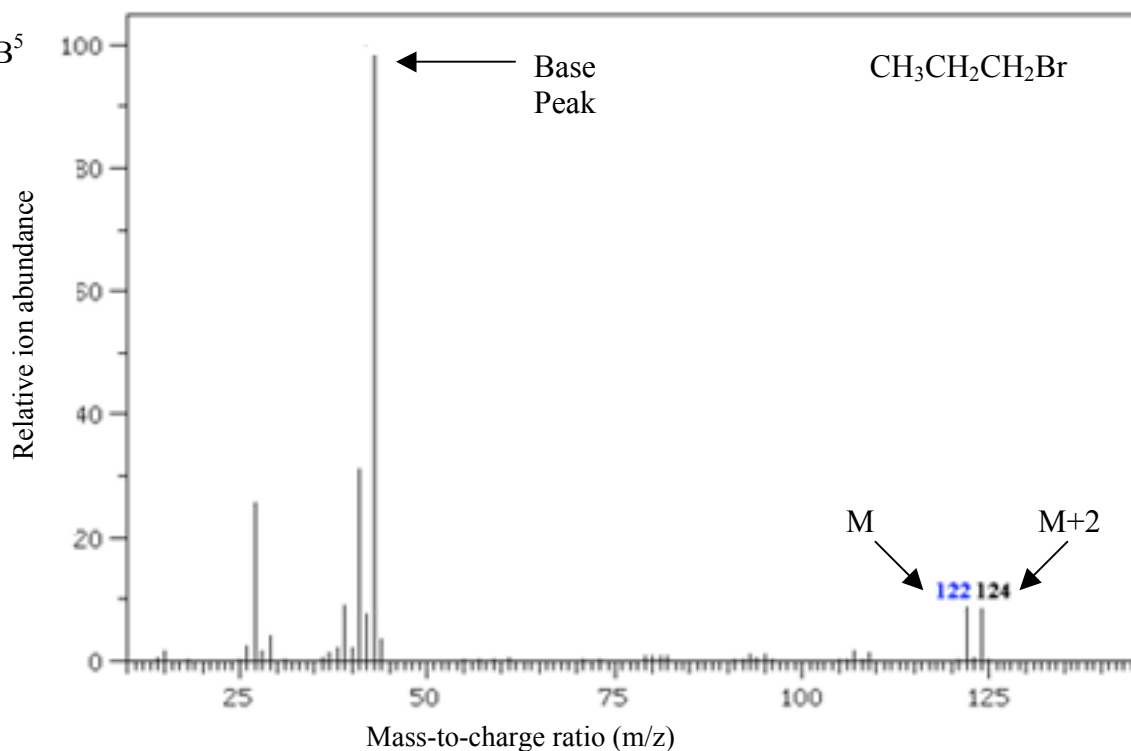
Step 3: The analyzer tube is surrounded by a curved magnetic field, which causes the path of the radical cation to be deflected in proportion to its **mass-to-charge ratio (m/z)**. The flight path of the ion depends on its molecular mass, its charge, and the strength of the magnetic field. Thus, at a given magnetic field strength, ions of only one specific mass collide with the detector and are recorded.

Step 4: The strength of the magnetic field is varied in increments to produce a **mass spectrum**, which is a plot of m/z (on the x axis) against relative abundance (on the y axis). If we assume that all ions have a charge of +1, then the peaks give the mass ratios and their heights give the proportions of ions of different masses.

Aston and Thomson used a process similar to the one outlined above to acquire the mass spectrum of neon in 1919. They observed that neon's mass spectrum had two peaks: one at m/z 20 (90% abundance) and one at m/z 22 (10%), but no peak at the atomic weight of Neon (20.20, which is the weighted average). Since Neon is inert and lacks chemical bonds, the peaks did not correspond to masses of fragments of the molecular ion, but to the masses of different isotopes of Neon. The experiment's conclusion was that "neon has two natural isotopes: ^{20}Ne (90% abundance) and ^{22}Ne (10% abundance)"⁴. This was the first time that an isotope had been detected for a non-radioactive substance. Note that modern spectrometers actually indicate that neon has a third isotope.

Interpreting a Mass Spectrum

*Figure B⁵



⁴ Quoted from Chem 14C Course Thinkbook by Professor Steven Hardinger, Summer 2006 Version, Pg. 215

⁵ Mass spectrum from <http://www.chem.ucalgary.ca/courses/351/Carey/Ch13/ch13-ms.html> (labels have been modified in Adobe Photoshop); Site visited on 8/24/06

The mass spectrum of 1-bromopropane shown on the previous page illustrates some characteristic features.

The **Base Peak** is the peak with the greatest intensity (usually set to 100% relative abundance) in the mass spectrum, corresponding to the most abundant ion. (M and the base peak are only the same if many of the molecular ions make it to the detector without breaking into fragments). Since M+1 and M+2 are always less intense than M, they can never be the base peak.

M is the molecular ion (un-fragmented molecule minus one electron) made up of “isotopes with the lowest mass numbers (H¹, C¹², etc)”⁶ This peak will most likely be indicated on an exam, but is usually the highest peak with the largest m/z.

- ✓ When we assume that z=1 (charge is usually +1), M provides the mass (in amu) of the compound with the lowest mass isotopes.
- ✓ To find the m/z for the M peak of a compound, refer to the table of natural isotopes (Chem 14C Thinkbook, Summer 2006, Pg. 42) and multiply the isotopic mass (not the atomic weight!) of each atom by the number of atoms of each in the formula.
- ✓ EX: We expect the M peak of CH₃CH₂CH₂Br should be at (3)(12)+(7)(1)+(1)(79)=122. This is verified by the mass spectrum above. Note that we use the isotopic mass, not the atomic weight, of each atom.

M+1 is next-door to M on the mass spectrum, and corresponds to the molecular ion with mass one higher than M due to presence of “one atom that is a heavier isotope”⁶

- ✓ EX: For 1-bromopropane, the M peak is at 122, so the M+1 peak should be at 122+1=123
- ✓ Only ¹³C, ¹⁵N, and ³³S contribute significantly to the M+1 peak, ¹³C is most important
- ✓ If M is scaled to 100%, then the M+1 intensity/1.1% gives an estimate for the number of carbons in the compound. BE CAREFUL TO AVOID MATH ERRORS HERE!

Note about rounding:

- ✓ If remainder is 0.4 or less, then round down
- ✓ If remainder is 0.7 or more, then round up
- ✓ It is important to be conservative in mass spectrometry, so if remainder is between 0.4-0.7, then consider two different carbon counts for formula candidates. Some of these may be rejected later based on other data.

EX: If the relative abundance of the M+1 peak (relative to M) is 4.95%, how many carbons are there in the formula?

ANSWER: $4.95/1.1 = 4.5$ There are 4 or 5 carbons!

M+2 is next-door to M+1 on the mass spectrum, and has a mass two higher than M.

- ✓ EX: For 1-bromopropane, the M peak is at 122, so the M+2 peak should be at 122+2=124
- ✓ For our purposes, the elements that make significant contributions to this peak are ³⁴S, ³⁷Cl, and ⁸¹Br.
- ✓ The M:M+2 ratio indicates the presence of S(100:4.4), Cl (100:31.9), or Br(100:97.2) in the compound.

⁶ Quoted from Chem 14C Course Thinkbook by Professor Steven Hardinger, Summer 2006 Version, Pg. 214

- ✓ **EX:** Notice that the M and M+2 peaks for 1-bromopropane are almost the same height, revealing that Br is a component of the molecule.

Getting the Formula from the Mass Spectrum⁷

The **Nitrogen Rule** states that if m/z for M is odd, then the molecular formula must have an odd number of nitrogens. If m/z for M is even, then the molecular formula must have an even number of nitrogens (this includes 0).

- ✓ **EX:** For 1-bromopropane, m/z for M=122. The even number is in accordance with the even number of nitrogens in the formula (zero).

The **Hydrogen Rule** states that the maximum number of hydrogens in the molecular formula is $2C+N+2$. In the formula, C: # of carbons, N: # of nitrogens

- ✓ **EX:** For $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$, there are three carbons, so the max # of hydrogens is $2(3)+2=8$

Getting the Molecular Structure from the Formula

One **Double Bond Equivalent (DBE)** (also known as a **degree of unsaturation**) is one pi bond or one ring. A triple bond counts as 2 DBE. Having 4 DBE indicates the possibility of a benzene ring, since benzene has three pi bonds plus one ring. The formula for DBE is the following:

$\text{DBE} = C - (\text{H}/2) + (\text{N}/2) + 1$	C: # of carbons H: # of hydrogens or halogens N: # of nitrogens
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* Formula⁸

Important Note: DBE can never be negative and can never be fractional! Beware of math errors!

- ✓ **EX:** For $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$, the DBE equals $3 - (8/2) + (0/2) + 1 = 0$. (No pi bonds, no rings.)

Putting it All Together

EX: Use the given mass spectrometry data to determine the molecular formula.

	m/z	Relative Intensity
M	59	100%
M+1	60	3.85%
M+2	61	0.0127%

ANSWER:

⁷ Nitrogen and Hydrogen Rules are outlined in the Chem 14C Course Thinkbook by Professor Steven Hardinger, Summer 2006 Version, Pg. 44-45

⁸ Formula from Chem 14C Course Thinkbook by Professor Steven Hardinger, Summer 2006 Version, Pg. 44-45

Step 1: Check to see if the relative intensity of the M peak is 100%. If not, you would have to rescale the values.

Step 2: Is the m/z value for the M peak even or odd? The M peak equals the molecular mass of the compound, which in this case is 59 amu. This is an odd number, so according to the Nitrogen Rule, there must be an odd number of nitrogen atoms in the compound. The minimum number of nitrogen atoms is one.

Step 3: Use the relative intensity of the M+1 peak to find the number of carbon atoms. Here, $3.85\%/1.1\% = 3.5$. This means that there are three or four carbons in the compound.

Step 4: Look at the M+2 peak to check for the presence of S, Cl, or Br. Since the intensity of the M+2 peak is less than 4% (approximate relative abundance of S), there are no S, Cl, or Br atoms in this molecule.

Step 5: Subtract the isotopic masses of the known atoms from the mass of the entire compound (m/z of M peak). The remaining value represents the amu left over for the other atoms. So,

$M - C_3 - N$ ← We must have at least 3 C and 1 N

$59 - (3(12) + 14) = 9$ amu left over for O, H, more N atoms (must be odd), or another C atom.

Step 6: Evaluate all possibilities for the molecular formula, and assess whether they are reasonable.

In this instance, there is no need to construct a chart for the number of each type of atom. 9 amu are not enough for oxygen (16 amu), nitrogen (14 amu each), or another carbon (12 amu). Thus, the 9 amu must come from nine hydrogen atoms.

In conclusion, the only possible molecular formula is C_3H_9N

EX: Assuming that the molecular ion is the base peak, create and fill out a chart containing the m/z and relative intensities for the M, M+1, and M+2 peaks for 2-chloropropane ($CH_3CHClCH_3$)

ANSWER:

	m/z	Relative Intensity
M	$3(12) + 7(1) + 35(1) = 78$	100% (we assume that it is the base peak)
M+1	$78 + 1 = 79$	$3(1.107\%) + 7(0.015\%) = 3.426\%$
M+2	$78 + 2 = 80$	$2(31.9\%) = 63.8\%$

^{37}Cl is the only significant contributor to the M+2 peak. It will increase the intensity of this peak only when one of the two chlorine atoms is ^{37}Cl (if they are both ^{37}Cl , then this contributes to the M+4 peak). We multiply the abundance of the isotope relative to M by 2 because there are two chlorine atoms. For the M+4 peak, since both chlorine atoms must be ^{37}Cl , we multiply the probabilities together: $31.9\%(31.9\%) = 10.176\%$