Ионная технология (ИТ МС)

- *используется для получения из пробы ионов в газовой фазе, их преобразования, задания и определения параметров траекторий*
- *является частью более общей ионно-плазменной технологии, широко применяемой также в микро-, нано-, вакуумной и плазменной электронике и т.д.*
- *основана на многодисциплинарной научной платформе физики, химии, биологии и ряда других наук*
- *применима практически к любым объектам для реализации МС исследования*

Direct Analysis in Real Time (DART) Малоугловая рентген/кристаллография, УФ спектроскопия г/ф
Desorption Electrospray Ionization (DESI) Desorption Electrospray Ionization (DESI) Electron Transfer
Dissociation (ETD) Мегадальтон

2000

Quantitative Proteomics and Metabolomics-Isotope Labels Nanostructure D/I DIOS Наночип-анализатор
Electron Capture Dissociation (ECD) MS imaging – ВИМС, МАЛДИ ИЦР ПФ
SELDI

MALDI post-source decay Nano ESI

90

Protein Mass Mapping LIAD, ЭДДИ
ЭСИ/ЭРИАД

МАЛДИ Tanaka, Karas, Hillenkamp R.Smith, капиллярный электрофорез

Н/ДО (H/DE) (ББА) термоспрей TSP

80

ББА (FAB)
Полевая Десорбция ИСП (ICP MS)

ПлазмД (PD MS)

АД ХИ (APCI) MIKES (1970) Organic Mol FDMS (1969) CID (1967)

70

ЖХ МС Peptide sequencing, metabolomics (1966)

ХИ (1966) ГХ МС (1956) MS imaging (1962), R.A.Markus, QET, RRKM

40

J.Hipple a.o. , метастабильные ионы

S.West a.o., разделение изотопов

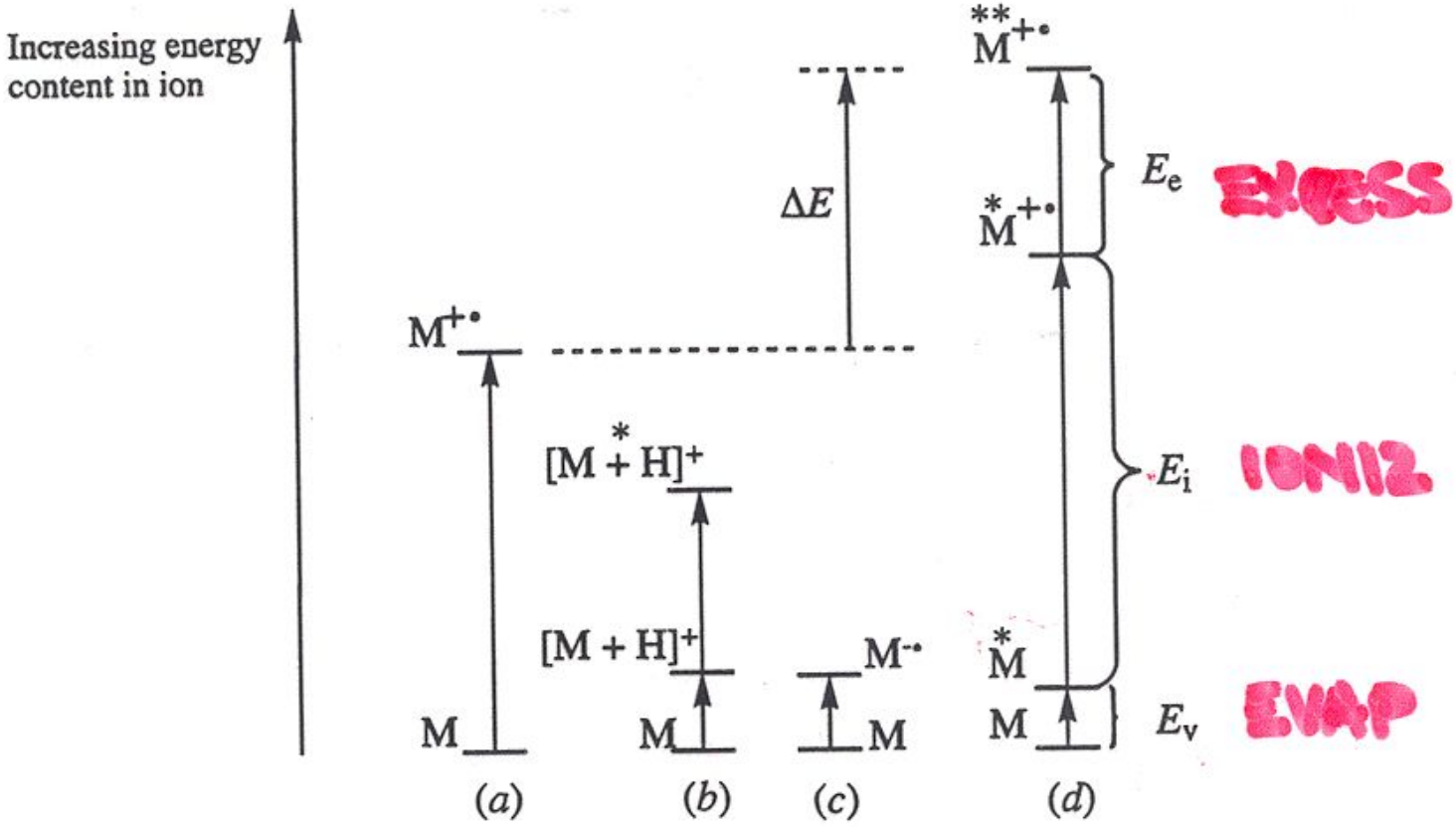
20

R.Conrad, приложения к органической химии
Ионизация электронами, A.J. Dempster

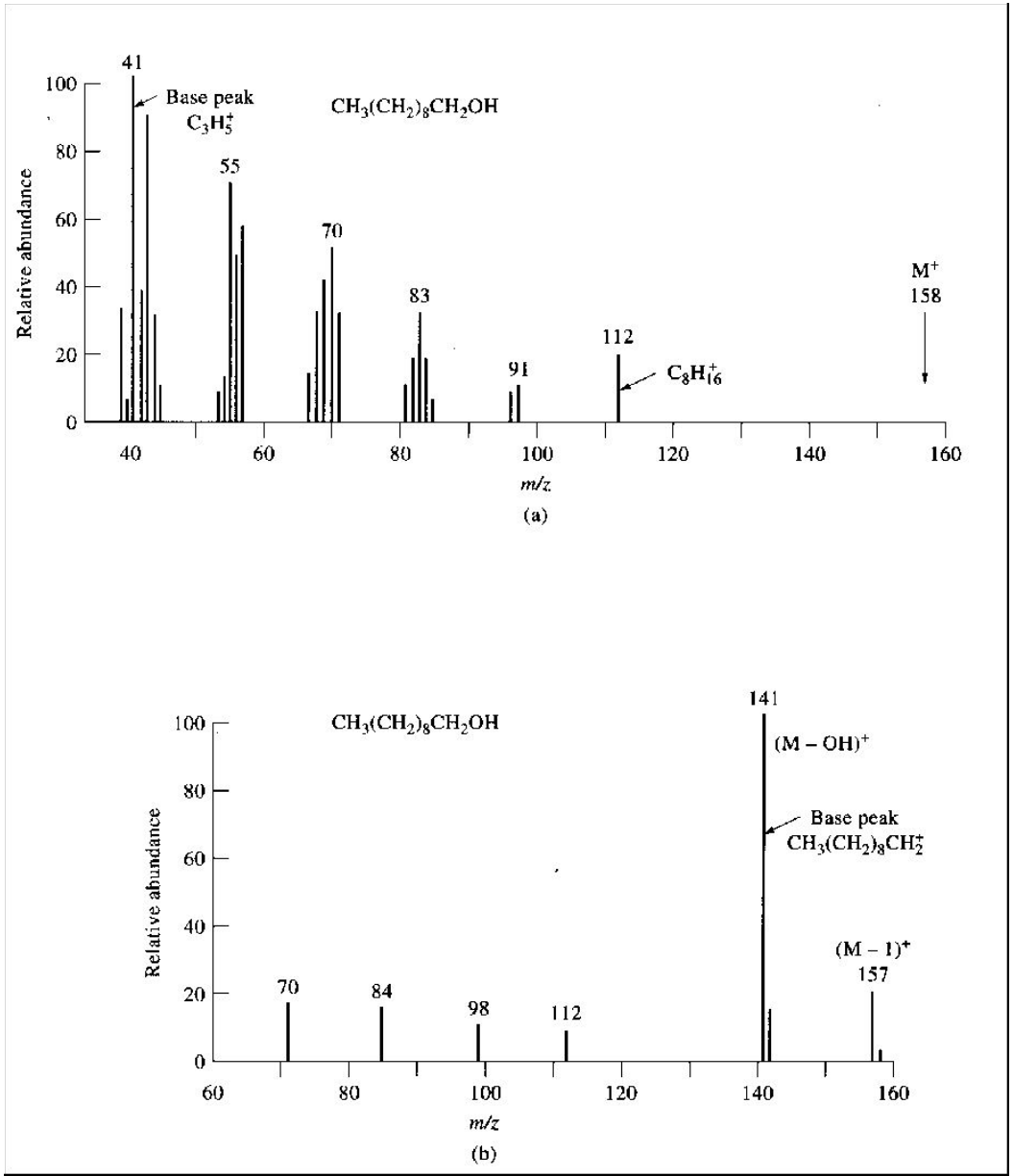
1900

Газовый разряд

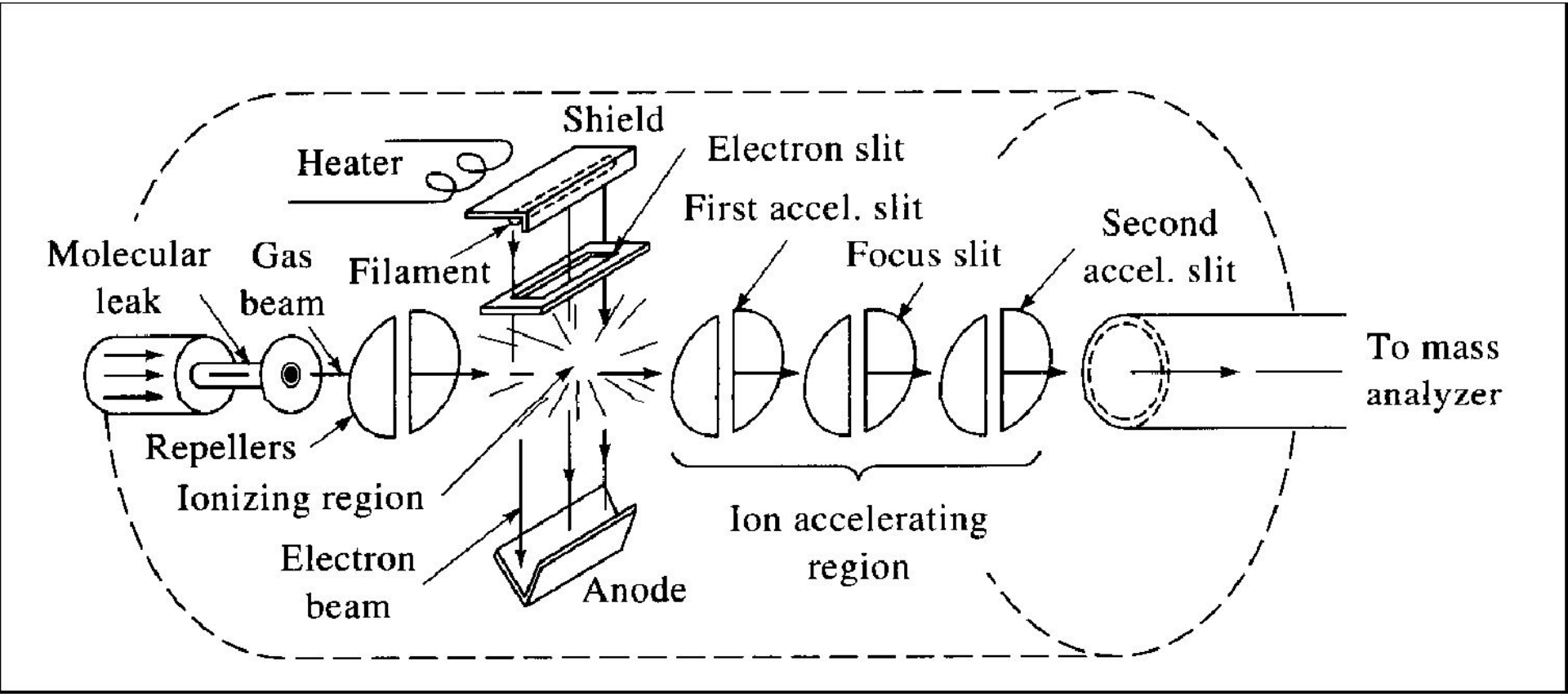
SOFT vs. HARD IONIZATION METHODS???



MS with “Hard” and “Soft” Sources



Electron Impact Source



Electron Ionization (EI) $M + e^- \rightarrow M^{\cdot +} + 2e^-$

Typical Reactions during Electron Impact

Molecular ion formation

Fragmentation

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

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

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

$$\rightarrow CD^\bullet + AB^+ \rightarrow B + A^+ \text{ or } A + B^+$$

$$\rightarrow AB^\bullet + CD^+ \rightarrow D + C^+ \text{ or } C + D^+$$

Rearrangement followed by fragmentation

$$ABCD^{\bullet +} \rightarrow ADBC^{\bullet +} \rightarrow BC^\bullet + AD^+ \text{ or } AD^\bullet + BC^+$$

Collision followed by fragmentation

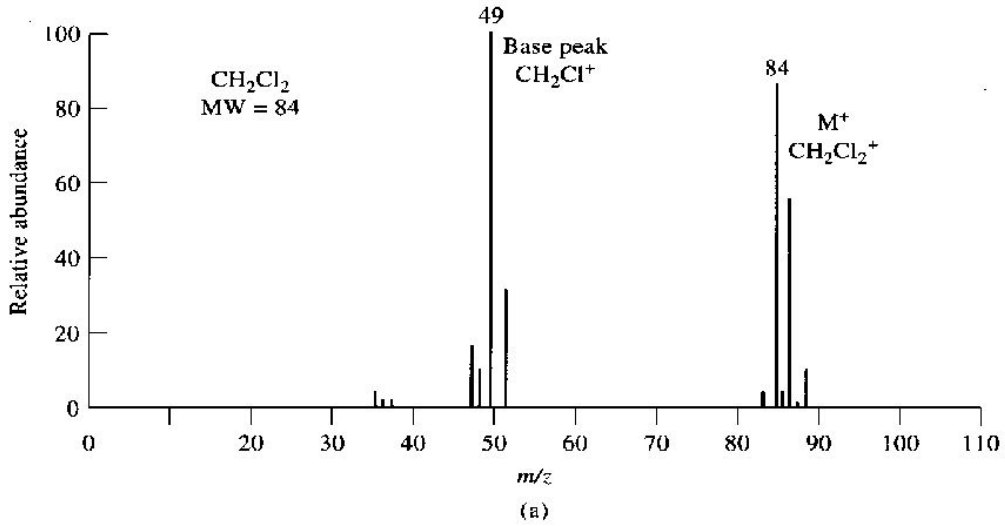
$$ABCD^{\bullet +} + ABCD \rightarrow (ABCD)^{\bullet 2+} \rightarrow BCD^\bullet + ABCDA^+$$

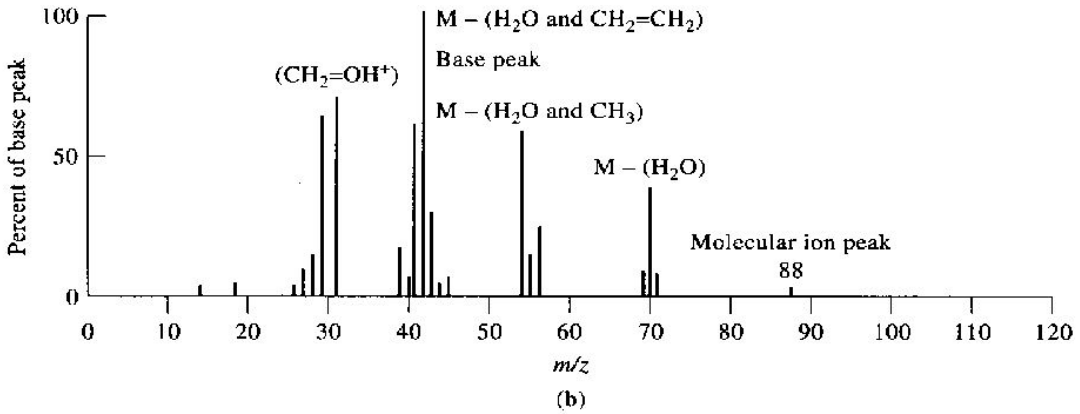
Energy = 70eV 6700 kJ/mol

$2(ABCD)^{\bullet +}$

Typical bond energies 200 to 600 kJ/mol EXTENSIVE FRAGMENTATION

Electron Impact Spectra

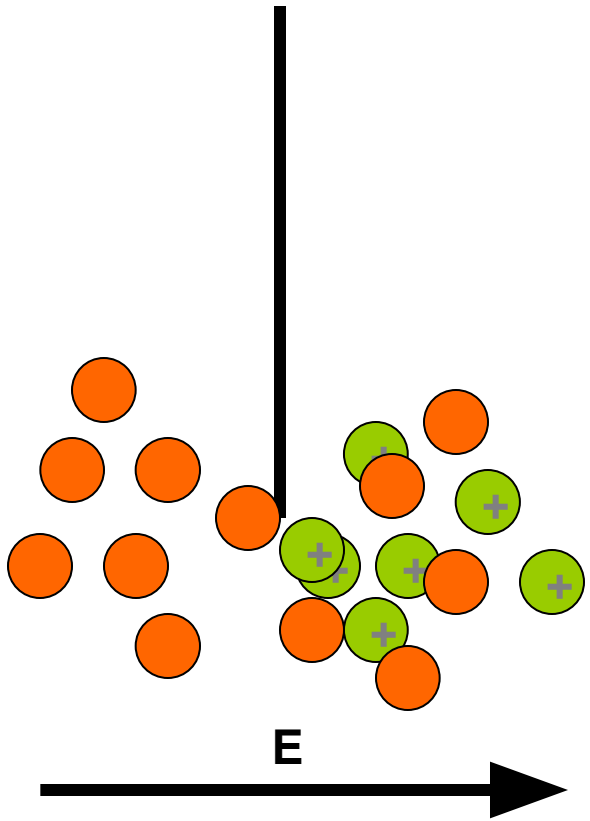




- Different molecules behave differently
- Good molecular ion little fragmentation
- No molecular ion extensive fragmentation
- Isotopes are extremely important!
- Molecular ion isotopic cluster

Ionization vs. Desorption?

FIELD IONIZATION **FIELD DESORPTION**



Field Ionization Sources

Apply large electric fields to carbon dendrites on a tungsten wire

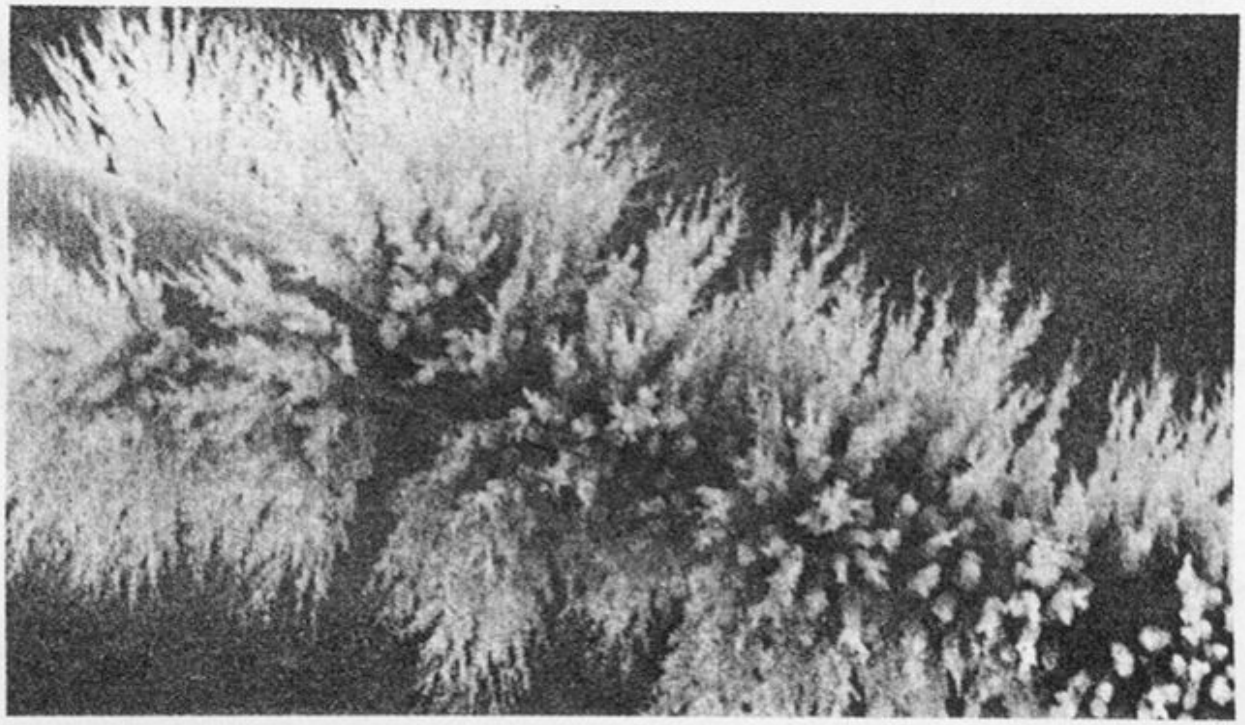
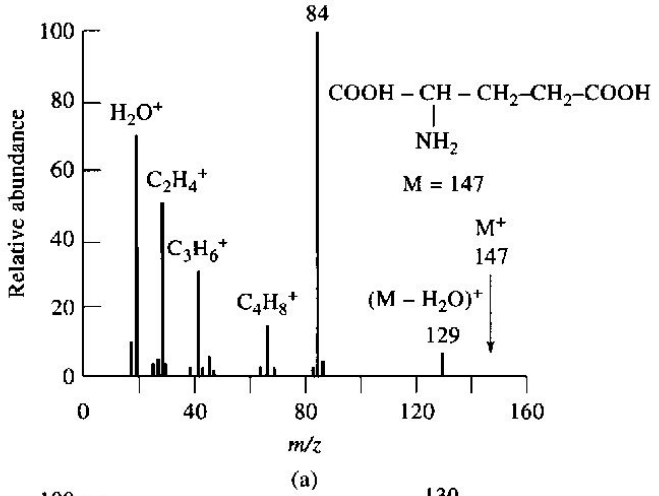
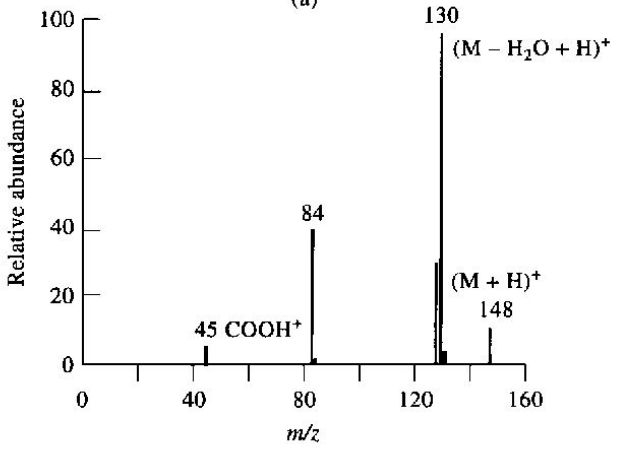


Fig. 6.1 Scanning electron micrograph (×500) of high temperature activated FD emitter. (Reprinted with permission from W.D. Reynolds *Anal. Chem.*, **51**, 283A[4]: Copyright (1979) American Chemical Society)

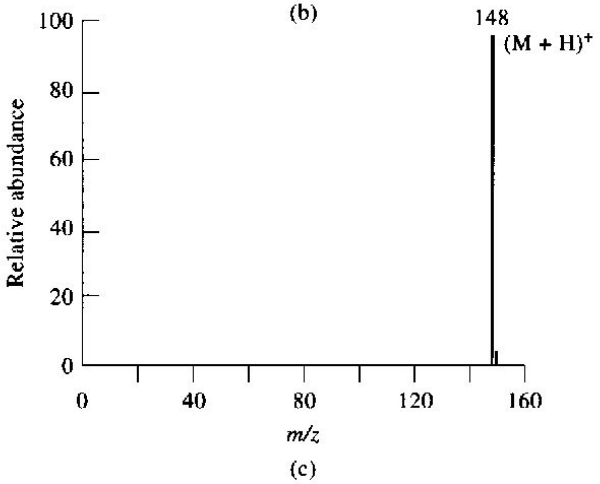
Glutamic Acid



Electron Impact (EI)



Field Ionization



Field Desorption

FAB Ionization

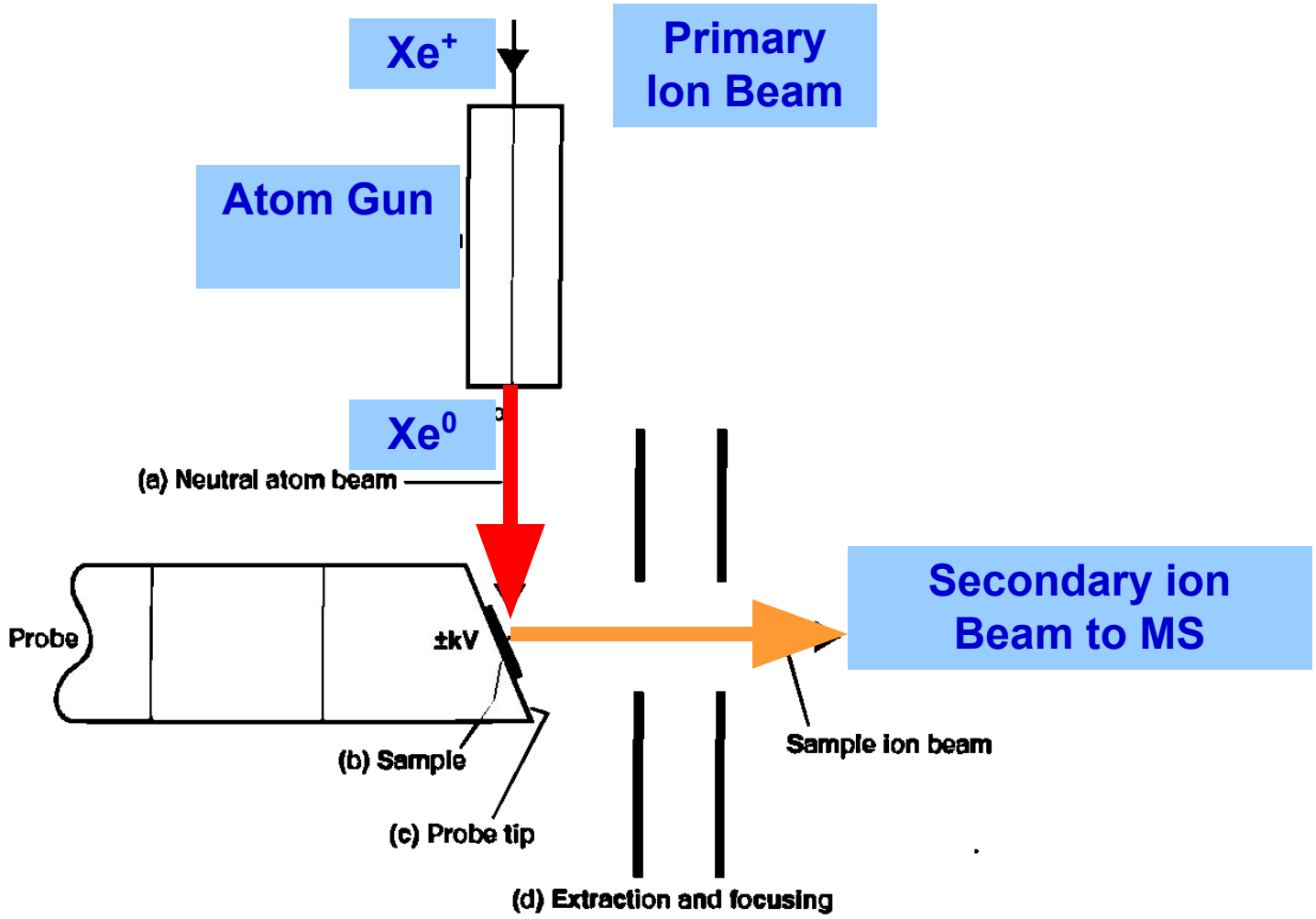
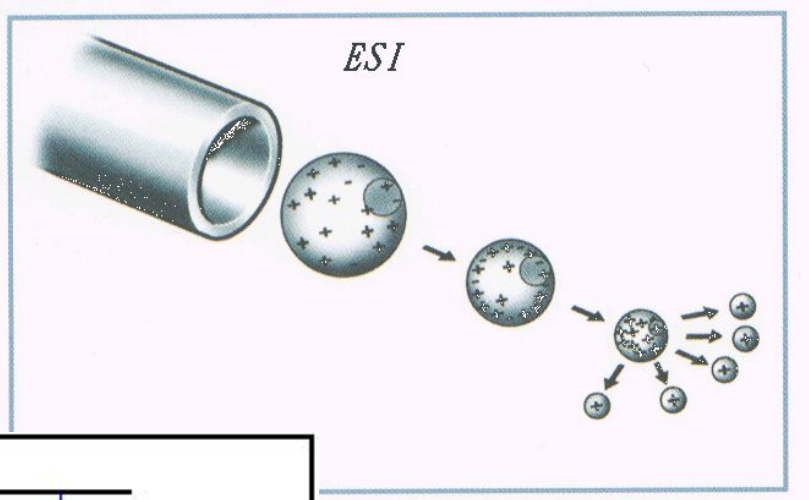
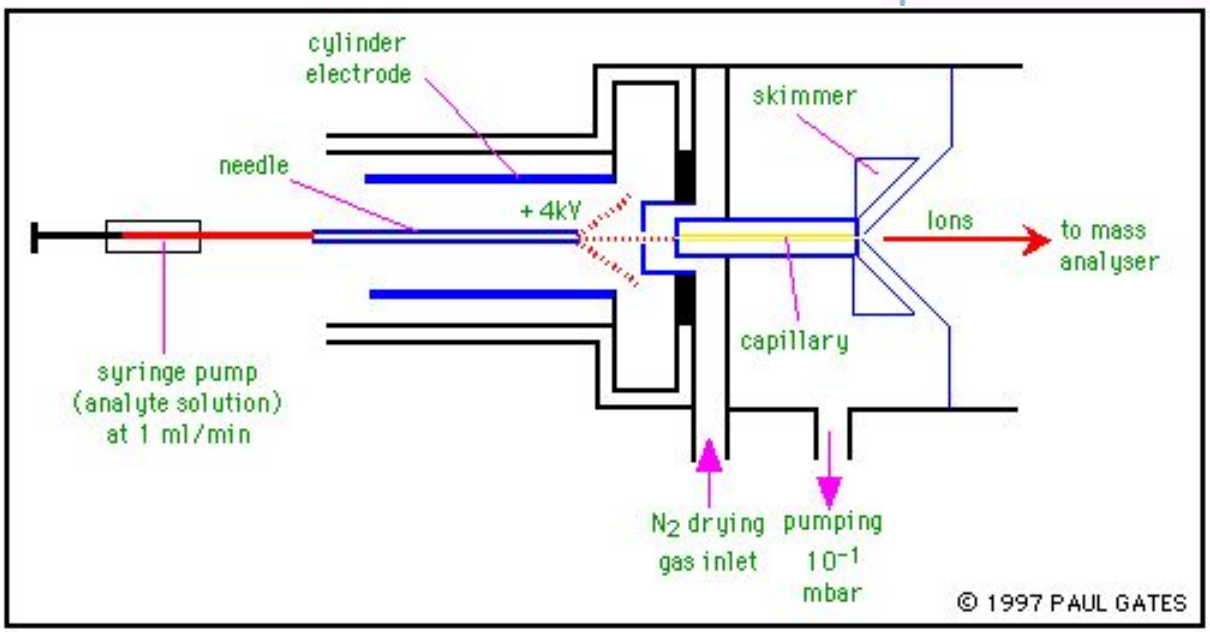


Fig. 5.4 Schematic diagram of fast ion bombardment ion source

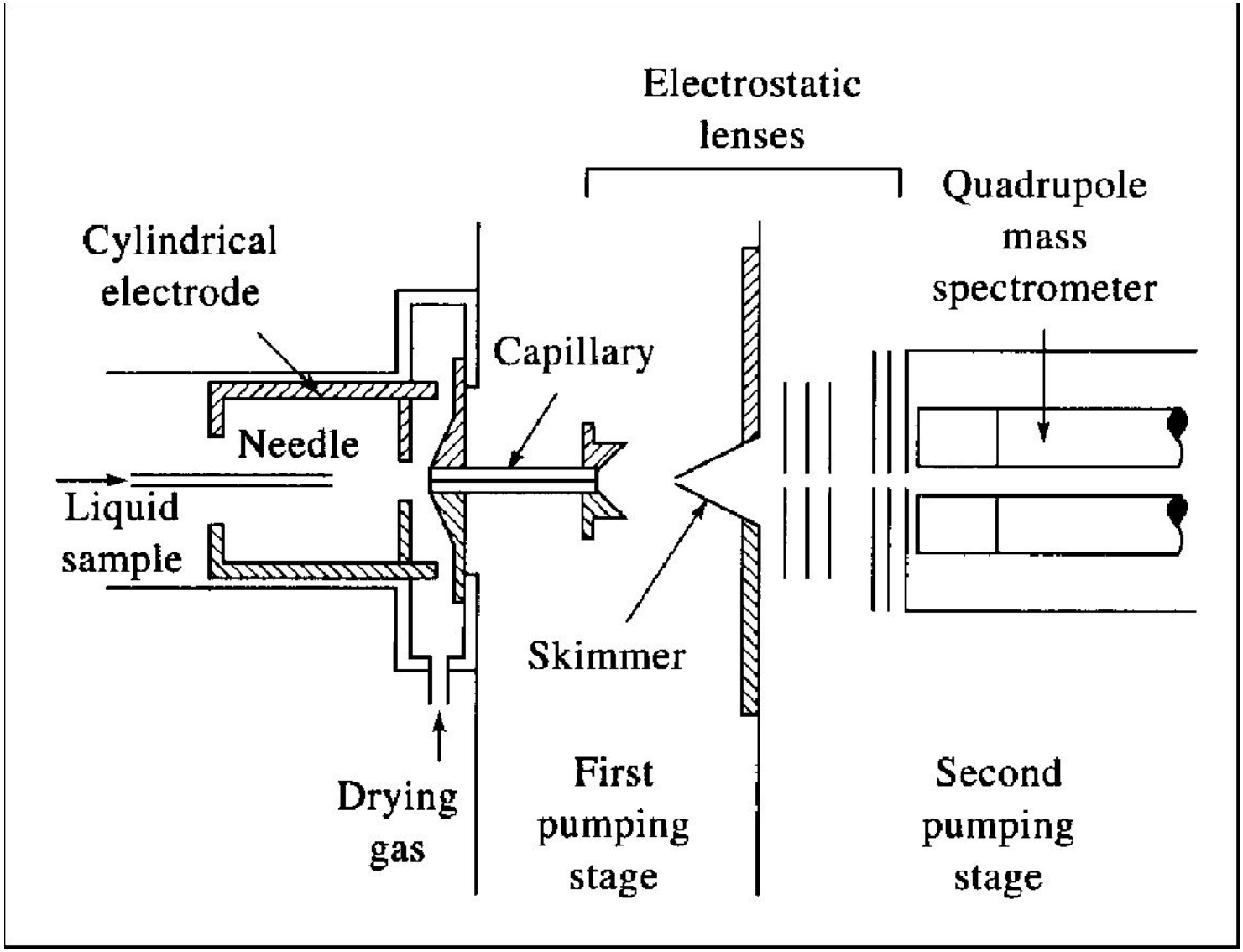
ESI

Растворители
Ацетонитрил 50%
MeOH 50%
0.1 HCOOH

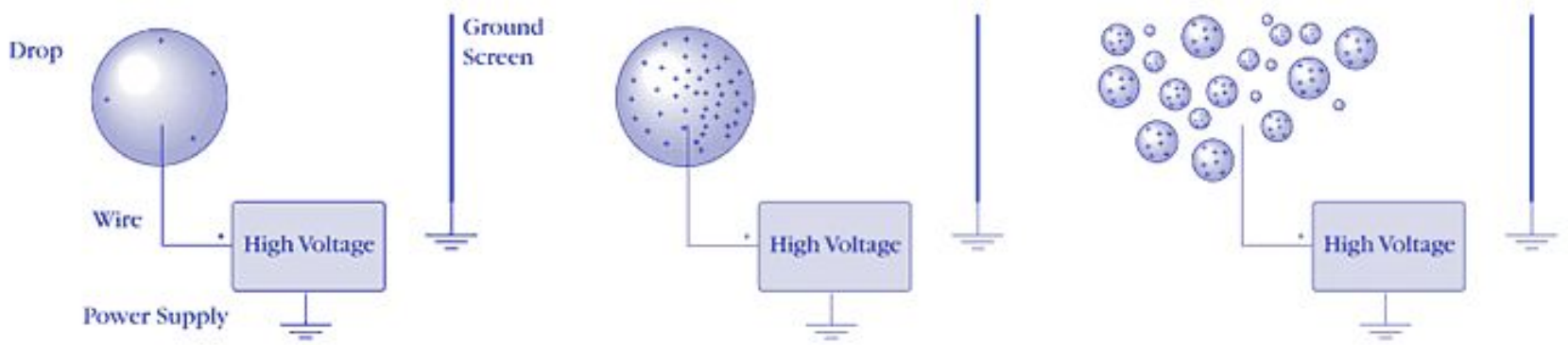


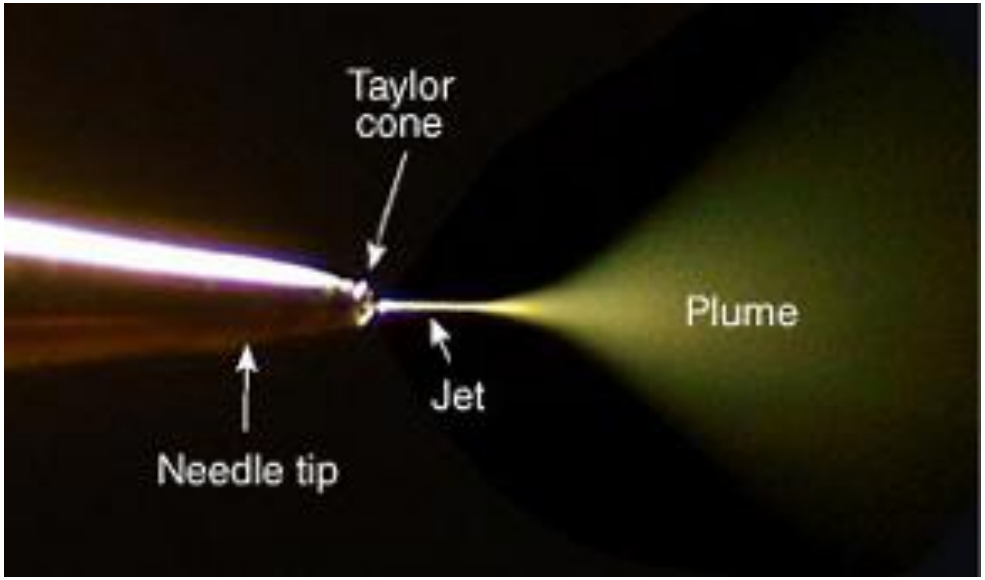


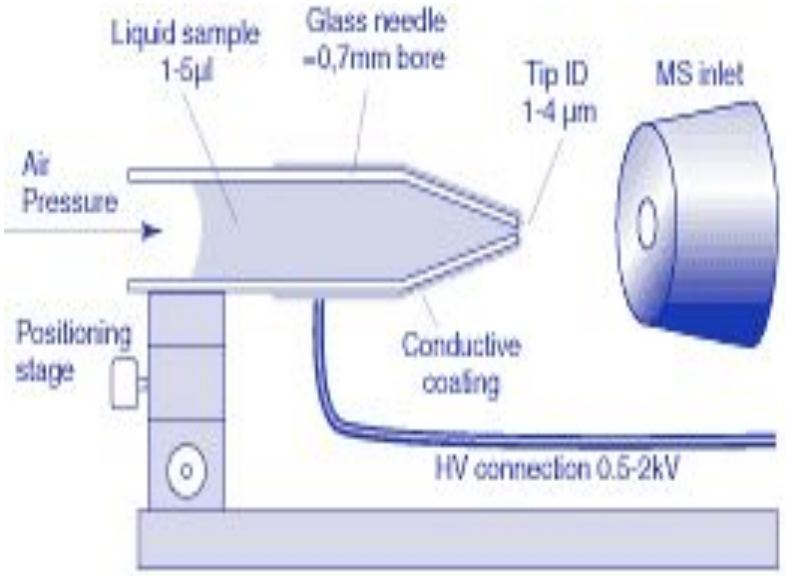
Electrospray Ionization Source



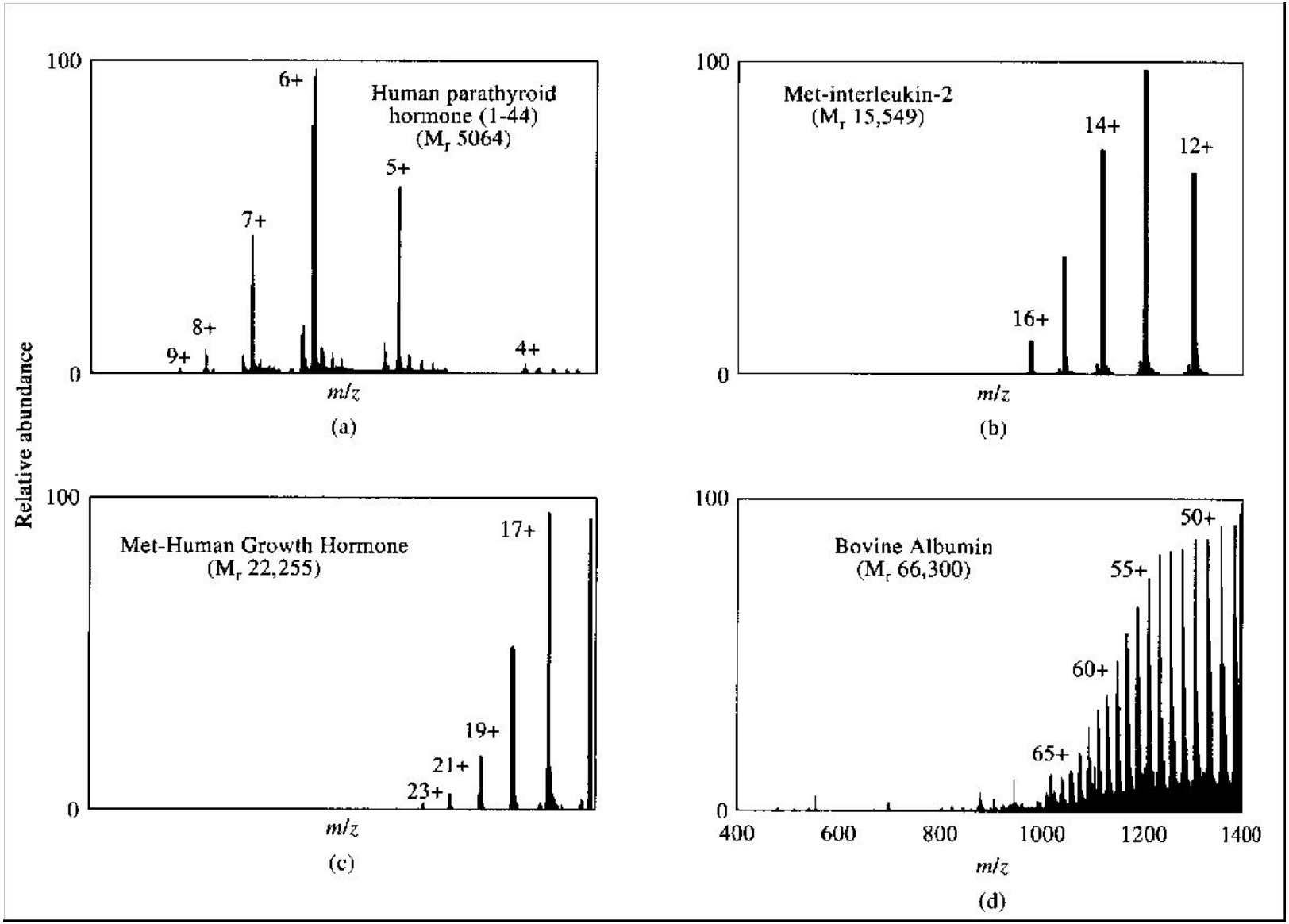
ELCTROSPRAY IONIZATION DETAILS





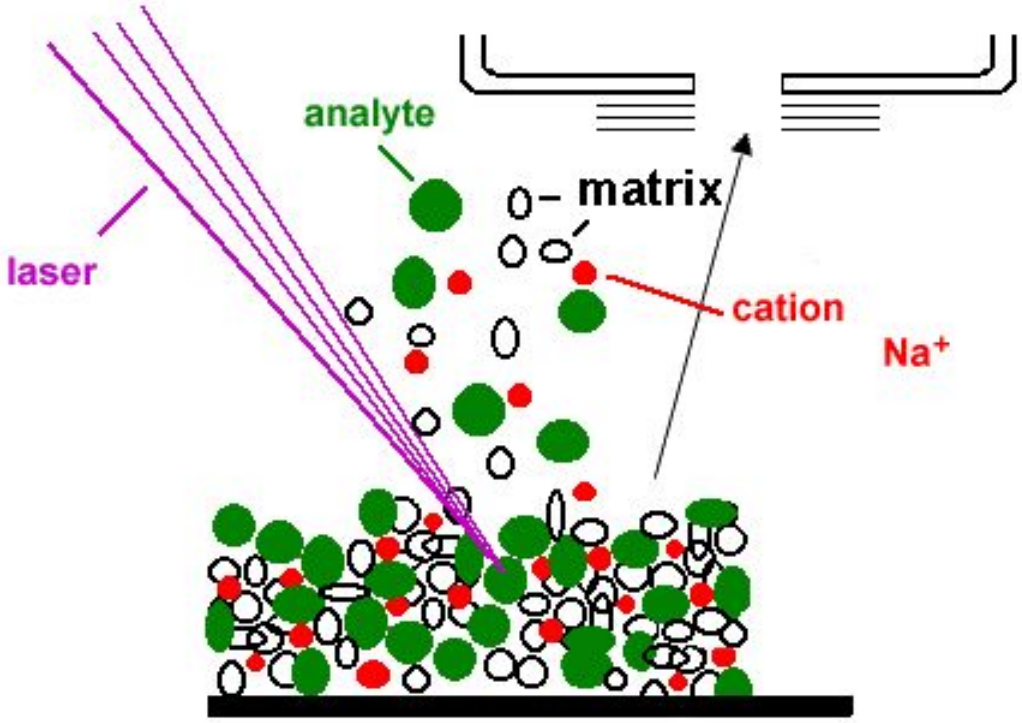


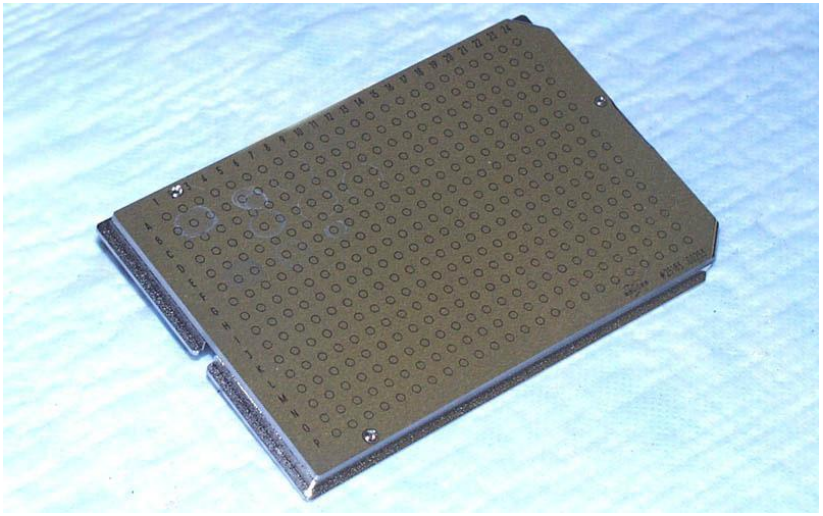
Electrospray Ionization MS of Proteins and Peptides



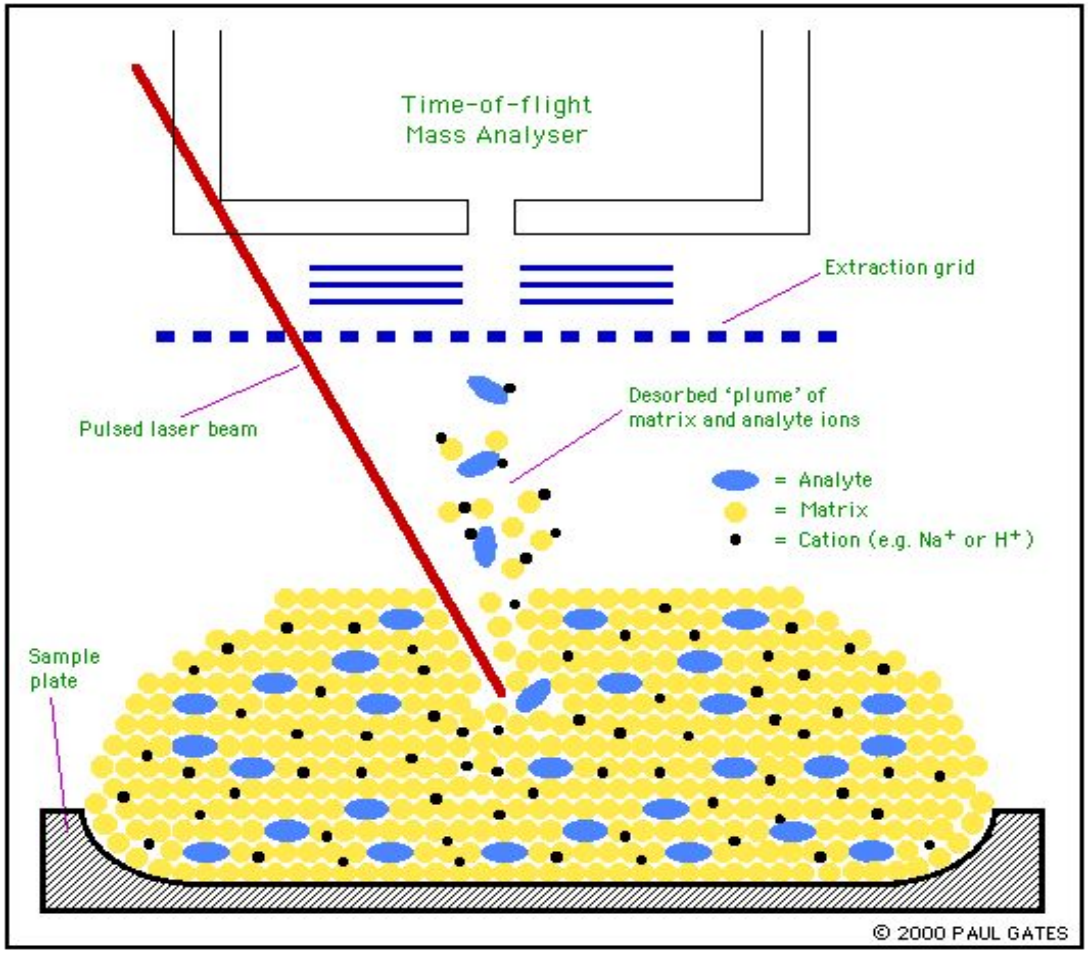
Источники ионов MALDI

MALDI - matrix assisted laser desorption / ionization
лазерная десорбция/ ионизация в присутствии вспомогательного вещества - матрицы





MALDI


Time-of-flight
Mass Analyser
Extraction grid
Pulsed laser beam
Desorbed 'plume' of
matrix and analyte ions
= Analyte
= Matrix
= Cation (e.g. Na+ or H+)
Sample
plate
© 2000 PAUL GATES

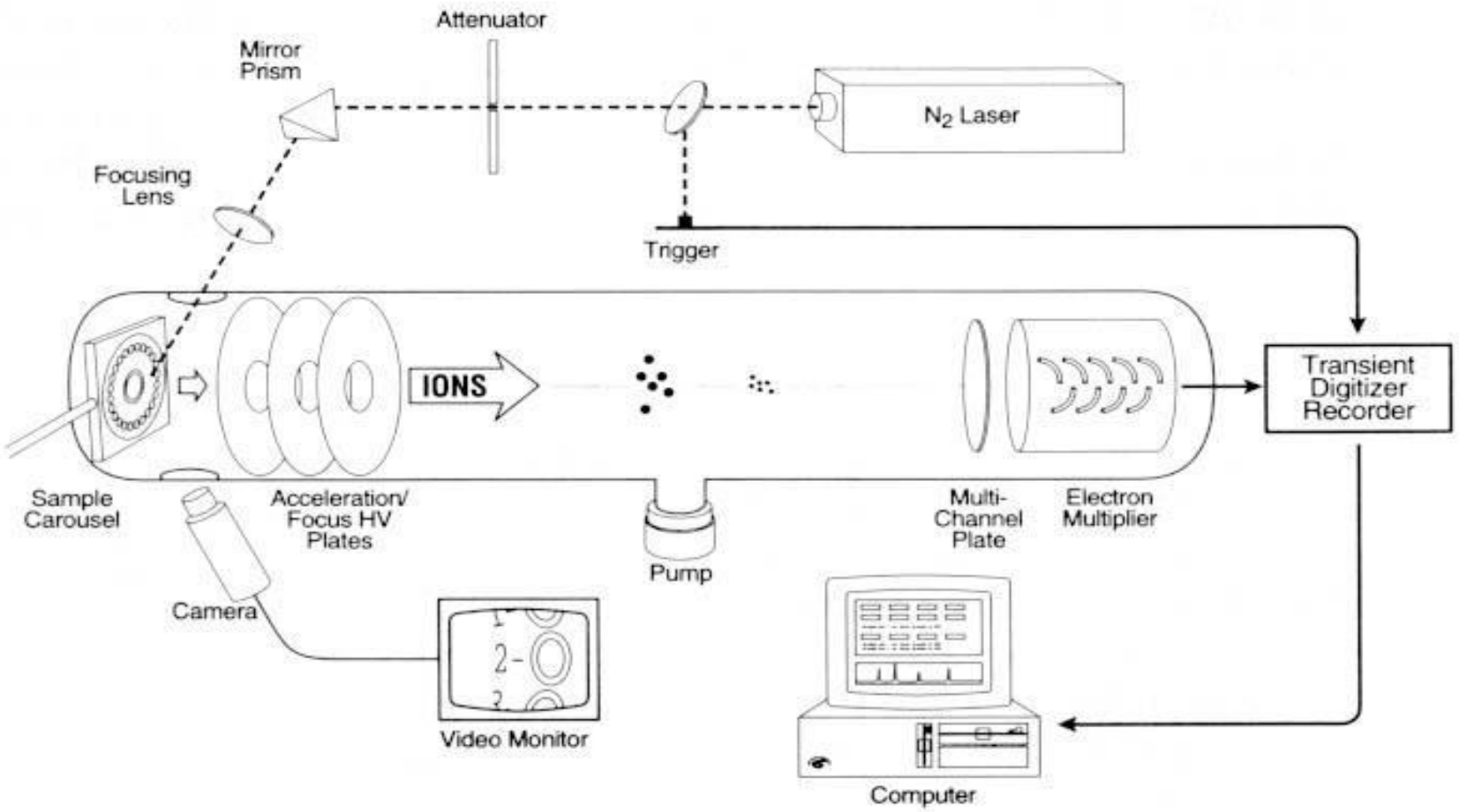
Solid Matrix Materials for MALDI

TABLE 20-4 Matrices Most Frequently Used for MALDI Together with the Usable Wavelengths*

Matrix	Wavelength (nm)
Nicotinic acid	266, 220–290
Benzoic acid derivatives:	
2,5-Dihydroxybenzoic acid	266, 337, 355
Vanillic acid	266
2-Amino-benzoic acid	266, 337, 355
Pyrazine-carboxylic acid	266
3-Aminopyrazine-2-carboxylic acid	337
Cinnamic acid derivatives:	
Ferulic acid	266, 377, 355
Sinapinic acid	266, 337, 355
Caffeic acid	266, 337, 355
3-Nitrobenzylalcohol	266

*From M. Karas and U. Bahr, *Trends Anal. Chem.*, **1990,** 9, 322.

MALDI-TOF


Attenuator
Mirror
Prism
N_2 Laser
Focusing
Lens
Trigger
IONS
Transient
Digitizer
Recorder
Sample
Carousel
Acceleration/
Focus HV
Plates
Multi-
Channel
Plate
Electron
Multiplier
Pump
Camera
Video Monitor
Computer