Chapitre 1

Spectrométrie de masse

Introduction

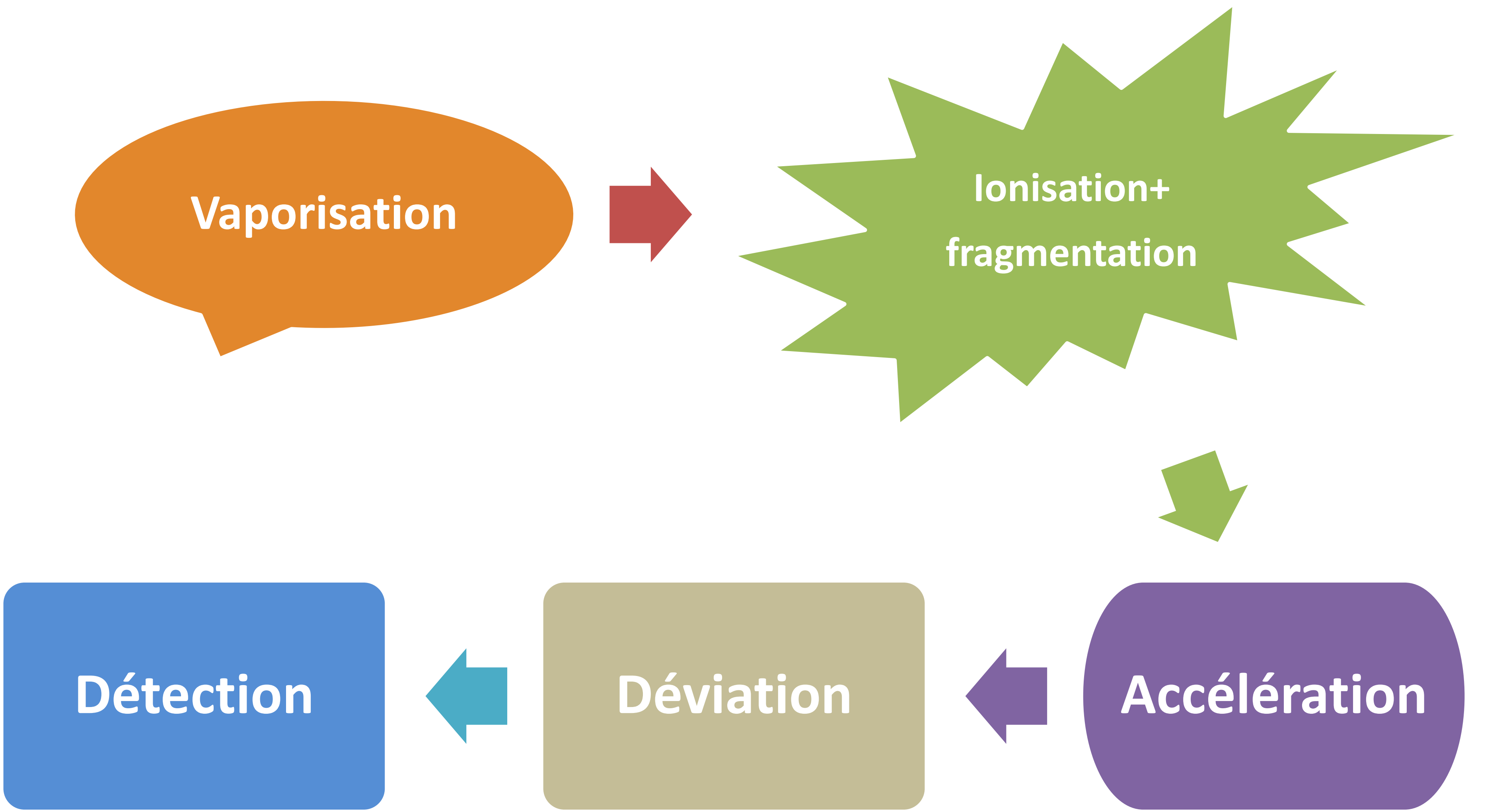
- Méthode d'analyse instrumentales (appareil)
- **Détermination de la masse molaire**
- **Analyses structurales**
- **Explication des mécanismes de ruptures de liaisons…**
- **Applicable pour des composés solides, liquides et gazeux.**
- **Méthode analytique destructive**

1. Principe

- Interaction électrons-matière
- Analyse de fragments moléculaires obtenus par ionisation

❖ *Impact électronique*

❖ *Ionisation chimique*


Vaporisation
Ionisation+
fragmentation
Accélération
Déviation
Détection

2. Terminologie en séquence

- Vaporisation
- Ionisation
- Fragmentation
- Accélération
- Déviation
- Détection

2.1. Vaporisation

- Echantillons solides ou liquides non volatiles.
- Faciliter leur ionisation.
- Energie thermique (typiquement 200°C).

2.2. Ionisation (électronique)

- On bombarde l'échantillon avec des électrons hautement énergétiques :

$A\text{-}B\text{-}C + 1e^- \rightarrow A\text{-}B\text{-}C^{+\cdot} + 2e^-$

$A\text{-}B\text{-}C^{+\cdot}$: ion moléculaire

2.2.1. Fragmentation

- L'ion moléculaire subit une fragmentation en donnant des ions, radicaux ou molécules neutres:

$$[A-B-C]^{+\cdot} \rightarrow AB^{+} + C^{\cdot}$$

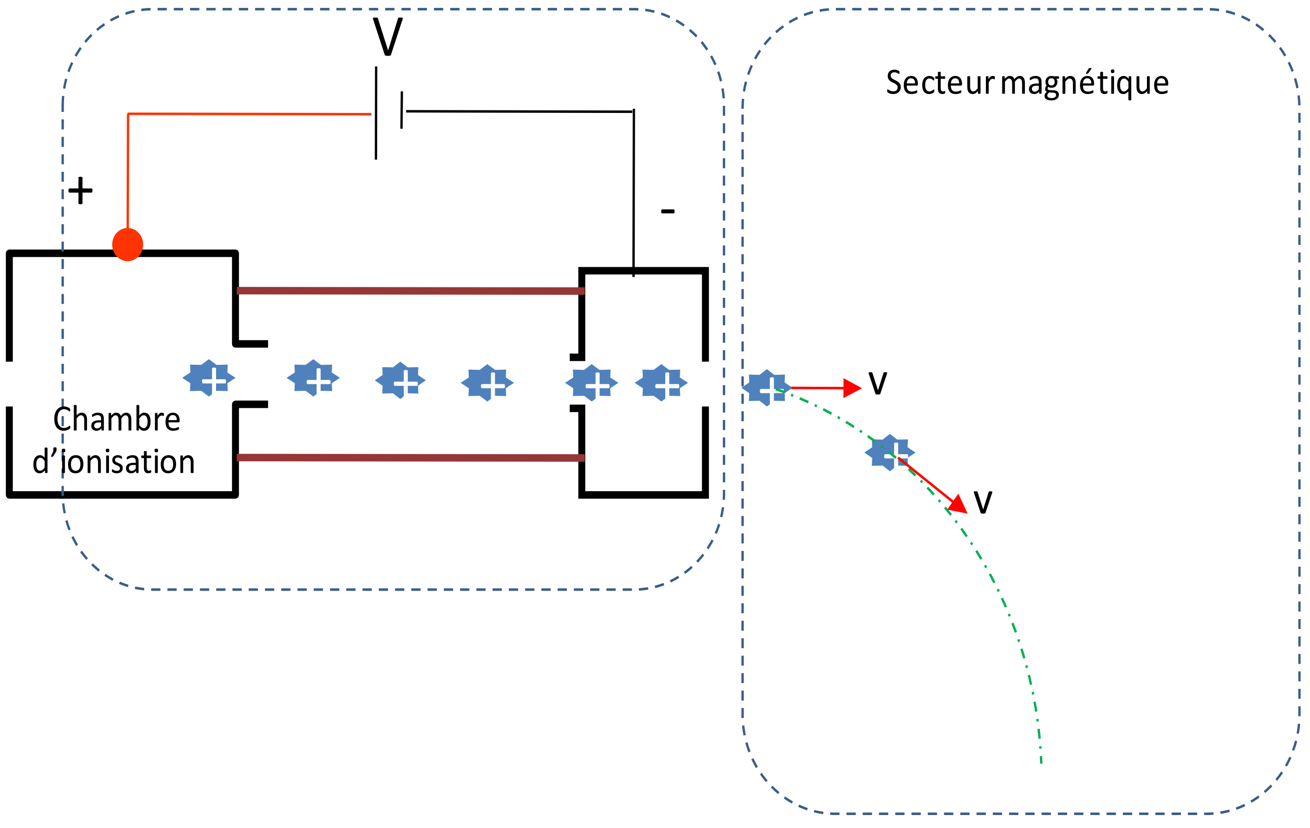
Ou

$$[A-B-C]^{+\cdot} \rightarrow AB^{\cdot} + C^{+}$$

2.3. Accélération

- **Accélération des particules chargées par un champ électrique**

$$qV = \frac{1}{2}mv^2 \Rightarrow v = \sqrt{\frac{2qV}{m}} \quad \ldots\ldots\ldots\ldots\ldots (1)$$


V
+
-
Chambre
d'ionisation
Secteur magnétique
v
v

2.4. Déviation

- Déviation des particules chargées par un champ magnétique
- Déviation proportionnelle à masse/charge : m/z

$$F_B = q \times v \times B$$

$$F_c = m\gamma$$

$$\gamma = \frac{v^2}{r}$$

$$en \Leftrightarrow : F_B = F_c$$

$$v = \frac{q \times B \times r}{m} \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$(1) + (2)$$

$$\frac{m}{z} = \frac{B^2 \times r^2}{2V}$$

Magnetic Sector Analyzer

- Ion kinetic energy when leaving source:
- Action of the magnetic field:
- Trajectory of ion is determined by equilibration of magnetic force and centripetal acceleration:
- Ions with the same momentum (*mv*) have the same R. This is a momentum analyzer.
- Taking into account the kinetic energy of the ions:

$$E_k = \frac{mv^2}{2} = qV_s$$

$$\vec{F}_M = q\,\vec{v} \times \vec{B}$$

$$qvB = \frac{mv^2}{R} = m\omega^2 R$$

$$R = \frac{mv}{qB}$$

$$\frac{m}{q} = \frac{R^2B^2}{2V_s}$$

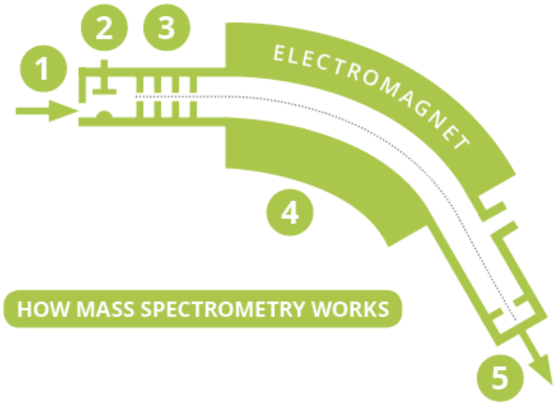
$$R = \frac{1}{B}\frac{\sqrt{2mE_k}}{q}$$

2.5. Détection

- Analyse : mesure de m/z de chaque fragment moléculaire

Nombre d'ions ayant un m/z donné ⇔ lié à l'intensité du pic correspondant

HOW MASS SPECTROMETRY WORKS



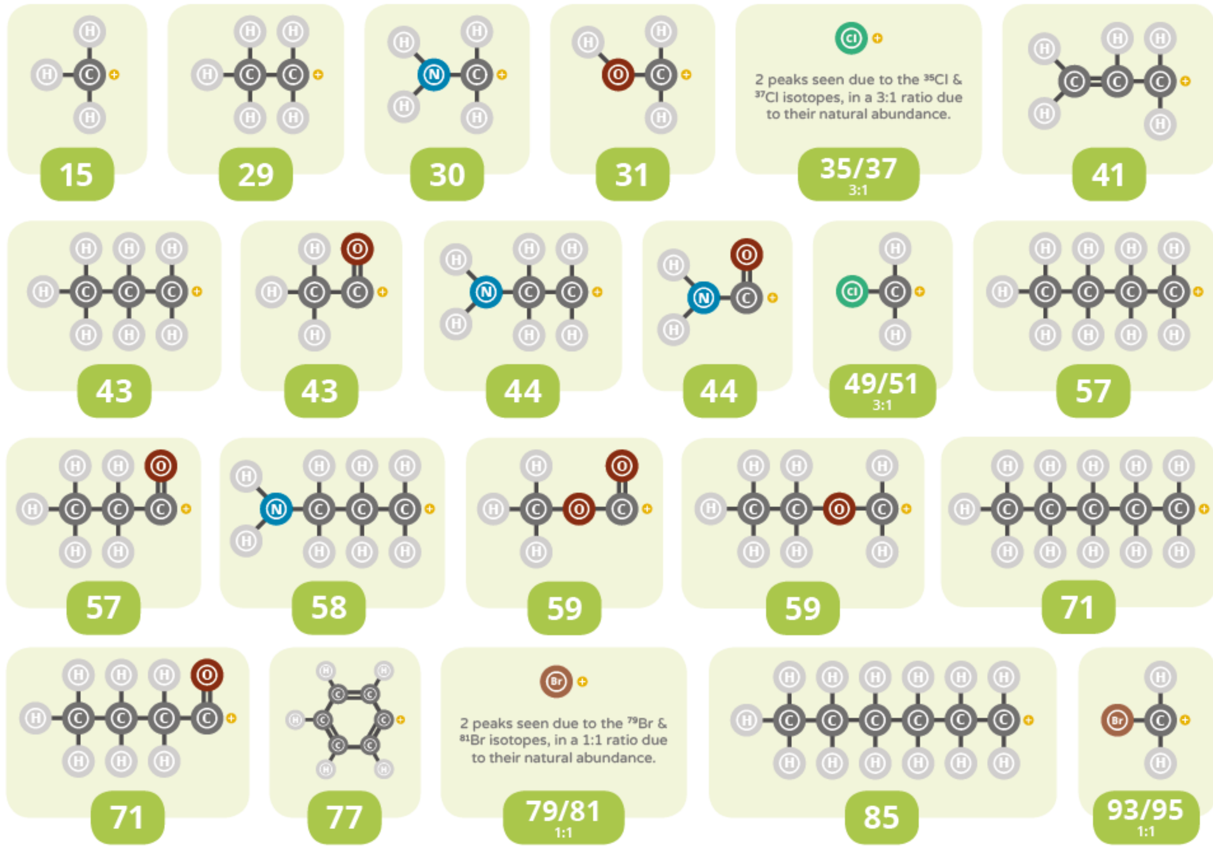
1. The sample is introduced to the mass spectrometer. Only very small samples are required. A heater is often present to vapourise the sample.

2. An electron gun ionises molecules in the sample by knocking out electrons, producing positive ions. Some molecules break into smaller ions & fragments.

3. The positive ions generated are passed through an electric field which accelerates them into a magnetic field generated by an electromagnet.

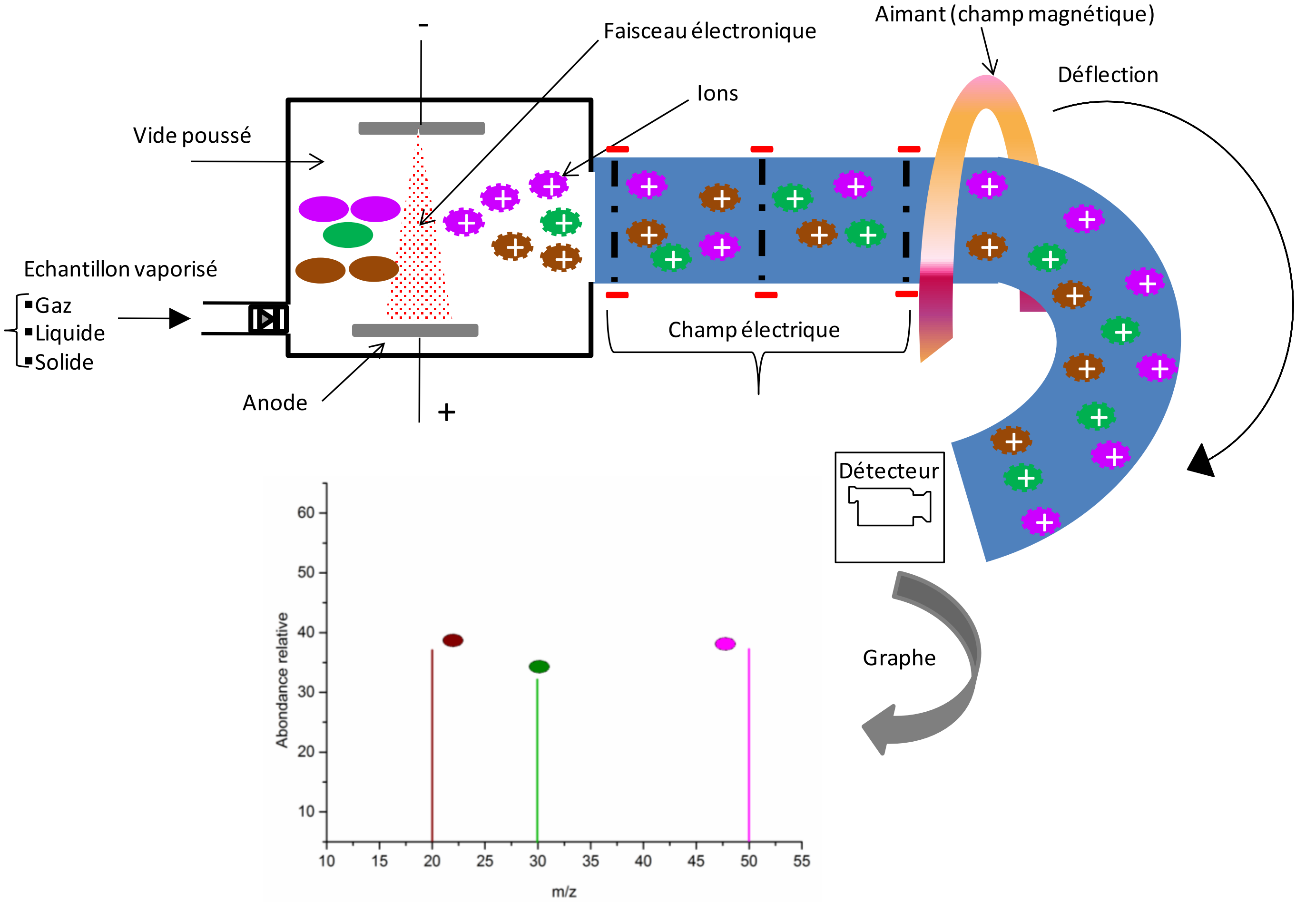
4. As the positive ions pass through the magnetic field, they are deflected. Lighter ions are deflected more than heavier ions, as are those with higher charges.

5. The positive ions hit a charged plate & accept electrons, creating a signal. The more ions that hit, the greater the signal. The output is a complex stick diagram.



Above are shown a selection of common fragment ions seen in mass spectra, along with their masses. Note that the structures shown are general representations, and it can also be possible for isomeric structures (those with the same constituent atoms, but a different structure) to cause the peaks in spectra. There are also many more fragments possible than those shown, but knowledge of these should suffice to interpret spectra of most simple molecules.

3. Expérimental

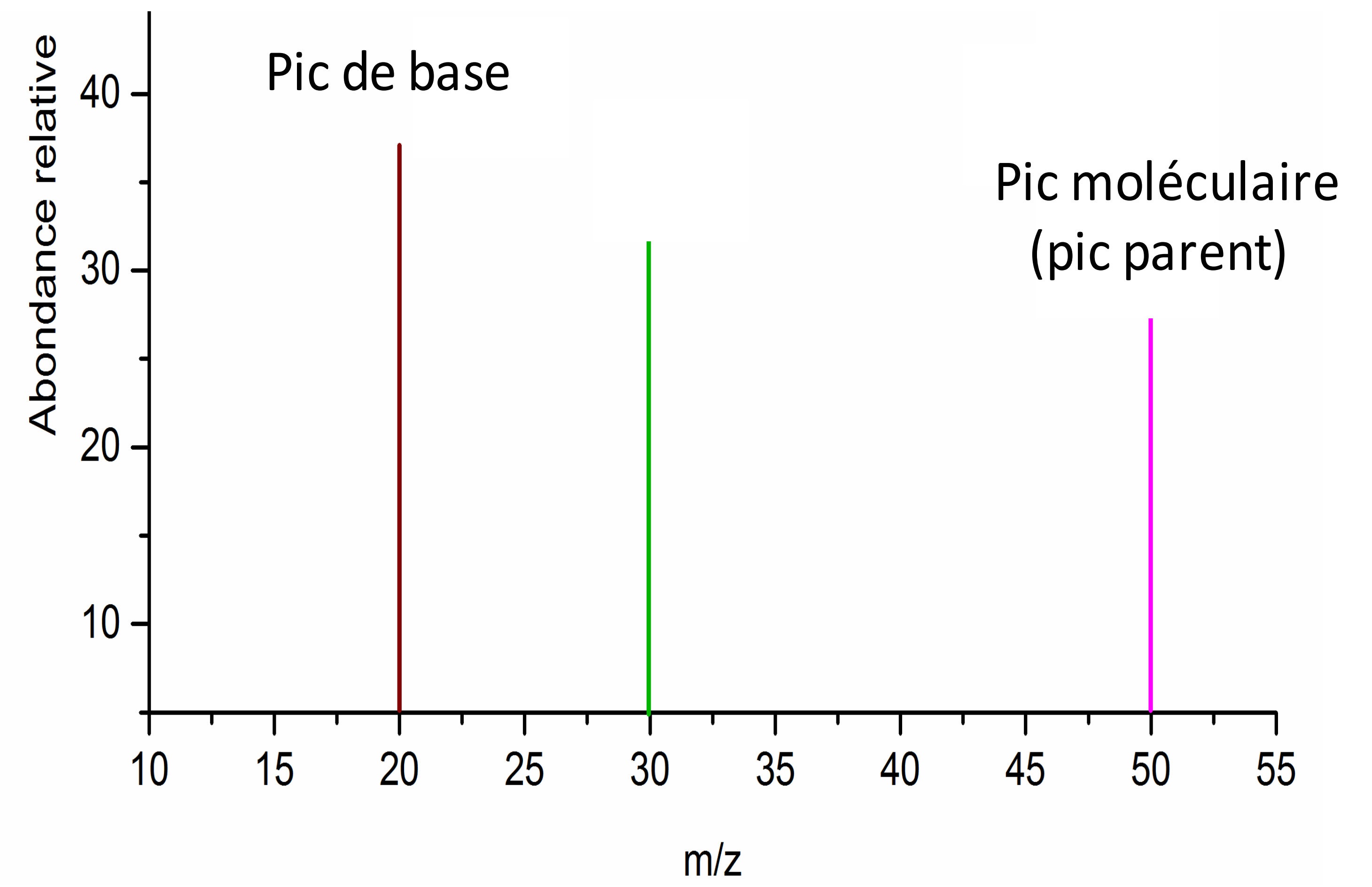


4. Abondances naturelle de certains nucléides

Nucléide	Isotopes	Masse	Abondances (%)
H	$^{1}_{1}H$	1.0078	99.985
	$^{2}_{1}H$	2.0140	0.015
C	$^{12}_{6}C$	12	98.89
	$^{13}_{6}C$	13.0034	1.11
Cl	$^{35}_{17}Cl$	34.9688	75.53
	$^{37}_{17}Cl$	36.9651	24.4
Br	$^{79}_{35}Br$	78.9183	50.54
	$^{81}_{35}Br$	80.9163	49.46

5. Spectre de masse

- Graphe
- Sous forme de pics (lignes verticaux)
- En abscisse: m/z
- En ordonnée: intensité (abondance relative des ions)


Pic de base
Pic moléculaire
(pic parent)
Abondance relative
40
30
20
10
10
15
20
25
30
35
40
45
50
55
m/z