# Fundamentals in Mass Spectrometry

*(Ionisation modes, coupling techniques, structure elucidation)*

**Introduction:**

Literature, History, Coupling Techniques, Vacuum., Atomic Masses

**MS-Analysers:**

Sectorfield-, Quadrupole-, Ion-Trap, TOF-Instruments, MS/MS, $MS^n$

**Ionisation modes and coupling (hyphenated) techniques:**

EI, CI, APCI, ESI, MALDI; GC-MS, LC-MS

**Interpretation of mass spectra I:**

The molecular ion, stabile isotopes, isotopic ratios

**Interpretation of mass spectra II:**

Ion-fragmentation mechanisms, fragmentation pattern of different chemical classes of substances

**Interpretation of mass spectra III:**

Particular fragmentations, rearrangements

# Literature

A) Mass Spectrometry: Principles and Applications
Second Edition; Edmond de Hoffmann, Vincent Stroobant
John Wiley & Sons, LTD, 2001

B) Mass Spectrometry, Second Edition; James Barker
John Wiley & Sons, LTD, 1999

C) Interpretation von Massenspektren; Fred W. McLafferty,
Franticek Turecek, Spektrum Verlag, 1993

D) GC/MS: A Practical User´s Guide; Marvin McMaster,
Christopher McMaster, VCH Wiley, 1998

# History of mass spectrometry I

| | |
|---|---|
| 1886 | E. Goldstein discovers anode rays (positive gas-phase ions) in gas discharge. |
| 1897 | J.J. Thompson discovers the electron and determines its m/z ratio. |
| 1898 | W. Wien analyses the anode rays (positive charge) by magnetic deflection. |
| 1901 | R. Kaufmann analyses cathodic rays using parallel electric and magnetic fields. |
| 1909 | R.A. Millikan and H. Fletcher determine the elementary unit of charge. |
| 1912 | J.J. Thompson constructs the first mass spectrometer |
| 1918 | A.J. Dempster develops the electron ionisation source and the first spectrometer with a sector shape magnet (180°) and direction focussing. |
| 1919 | F.W. Aston develops the first mass spectrometer with velocity focussing. |
| 1948 | A.E. Comeron, D.F. Eggers develop the first TOF device. |
| 1952 | E.G. Johnson, A.O. Nier develop double-focussing instruments. |
| 1953 | W. Paul, H.S. Steinwedel describe the quadrupole analyser. |
| 1956 | First spectrometers coupled with a GC by F.W. McLafferty, R.S. Gohlke. |

# History of mass spectrometry II

1966 M.S.B. Munson, F.H. Field discover chemical inonistion (CI).

1969 H.D. Beckey demonstrates field desorption (FD) mass spectrometry.

1974 E.C. Horning et al. discover atmospheric pressure chemical ionisation (APCI).

1974 First HPLC-MS coupling by P.J. Arpino et al..

1976 R.D. McFarlane, D.F. Torgesson introduce the plasma desorption (PD) source.

1978 R.A. Rost, C.G. Enke build the first triple quadrupole MS

1980 R.S. Houk et al. demonstrate the potential of ICP-MS.

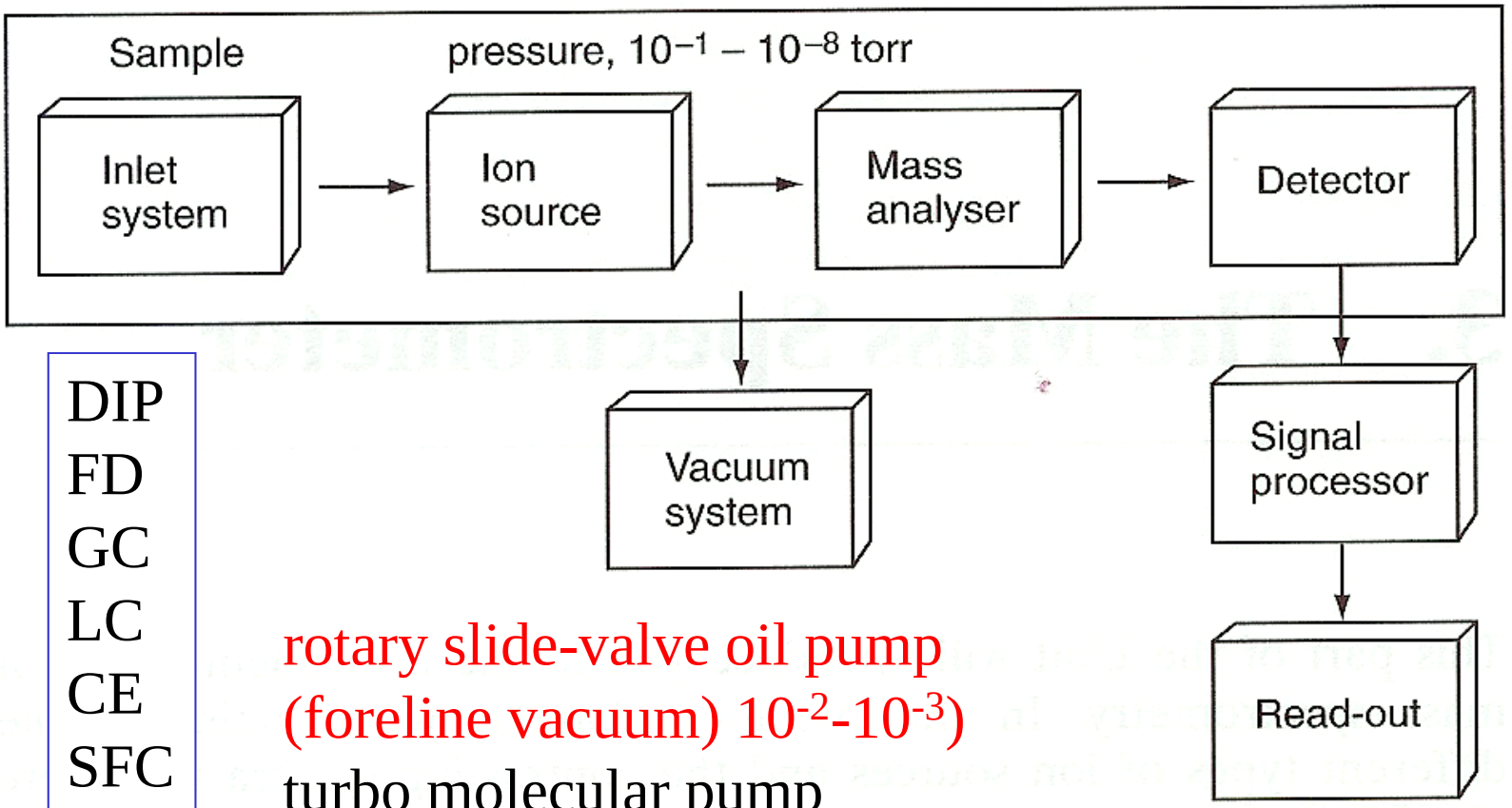
1981 M. Barber et al. describe the first atom bombardment (FAB) source.

1982 First complete spectrum of insulin (5750 Da) by FAB and PD.

1987 M. Karas et al. discover matrix-assisted laser desorption/ionisation (MALDI).

1987 R.D. Smith describes the coupling of capillary electrophoresis (CE) with MS.

1988 J. Fenn develops the electrospray (ESI) for ionisation. First spectra of proteins above 20000 Da.




DIP
FD
GC
LC
CE
SFC

rotary slide-valve oil pump
(foreline vacuum) $10^{-2}$-$10^{-3}$)
turbo molecular pump
(source, analysator)

The components of a mass spectrometer

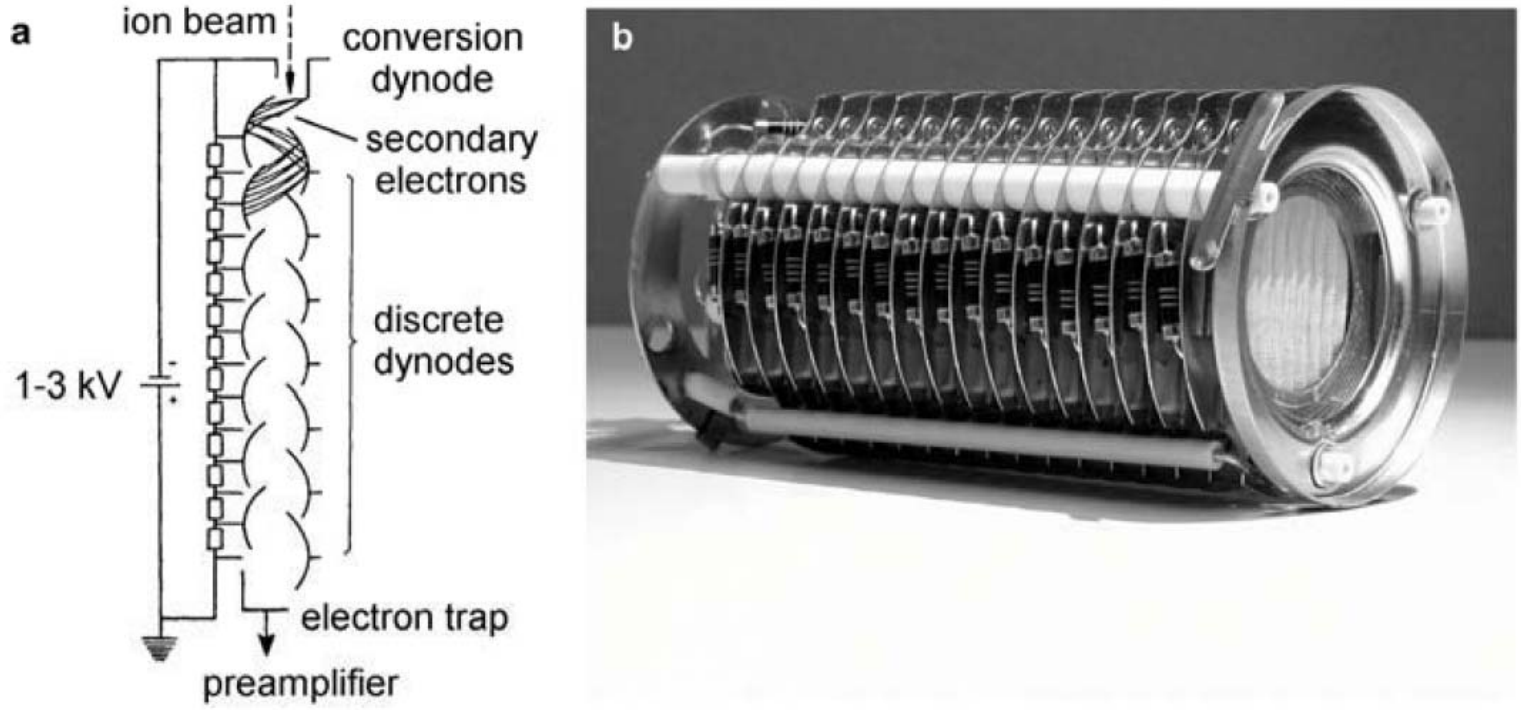



**Fig. 4.57.** Discrete dynode electron multipliers. (**a**) Schematic of a 14-stage SEM. (**b**) Photograph of an old-fashioned 16-stage Venetian blind-type SEM clearly showing the resistors and ceramics insulators between the stacking dynodes at its side. (**a**) Adapted from Ref. [238] by permission. © Springer-Verlag Heidelberg, 1991.

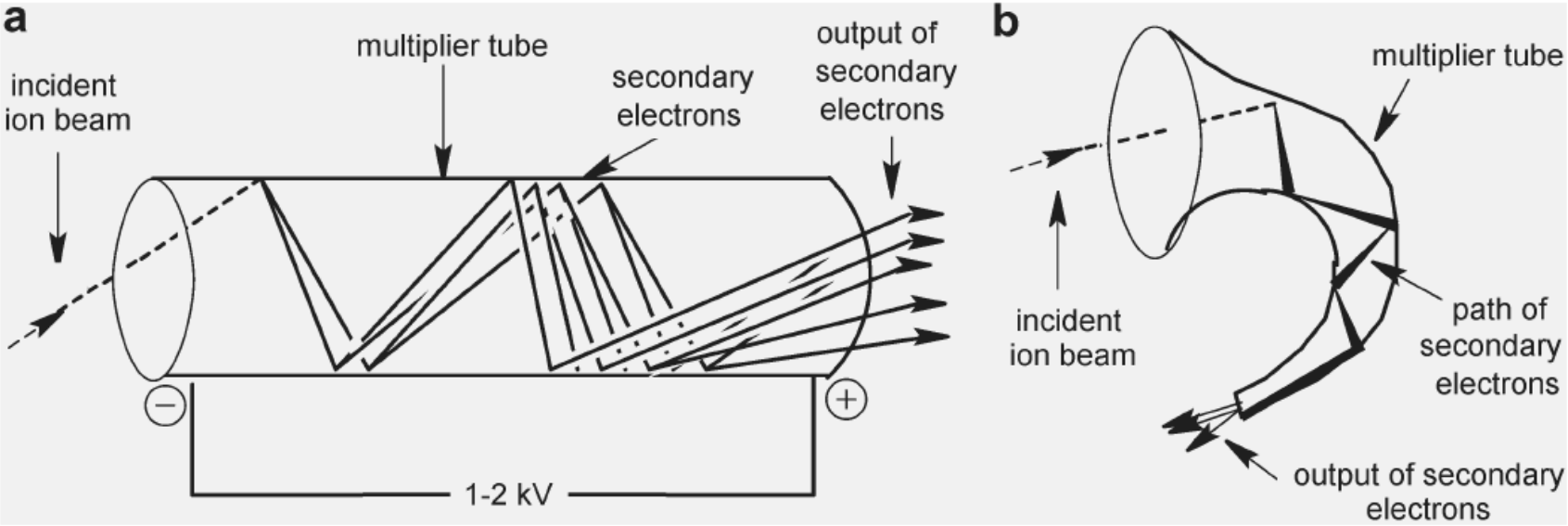



**Fig. 4.58.** Schematic of linear channel electron multiplier (**a**) and curved channel electron multiplier (**b**). By courtesy of Waters Corporation, MS Technologies, Manchester, UK..

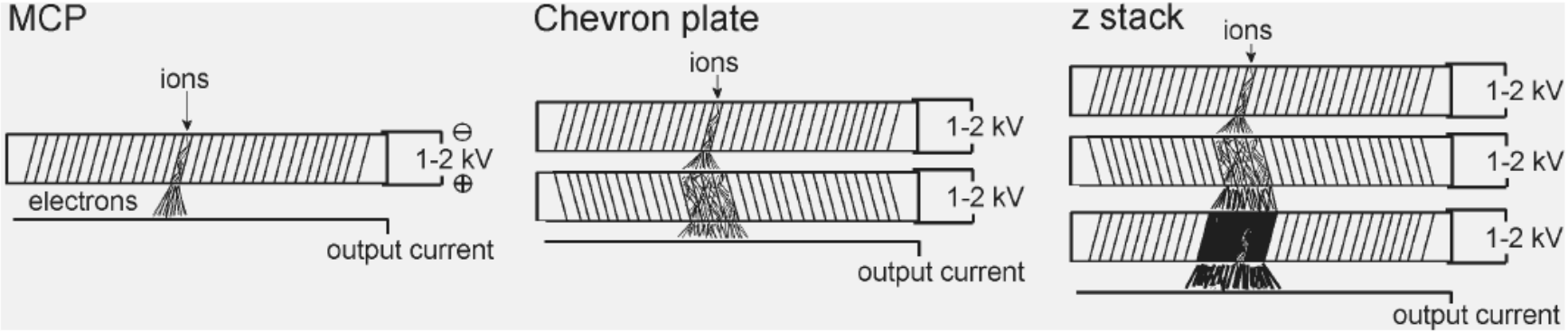
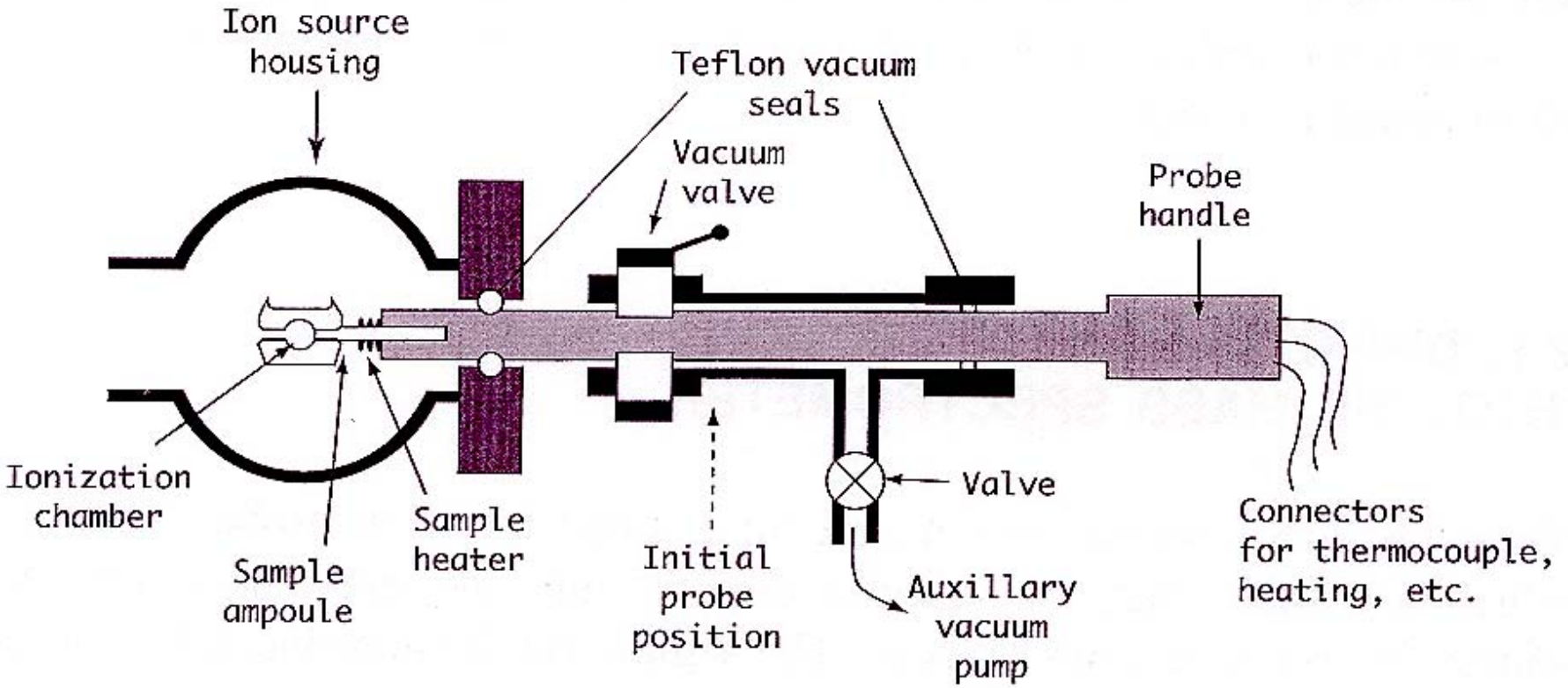


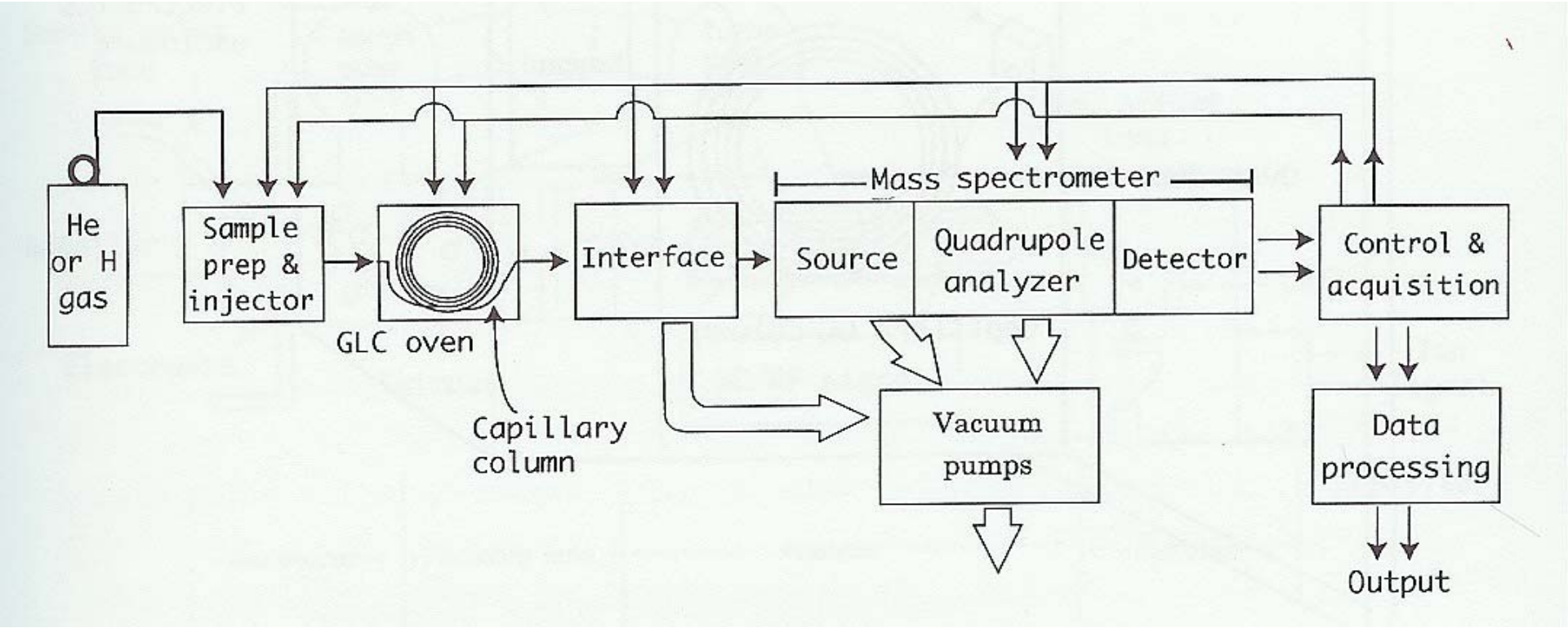

**Fig. 4.61.** Stacking of MCPs to increase gain. From left: single MCP, Chevron plate, and z-stack configuration. Note the loss of spacial resolution upon stacking.

# Direct coupling to MS



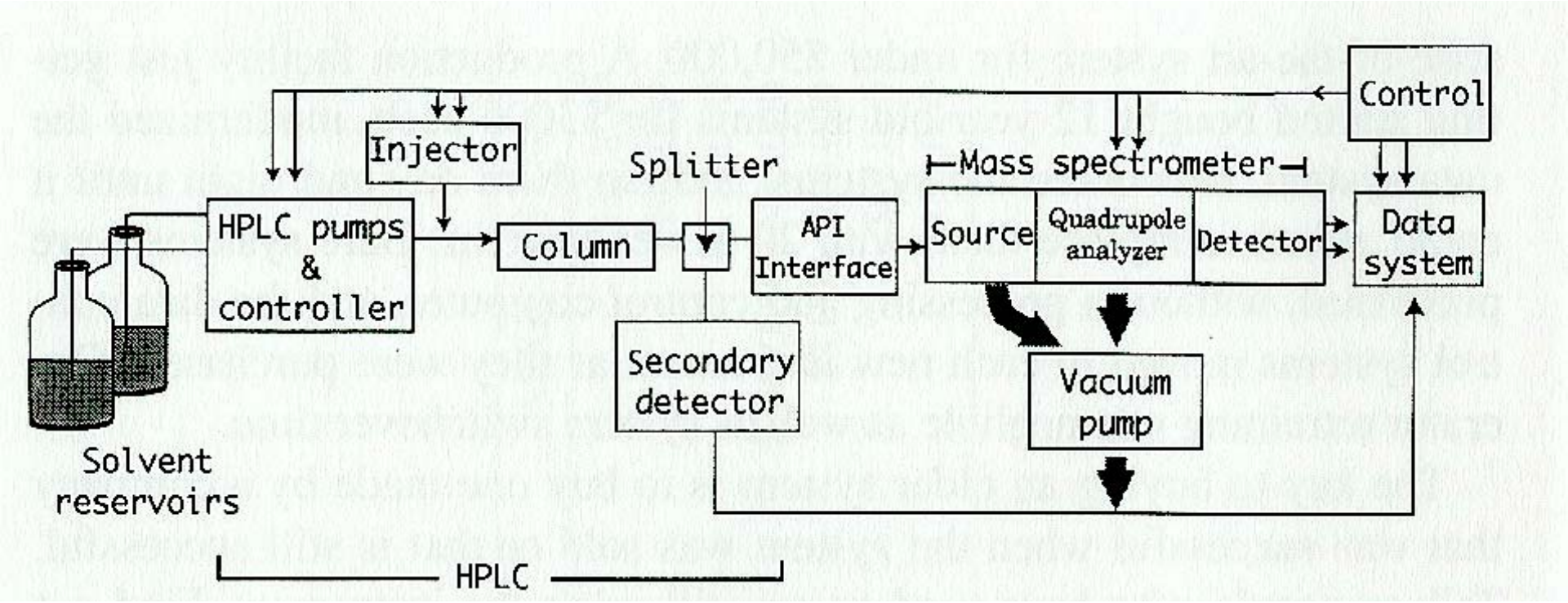

Direct insertion probes

# Direct coupling of chromatographic techniques to MS



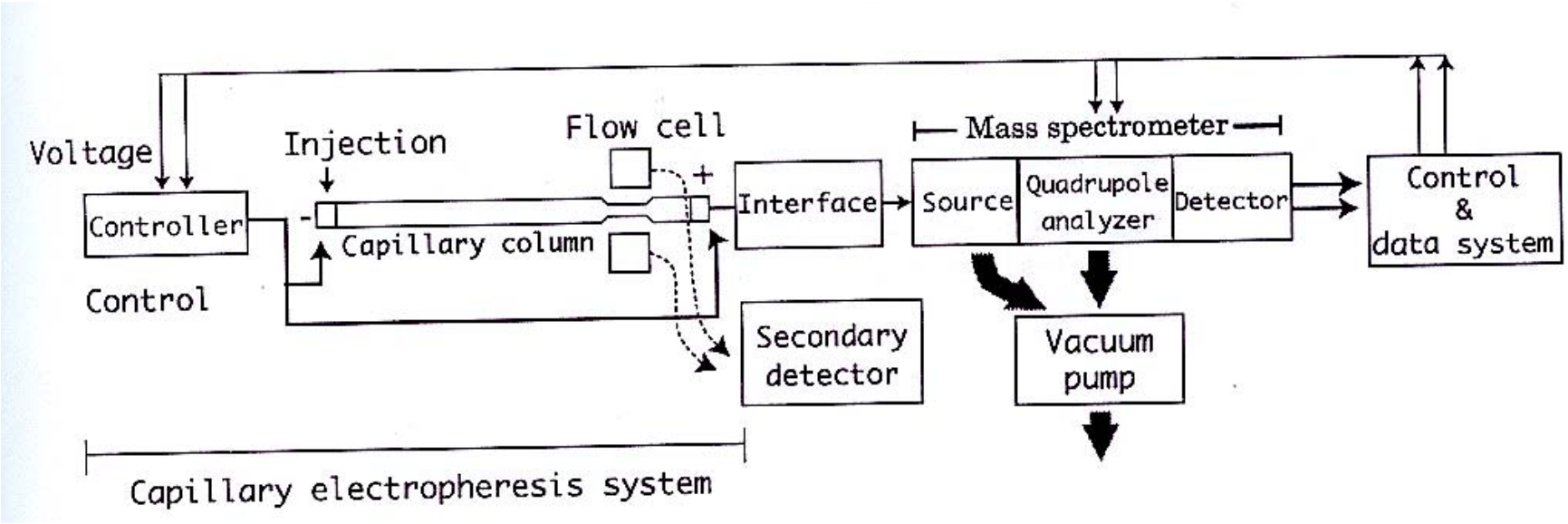

A typical GC/MS system diagram

# Direct coupling of chromatographic techniques to MS



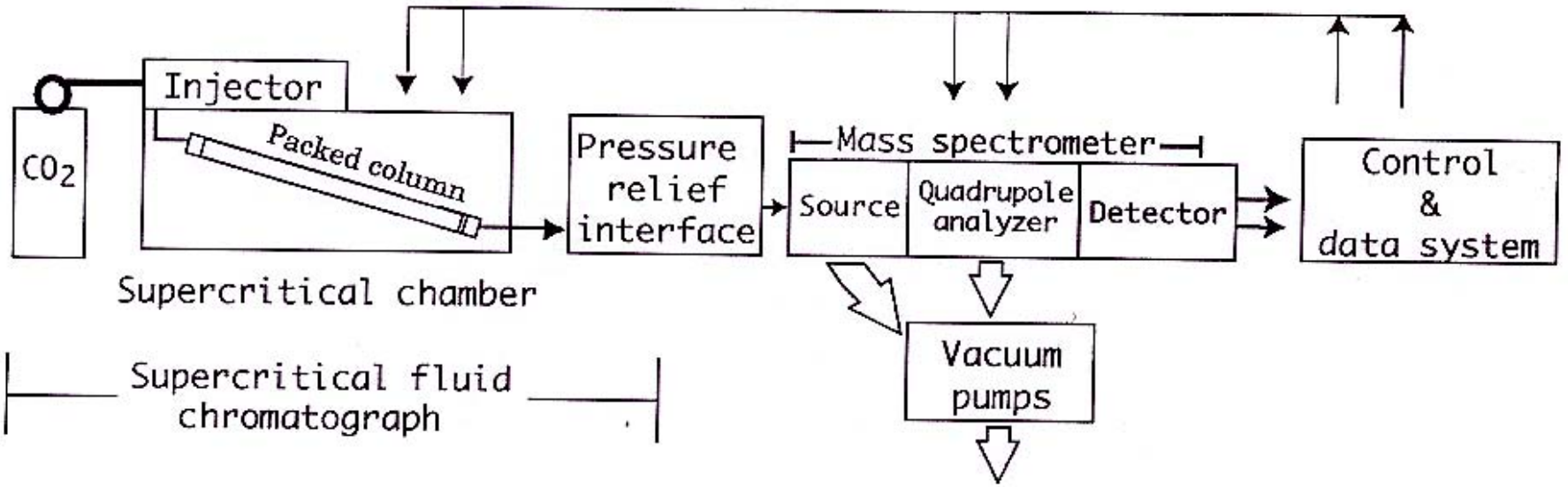

A typical LC/MS system diagram

# Direct coupling of electrophoretic techniques to MS

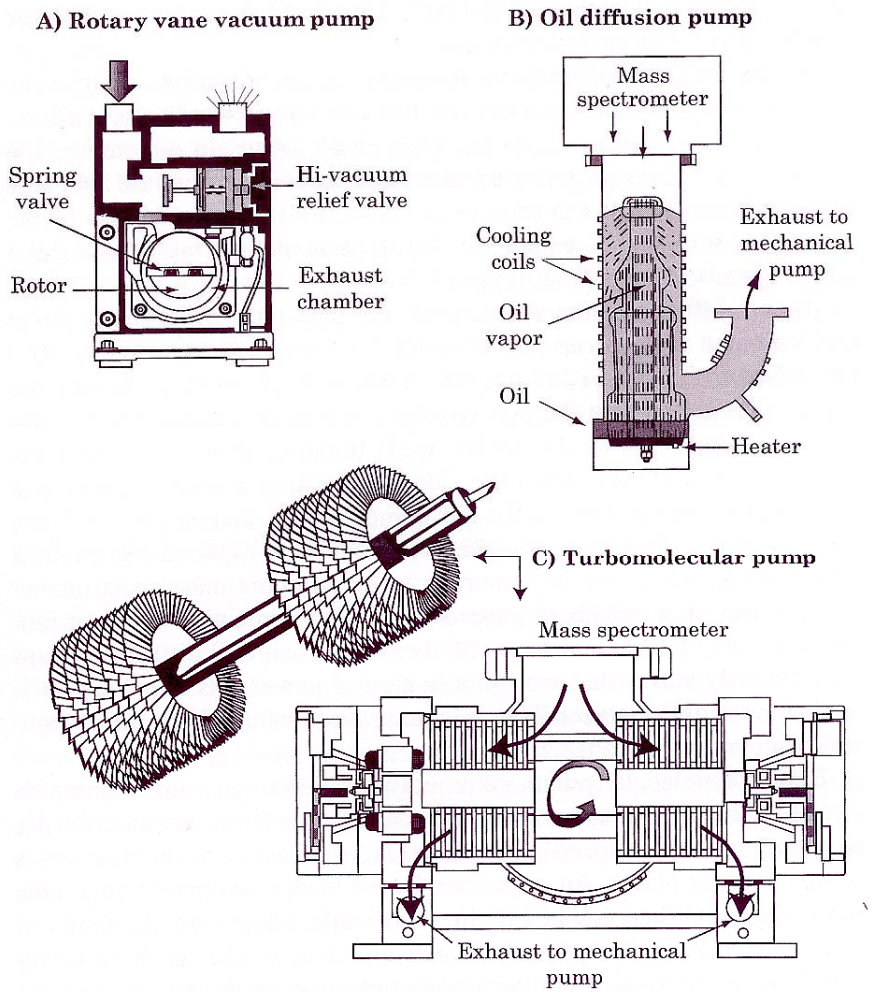



A typical CZE/MS system diagram

# Direct coupling of chromatographic techniques to MS



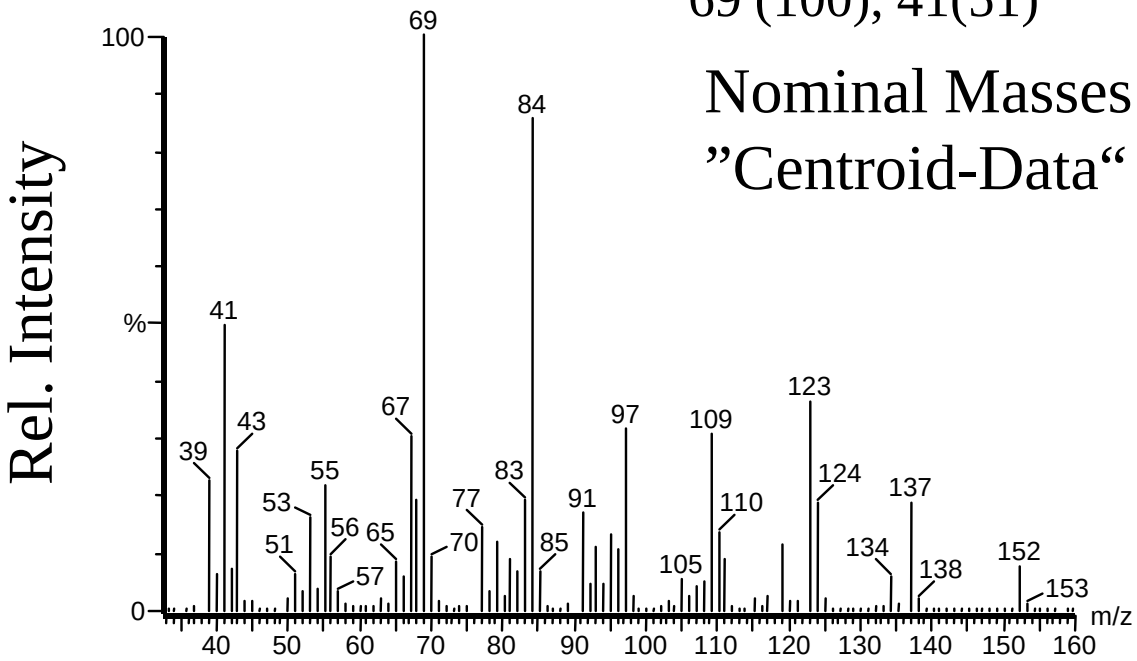

A typical SFC/MS system diagram




# Mass spectrometer vacuum pumps

152 ([$M^{+\cdot}$] 11), 137 (19), 124 (22),
123 (33), 109 (30), 97 (31), 84 (85),
69 (100), 41(51)

Nominal Masses
”Centroid-Data“

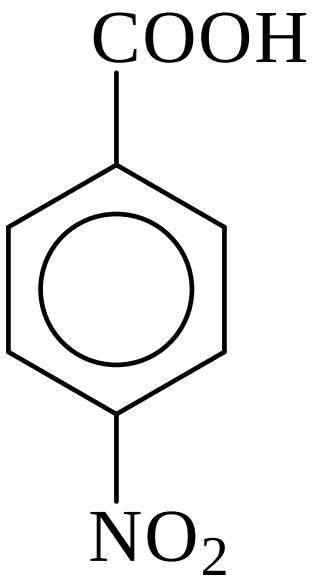



m/z

Representive GC-Low Resolution Mass Spectrum

[4-Hydroxy-mentha-1,8-diene]

Introduction




* $^{12}C$, $^{1}H$, $^{14}N$ und $^{16}O$

$C_7H_5NO_4$ empirical formula

167.12 nominal molecular weight

167.021857 accurate molecular weight*

C 50.31% H 3.02% N 8.38% O 38.29%

elemental composition % (w/w)

## Introduction

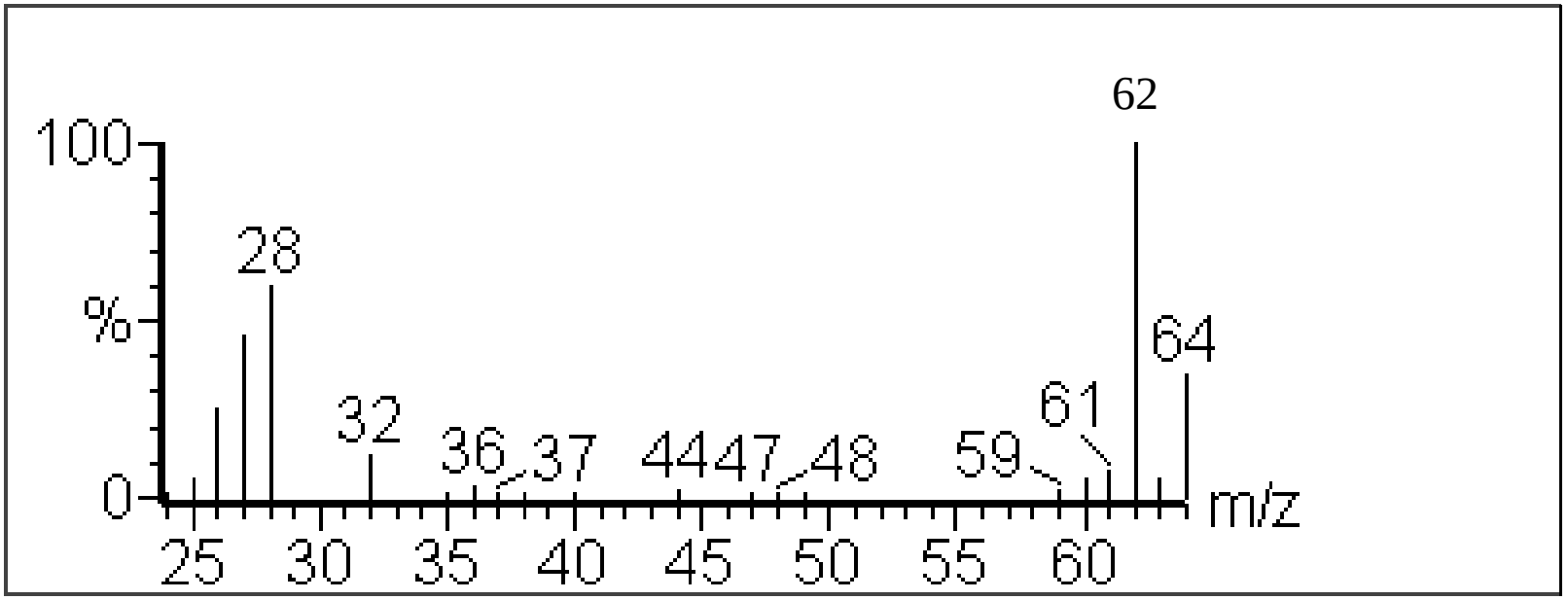
# $E = m \times c^2$

Mass defect of the chlorine isotope with the nominal mass of 35 u

| | |
|---|---|
| 17 Protons: | 17 x 1.007276 u |
| 18 Neutrons | 18 x 1.008665 u |
| 17 Electrons | 17 x 0.000549 u |
| total of masses | 35.288995 u |
| mass determined | 34.968853 u |

| | |
|---|---|
| Mass defect (nuclear bonding energy) | 0.320142 u<br>equals an energy of<br>$E = 4.8\ 10^{-11}$ J per atom<br>and $2.9\ 10^{13}$ J per mol |

| Symbol | Nominal Mass | %-Ratiol | accurate mass of the isotope | nominal atomic weight |
|---|---|---|---|---|
| H | 1 | 99.985 | 1.007825 | |
| D | 2 | 0.015 | 2.014 | 1.00794 |
| C | 12 | 98.90 | 12.000000 | |
| | 13 | 1.10 | 13.003355 | 12.011 |
| N | 14 | 99.63 | 14.003074 | |
| | 15 | 0.37 | 15.000108 | 14.00674 |
| O | 16 | 99.76 | 15.994915 | |
| | 17 | 0.04 | 16.999133 | |
| | 18 | 0.20 | 17.999160 | 15.9994 |
| S | 32 | 95.03 | 31.972070 | |
| | 33 | 0.75 | 32.971456 | |
| | 34 | 4.22 | 33.967866 | 32.066 |
| Cl | 35 | 75.77 | 34.968852 | |
| | 37 | 24.23 | 36.96903 | 35.453 |




Mass spectrum of chloroethene

* $^{12}C$, $^{1}H$, $^{35}Cl$

| | |
|---|---|
| $C_2H_3Cl$ | empirical formula |
| 62.49 g $mol^{-1}$ | nominal molecular weight |
| 61.9923 g $mol^{-1}$ | accurate molecular weight* |
| C 38.44%, H 4.84%, Cl 56.73% | elemental composition |

TIC = total ion count /chromatogram

SIC = single ion count/chromatogram

SIM = single ion monitoring

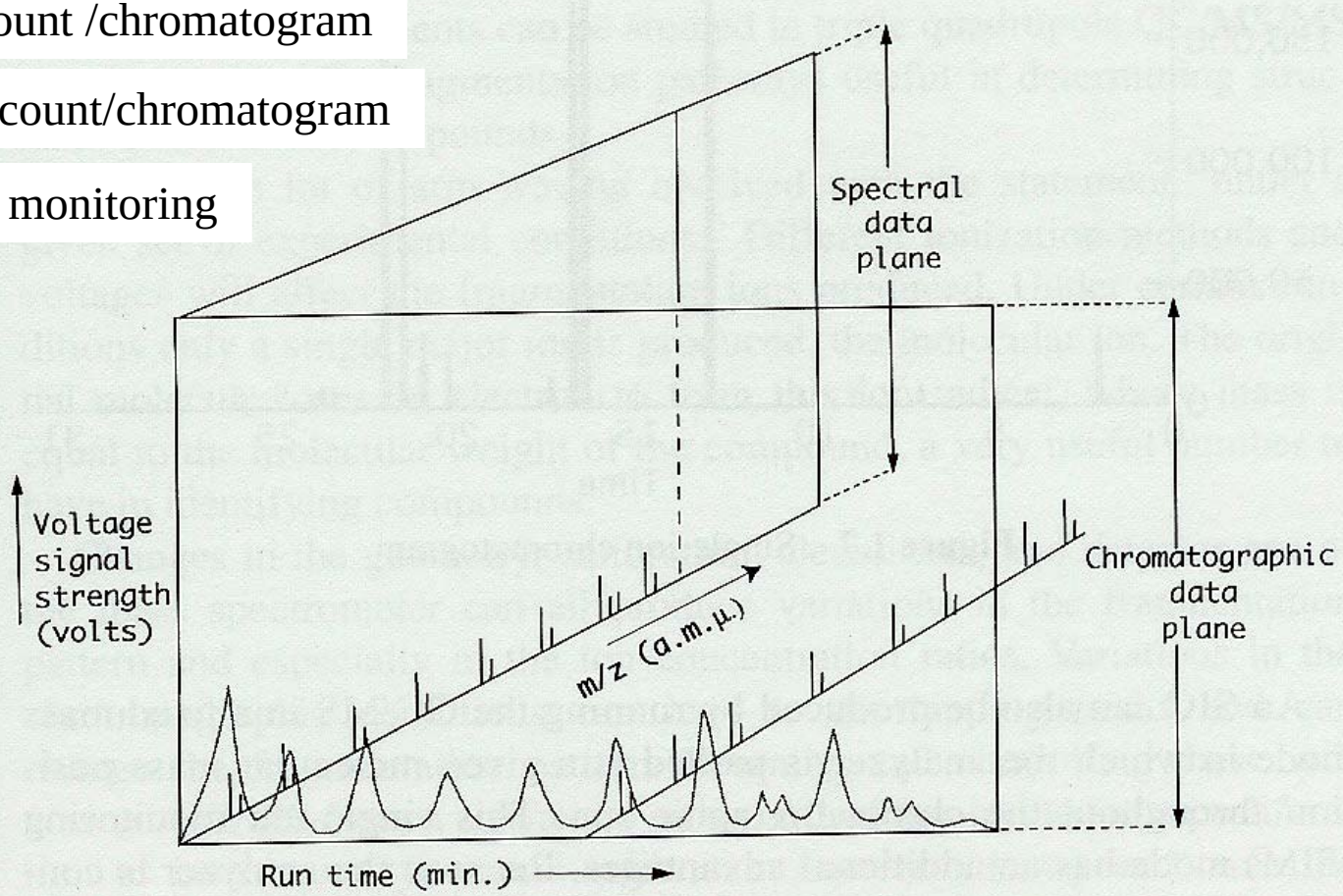



**Figure 1.6** Three-dimensional GC/MS data block.

Three-dimensional GC/MS data block