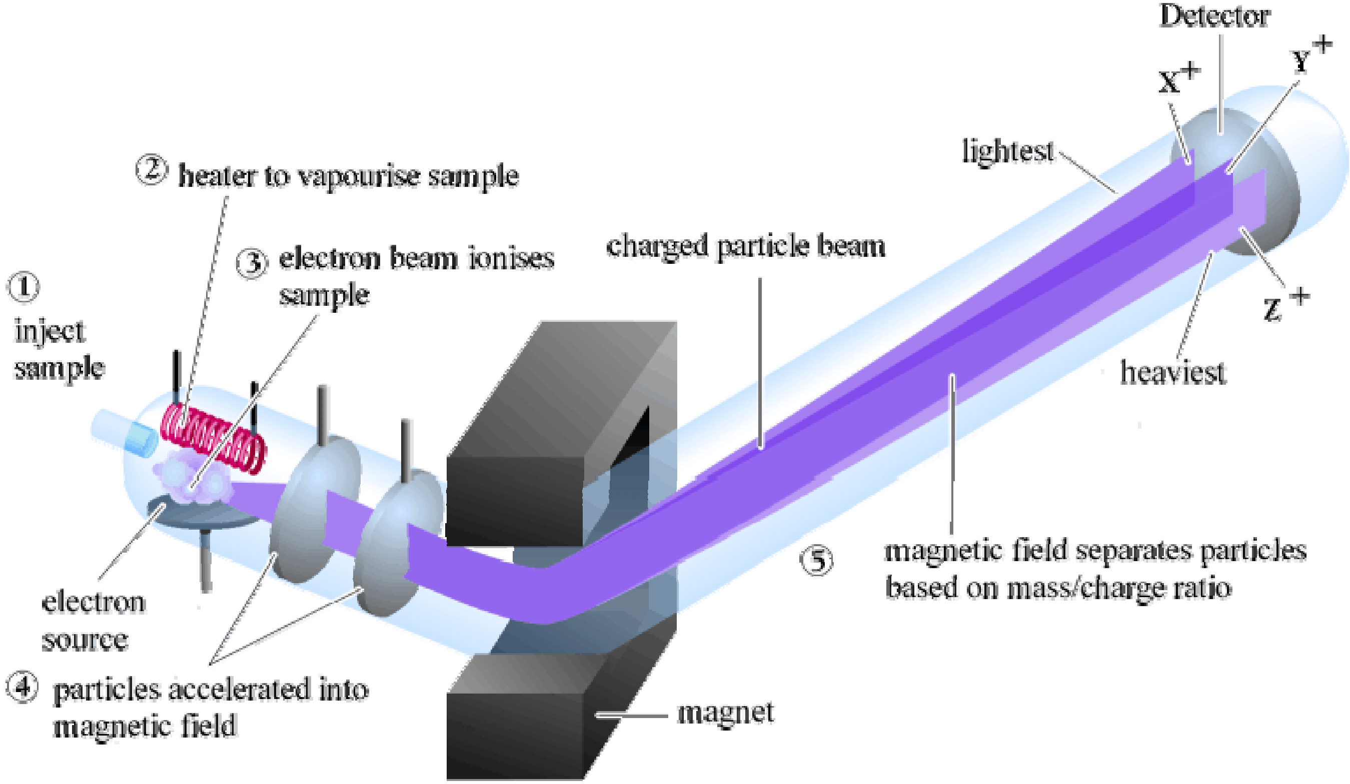
Mass spectrometry and elemental analysis

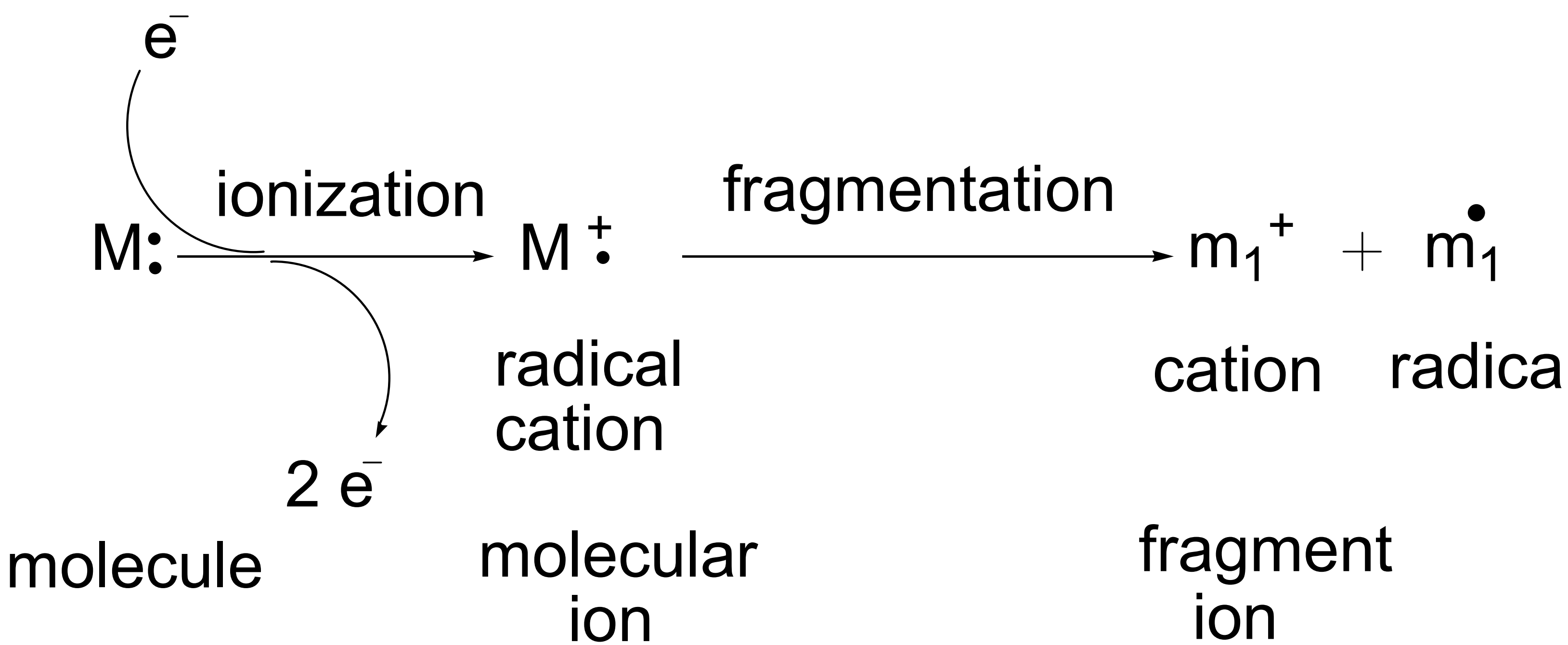
A schematic representation of a single-focusing mass spectrometer

with an electron-impact (EI) ionization source.

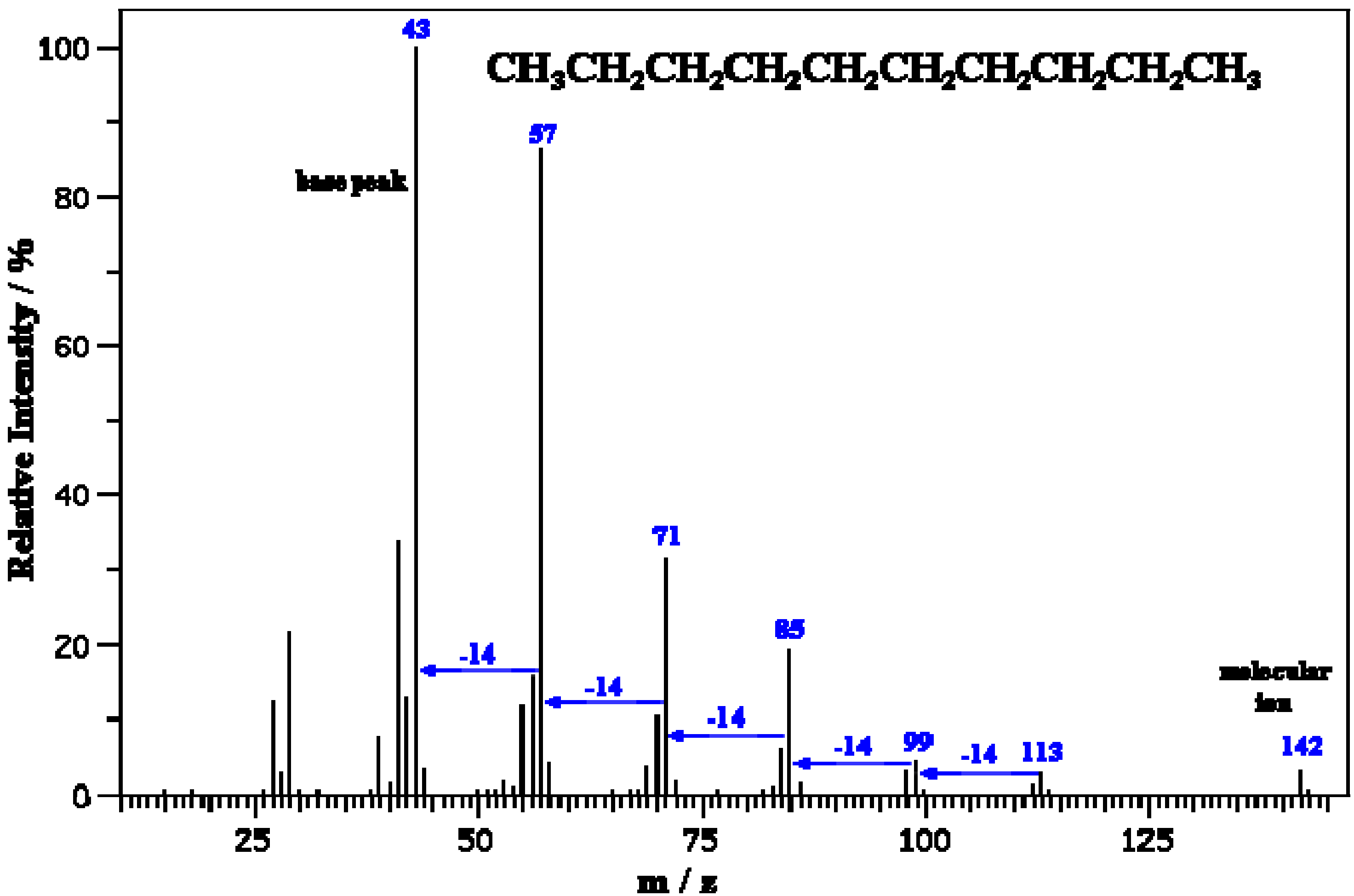
$$M: \quad + \quad e^{-} \longrightarrow M^{+\cdot} \quad + \quad 2e^{-}$$



Ionization and fragmentation processes in the EI ionization source of a mass spectrometer.



EI mass spectrum of *n*-decane. Note the molecular ion peak (M+• or M+) at m/z 142 and the base peak (the most intense peak) at m/z 43



Glossary

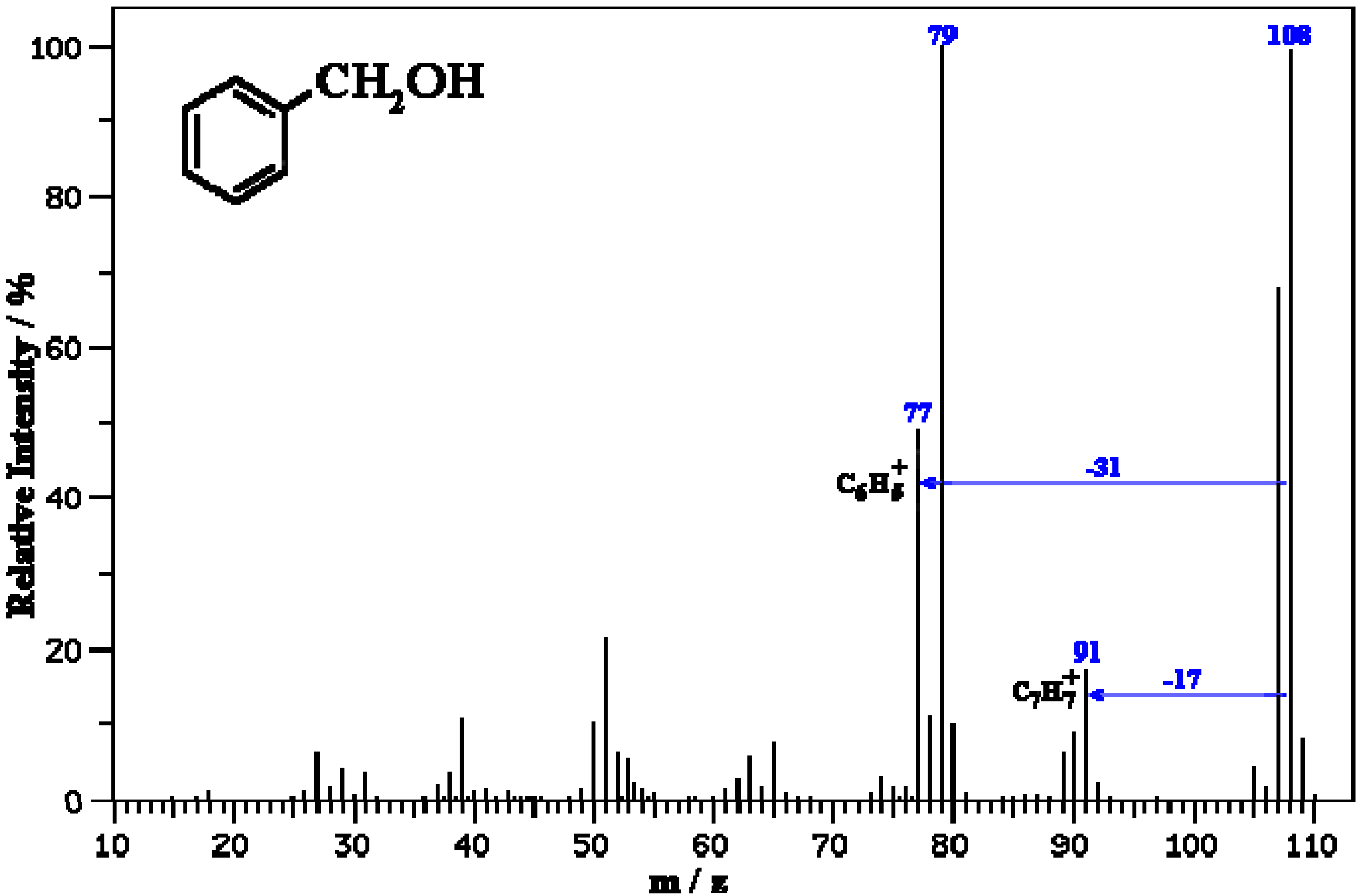
Molecular ion (**M+•** or **M+**) – The ion generated by the loss of an electron from the molecule (M••).

Radical cation – Positively charged species with an odd number of electrons.

Fragment ions – Lighter cations formed by the decomposition of the molecular ion. These often correspond to stable carbocations.

Base peak – The most intense peak in the mass spectrum, assigned 100% intensity.

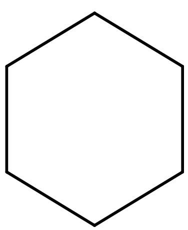
EI mass spectrum of benzyl alcohol



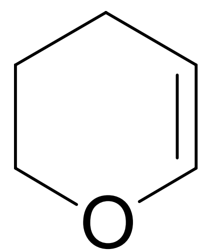
The low resolution mass spectra of different compounds with the same nominal molecular weight are often similar and cannot be used to differentiate between them.

Examples are the mass spectra of cyclohexane and 3,4-dihydro-2*H*-pyran with the molecular ion peak at m/z 84 and fragment ion peaks at m/z 69, 55, and 41 in both cases.

Cyclohexane



3,4-Dihydro-2H-pyran



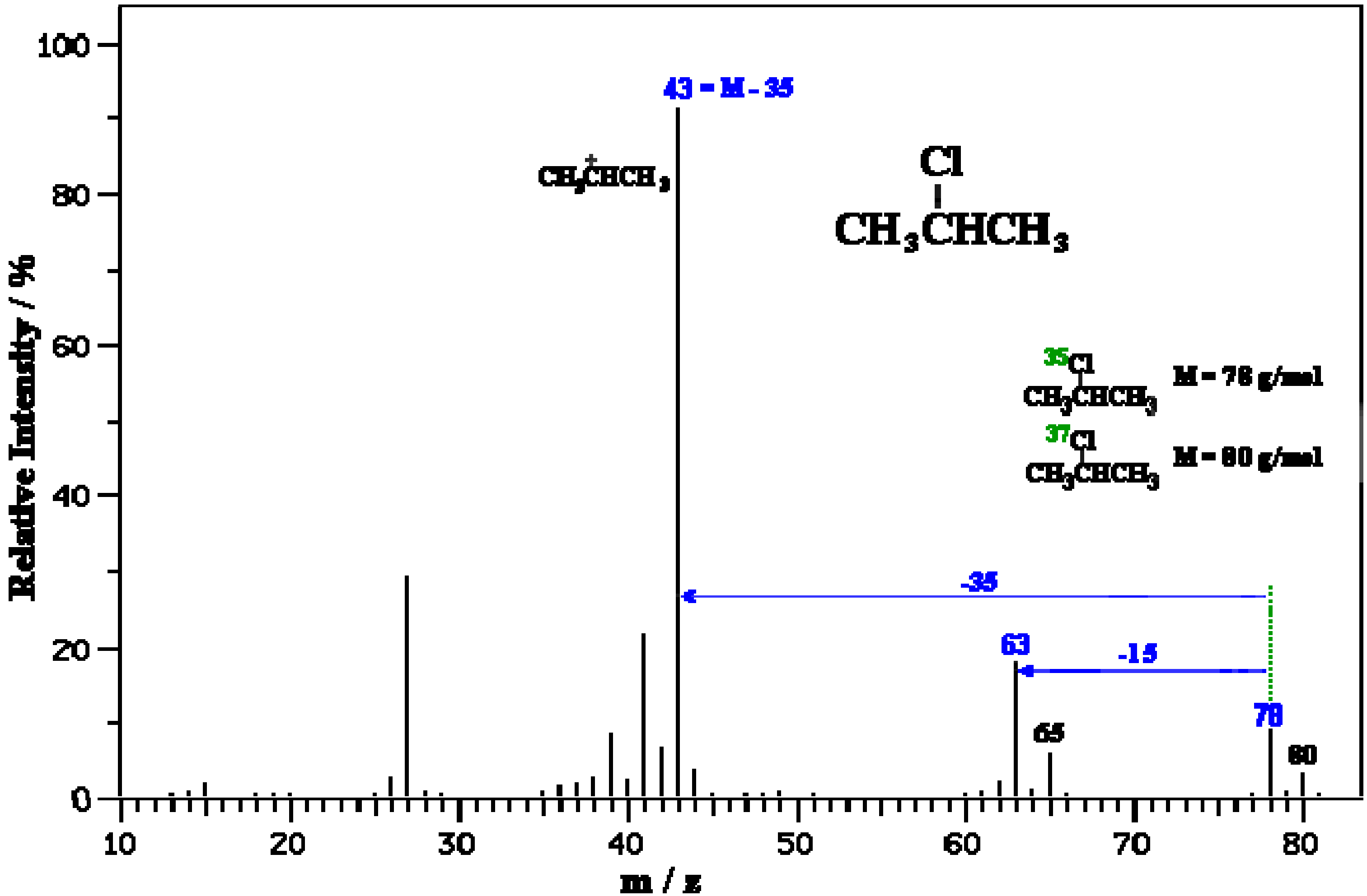
Selected elements and their isotopes

Element	Atomic weight	Isotope	Abundance	Mass
Hydrogen	1.00797	^{1}H	99.985	1.00782
		^{2}H	0.015	2.01410
Carbon	12.01115	^{12}C	98.90	12.00000
		^{13}C	1.10	13.00336
Nitrogen	14.0067	^{14}N	99.634	14.00307
		^{15}N	0.366	15.00010
Oxygen	15.9994	^{16}O	99.762	15.99491
		^{17}O	0.038	16.99913
		^{18}O	0.200	17.99916
Fluorine	18.9984	^{19}F	100.00	18.9984
Sulfur	32.064	^{32}S	95.02	31.97207
		^{33}S	0.75	32.97146
		^{34}S	4.21	33.96786
Chlorine	35.453	^{35}Cl	75.77	34.96885
		^{37}Cl	24.23	36.96590
Bromine	79.909	^{79}Br	50.69	78.91839
		^{81}Br	49.31	80.91642

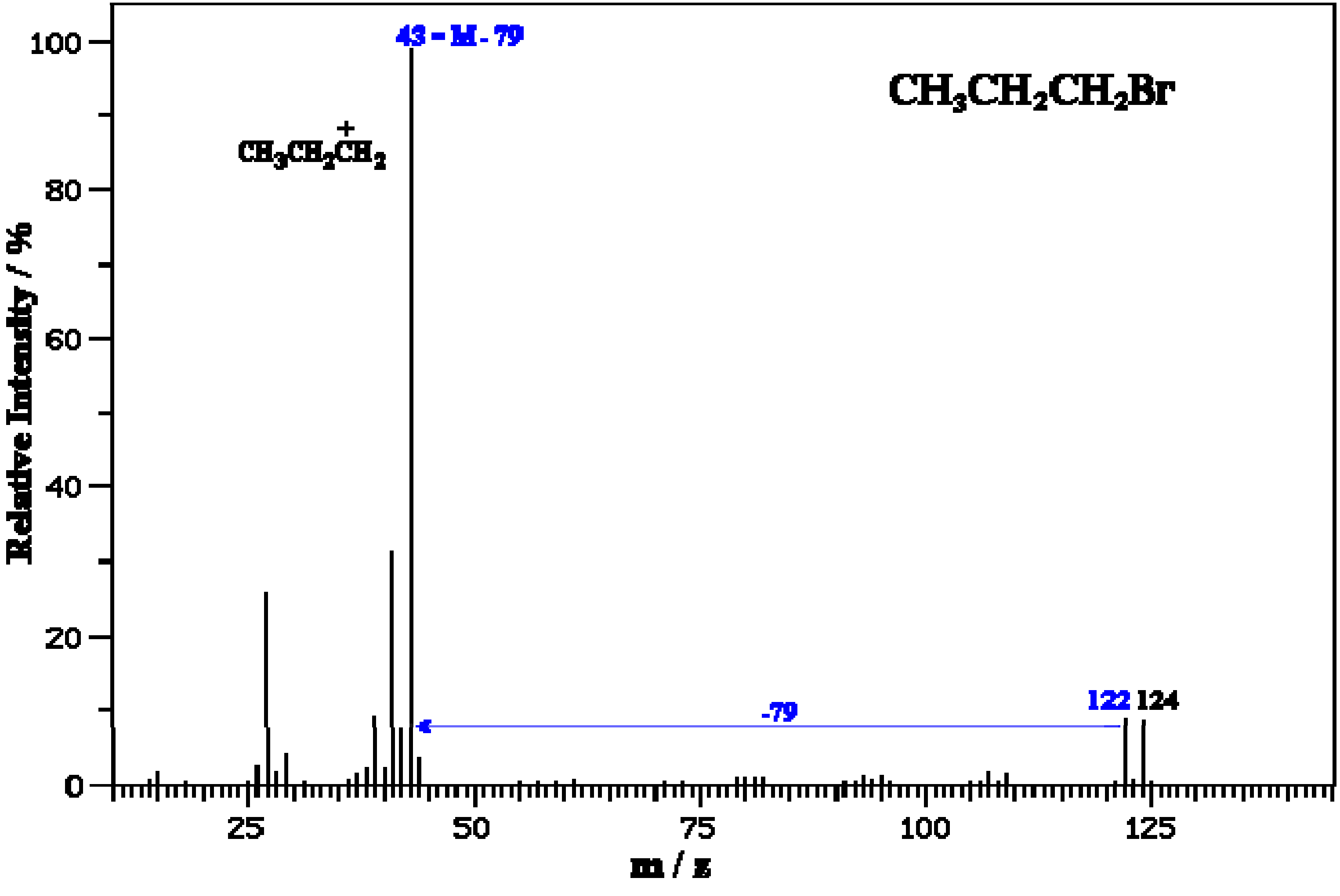
Summary

Low-resolution mass spectrometer is capable of separating and detecting individual ions even those that only differ by a single atomic mass unit. As a result, molecules containing different isotopes can be distinguished. This is most apparent when atoms such as bromine or chlorine are present. Natural bromine contains two isotopes, ^{79}Br and ^{81}Br, with the relative intensity of 1:1. Chlorine contains two isotopes, ^{35}Cl and ^{37}Cl, with the relative intensity of 3:1. Accordingly, the mass spectrum of a molecule containing a single chlorine atom will show two molecular ion peaks for ^{35}Cl-M+• and ^{37}Cl-M+• in the ratio of 3:1. The mass spectrum of a molecule containing a single bromine atom will show two molecular ion peaks for ^{79}Br-M+• and ^{81}Br-M+• in the approximate ratio of 1:1. The intensity ratios in the isotope patterns are due to the natural abundance of the isotopes. The low-intensity "M+1" peaks are seen due the presence of ^{13}C and ^{2}H.

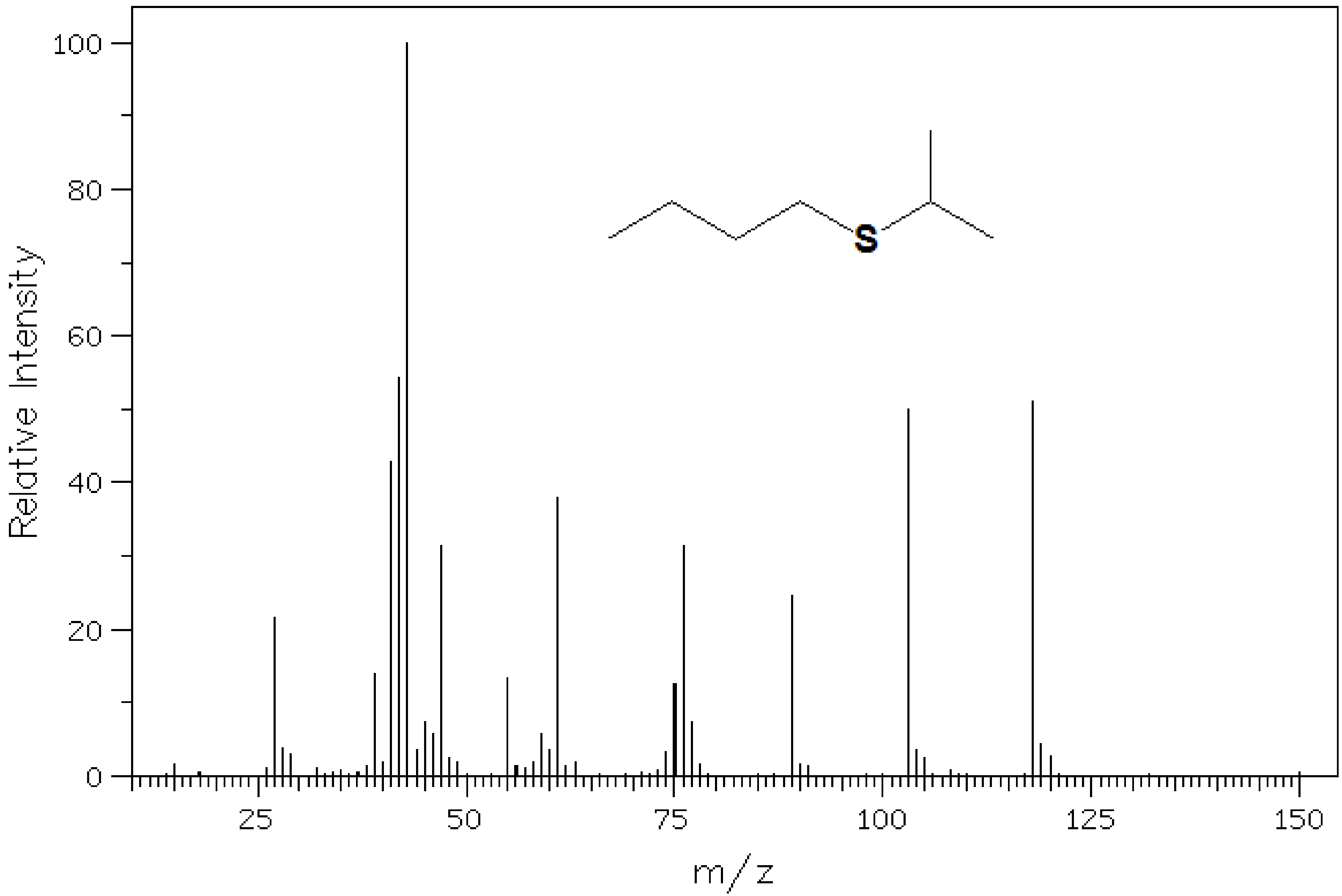
EI mass spectrum of 2-chloropropane.



EI mass spectrum of 1-bromopropane.



EI mass spectrum of *n*-butyl isopropyl sulfide



Soft ionization techniques

- *Chemical ionization (CI).* The CI method generates low-energy protonated ions MH^+ that undergo little fragmentation. Chemical ionization of the molecule $M^{\cdot\cdot}$ in the presence of methane as the reagent is shown below.

$$CH_4 + e^- \rightarrow CH_4^{+\bullet} + 2e^-$$
$$CH_4^{+\bullet} + CH_4 \rightarrow CH_5^+ + {}^{\bullet}CH_3$$
$$M^{\bullet\bullet} + CH_5^+ \rightarrow MH^+ + CH_4$$

Soft ionization techniques (contd.)

- *Electrospray ionization (ESI).* ESI works by converting the high-performance-liquid-chromatography (HPLC) effluent (solution) into an aerosol in a chamber under high voltage conditions. The solvent is quickly evaporated and the charged sample, including polymers, enters the mass spectrometer. This technique often produces $(M + H)^+$ ions.

Soft ionization techniques (contd.)

- *Fast atom bombardment (FAB).* A needle is immersed in a solution containing a high molecular weight compound and then the solvent is evaporated under a very low pressure. A beam of energetic atoms, typically Ar, is sprayed onto the needle with the adsorbed molecules to induce ionization of the molecules and desorption of the resultant ions. The ions are forced to travel to the m/z analyzer of the mass spectrometer.

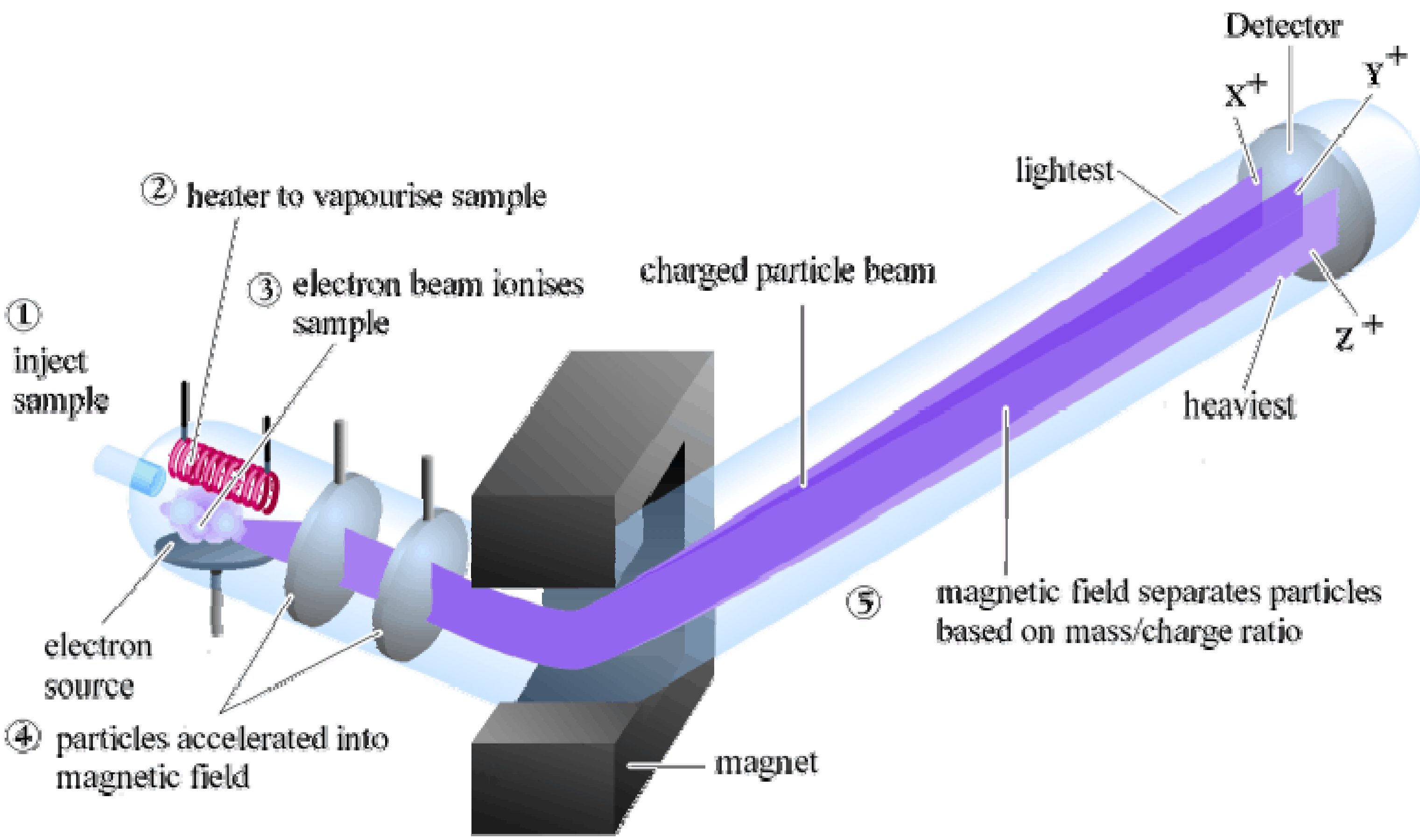
Soft ionization techniques (contd.)

- *Matrix-assisted laser desorption/ionization (MALDI).* The sample, including large biopolymers (DNA fragment, protein), is irradiated with an intense beam of photons. Ionization of the molecules and desorption of the ions are facilitated by mixing the sample with a compound that enhances light absorption (matrix). The MALDI process generates protonated molecular ions MH^+ that are relatively stable and which undergo little fragmentation.

High-resolution mass spectrometry (HR-MS)

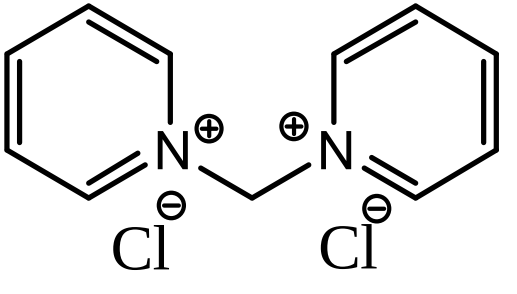
- The single magnetic-sector mass spectrometer can unmistakably distinguish between ions differing in one mass unit. By adding an electric-field sector in tandem to the low resolution magnetic-field sector of the mass spectrometer, the resolution of ions is improved enormously (a double-focussing mass spectrometer). Its mass resolution can be accurate up to six decimal places. HR-MS can be used to identify atomic composition of a molecule (molecular formula).

(Magnetic-field sector) + (electric-field sector) = high resolution mass spectrometer



Molecular formula by HR-MS

- The molecular formula $C_{11}H_{12}N_2$ was supported by ESI-MS.
- Calculated m/z 86.04948 for M^{2+}
- (z = 2, m = 172.09896)
- Experimental m/z 86.04937 (m = 172.09874)
- The presence of Cl^- cannot be observed by a positive ion mode mass spectrometry.

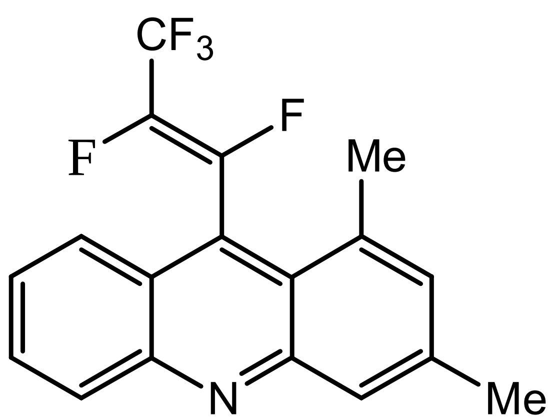


Elemental analysis (microanalysis or combustion analysis)

- A small sample (1-3 mg) is weighed on an electronic balance.
- The sample is burned in the elemental analyzer.
- The final gaseous products are CO_2, H_2O, and N_2 only.
- These products are separated on a gas chromatograph and quantified.
- The results are expressed as percentages of C, H, and N in the original sample.
- In the absence of other elements the oxygen content is calculated by subtracting the percentage sum of C, H, and N from 100%.
- The empirical formula can be calculated.

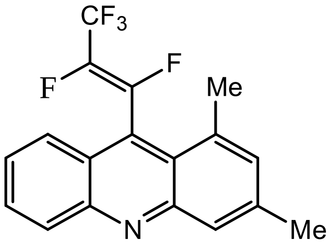
Elemental analysis: an example

- A student synthesized a new compound the spectral analysis of which by ^{19}F NMR, ^{1}H NMR, and ^{13}C NMR suggested the structure given below.
- The elemental analysis gave the following results: C, 63.94; H, 3.48; N, 4.07. The fluorine content can be calculated as 100 – 63.94 – 3.48 – 4.07 = 28.51



Elemental analysis: an example (contd.)

- In order to calculate the molar percentage of atoms in the molecule, the weight percentage of each individual element (by weight, as referred to 100 g or 100%) is divided by the respective atomic weight:
- C: 63.94/12.01 = 5.324
- H: 3.48/1.008 = 3.452
- N: 4.07/14.007 = 0.291
- F: 28.51/19.00 = 1.501
- The empirical formula: $C_{5.324}H_{3.452}F_{1.501}N_{0.291}$ or $C_{18.29}H_{11.86}F_{5.16}N$ (divided by the smallest number)
- With the rounded numbers: $C_{18}H_{12}F_5N$.



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