Electron Ionization (EI)

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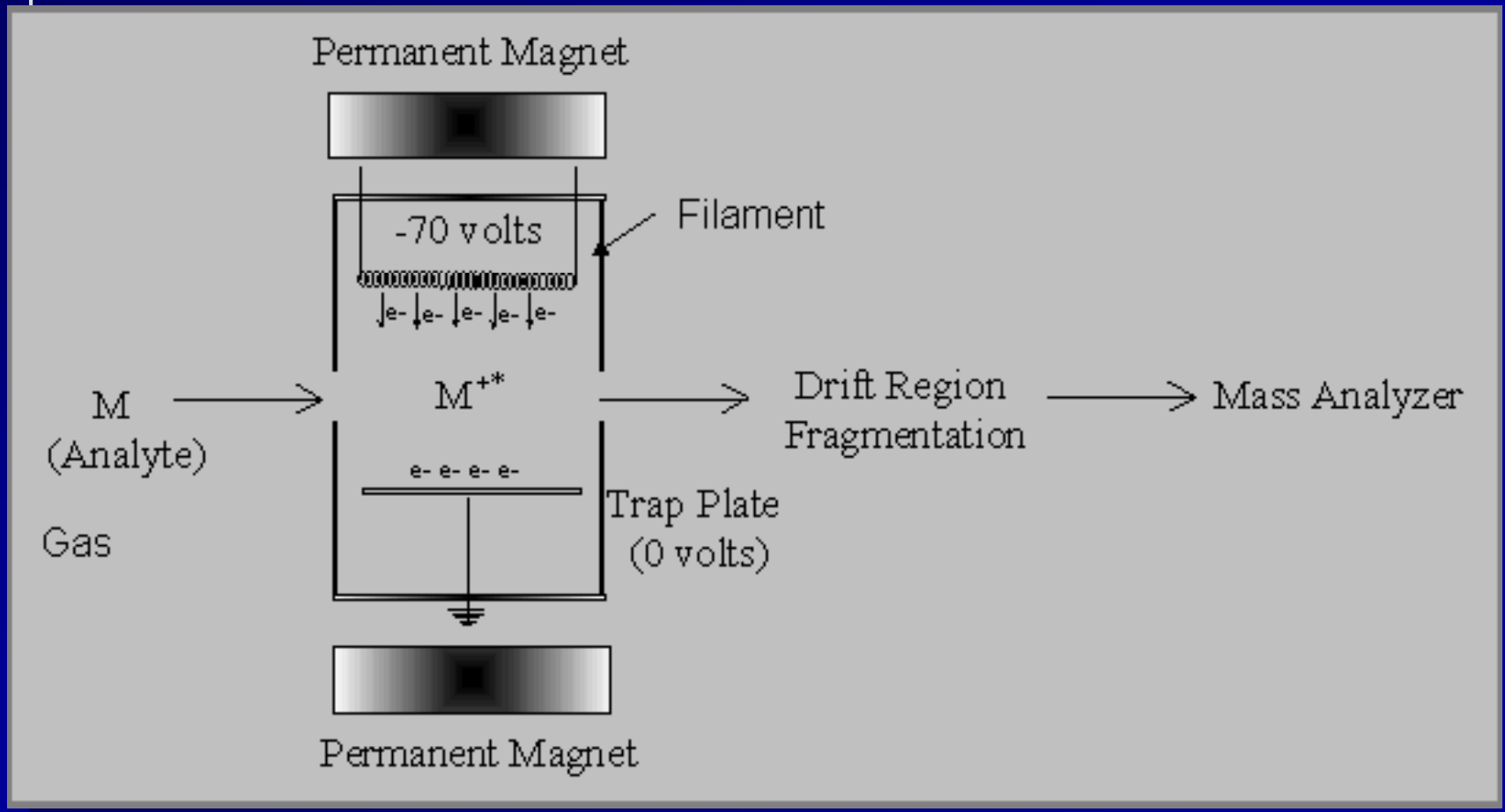


http://www.noble.org/PlantBio/MS/ion_tech_main.html

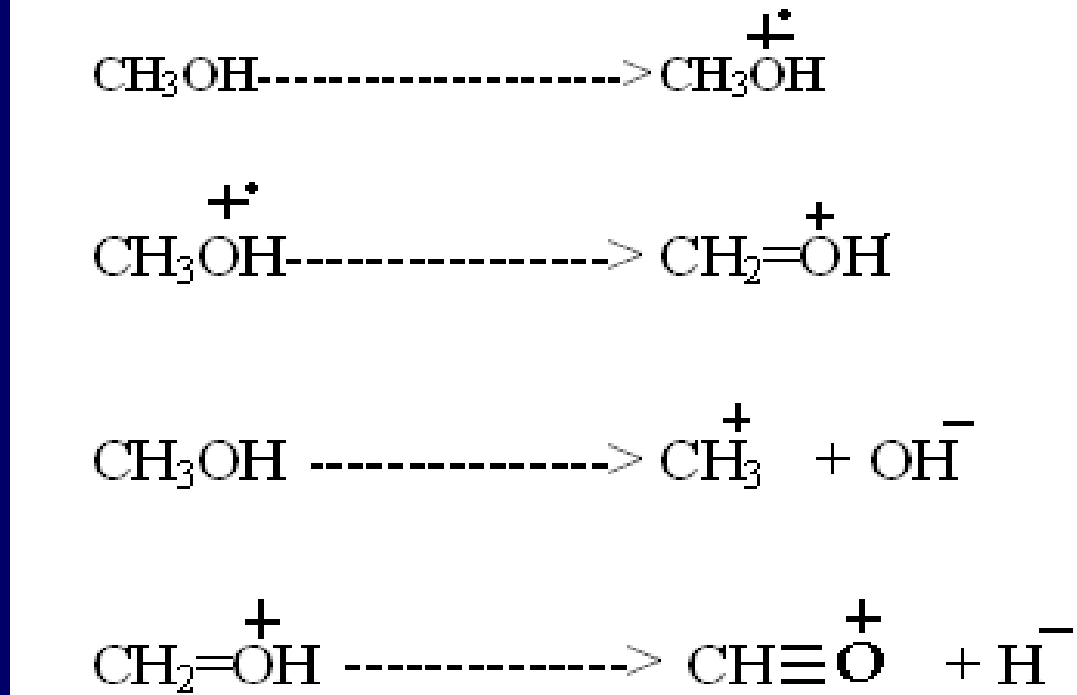
Electron Ionization (EI)

- Electron beam from a tungsten filament to knock off an electron from analyte to form an ion
- Electrons are usually accelerated by a potential of 70eV
- The paths of the electrons and the molecules are at right angles and they intersect at the source where collisions and ionizations occur
- Excess energy results in “daughter ions”
- Hard ionization technique
- “Daughter ions” can be used to identify target compounds

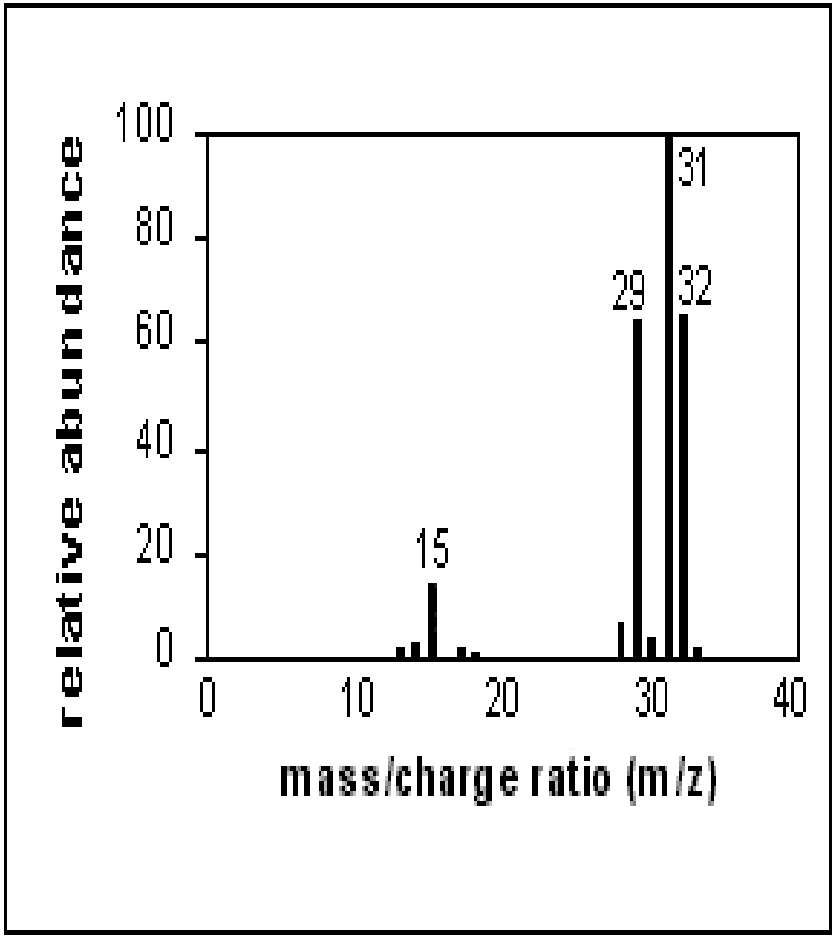
Electron Ionization (EI) (contd…)

- Can be performed in direct probe as well as interfaced
- Sample can be solid, liquid or gas — has to be volatile
- High sensitivity can be obtained

EI Fragmentation of MeOH



EI Mass Spectrum of MeOH



ions	m/z
$CH_3OH^{+\bullet}$	32
$H_2C{=}OH^{+}$	31
$HC{\equiv}O^{+}$	29
H_3C^{+}	15

Typical Reactions In EI Source

Molecular ion formation

$$ABCD + e^- \rightarrow ABCD^{\bullet +} + 2e^-$$

Fragmentation

$$ABCD^{\bullet +} \rightarrow A^+ + BCD^\bullet$$

$$\longrightarrow A^\bullet + BCD^+ \rightarrow BC^+ + D$$

$$\longrightarrow CD^\bullet + AB^+ \longrightarrow \begin{cases} \rightarrow B + A^+ \\ \rightarrow A + B^+ \end{cases}$$

$$\longrightarrow AB^\bullet + CD^+ \longrightarrow \begin{cases} \rightarrow D + C^+ \\ \rightarrow C + D^+ \end{cases}$$

Rearrangement followed by fragmentation

$$ABCD^{\bullet +} \rightarrow ADBC^{\bullet +} \longrightarrow \begin{cases} \rightarrow BC^\bullet + AD^+ \\ \rightarrow AD^\bullet + BC^+ \end{cases}$$

Collision followed by fragmentation

$$ABCD^{\bullet +} + ABCD \rightarrow (ABCD)^{\bullet 2+} \rightarrow BCD^\bullet + ABCDA^+$$

PLUS and MINUS of EI

Advantages of EI

- Reproducible method
- High Ionization Efficiency
- Ionization is non-selective
- Extensive fragmentation occurs
- Interface to GC possible
- Libraries of EI spectra help ID
- Improved sensitivity by having no suppression
- All vaporized molecules can be ionized (non polar and insoluble)
- Molecular structural information

Disadvantages of EI

- Only +ve ions are formed
- Sample has to be volatile
- Large internal energy method
- No interface to LC
- Solid probes need skilled operator
- Not ideal for some classes of compounds
- Rearrangement process complicates spectra
- Limits to 600Da or less MW
- Limits value in MW determination due to extensive fragmentation