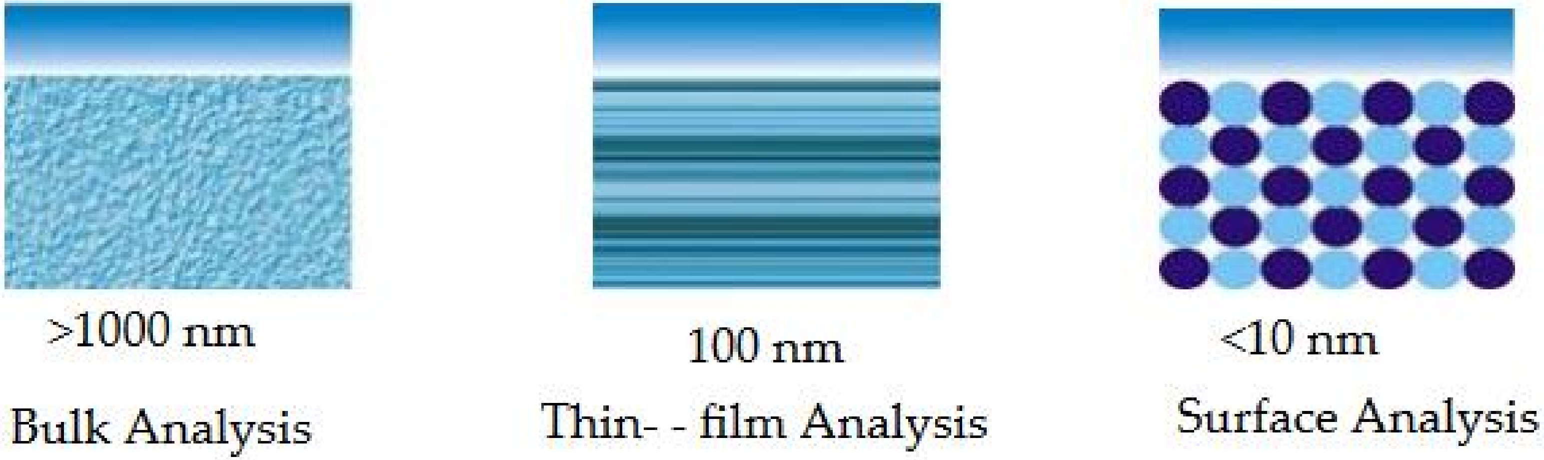
Surface Chemistry

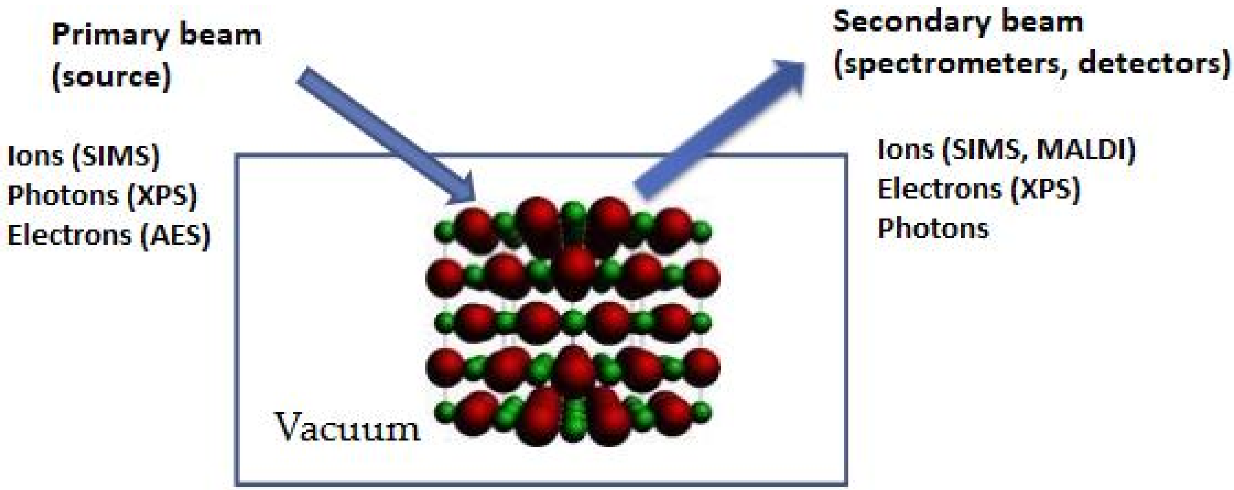
XPS
X-Ray Photoelectron Spectroscopy

SIMS
Secondary Ion Mass Spectrometry

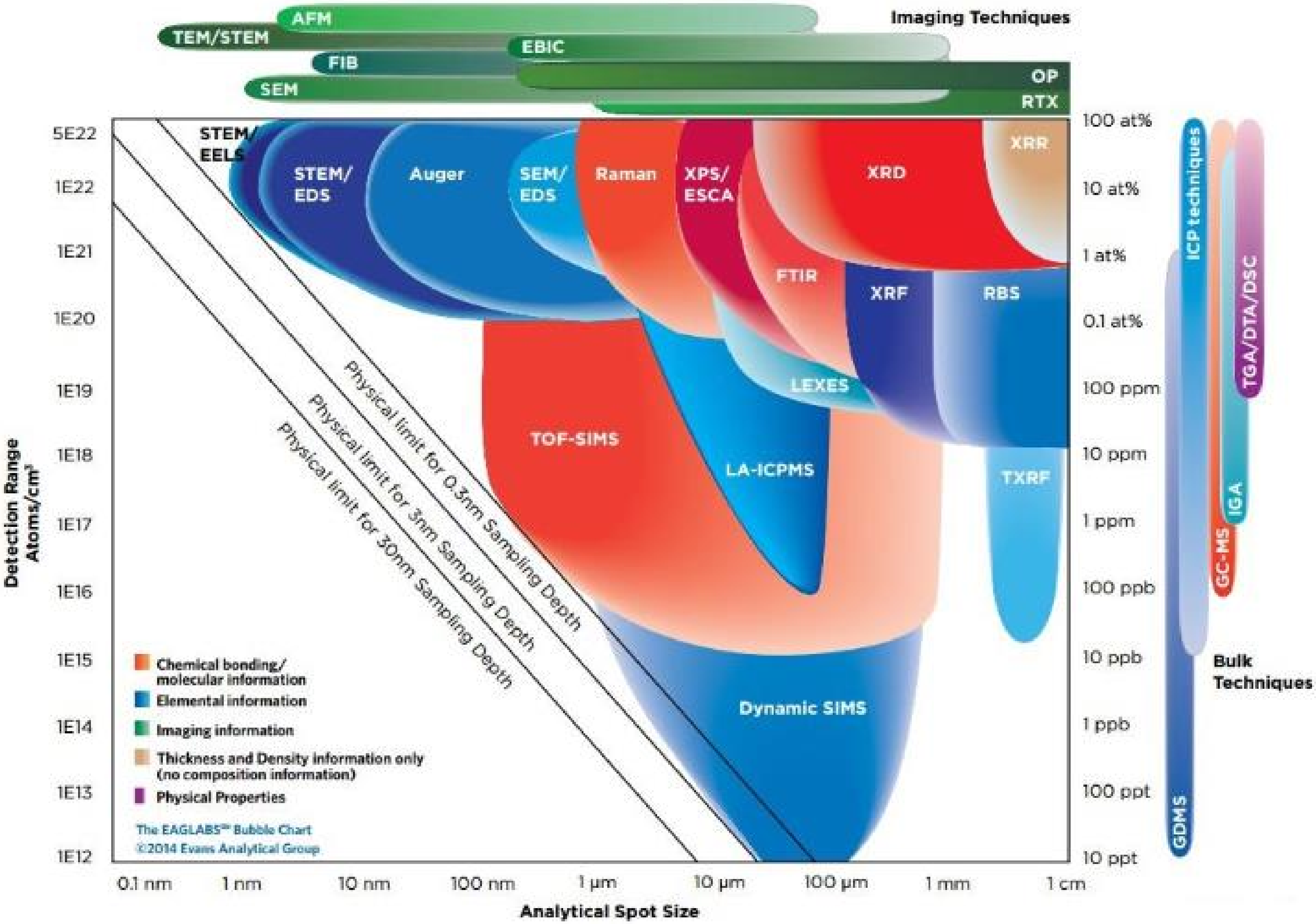
MALDI
Matrix Assisted Laser Desorption Ionization

Surface and Surface Analysis

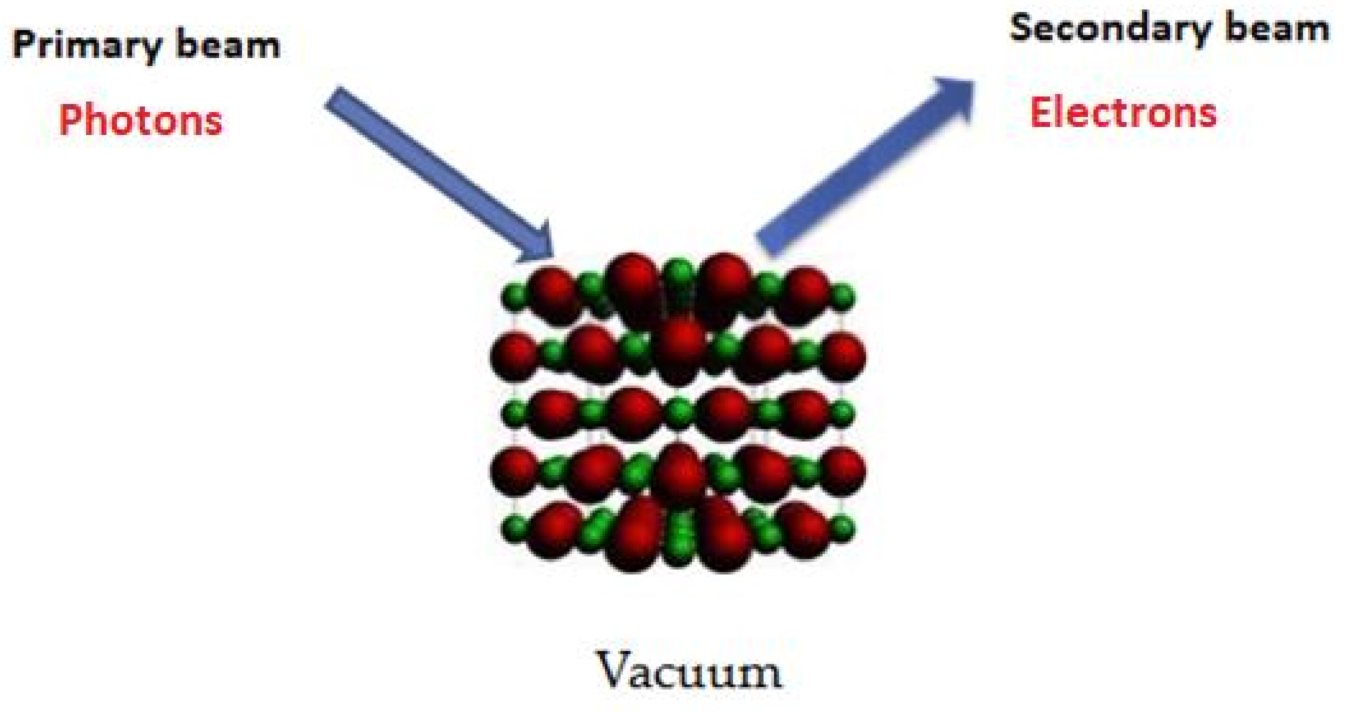




Analytical Resolution vs. Detection Limit



X-Ray Photoelectron Spectroscopy, XPS



History of XPS

1905
- Photoelectric effect by Einstein

1914
- Rutherford and coworkers, $E_{kin} = h\nu - E_{binding}$

1923
- while studying electron emission induced by X-ray excitation in a Wilson cloud chamber, Pierre Victor Auger observed electron emitted with constant energy independent of the X-ray energy.

1930
- Robinson and Young, who observed the line shift caused by chemical bonding.

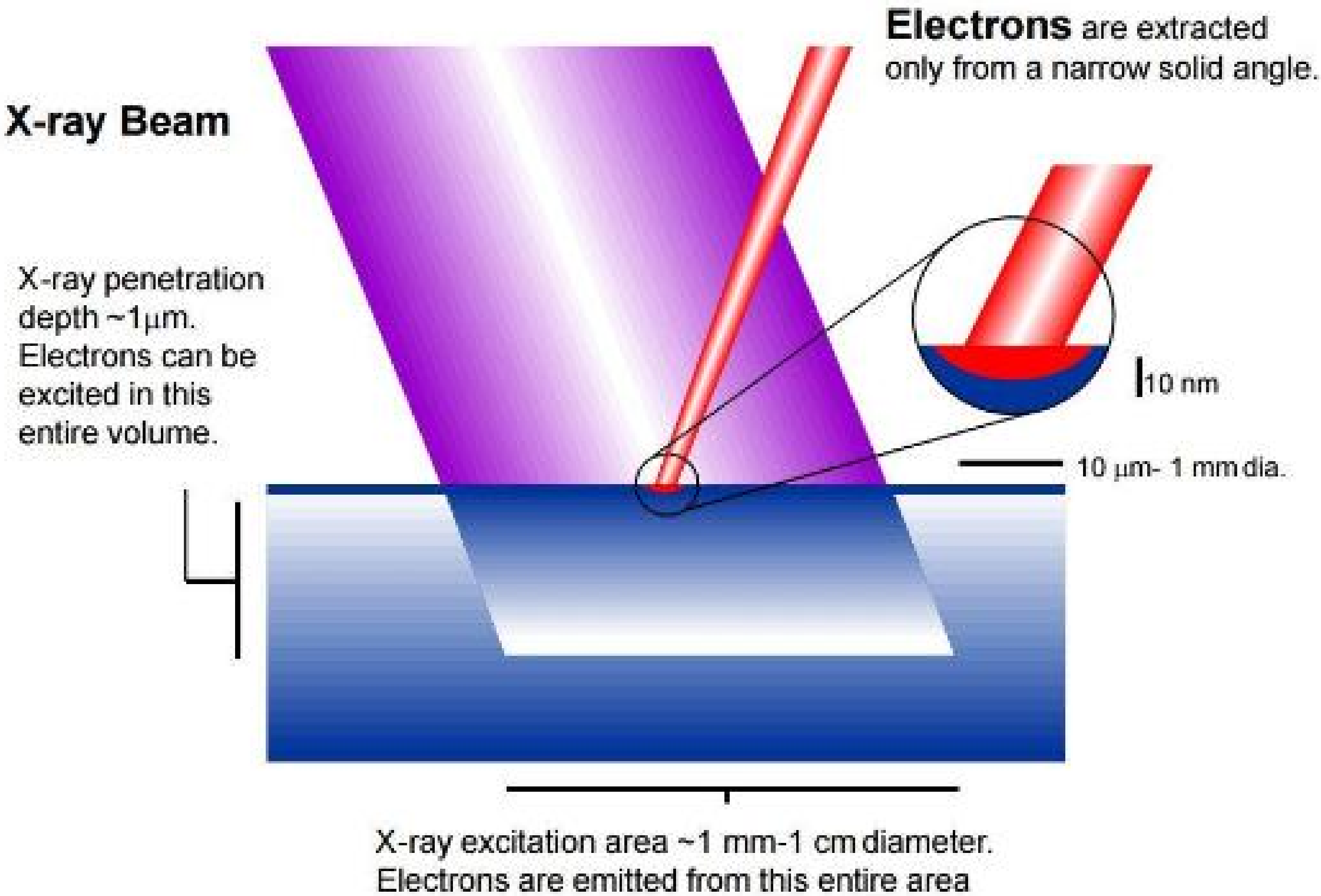
1950
- The development of electron spectrometers in Uppsala by Kai Siegbahn, the first XPS spectra with high resolution, investigation of core level binding energies and their shifts due to chemical bonding.

1981
- Siegbahn received the Nobel Prize in physics for his achievements in ESCA (he also coined the acronym ESCA).

1969
- The first commercial AES instruments for surface analysis.

1985
- the use of XPS in materials increased dramatically with the development of digital instruments with multichannel detection and with higher analyzer transmission.

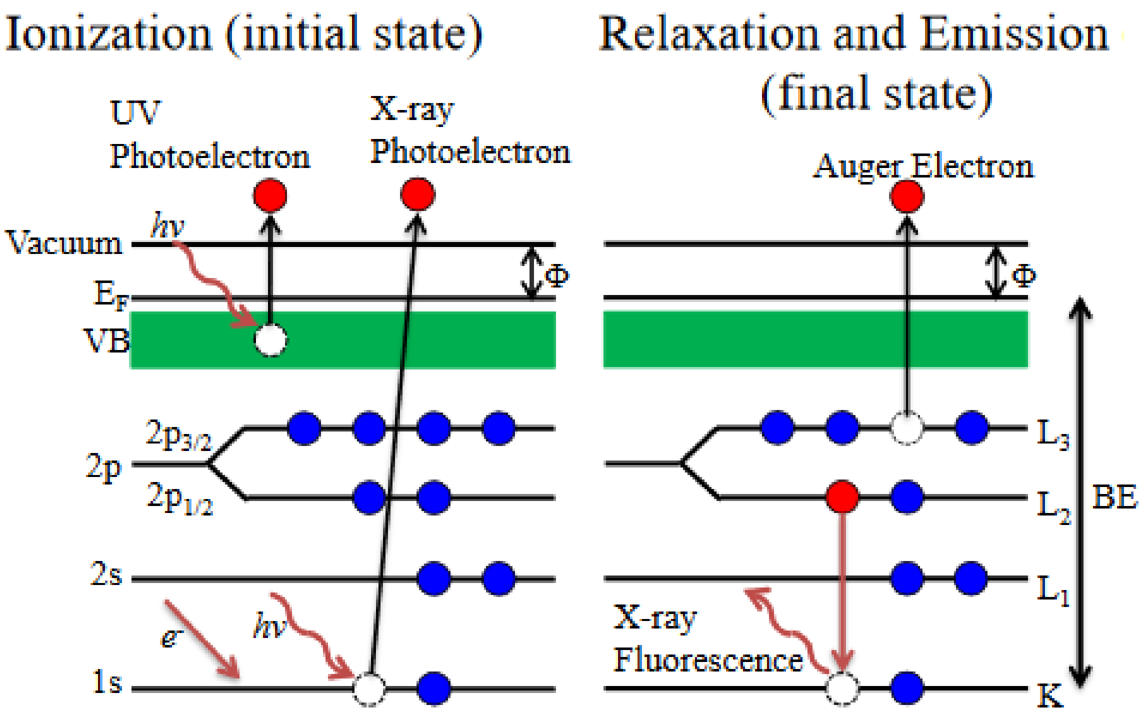
Scattering of Photoelectrons

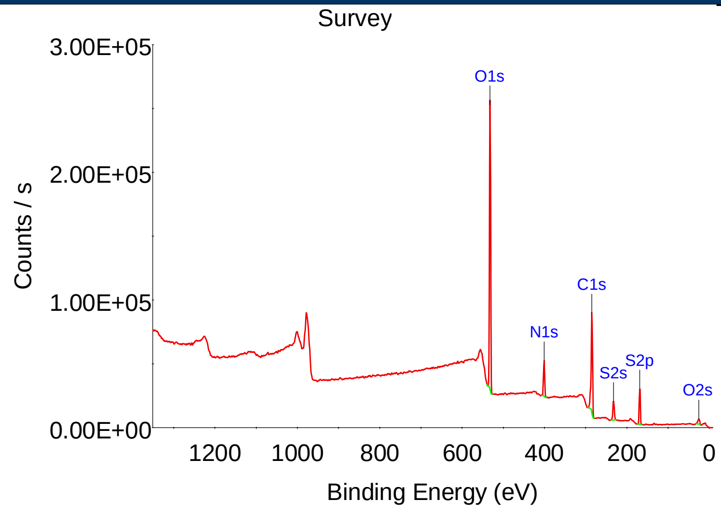


Introduction to XPS

XPS
X-Ray Photoelectron Spectroscopy

ESCA
Electron Spectroscopy for Chemical Analysis





$$E_k(e^-) = h\nu - E_b$$

$E_k(e^-)$ Kinetoc Energy of ejected photoelectron

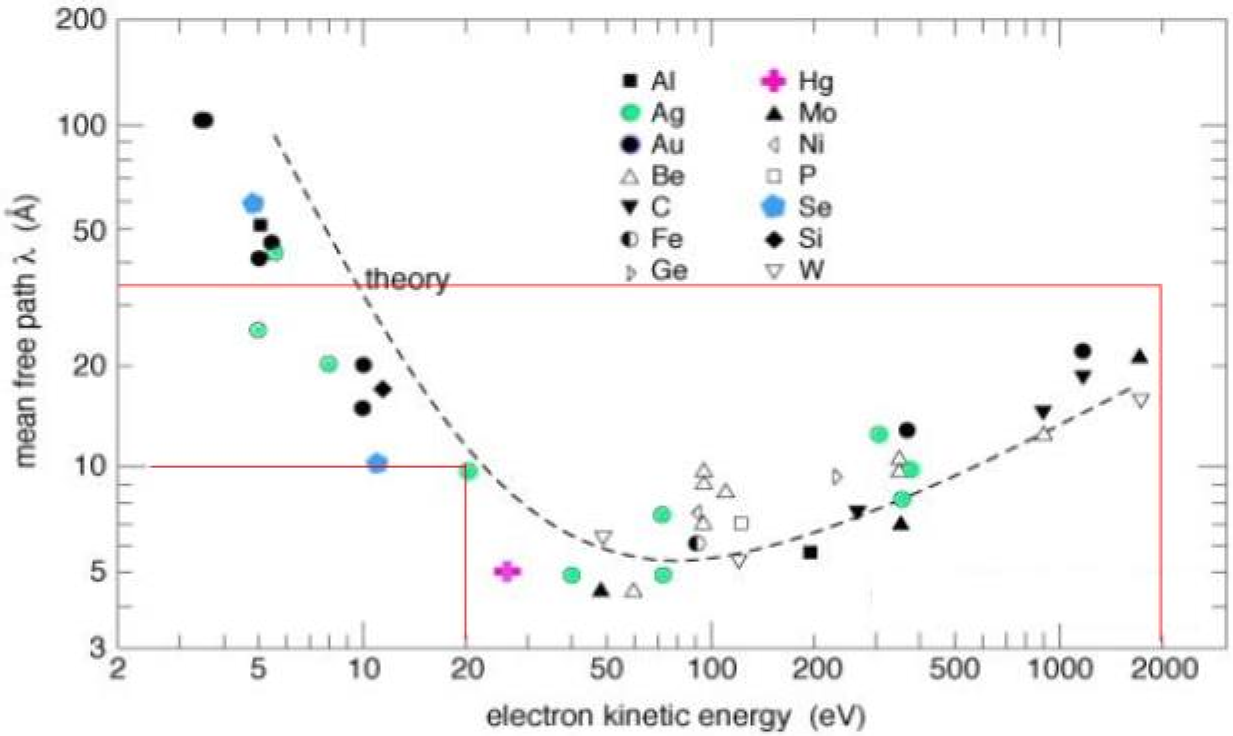
h3 characteristic energy of X-ray photon

E_b Binding Energy of the atomic orbital from which the electron originates

Elecron Inelastic Mean Free Path, IMFP

The average distance an electron travels through a solid before losing energy through inelastic collisions.

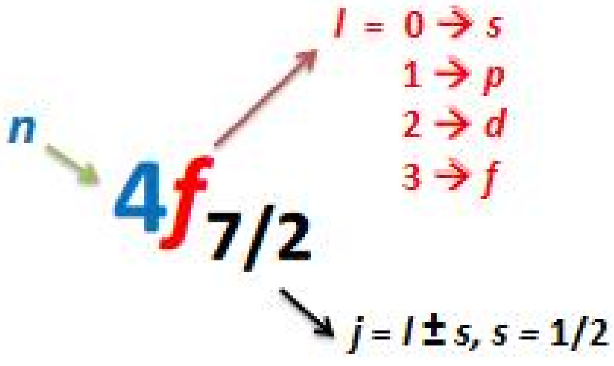
"Universal Curve" - λ (IMFP) *vs* kinetic



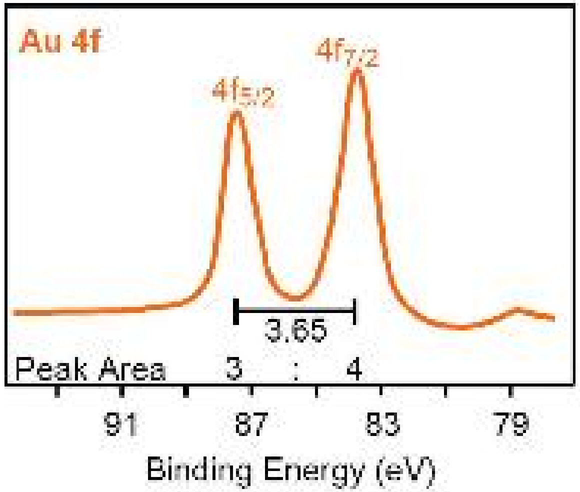
$\lambda = 1 \sim 3.5$

for X-ray photoelectrons

XPS Peak Notation

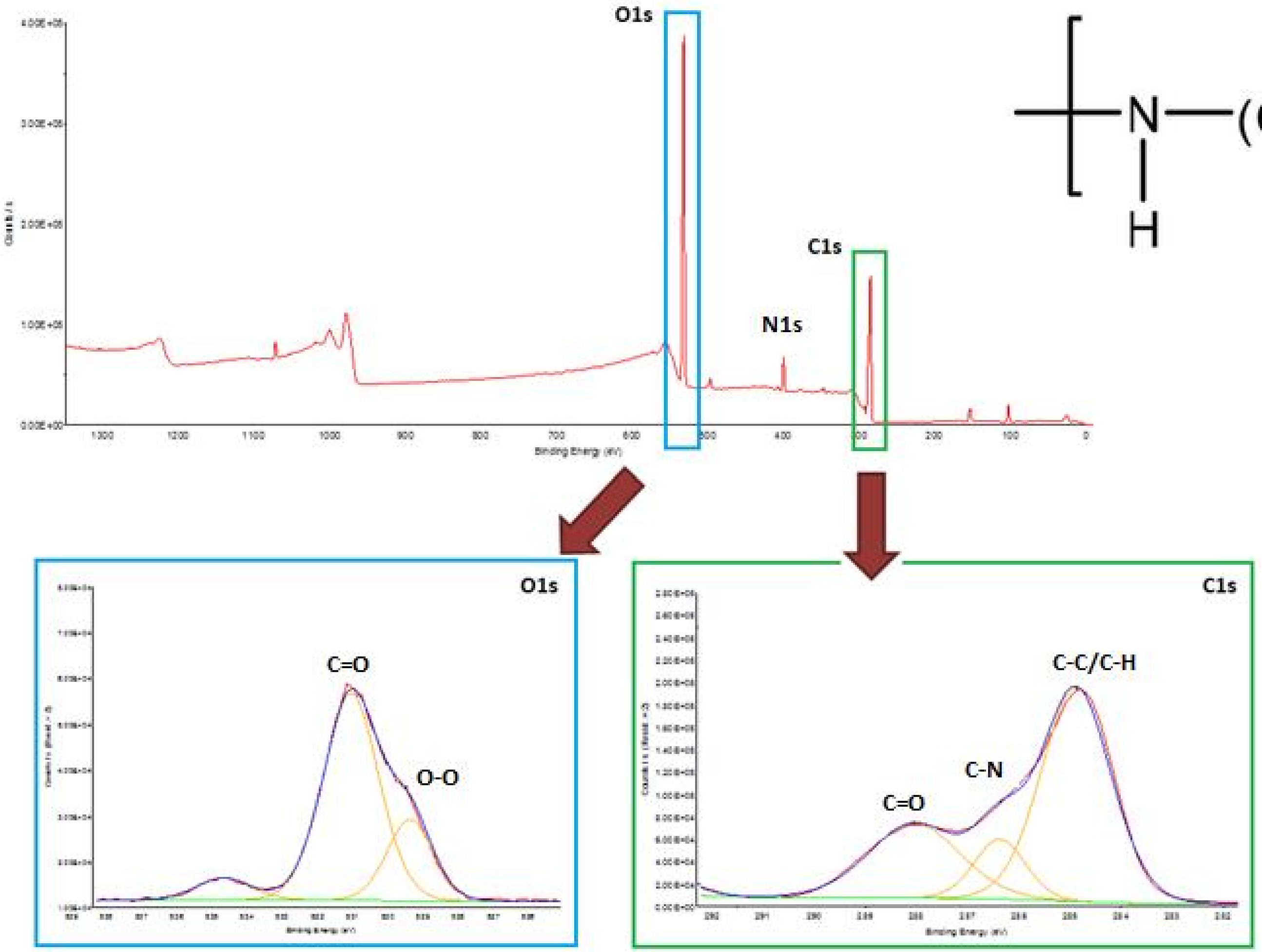


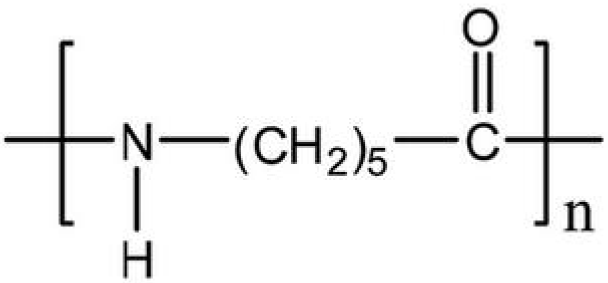
Spin-orbital splitting with $l > 0$



Orbital	l	j	Degeneracy ($2j + 1$)	Peak area ratio	Electron level
s	0	1/2	1	-	1*s*
p	1	1/2, 3/2	2, 4	1 : 2	$2p_{1/2}$, $2p_{3/2}$
d	2	3/2, 5/2	4, 6	2 : 3	$3d_{3/2}$, $3d_{5/2}$
f	3	5/2, 7/2	6, 8	3 : 4	$4f_{5/2}$, $4f_{7/2}$

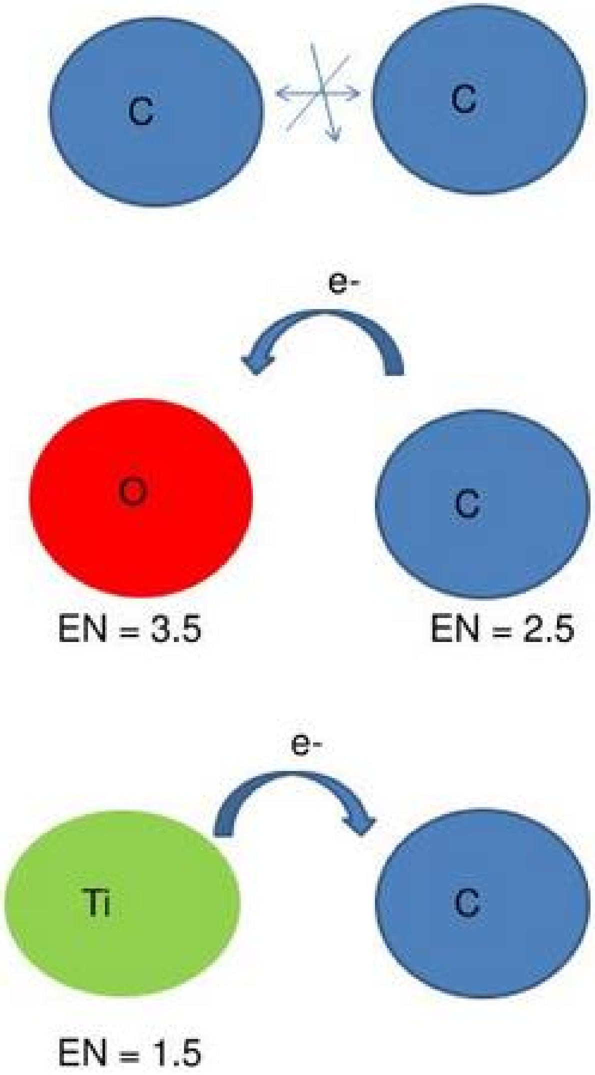
Analysis of XPS Data, Surface Spectroscopy





Polyamide 6

Chemical Shifts



Elemental C: binding energy = 285.0 eV

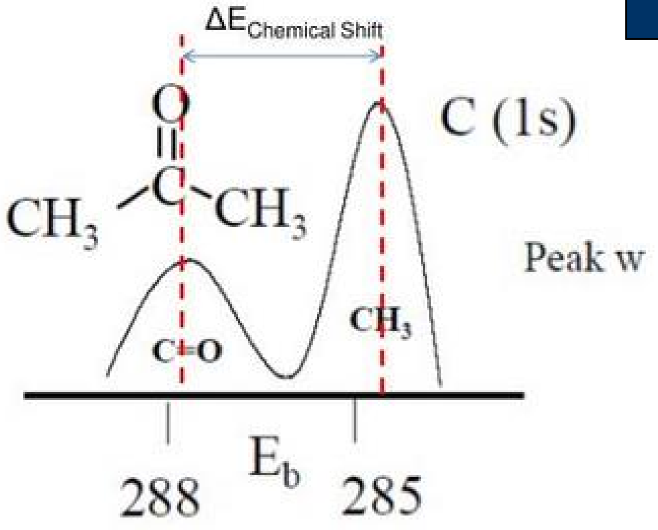
O withdraws valence charge from C:
C(1s) shifts to higher BE relative to elemental C (diamond) at 285.0 eV

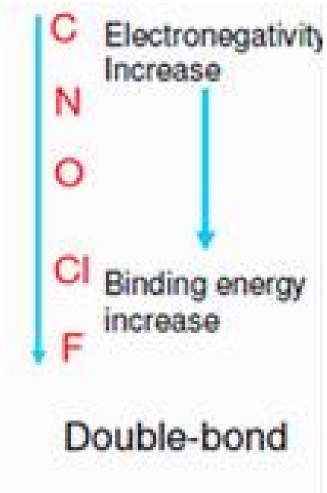
Ti donates charge to C, binding energy shifts to smaller values relative to 285 eV

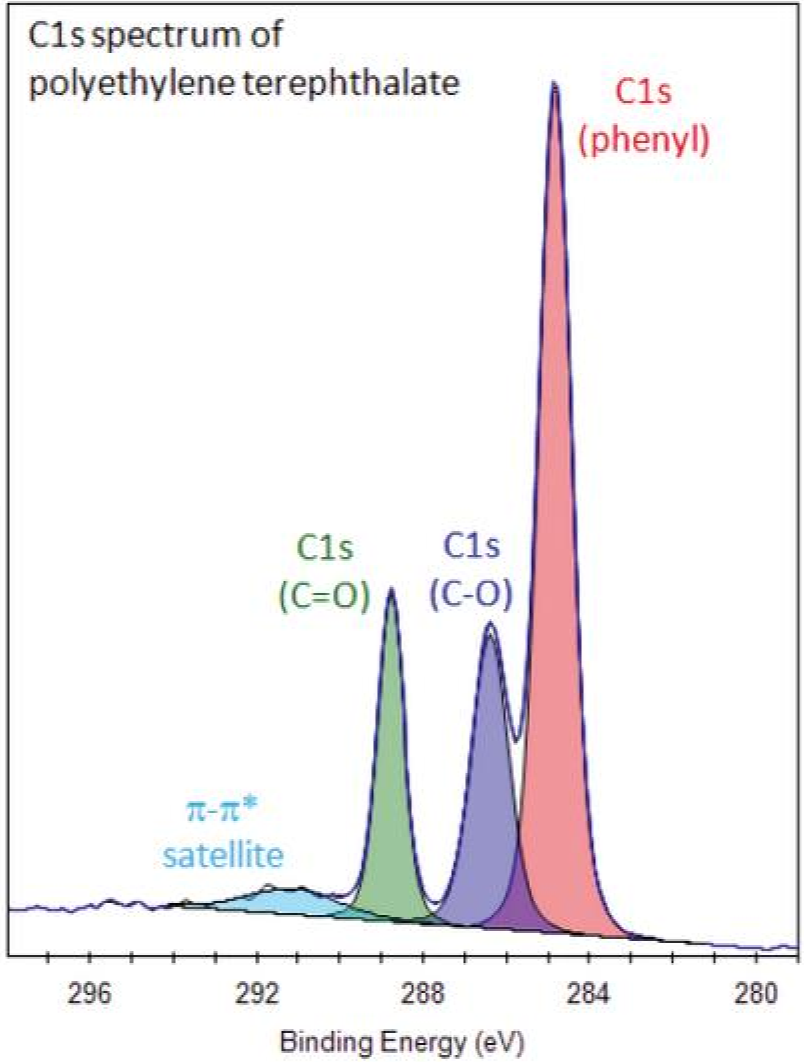
- change in binding energy of a core electron of an element due to a change in the chemical bonding of that element

- very powerful tool for functional group and oxidation state

Chemical Shifts



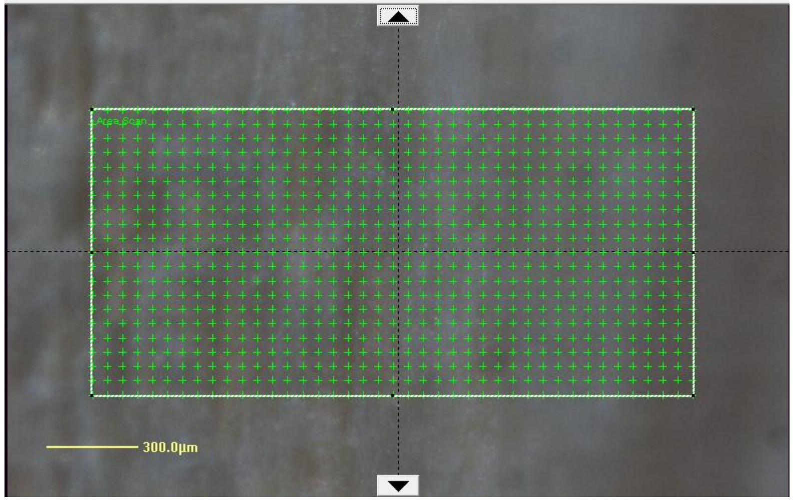


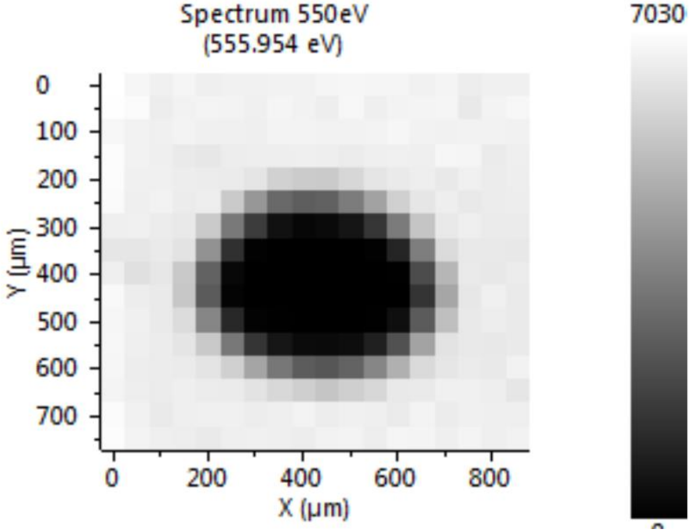


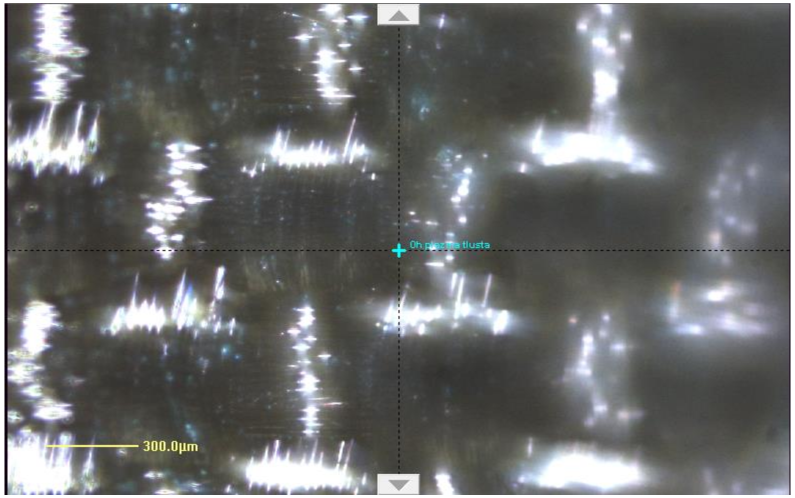
Functional Group		Binding Energy (eV)
hydrocarbon	C-H, C-C	285.0
amine	C-N	286.0
alcohol, ether	C-O-H, C-O-C	286.5
Cl bound to C	C-Cl	286.5
F bound to C	C-F	287.8
carbonyl	C=O	288.0

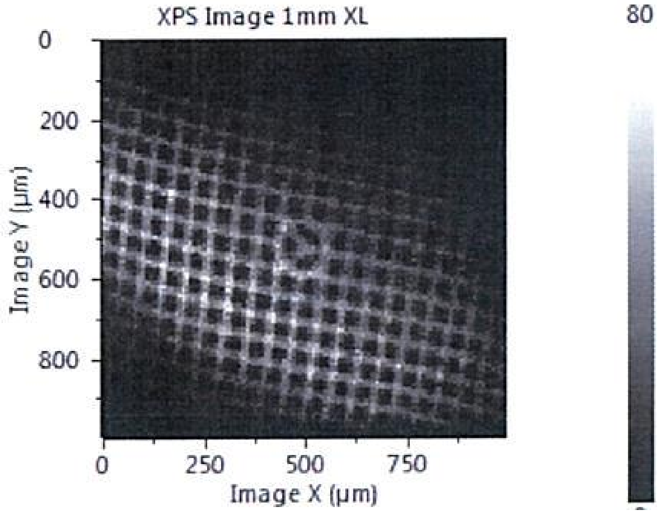
ý

Mapping & Imaging

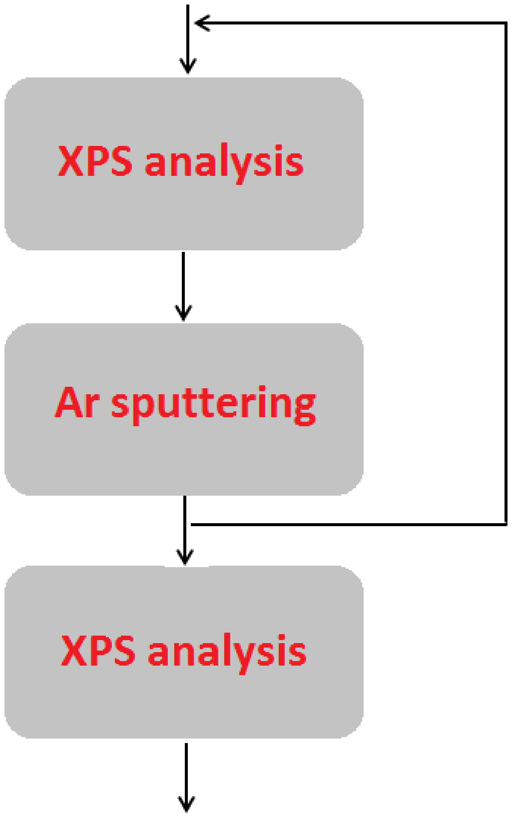


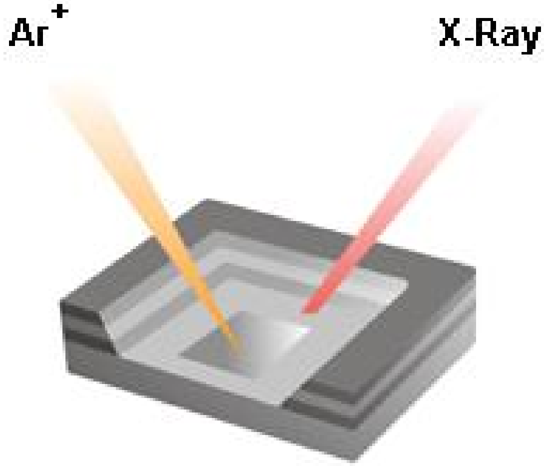


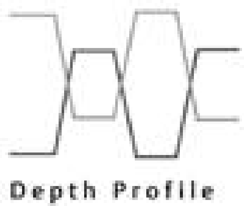


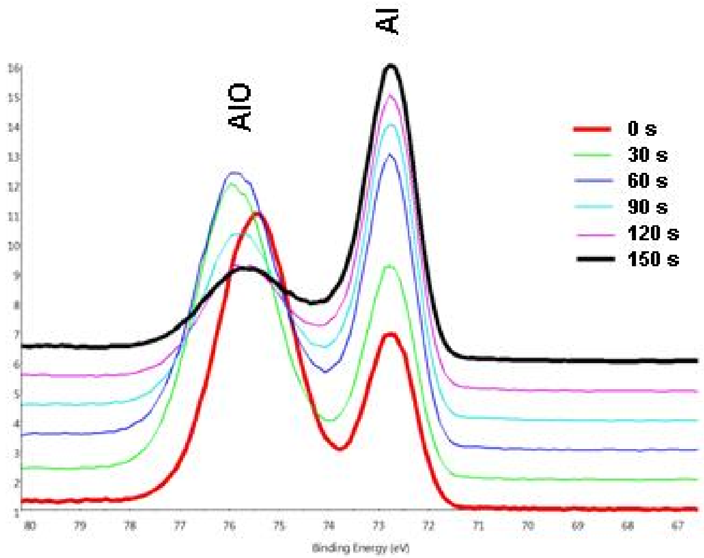


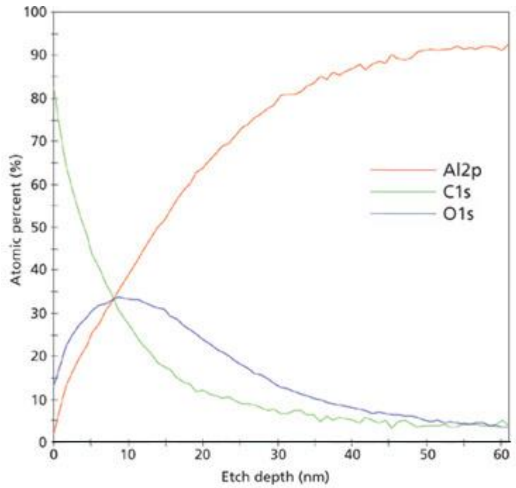
XPS Depth Profile



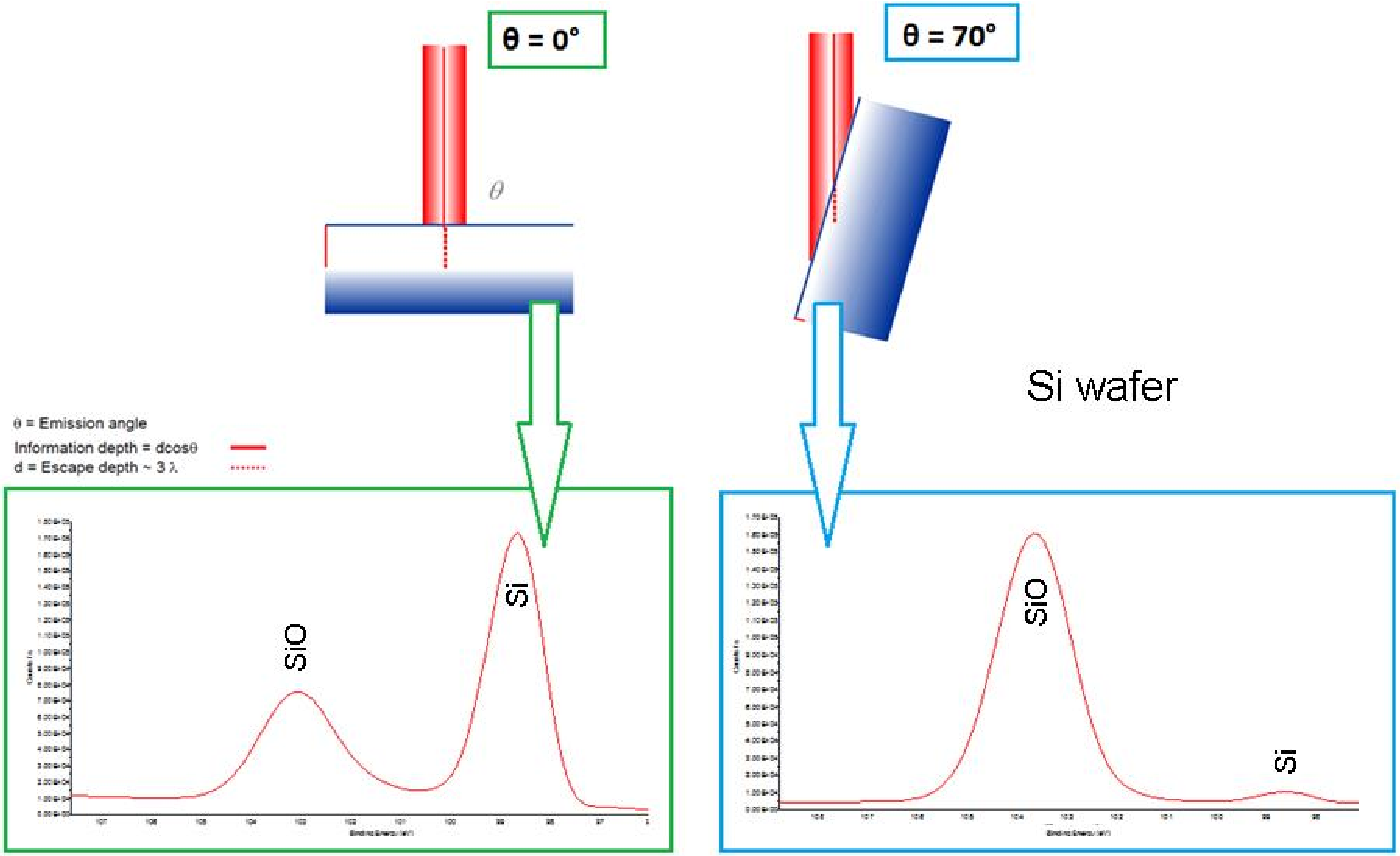






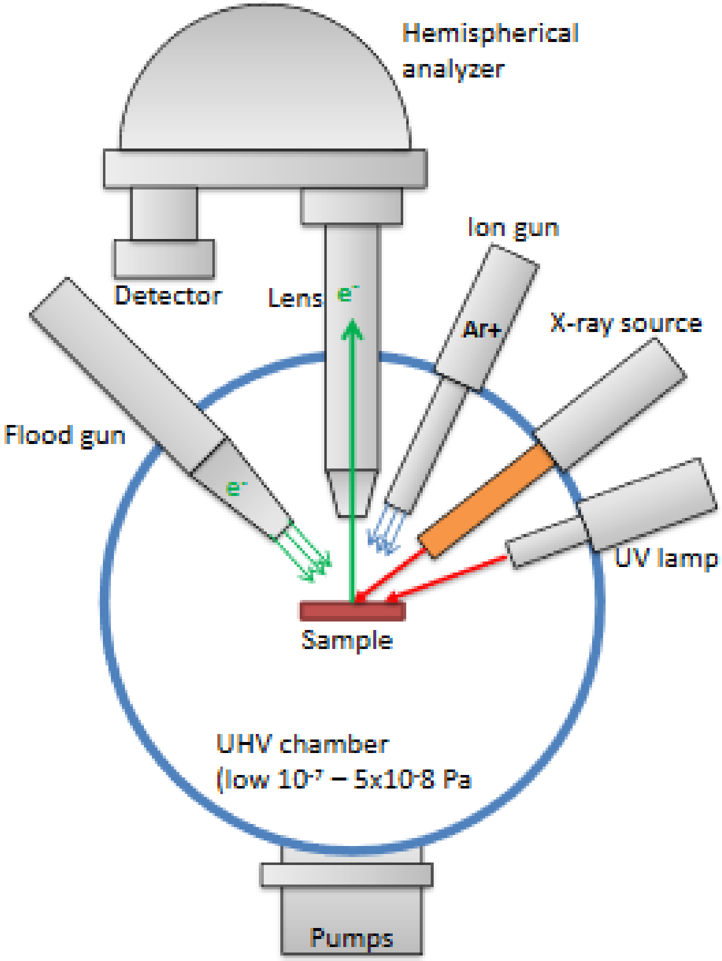


Angle Resolved XPS



Instrumentation

Thermo Scientific Escalab250Xi



UHV system (< 10^{-8} Torr)

- Surface clean
- Longer photoelectron path length

Electron analyzer

- Lens to collect photoelectrons
- Analyzer to filter electron energies
- Detector to count electrons

X-ray source

- Al Kα 1486.6 eV; Mg Kα 1256.6 eV
- Monochromated using quartz crystal

Low-energy electron flood gun

- Insulating samples

Ion gun

- Sample cleaning
- Depth profiling
- For polymers, cluster ion sources may be required

Thermo Scientific Escalab250Xi

Å Identification of all elements (except H & He)
Å Quantitative
Å Chemical state identification
Å Chemical state distributions
Ÿ Photoelectron Spectroscopy
- Energy Resolution FWHM Ò0.45 eV of the Ag $3d_{5/2}$ peak
- Spatial Resolution Ò20 µm

Ÿ Lateral (x,y)
- Mapping with < 25 µm resolution
- Imaging with < 3 µm resolution

Ÿ Depth (z)
- Sputter depth profiling
- Angle dependent depth profiling

Thermo Scientific Escalab250Xi,

Analysis Capabilities

Å Catalysis

Å Polymers

Å Coatings

Å Surface functionalization

Å Corrosion

Å Semiconductors

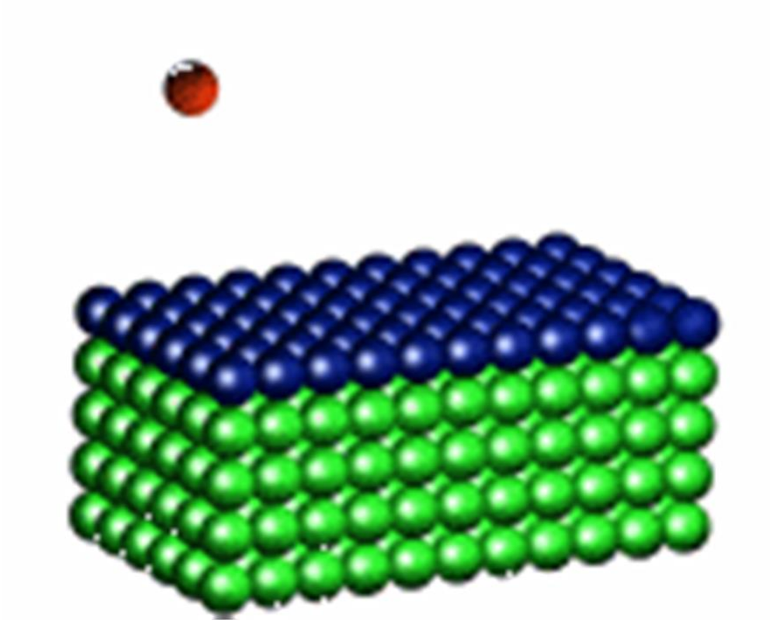
Å Thin films

Å Adhesions

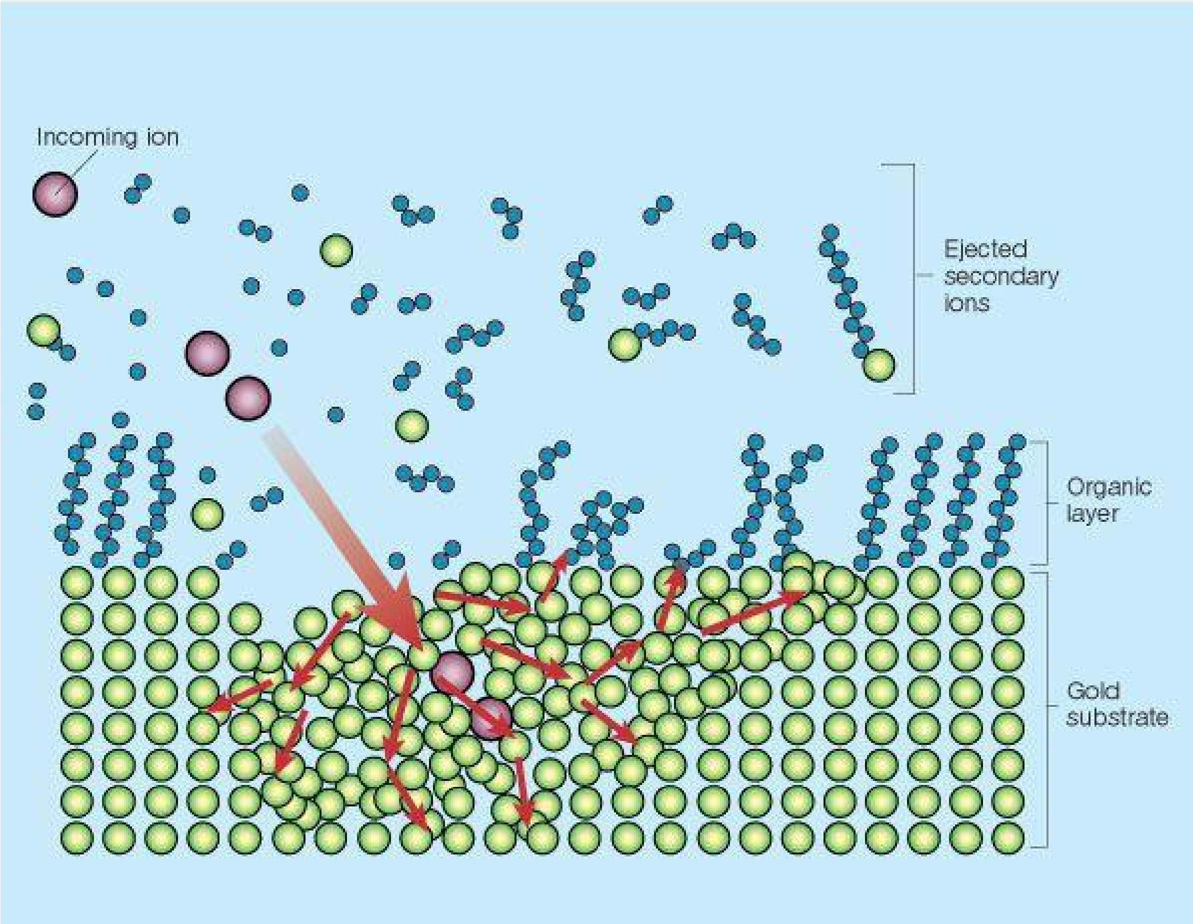
Secondary Ion Mass Spectrometry, SIMS

Å SIMS is a surface analysis technique used to characterize the surface and sub-surface region of materials.

Å It effectively employs the mass spectrometry of ionised particles – ***secondary ions*** which are emitted when a solid surface is bombarded by energetic ***primary ions***.



Sputtering process, Collision Cascade



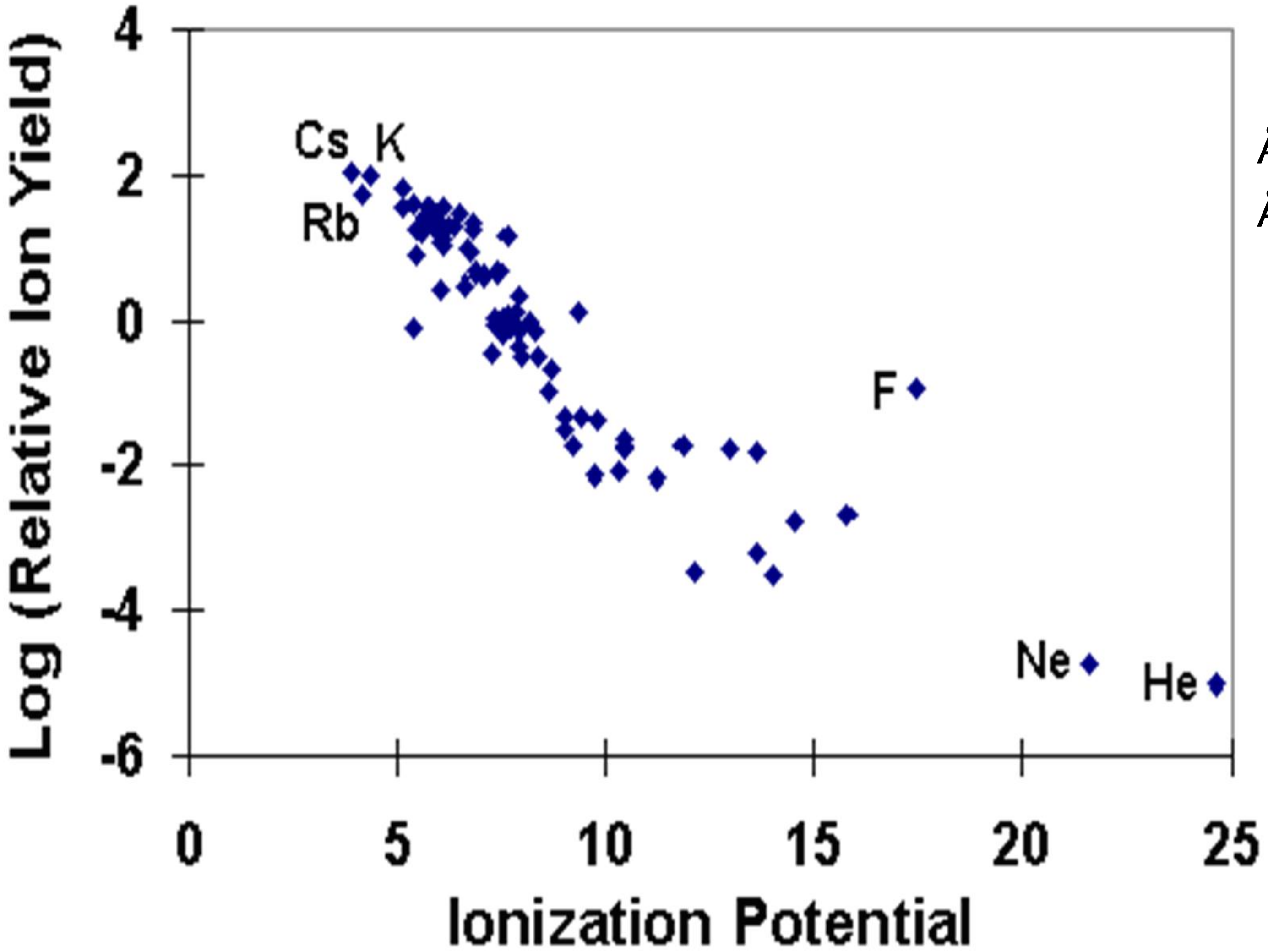
Excitation

- Bombardment with primary ions
- (Ga+, Bi1-3+, C60+...)
- energy ~ 10-60 keV
- collision cascade in solid

Results

-Desorption of neutrals, secondaty ions (+/-)
- depth of origin 1-2 monolayers
- implantation of primary ions
-Atoms mixing
- damaging of organic molecules

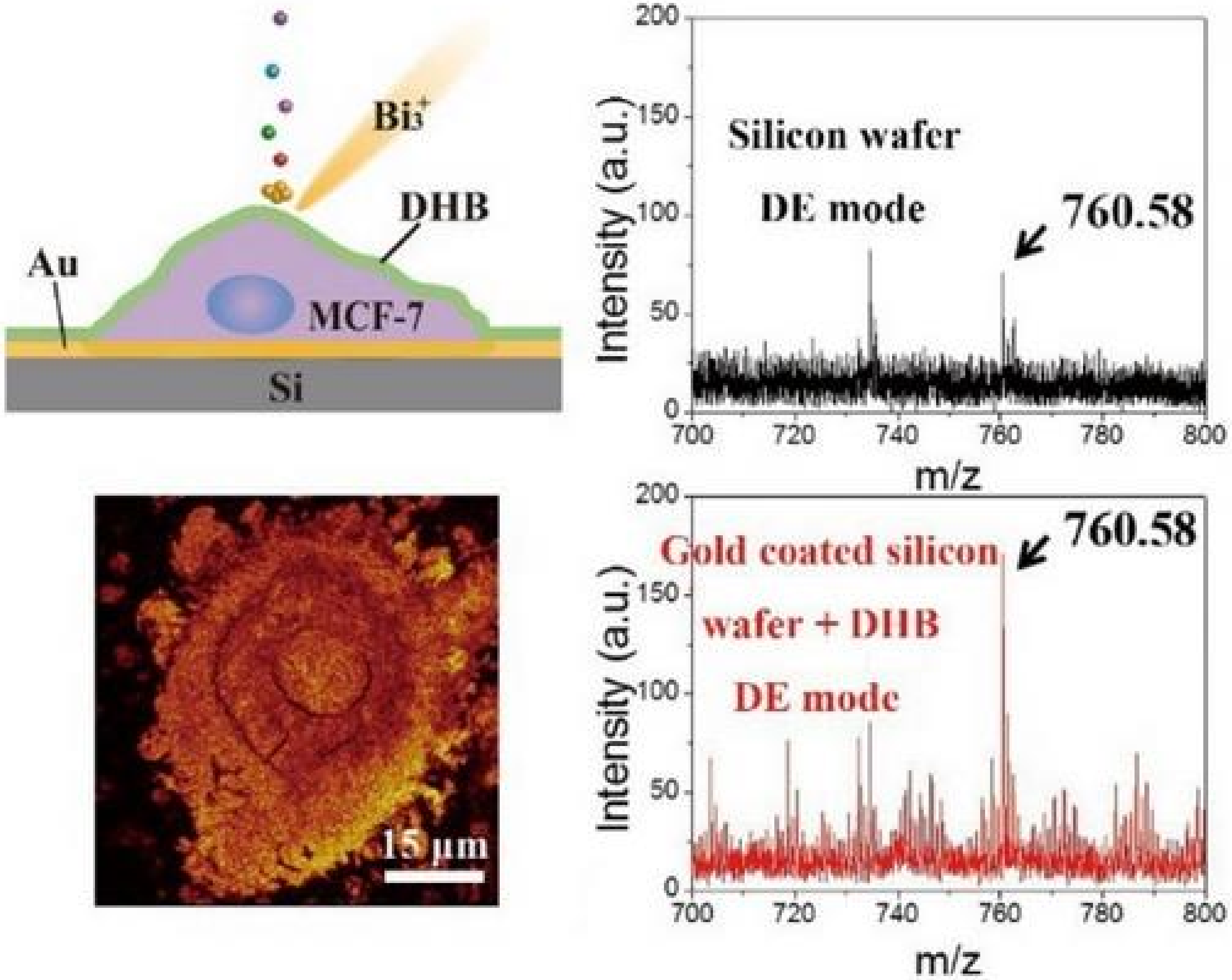
Secondary Ion Yields



Å Sputtering Yield

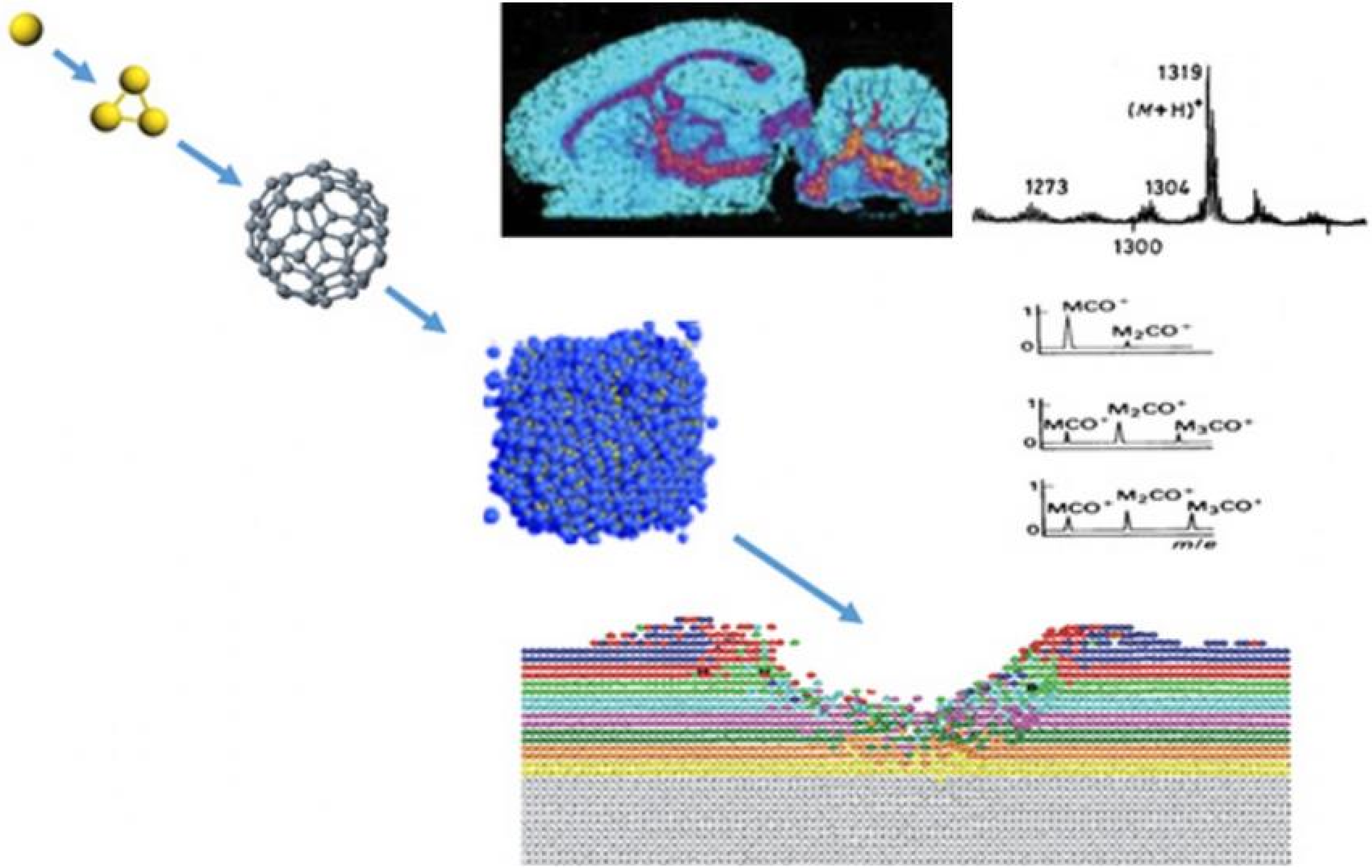
Å Ion Sputtering Yield

SIMS Matrix Effect

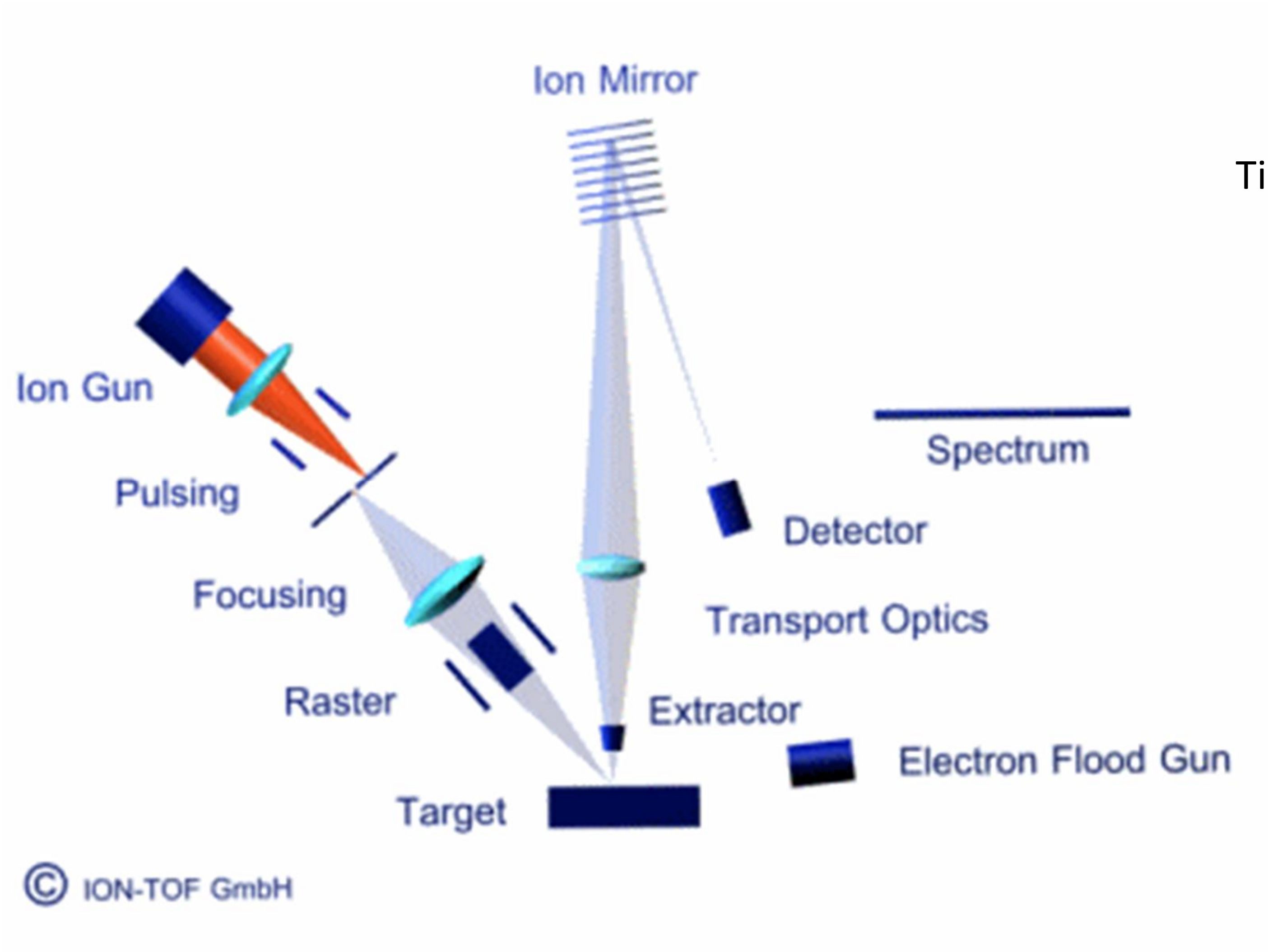


Metal substrate and matrix material enhance ToF-SIMS signal of single cell lipids.

Effect of Primary Ions



Secondary Ion Mass Spectrometry, SIMS



Time of Flight
TOF

Modes of Operation

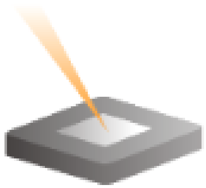
Quasi non-destructive surface analysis of the outer monolayers

Elemental and molecular information

Resolution: 11,000 @ 200u

Mass range: 12,000 u

ppm/ppb sensitivity



Surface Spectrometry

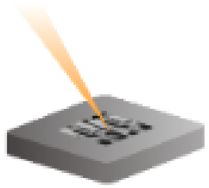
Chemical mapping of the surface

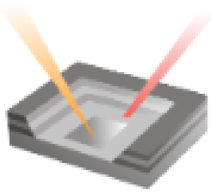
Lateral distribution of elements and molecules

Lateral resolution down to 50 nm

Parallel acquisition of all masses / images

Surface Imaging





Depth Profiling

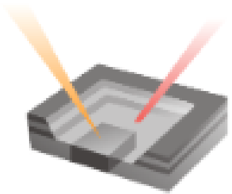
Analysis of the in-depth distribution

Elemental and molecular information

From a few nm to several µm

Depth resolution < 1 nm

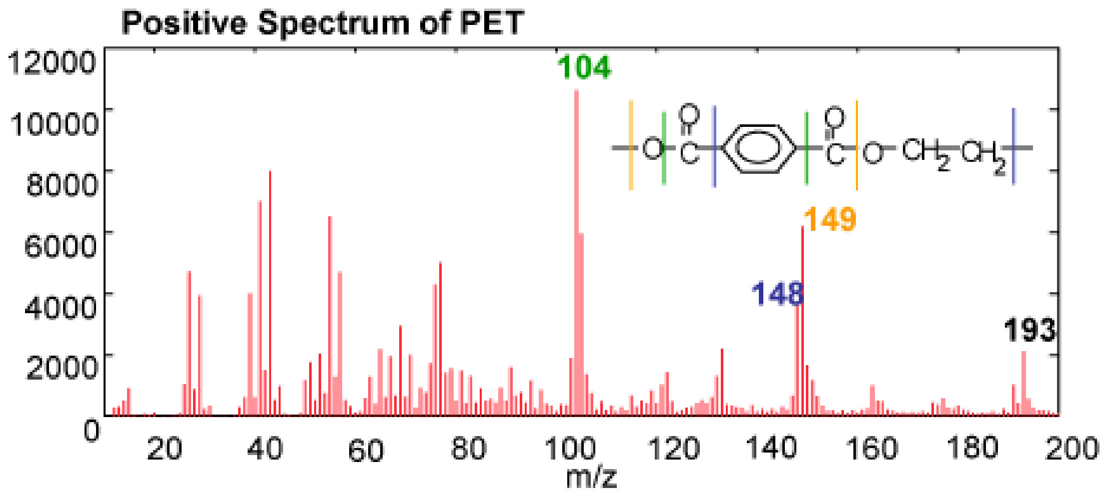
3D Analysis

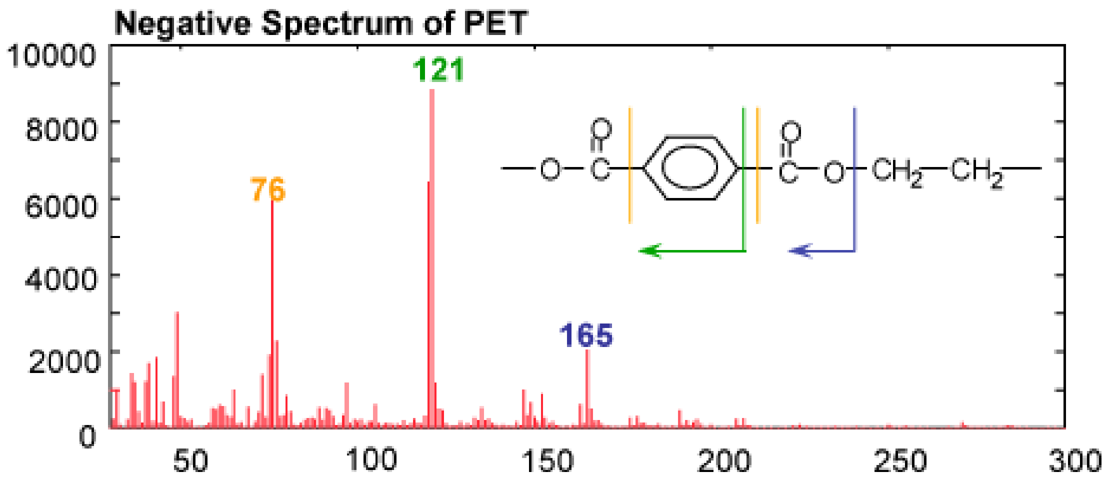


Combination of imaging and in-depth information

Elemental and molecular information

Surface Spectrometry, PET

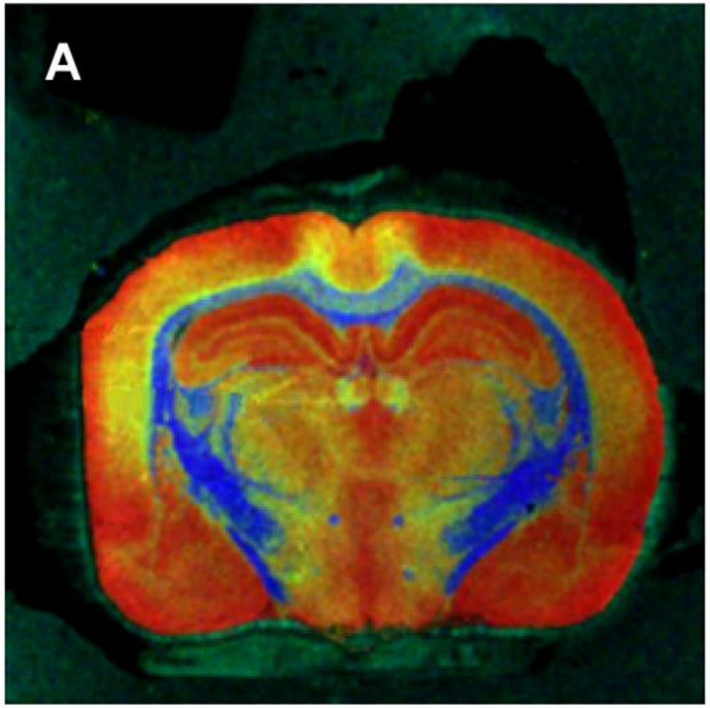




Fingerprint of polymers

Surface Imaging, Rat Brain CrossSection

Field of View: 18 x 18 mm^2



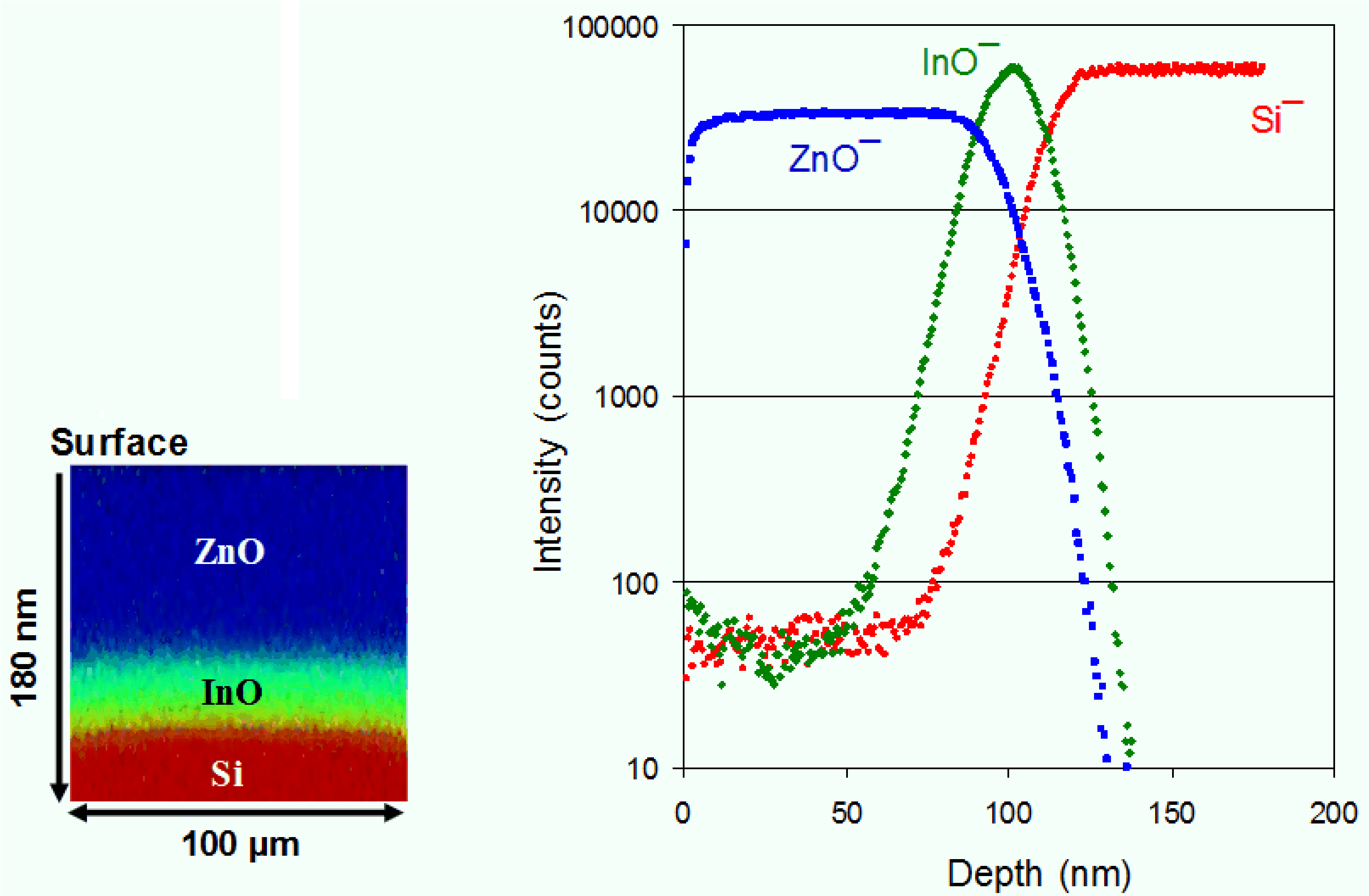
red=(255+283)
green=892 blue=771

red=283
blue=255

255 Carboxylate
283 C18 Fatty acid
771 Phospholipid
892 Triclyceride

A. Brunelle et. al. ICSN, CNRS, France

Depth Profiling,

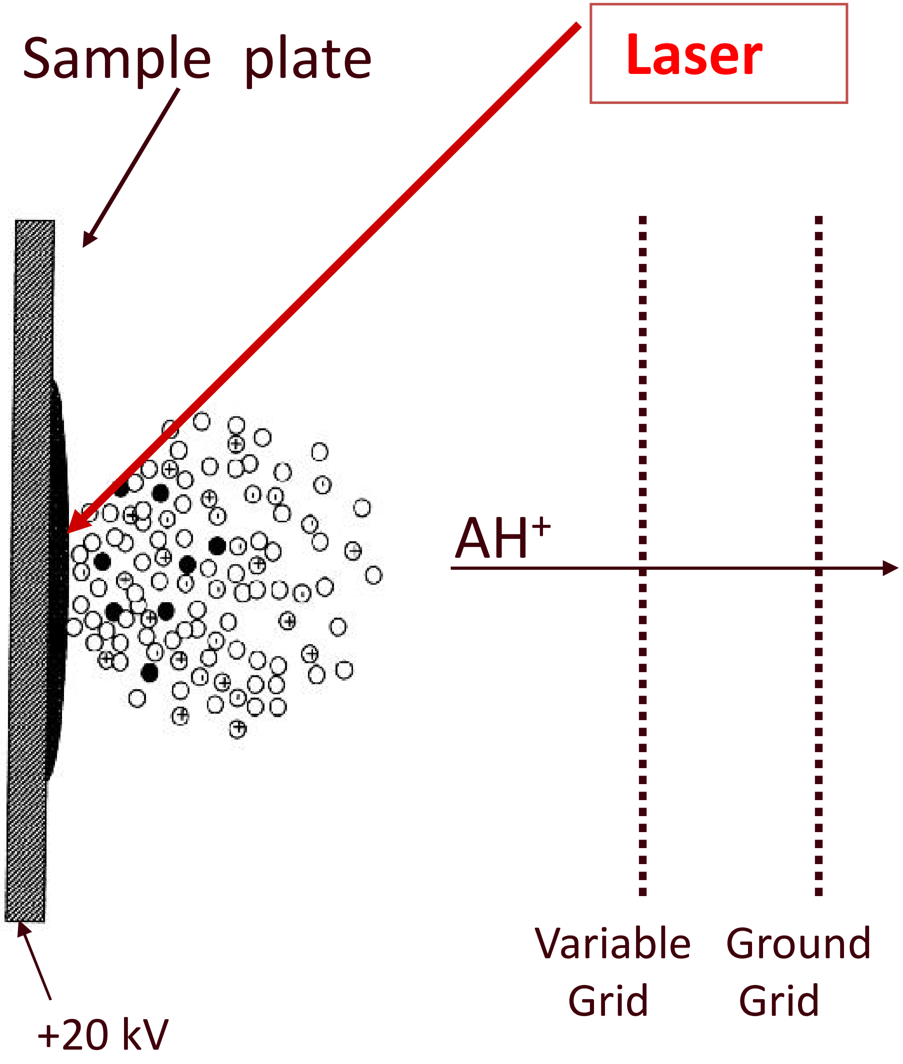


SIMS, Analysis Capabilities

- composition of organic, inorganic solids at the outer 5 nm of sample
- detection of all elements and izotopes
- composition of sample at varying spatial and depth resolution → spatial or depth profile of elemental or molecular concentrations
- detection of impurities and trace elements
- detection limit ppm-ppb
- spatial resolution ~ 100 nm

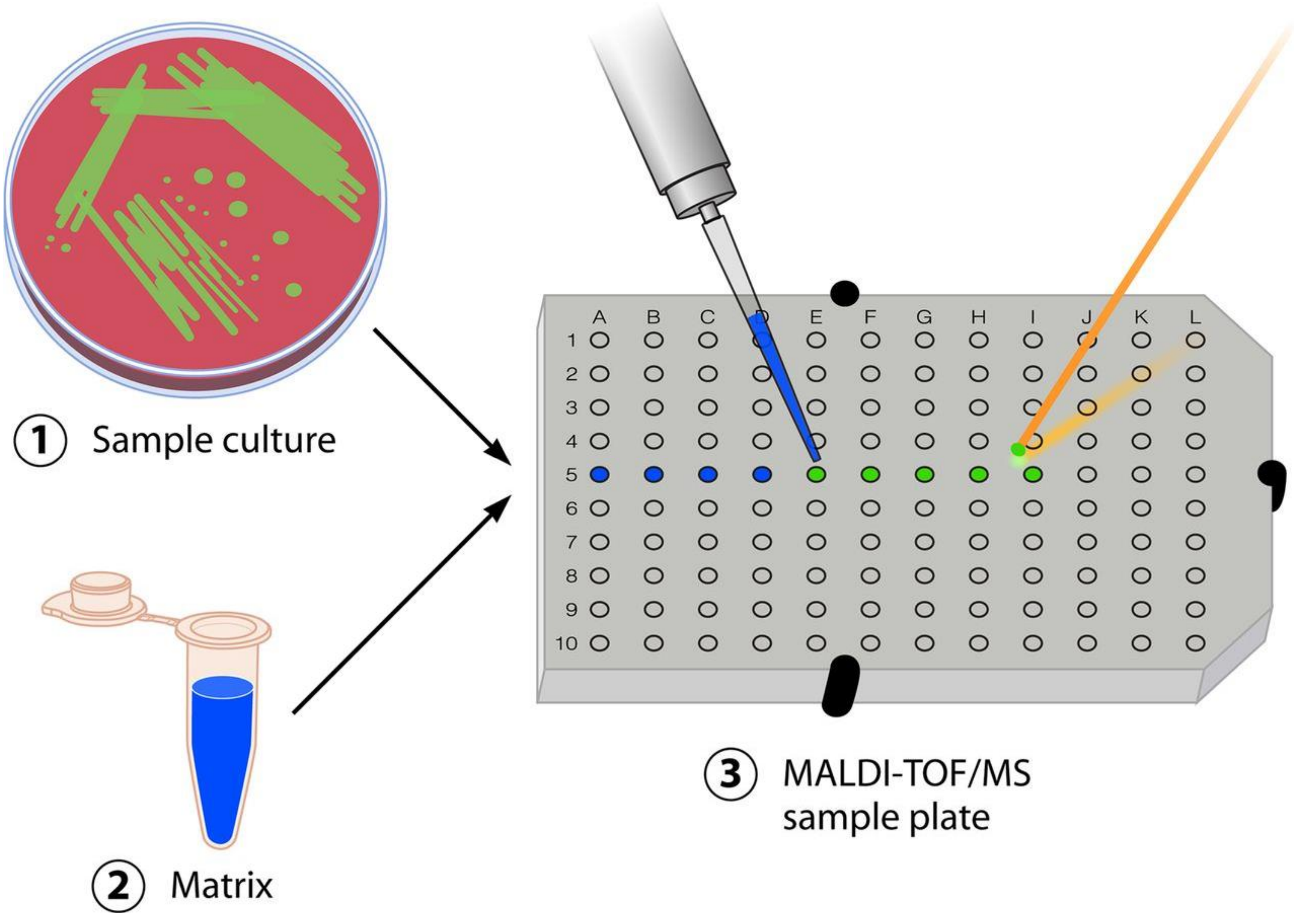
Matrix Assisted Laser Desorption Ionization

MALDI



- Soft ionization - analyze intact biomolecules and synthetic polymers
- Broad mass range - analyze a wide variety of biomolecules
- Simple mixtures are okay
- Relatively tolerant of buffers and salts
- Fast data acquisition
- Easy to use and maintain, no water or gas hook ups required
- *High sensitivity, superior mass resolution and accuracy*

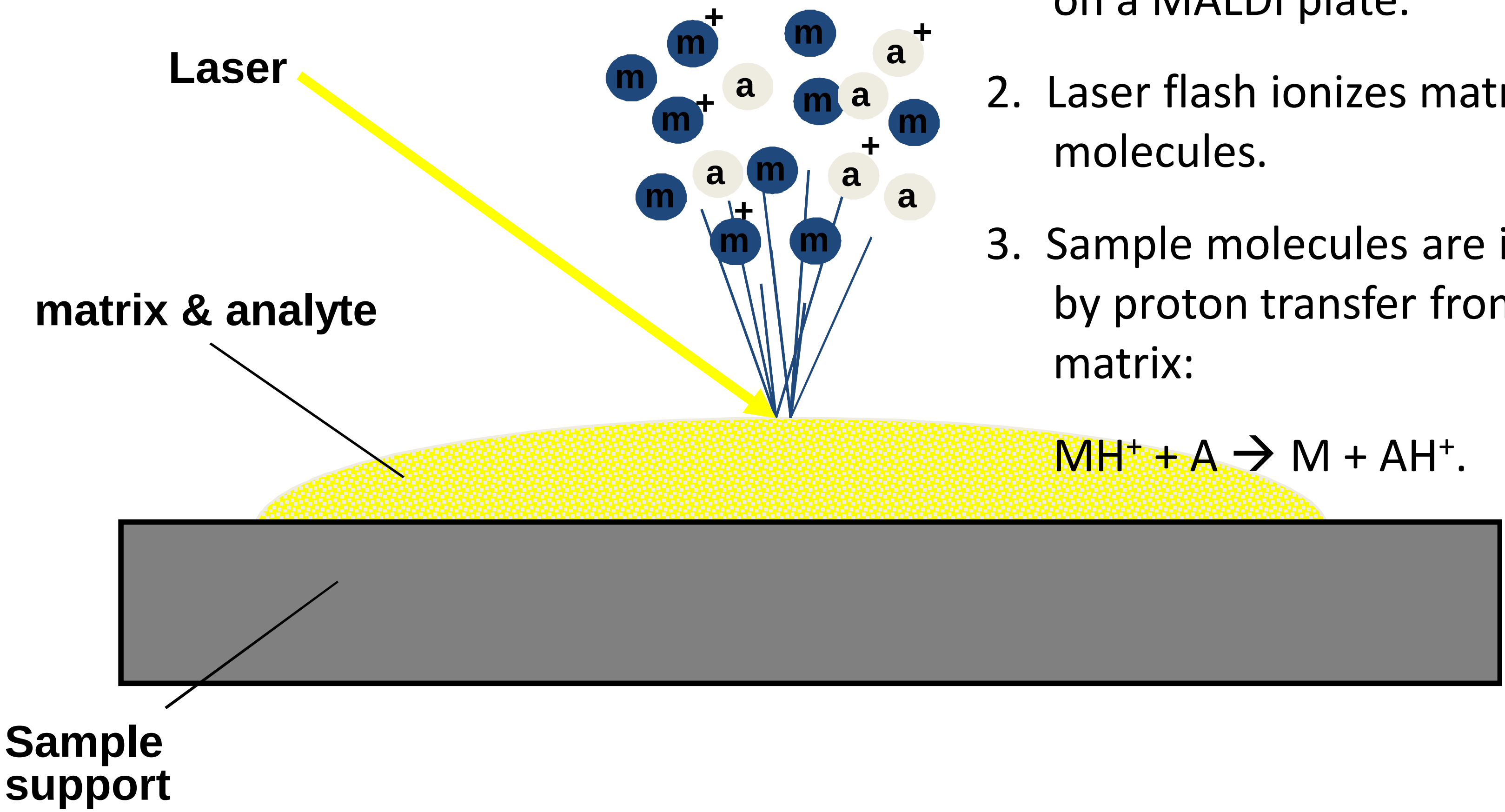
MALDI, Sample preparation



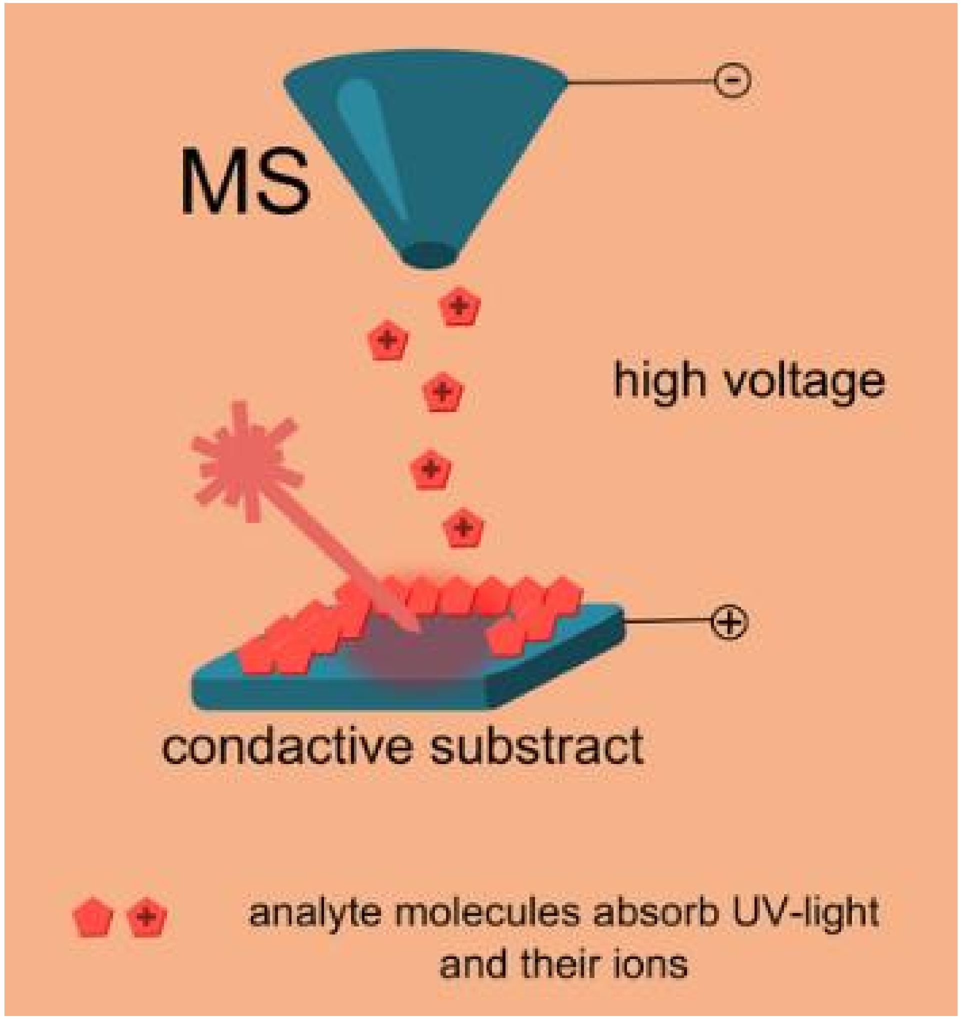
MALDI/LDI mechamism

1. Sample (A) is mixed with excess matrix (M) and dried on a MALDI plate.
2. Laser flash ionizes matrix molecules.
3. Sample molecules are ionized by proton transfer from matrix:

$$MH^{+} + A \rightarrow M + AH^{+}.$$

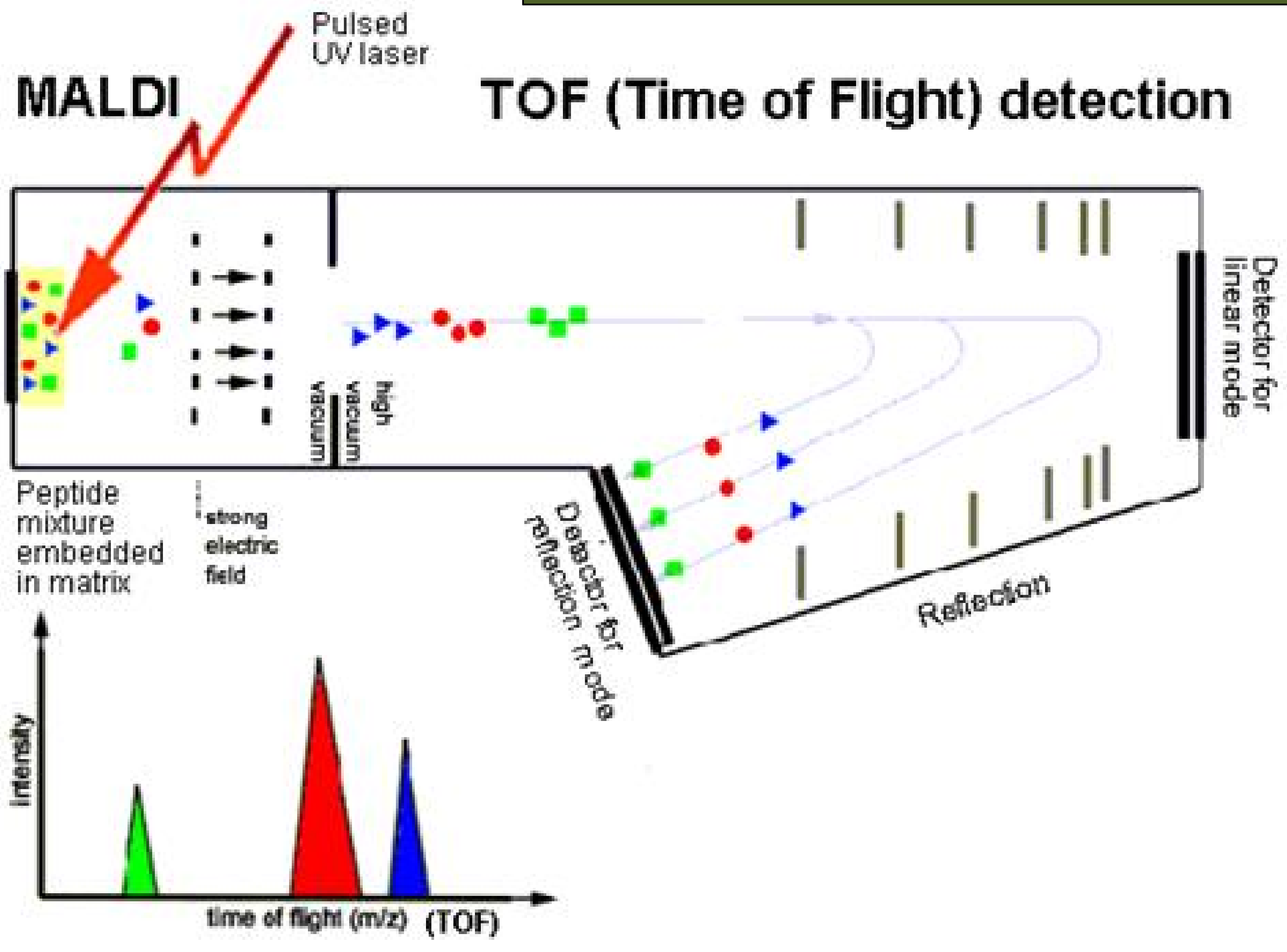


LDI mechanism



Matrix Assisted Laser Desorption Ionization

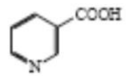
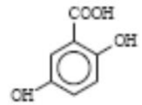
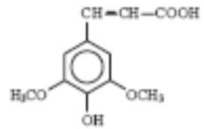
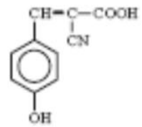
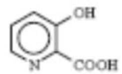
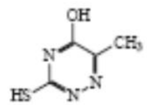
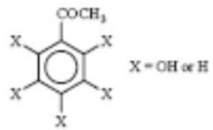
MALDI



MALDI Matrix

matrix properties and requirements:

- Be able to embed and isolate analytes (e.g. by co-crystallization)
- Be soluble in solvents compatible with analyte
- Be vacuum stable
- Absorb the laser wavelength
- Cause co-desorption of the analyte upon laser irradiation
- Promote analyte ionization

Matrix	*Structure*	*Wavelength*	*Major applications*
Nicotinic acid		UV 266nm	Proteins, peptides, adduct formation
2,5-Dihydroxybenzoic acid (plus 10% 2-hydroxy-5-methoxybenzoic acid)		UV 337nm, 353nm	Proteins, peptides, carbohydrates, synthetic polymers
Sinapinic acid		UV 337nm, 353nm	Proteins, peptides
α-Cyano-4-hydroxycinnamic acid		UV 337nm, 353nm	Peptides, fragmentation
3-Hydroxy-picolinic acid		UV 337nm, 353nm	Best for nucleic acids
6-Aza-2-thiothymine		UV 337nm, 353nm	Proteins, peptides, non-covalent complexes; near-neutral pH
k,m,n-Di(tri)hydroxy-acetophenone		UV 337nm, 353nm	Protein, peptides, non-covalent complexes; near-neutral pH
Succinic acid	HOOC–CH_2-CH_2-COOH	IR 2.94 µm, 2.79 µm	Proteins, peptides
Glycerol	H_2C–CH–CH_2 (OH OH OH)	IR 2.94 µm, 2.79 µm	Proteins, peptides, liquid matrix

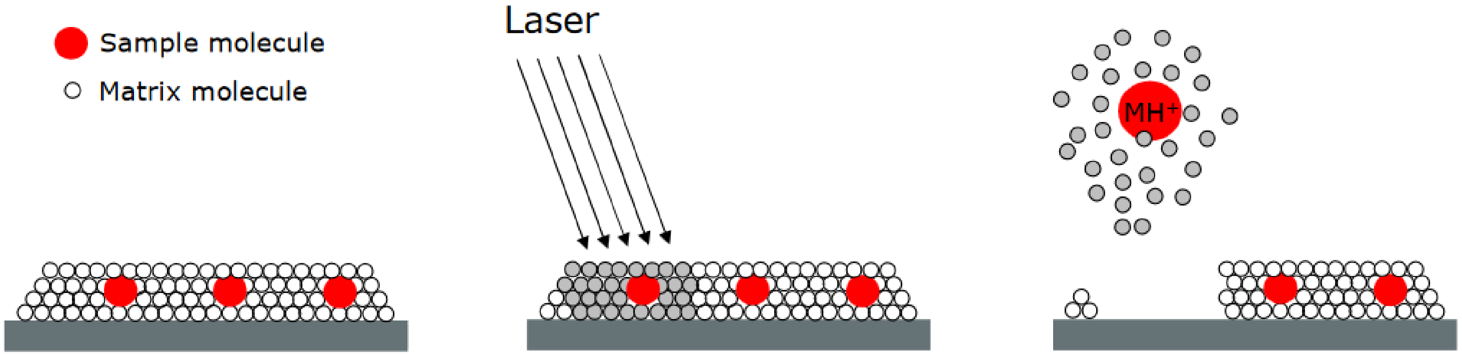
MALDI Matrix

What role does the **MALDI matrix** play?

The matrix transfers the energy needed for ionization from the laser light to the sample molecules.

Positive ionization mode:

Sample embedded in light-absorbing matrix	Excitation of matrix molecules by laser light	Desorption/protonation of sample molecules



$$M \xrightarrow[\text{Matrix}]{\text{Laser energy}} [M+H]^+$$

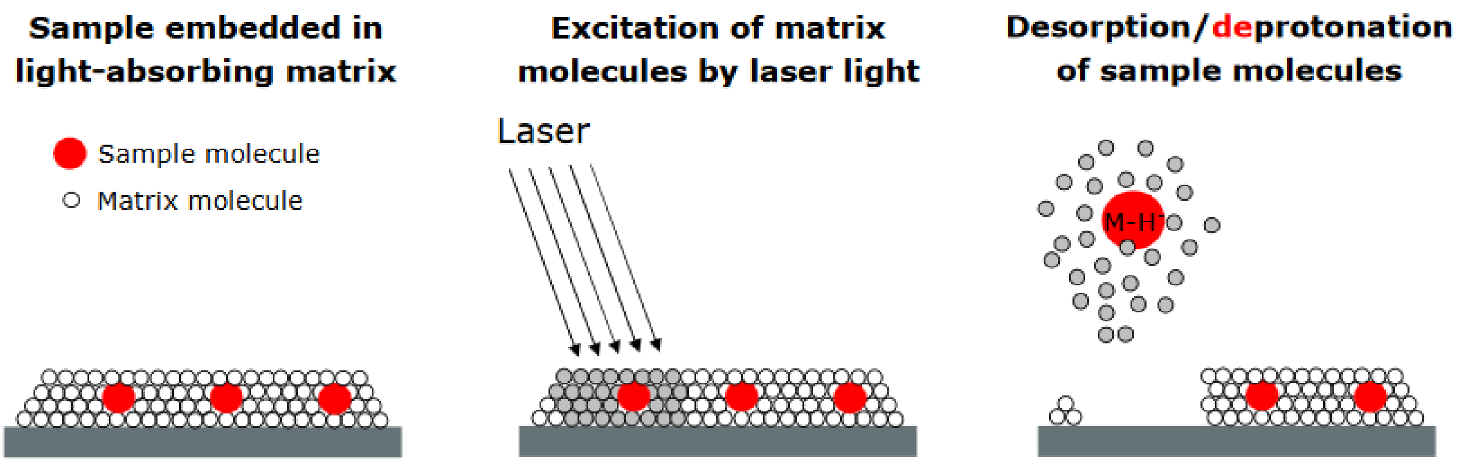
Formation of alternative adducts depends on the presence of respective cations (either being ubiquitary present or actively added – depending on type of sample): $[M+Na]^+$; $[M+K]^+$; $[M+Cu]^+$; $[M+Li]^+$; $[M+Ag]^+$

MALDI Matrix

What role does the **MALDI matrix** play?

The matrix transfers the energy needed for ionization from the laser light to the sample molecules.

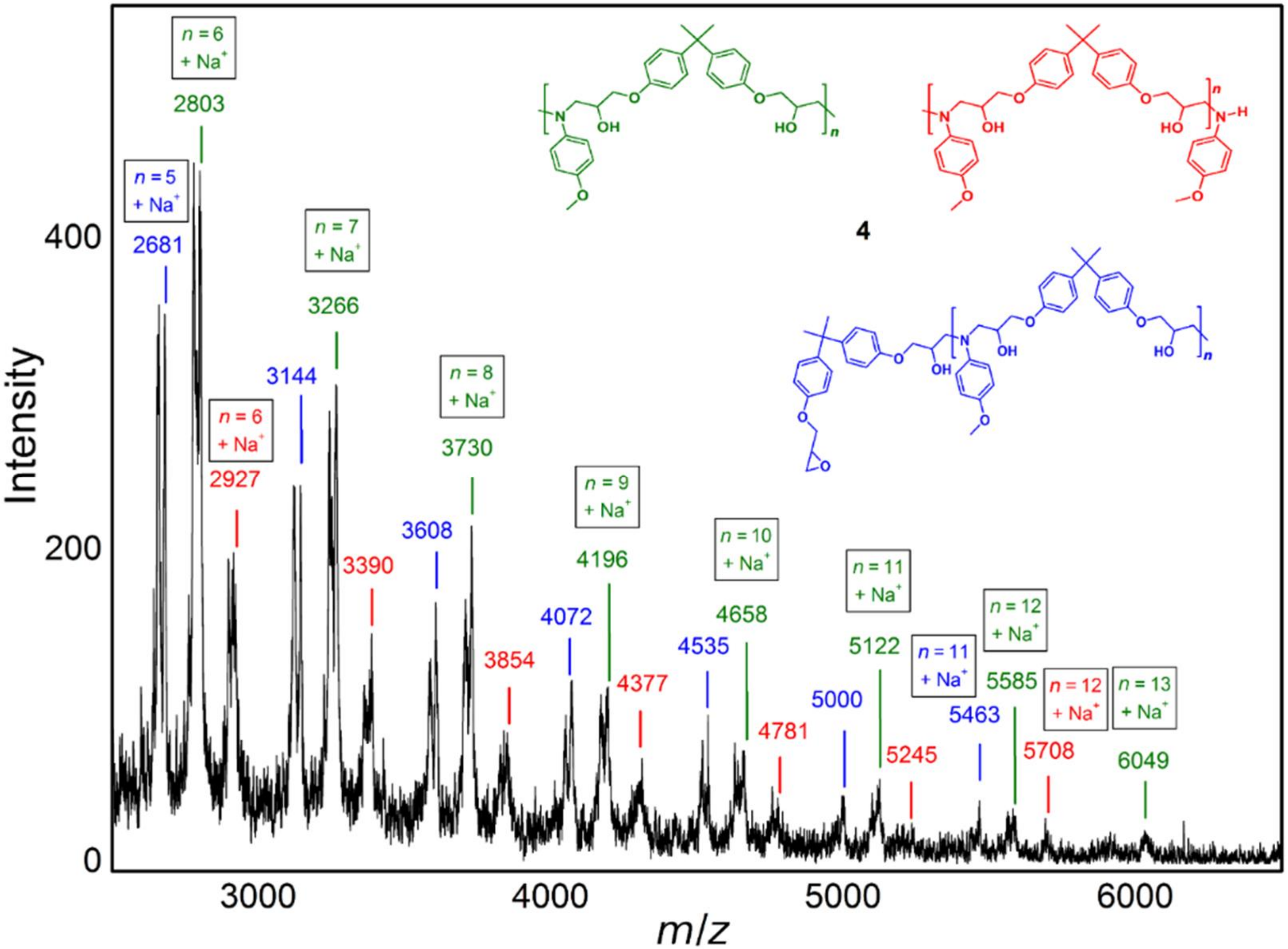
Negative ionization mode:



$$M \xrightarrow[\text{Matrix}]{\text{Laser energy}} [M-H]^-$$

Matrix Assisted Laser Desorption Ionization

MALDI



MALDI, Analysis capabilities