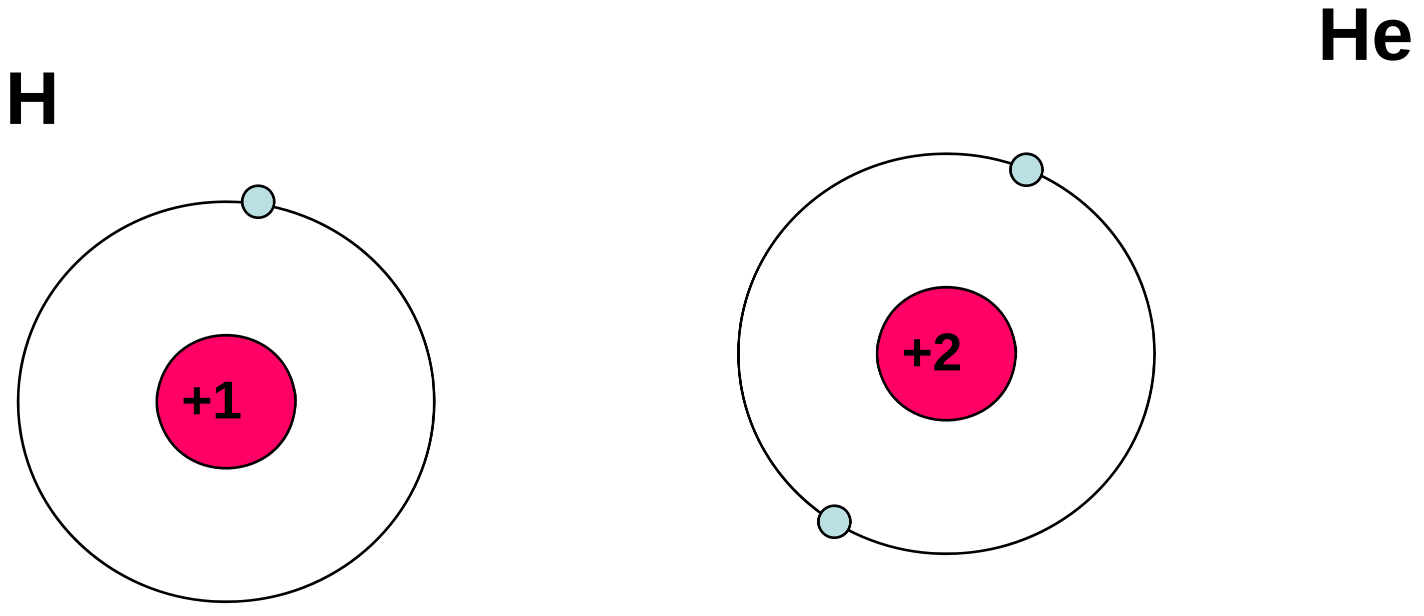
X-ray Photoelectron Spectroscopy (XPS)
Electron Energy Loss Spectroscopy (EELS)

General terms related to the structure of atoms

Orbital energy levels in atoms
Electron configurations in multielectron atoms
Rules for orbital occupation by electrons

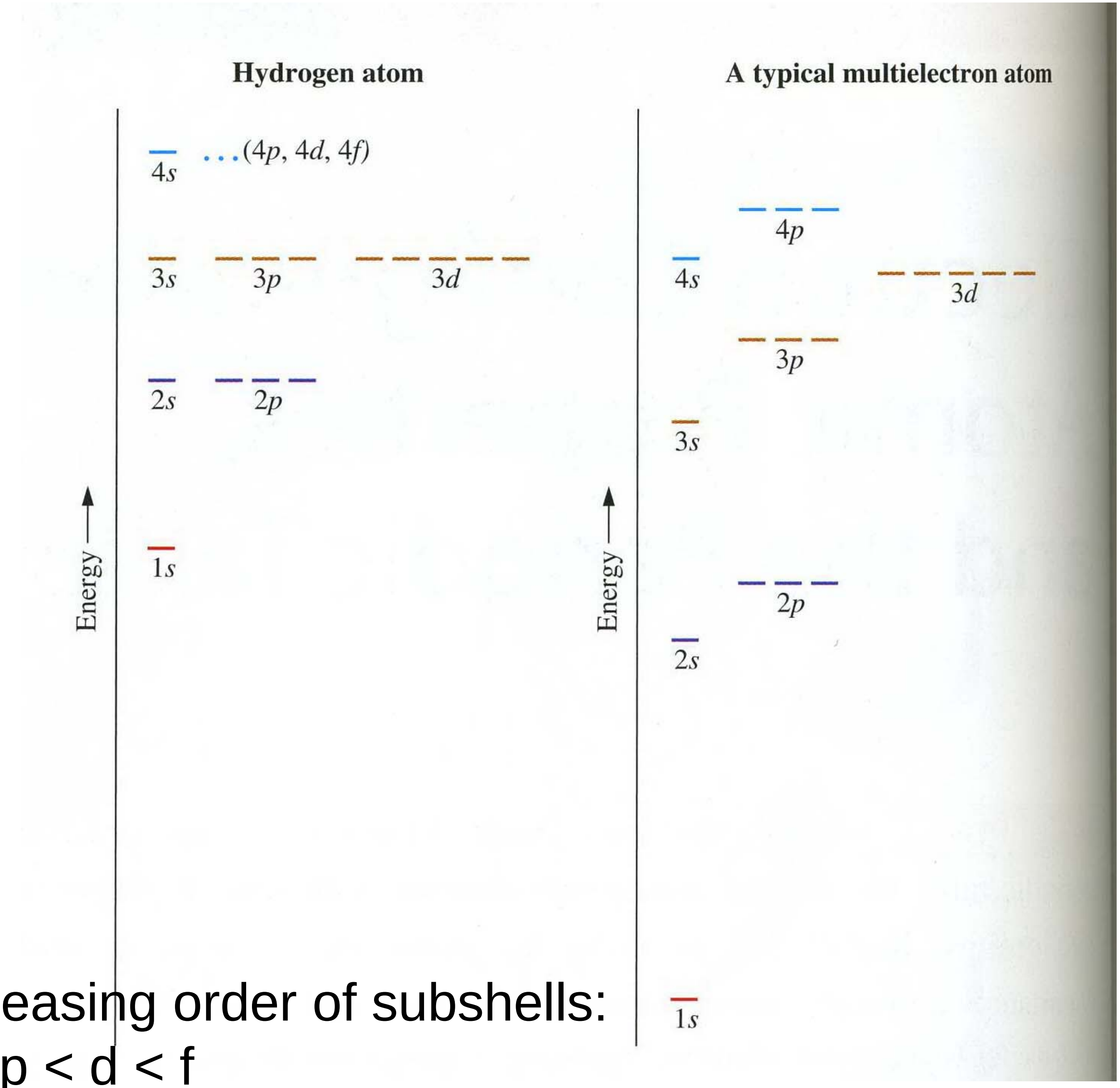
Electronic structure of H and He atoms



Ground state

Only valence electrons responsible for bondings and properties of material - outer shell

Orbital energy diagrams in atoms



Increasing order of subshells:
s < p < d < f

n – number of shell
Quantum number

Electron configurations: s p d f notation

Electrons are in the l=0 (s) subshell

2 electrons in the 1s subshell

$$1s^2$$

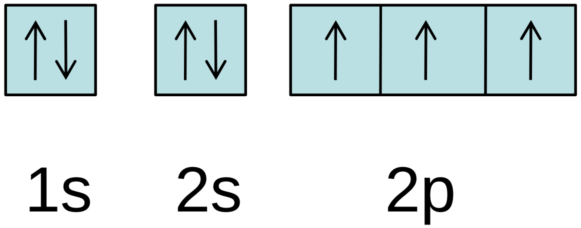
Electrons occupy the n=1 energy level

$1s^2 2s^2 2p^3$ number of electrons = 7, Z=7

$1s^2 2s^2 2p_x 2p_y 2p_z$

Electron configurations: representation of orbitals and spins

$1s^2 2s^2 2p_x 2p_y 2p_z$



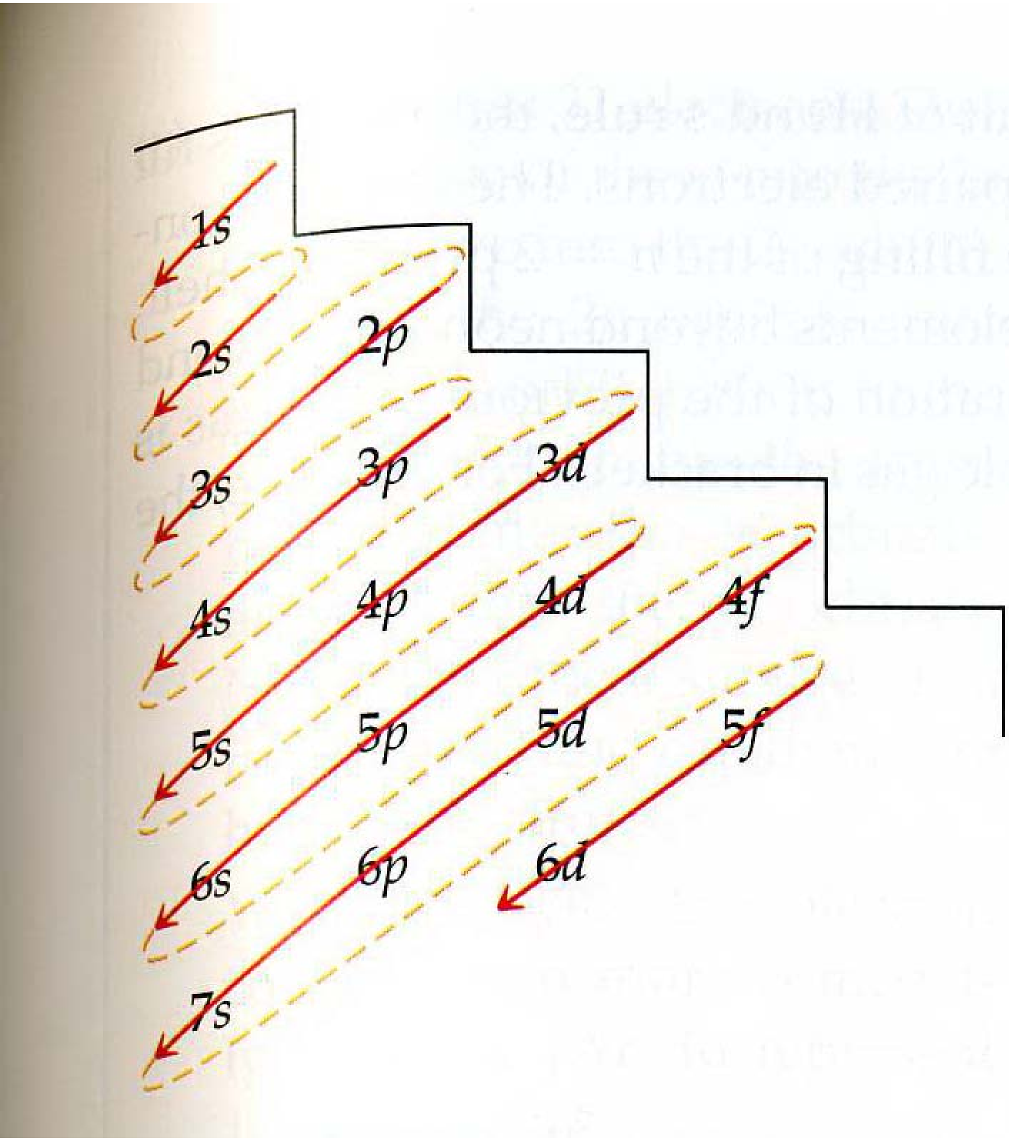
N, nitrogen

Electrons with opposing spins are paired

Electrons with parallel spins

Why only 2 electrons in one orbital?
Why they have opposing spins?
Why are orbitals in a subshell singly occupied before pairing occurs?
Why parallel spin?

Rules for Electron Configurations

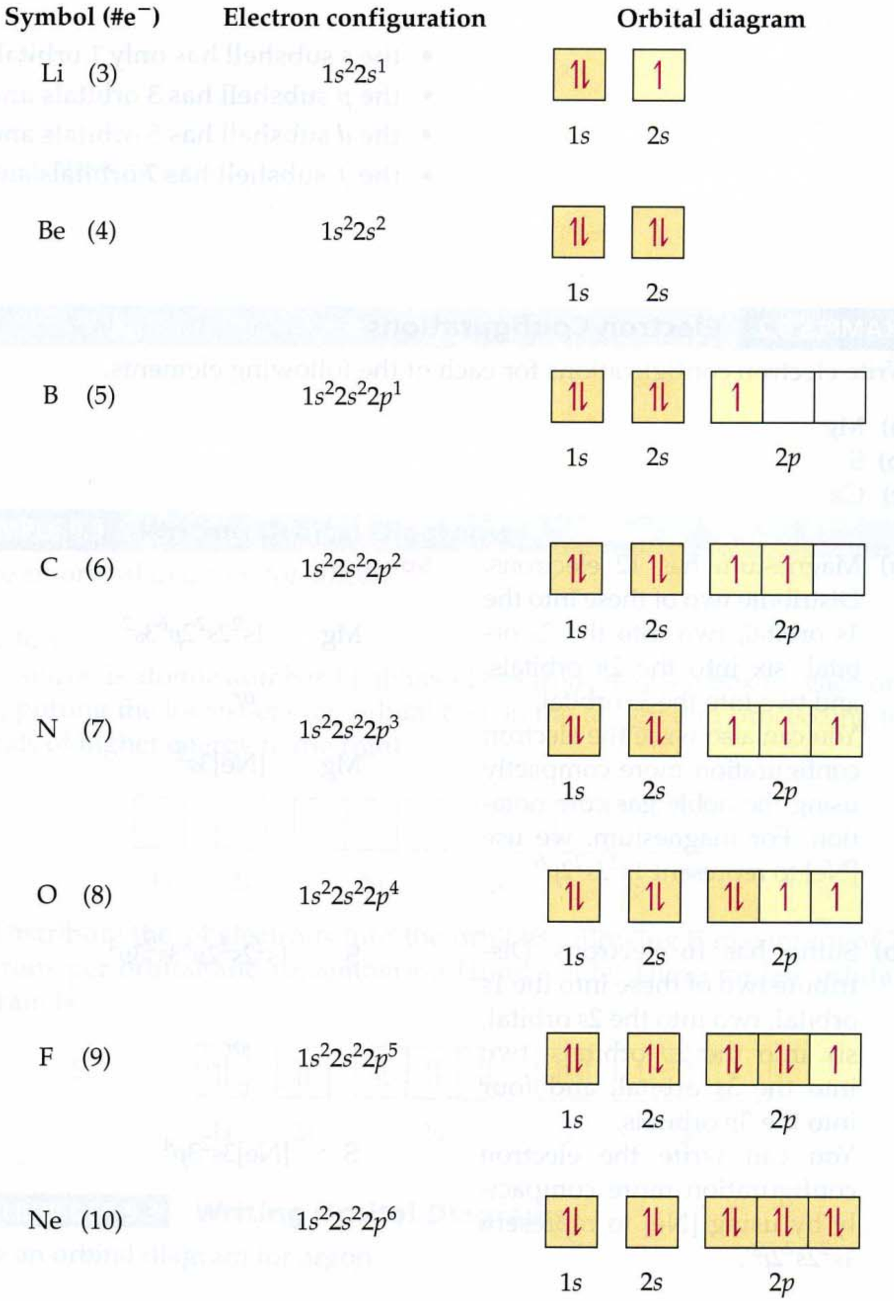


The order in which subshells are filled with electrons

1. Electrons occupy orbitals of the lowest energy,
2. No two electrons in the same atom may have all 4 quantum numbers alike,
3. In a group of orbitals of identical energy, electrons enter empty orbitals. Half filled orbitals have parallel spins, Hund’s rule

1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p…

An atomic orbital can accommodate only 2 electrons with opposing spins, Pauli exclusion principle



Symbol (#e⁻)	Electron configuration	Orbital diagram
Li (3)	$1s^2 2s^1$	1s ⇅ · 2s ↑
Be (4)	$1s^2 2s^2$	1s ⇅ · 2s ⇅
B (5)	$1s^2 2s^2 2p^1$	1s ⇅ · 2s ⇅ · 2p ↑ ☐ ☐
C (6)	$1s^2 2s^2 2p^2$	1s ⇅ · 2s ⇅ · 2p ↑ ↑ ☐
N (7)	$1s^2 2s^2 2p^3$	1s ⇅ · 2s ⇅ · 2p ↑ ↑ ↑
O (8)	$1s^2 2s^2 2p^4$	1s ⇅ · 2s ⇅ · 2p ⇅ ↑ ↑
F (9)	$1s^2 2s^2 2p^5$	1s ⇅ · 2s ⇅ · 2p ⇅ ⇅ ↑
Ne (10)	$1s^2 2s^2 2p^6$	1s ⇅ · 2s ⇅ · 2p ⇅ ⇅ ⇅

First and second shell filled

Building up atom with electron configuration

Distribution of electrons on the atomic orbitals

H (Z =1) $1s^1$
He (Z=2) $1s^2$
Li (Z=3) $s^2 2s^1$

Na (Z=11) $[Ne]3s^1$

Electron capacity of shells and subshells

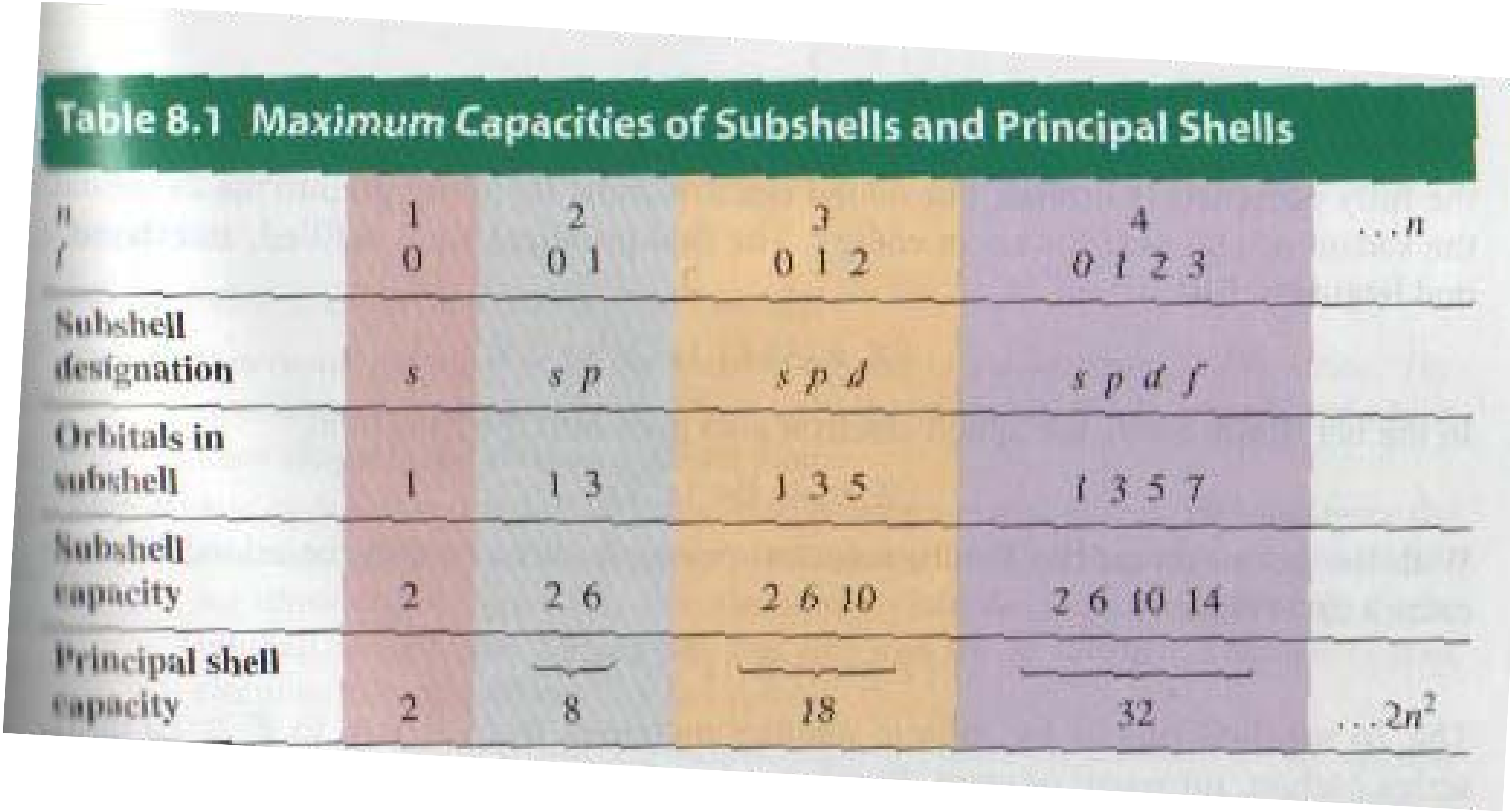
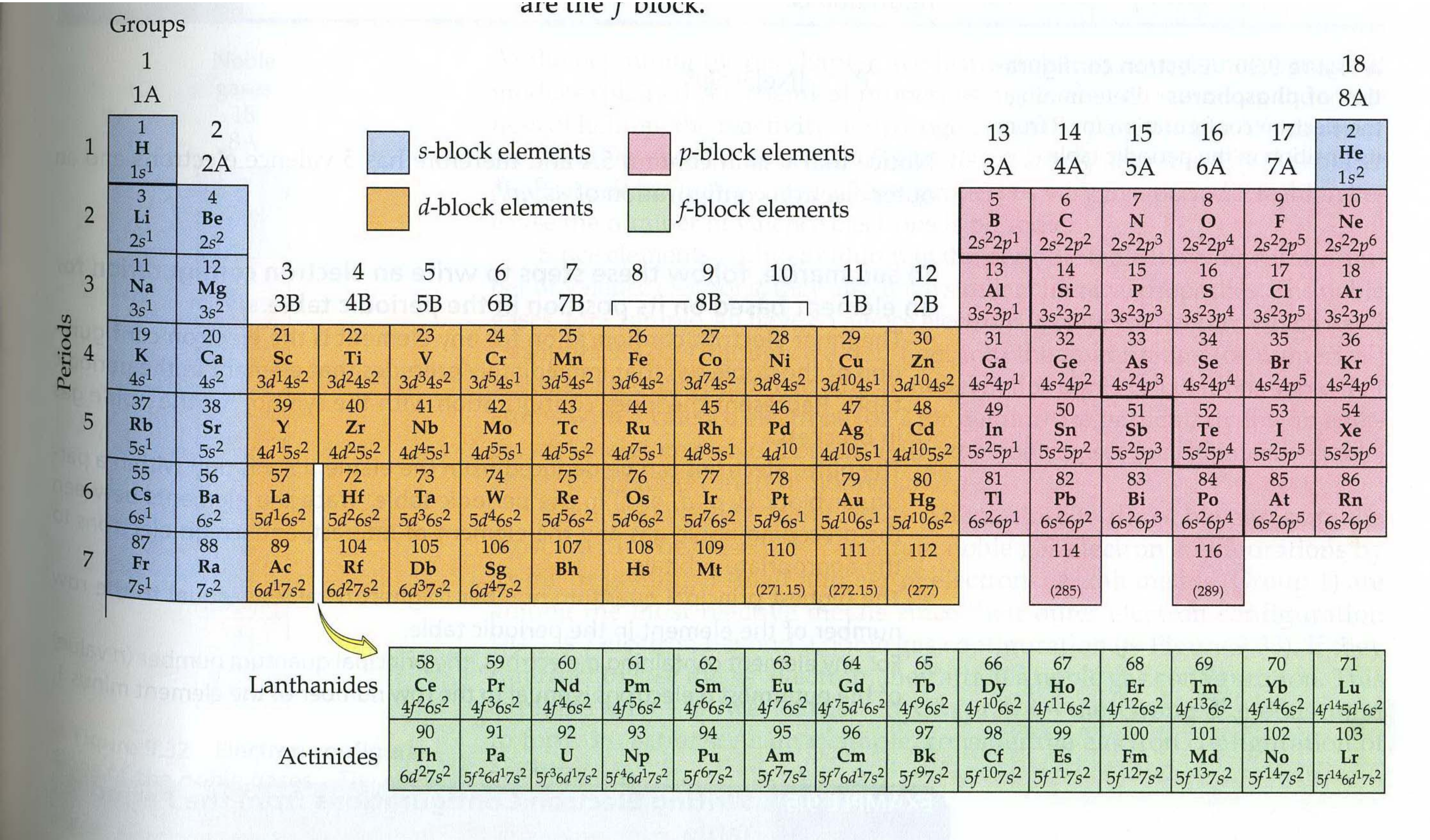


Table 8.1 Maximum Capacities of Subshells and Principal Shells

n	1	2	3	4	. . . *n*
l	0	0 1	0 1 2	0 1 2 3	
Subshell designation	*s*	*s p*	*s p d*	*s p d f*	
Orbitals in subshell	1	1 3	1 3 5	1 3 5 7	
Subshell capacity	2	2 6	2 6 10	2 6 10 14	
Principal shell capacity	2	8	18	32	. . . $2n^2$

Electron configurations: how electrons occupy orbitals



are the *f* block.

Groups

s-block elements
d-block elements
p-block elements
f-block elements

Periods	1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1	1 **H** $1s^1$																	2 **He** $1s^2$
2	3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^2 2p^1$	6 **C** $2s^2 2p^2$	7 **N** $2s^2 2p^3$	8 **O** $2s^2 2p^4$	9 **F** $2s^2 2p^5$	10 **Ne** $2s^2 2p^6$
3	11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^2 3p^1$	14 **Si** $3s^2 3p^2$	15 **P** $3s^2 3p^3$	16 **S** $3s^2 3p^4$	17 **Cl** $3s^2 3p^5$	18 **Ar** $3s^2 3p^6$
4	19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $3d^1 4s^2$	22 **Ti** $3d^2 4s^2$	23 **V** $3d^3 4s^2$	24 **Cr** $3d^5 4s^1$	25 **Mn** $3d^5 4s^2$	26 **Fe** $3d^6 4s^2$	27 **Co** $3d^7 4s^2$	28 **Ni** $3d^8 4s^2$	29 **Cu** $3d^{10} 4s^1$	30 **Zn** $3d^{10} 4s^2$	31 **Ga** $4s^2 4p^1$	32 **Ge** $4s^2 4p^2$	33 **As** $4s^2 4p^3$	34 **Se** $4s^2 4p^4$	35 **Br** $4s^2 4p^5$	36 **Kr** $4s^2 4p^6$
5	37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $4d^1 5s^2$	40 **Zr** $4d^2 5s^2$	41 **Nb** $4d^4 5s^1$	42 **Mo** $4d^5 5s^1$	43 **Tc** $4d^5 5s^2$	44 **Ru** $4d^7 5s^1$	45 **Rh** $4d^8 5s^1$	46 **Pd** $4d^{10}$	47 **Ag** $4d^{10} 5s^1$	48 **Cd** $4d^{10} 5s^2$	49 **In** $5s^2 5p^1$	50 **Sn** $5s^2 5p^2$	51 **Sb** $5s^2 5p^3$	52 **Te** $5s^2 5p^4$	53 **I** $5s^2 5p^5$	54 **Xe** $5s^2 5p^6$
6	55 **Cs** $6s^1$	56 **Ba** $6s^2$	57 **La** $5d^1 6s^2$	72 **Hf** $5d^2 6s^2$	73 **Ta** $5d^3 6s^2$	74 **W** $5d^4 6s^2$	75 **Re** $5d^5 6s^2$	76 **Os** $5d^6 6s^2$	77 **Ir** $5d^7 6s^2$	78 **Pt** $5d^9 6s^1$	79 **Au** $5d^{10} 6s^1$	80 **Hg** $5d^{10} 6s^2$	81 **Tl** $6s^2 6p^1$	82 **Pb** $6s^2 6p^2$	83 **Bi** $6s^2 6p^3$	84 **Po** $6s^2 6p^4$	85 **At** $6s^2 6p^5$	86 **Rn** $6s^2 6p^6$
7	87 **Fr** $7s^1$	88 **Ra** $7s^2$	89 **Ac** $6d^1 7s^2$	104 **Rf** $6d^2 7s^2$	105 **Db** $6d^3 7s^2$	106 **Sg** $6d^4 7s^2$	107 **Bh**	108 **Hs**	109 **Mt**	110 (271.15)	111 (272.15)	112 (277)		114 (285)		116 (289)		

Lanthanides	58 **Ce** $4f^2 6s^2$	59 **Pr** $4f^3 6s^2$	60 **Nd** $4f^4 6s^2$	61 **Pm** $4f^5 6s^2$	62 **Sm** $4f^6 6s^2$	63 **Eu** $4f^7 6s^2$	64 **Gd** $4f^7 5d^1 6s^2$	65 **Tb** $4f^9 6s^2$	66 **Dy** $4f^{10} 6s^2$	67 **Ho** $4f^{11} 6s^2$	68 **Er** $4f^{12} 6s^2$	69 **Tm** $4f^{13} 6s^2$	70 **Yb** $4f^{14} 6s^2$	71 **Lu** $4f^{14} 5d^1 6s^2$
Actinides	90 **Th** $6d^2 7s^2$	91 **Pa** $5f^2 6d^1 7s^2$	92 **U** $5f^3 6d^1 7s^2$	93 **Np** $5f^4 6d^1 7s^2$	94 **Pu** $5f^6 7s^2$	95 **Am** $5f^7 7s^2$	96 **Cm** $5f^7 6d^1 7s^2$	97 **Bk** $5f^9 7s^2$	98 **Cf** $5f^{10} 7s^2$	99 **Es** $5f^{11} 7s^2$	100 **Fm** $5f^{12} 7s^2$	101 **Md** $5f^{13} 7s^2$	102 **No** $5f^{14} 7s^2$	103 **Lr** $5f^{14} 6d^1 7s^2$

Valence electrons and core electrons

Valence electrons: highest quantum number n,
outermost shell

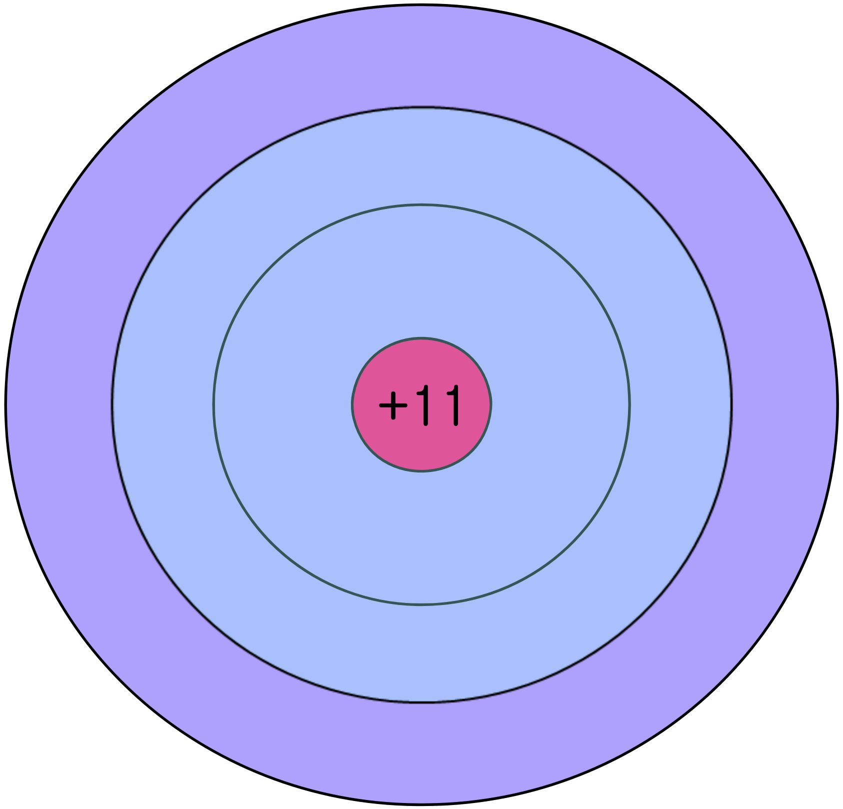
Core: electrons in inner shell

Examples : Ca [Ar]$4s^2$

Br [Ar]$3d^{10}4s^24p^5$

Electronic structure of an multishell atom

Na

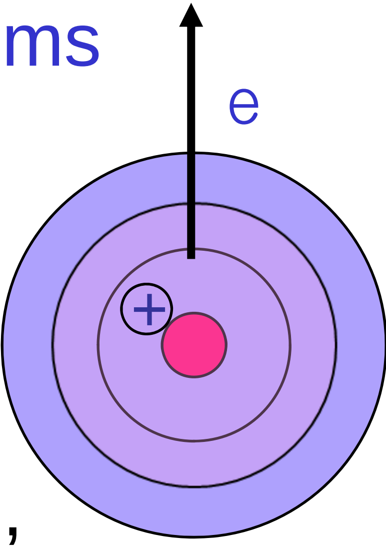


Na (Z=11) [Ne]$3s^1$

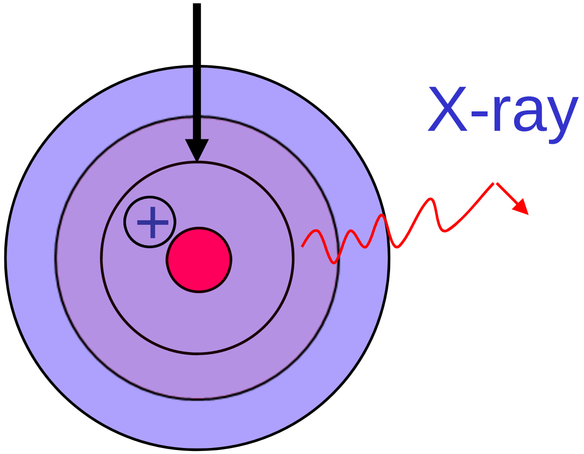
Each atom
(except H and He)
possesses core
electrons, inner
shells

Valence electrons responsible for bondings and properties are located on the outer shell

Phenomena from the bombardment of atoms with energetic particles or photons

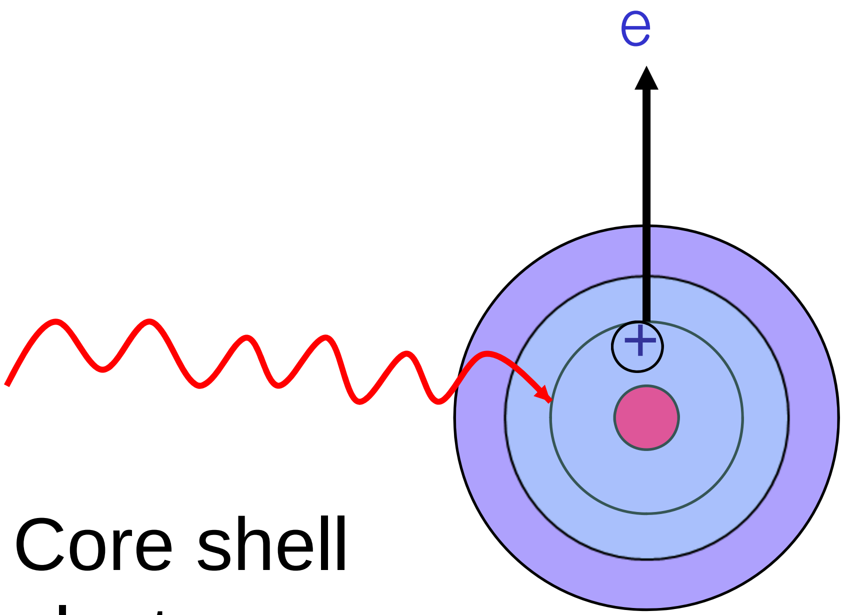


1. Ejection of electrons from the target atoms, which leave vacances,
2. Filling up the vacancies with outer shell electrons followed by the emission of characteristic X-rays



Electron ejection:
Removing electron from the atomic shell

XPS is based on emission of electrons from the core level by irradiation with low energetic X-ray photons



Core shell
electrons

Photoemission,
Photoelectric effect,
Photoionisation,
Photoelectrons

The electrons are detected, the energy of electrons is measured and the binding energy in the atom is determined

X-ray Photoelectron Spectroscopy (XPS)

XPS is a most powerful **surface analysis technique** currently available that can be used to analyze the surface chemistry of a material.

Also known as **ESCA**, an abbreviation for **Electron Spectroscopy for Chemical Analysis**.

Discovery history

1981 – Kai Siegbahn, Upsalla, Sweden aworded with Nobel Preize for the pioneering work in development of XPS

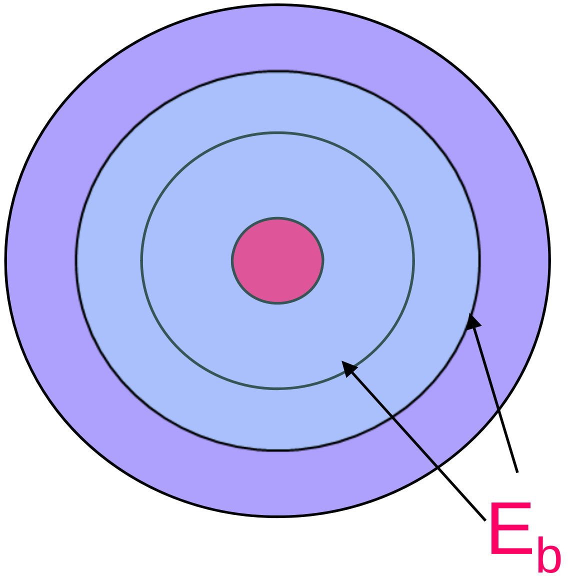
Basic principles

Sample is excited by a controllable energy source and responses to the excitation with emission of electrons.

Excitation: irradiation with monochromatic X-rays that cause photoionisation of atoms

Response of atoms: photoemission – emission of electrons, which can be observed and their energy can be measured

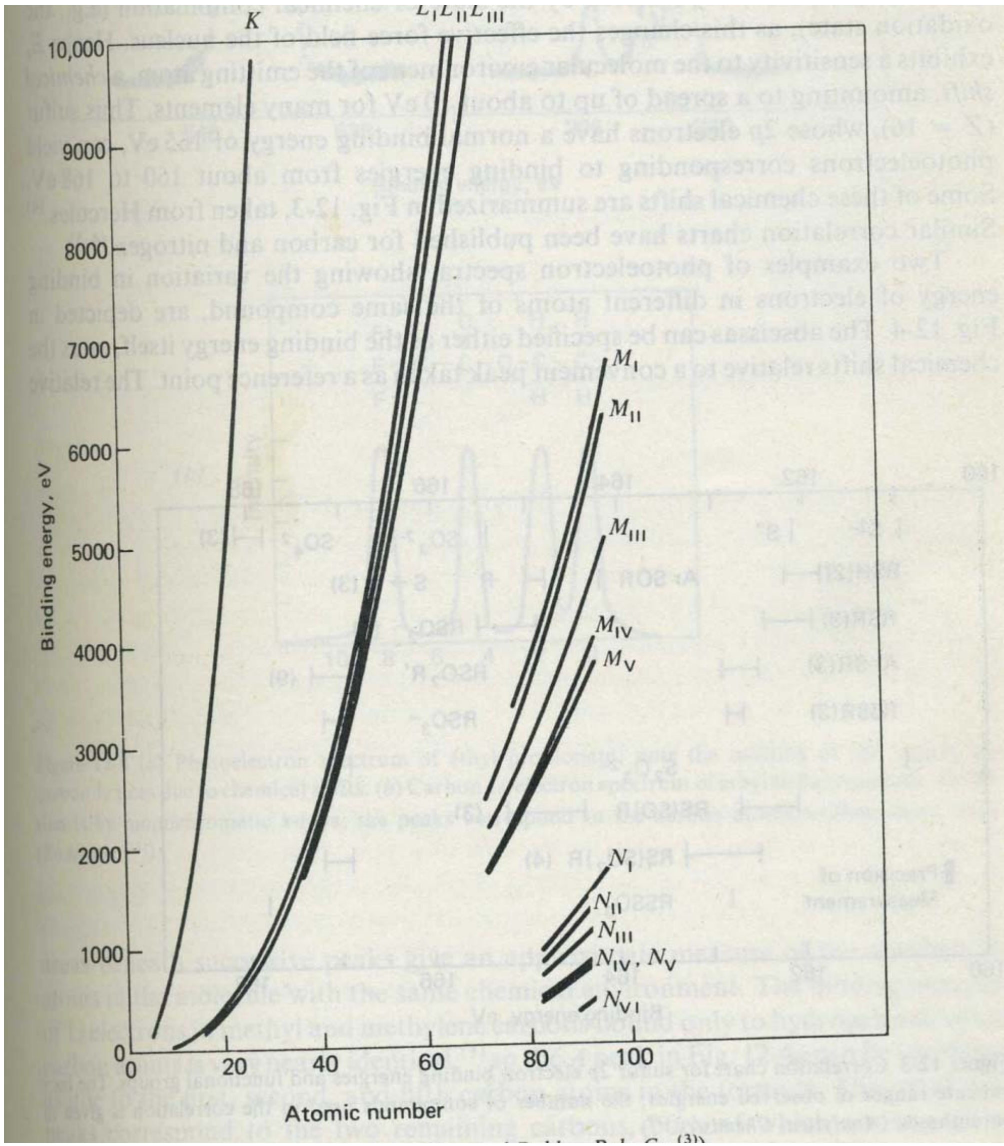
Kinetic energy of photoelectrons

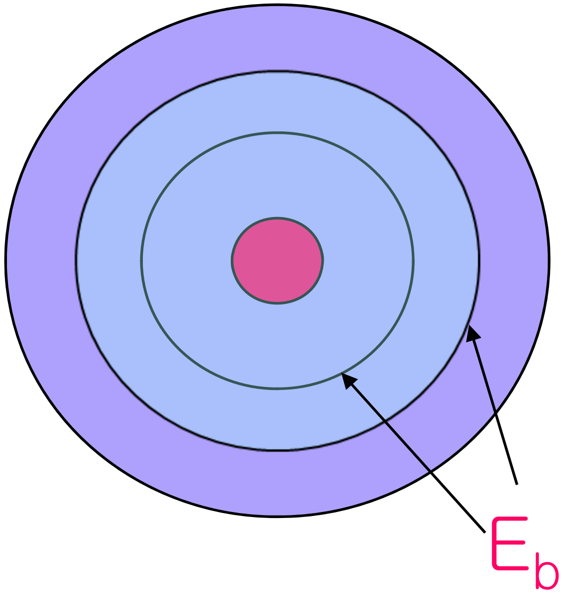


Since the energy levels in atoms are quantized (different energy in different shells), the emitted photoelectrons have a different kinetic energy depending on which shell of the atom they belong to.

The kinetic energy of photoelectrons reflects the electronic shell structure of atom

What does it mean binding energy E_b of core electron?





attraction energy of an electron in the core shell, or energy to be introduced to extract an electron from that shell

Core level electron binding energies measured by XPS in eV

Element	1s	2s	2p	3s	3p	4s
B	188					
C	284					
N	399					
O	532	24				
F	686	31				
Si		149	100			
S		229	165			
Cl		270	202			
Ge		1249	1217	181	129	
Br				232	168	27

Photoelectric effect

If the photoelectrons have sufficient kinetic energy they can escape from the surface of material overcoming the work function.

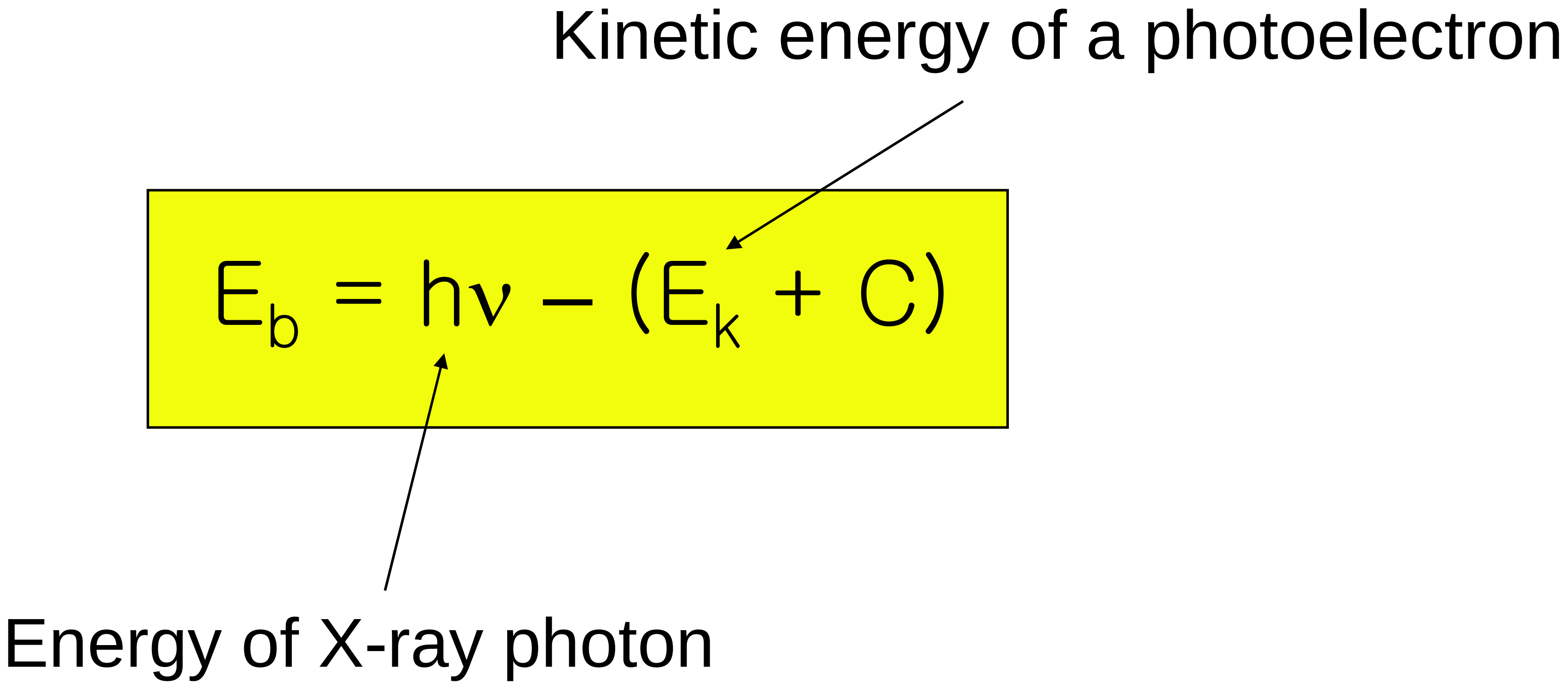
Photoemission may be observed from gases, liquids or solids, but is most interesting for solid samples.

Core level electron binding energies are characteristic for the type of atom to which the electron is bound. Measuring the binding energies of a sample allows qualitative elemental analysis.

The number of photoelectrons produced from any core level of an atom depends on the irradiation conditions. For a specific apparatus the intensity of photoemission may be used as for element determination as a basis for quantitative elemental analysis.

Questions

Determination of binding energy



Kinetic energy of a photoelectron

$$E_b = h\nu - (E_k + C)$$

Energy of X-ray photon

Basic requirements for XPS

In the basic XPS experiment, the sample surface is irradiated by low energy X-rays under ultra-high vacuum conditions.

Electron energy analyser for the emitted photoelectrons

How to obtained XPS spectra?

XPS spectra are obtained by irradiating a material with a beam of X-rays and simultaneously measuring the kinetic energy and number of electrons that escape from the top layer of 1 to 10 nm of the material surfaces.

XPS requires ultra high vacuum (UHV) conditions.

Instrumentation for XPS

1. Ultra-high vacuum, UHV environment
2. Controlled source of X-ray, suitable for excitation of core electrons of all elements (energy from 1eV to more then 1000 eV), Mg and Al
3. Sample manipulation system,
   powder on adhesive tape or pressed on In foil, fiber, bulk solid
4. Electron detection and energy analyzing system
5. Data recording and processing

How to obtained XPS spectra?

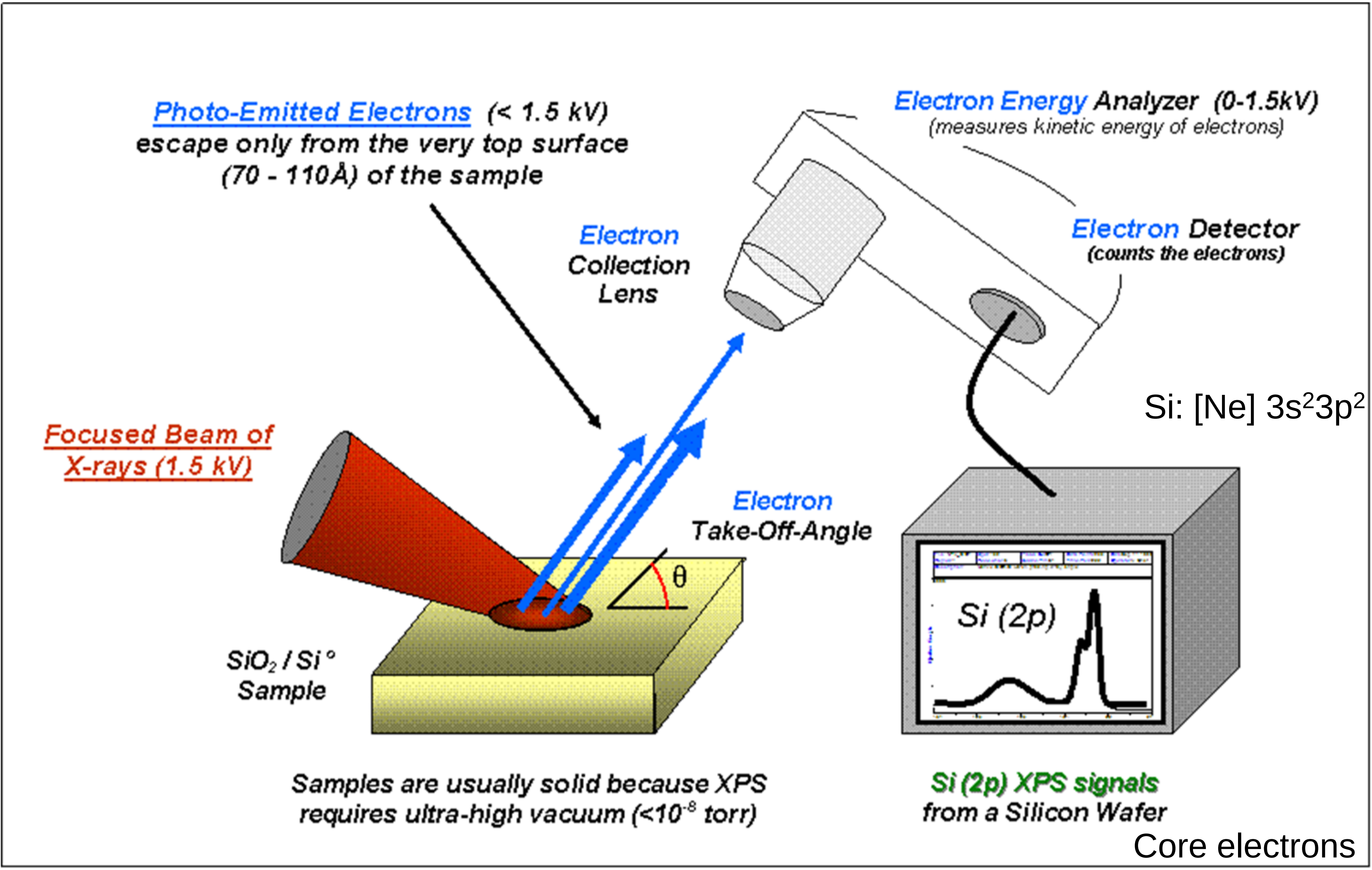


Photo-Emitted Electrons (< 1.5 kV) escape only from the very top surface (70 - 110Å) of the sample

Electron Energy Analyzer (0-1.5kV) (measures kinetic energy of electrons)

Electron Detector (counts the electrons)

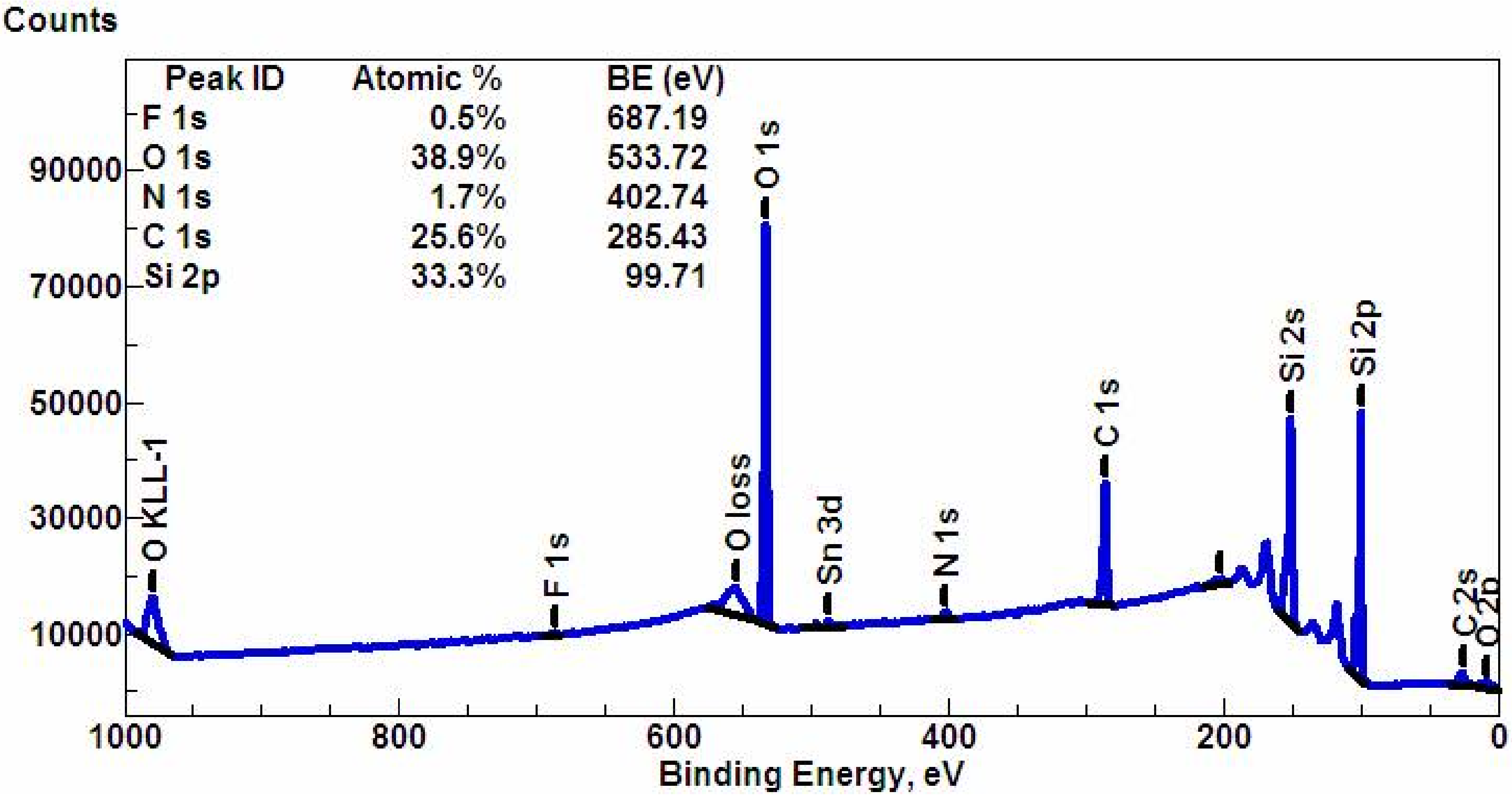
Samples are usually solid because XPS requires ultra-high vacuum ($<10^{-8}$ torr)

Si (2p) XPS signals from a Silicon Wafer

Si: [Ne] $3s^2 3p^2$

Core electrons

Typical XPS Spectrum



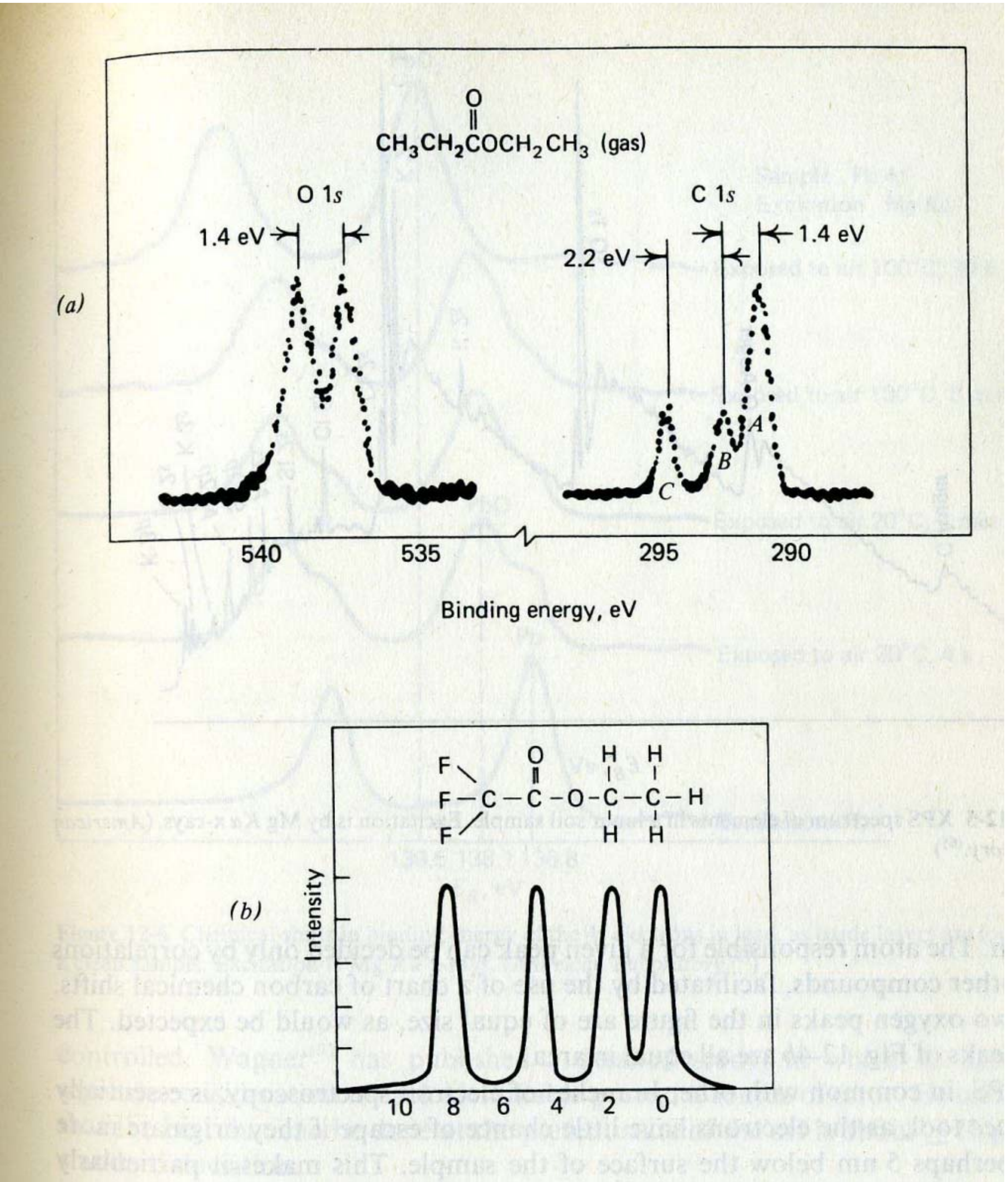
Peak ID	Atomic %	BE (eV)
F 1s	0.5%	687.19
O 1s	38.9%	533.72
N 1s	1.7%	402.74
C 1s	25.6%	285.43
Si 2p	33.3%	99.71

a plot of the number of electrons detected (Y-axis) versus the binding energy (X-axis) of the electrons detected

Application of XPS

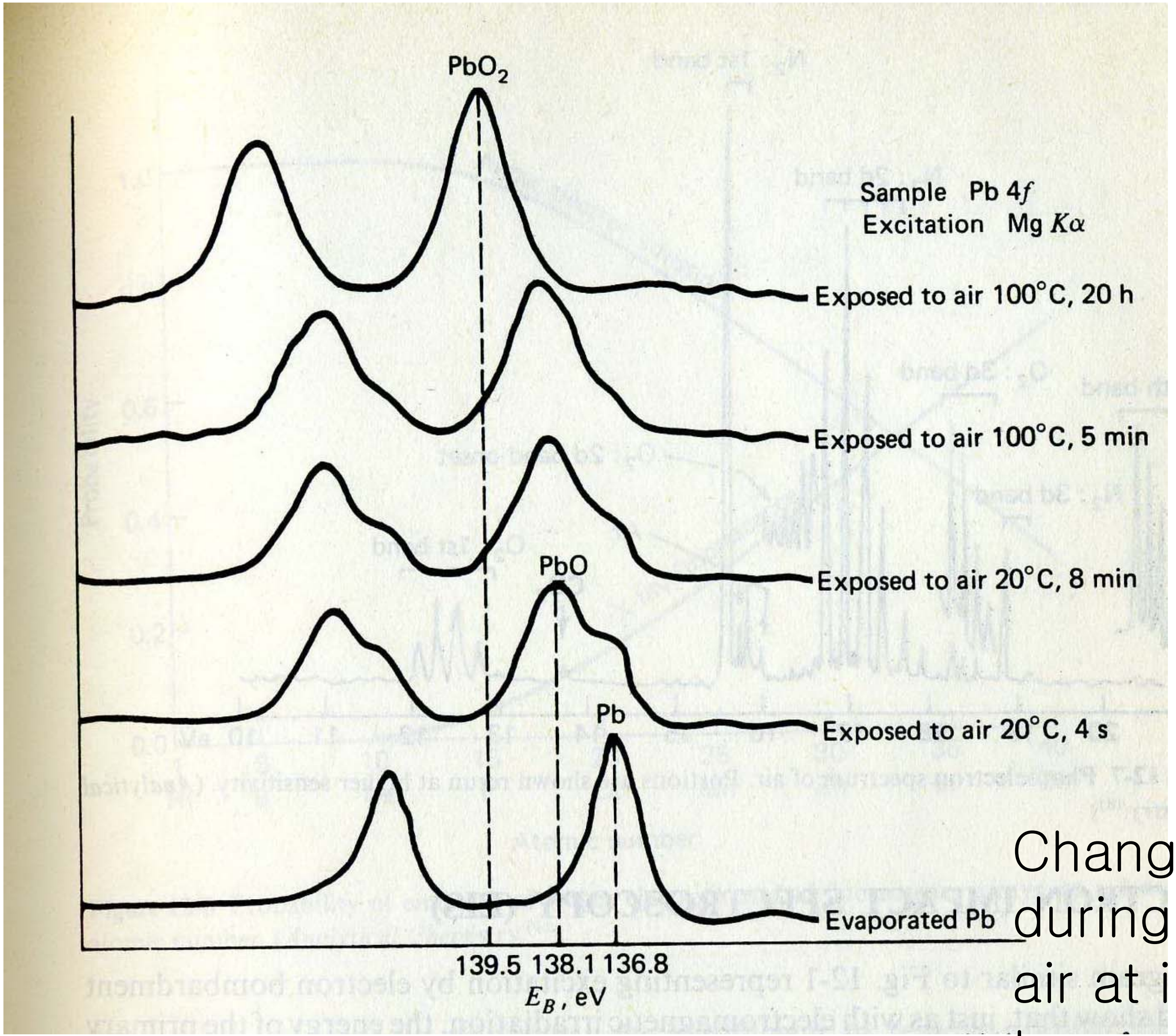
In a large number of research areas:
characterisation of surface in polymers,
thin layers, coatings, films
small particles, fibers, nanowires,
nanotubes

Examples of photoelectron spectra



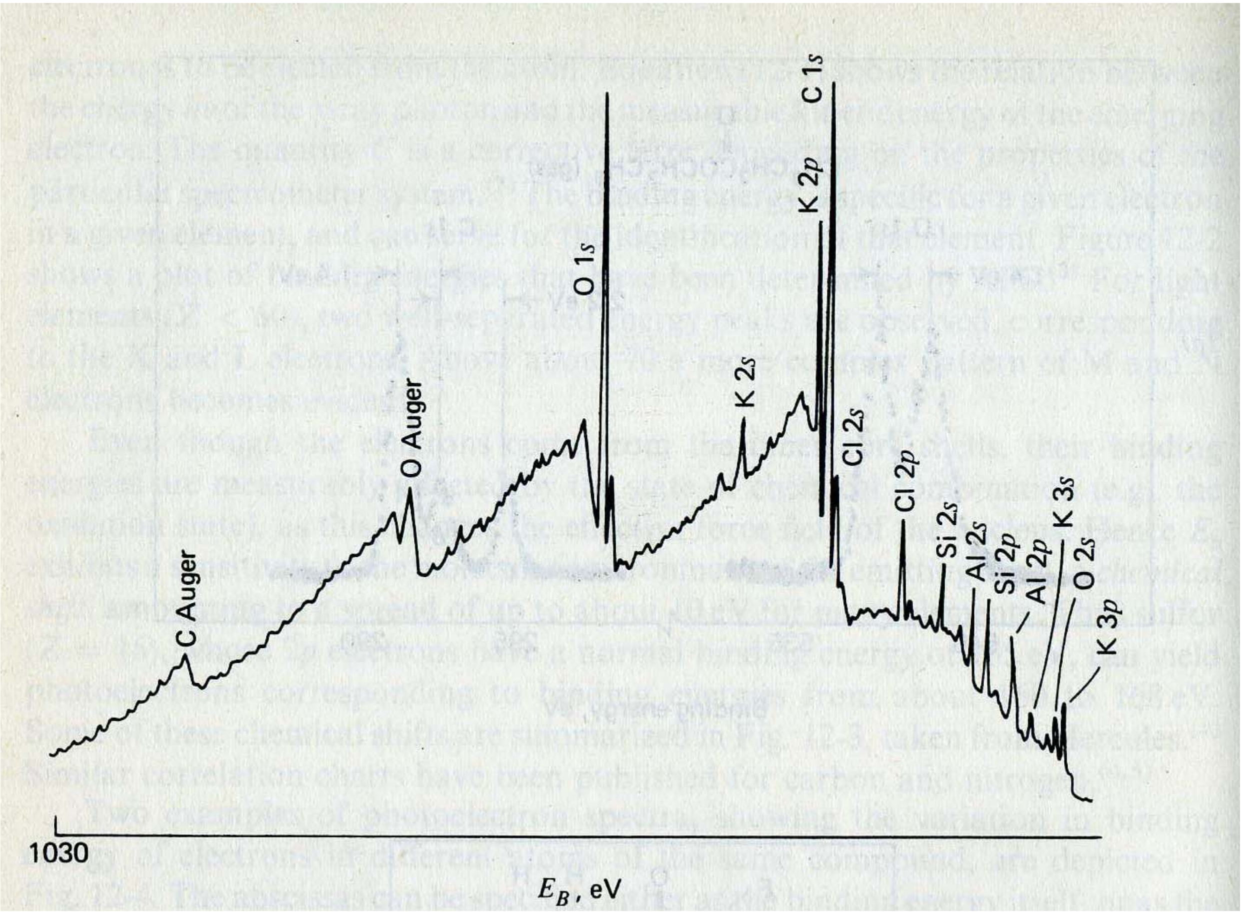
Binding energy in different atoms (different chemical environment) of the same compound

Examples of photoelectron spectra



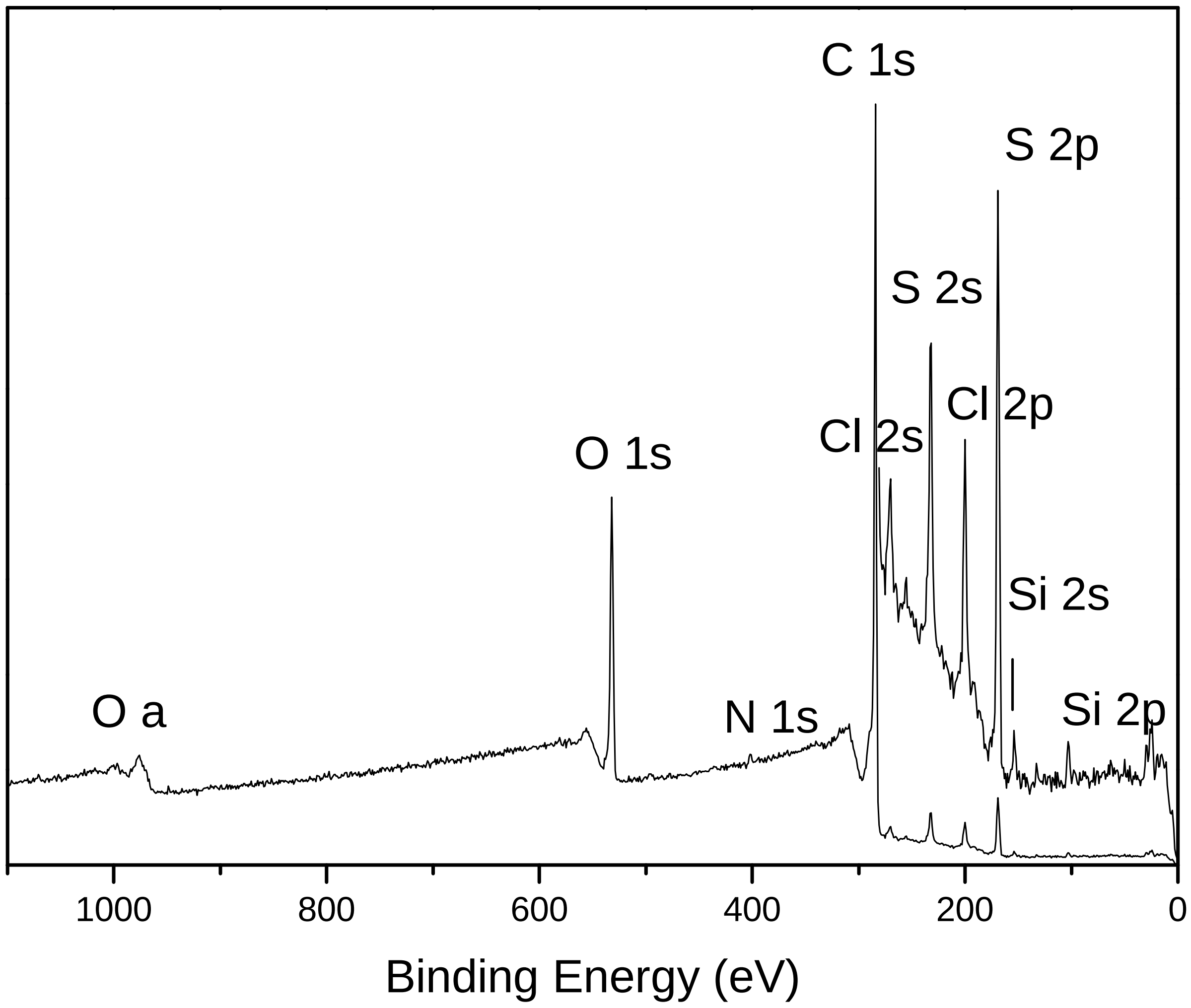
Changes in XPS during exposure to air at increasing temperature – oxidatio

Examples of structure determination and compositi

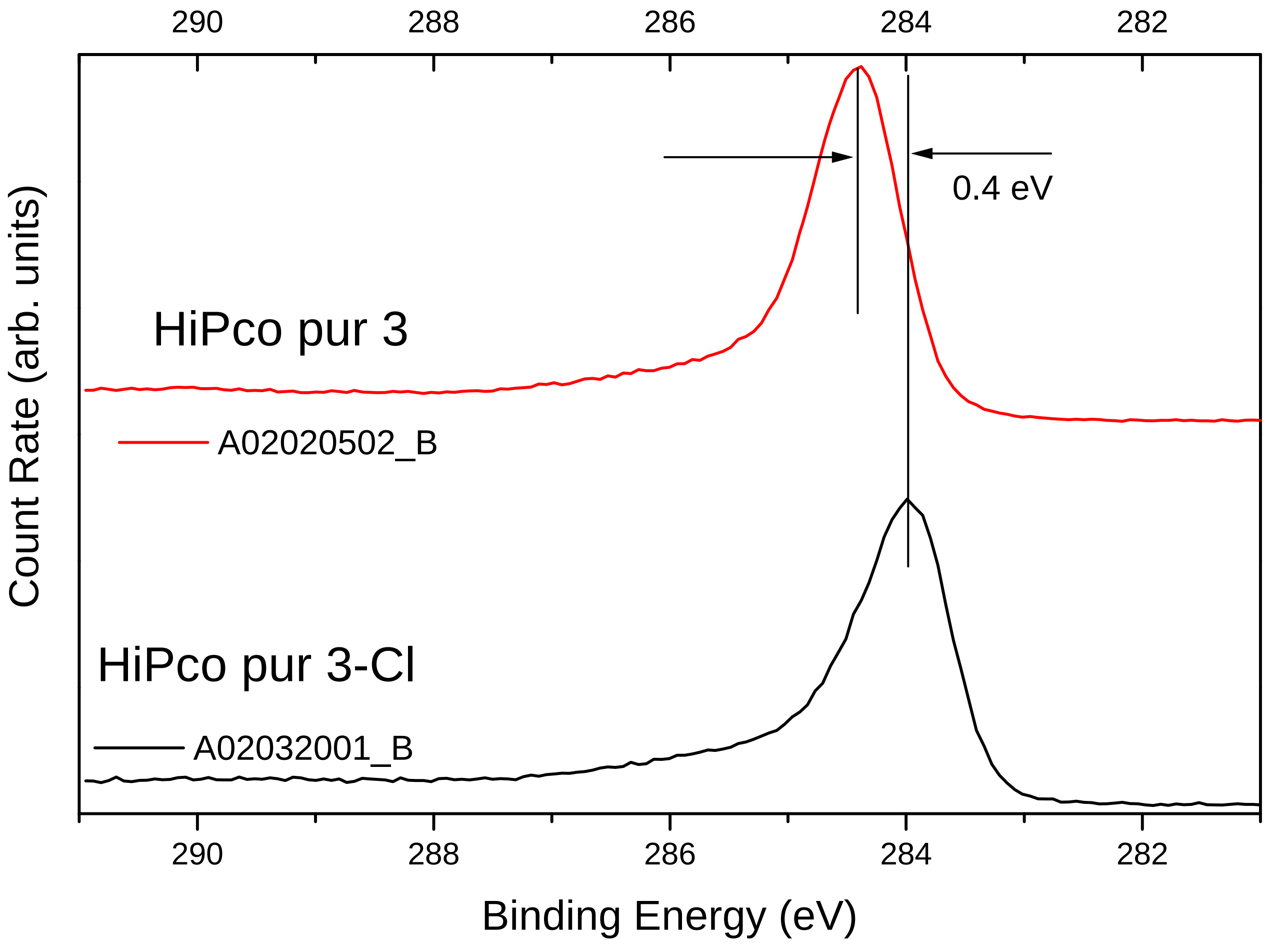


Spectrum of elements in a lunar soil sample, (American lab)

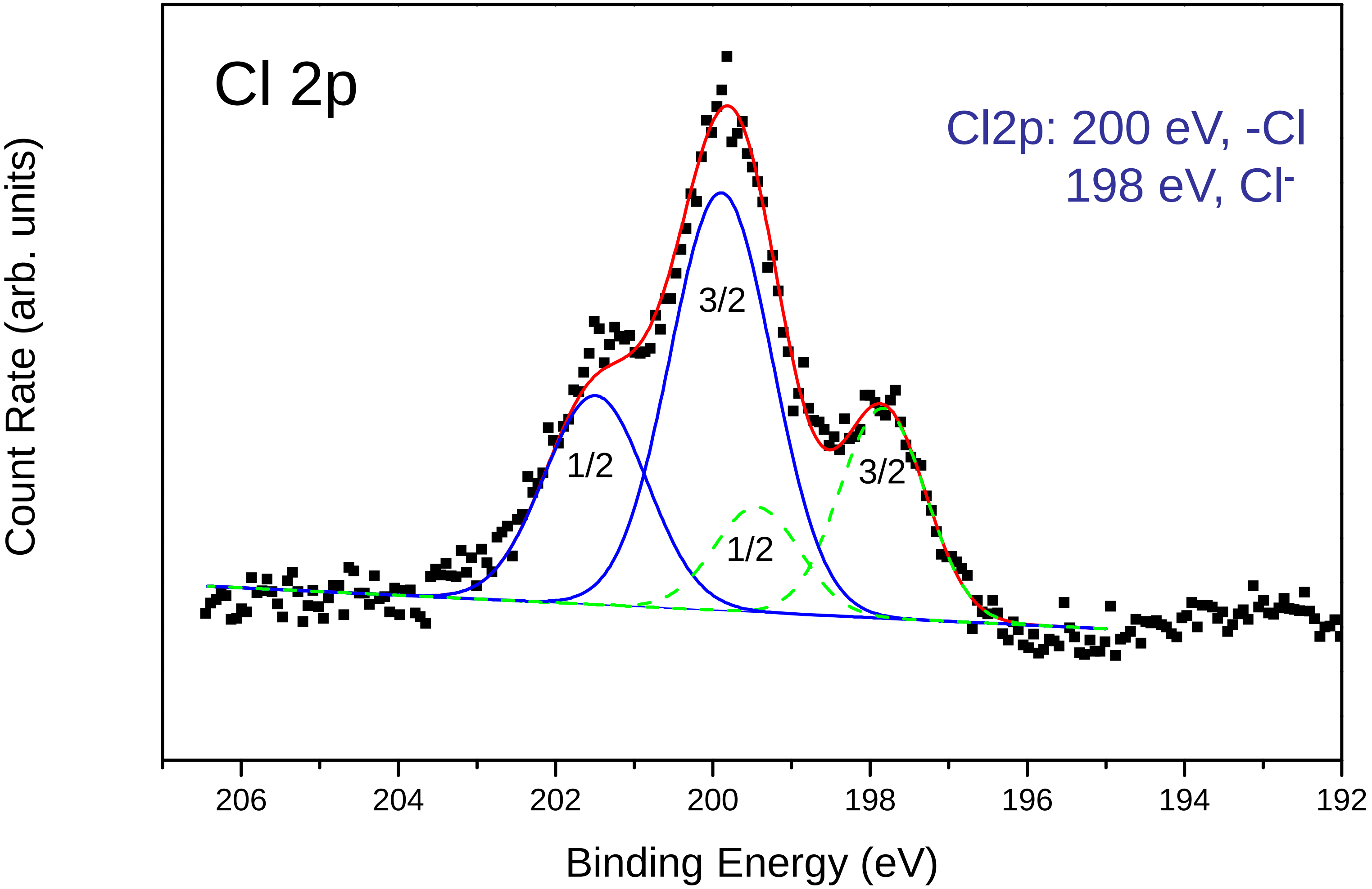
XPS spectra of chemically modified SWNTs



XPS Spectra of modified SWNTs, exposure to SOCl2



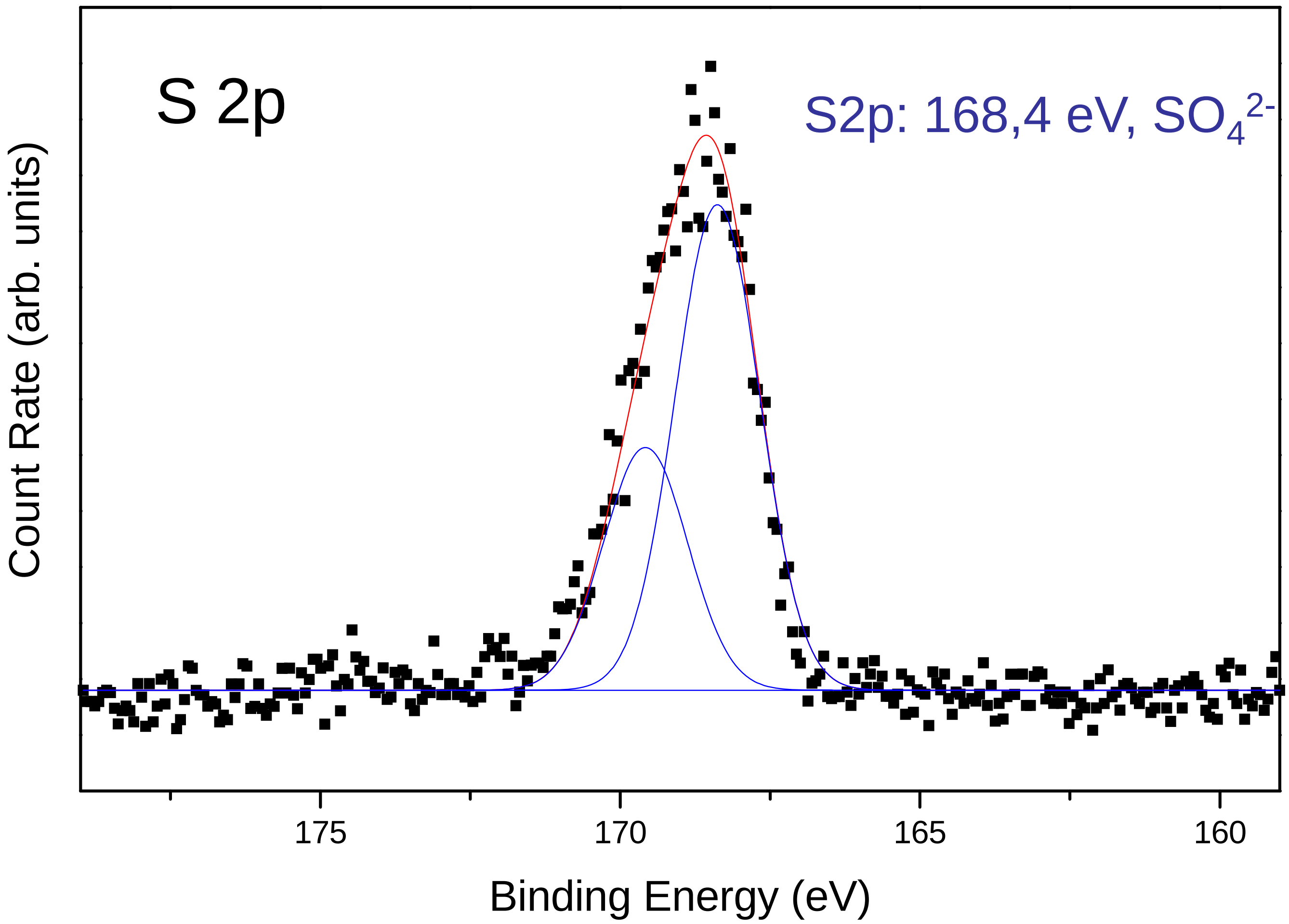
XPS Spectra of modified SWNTs, after SOCl2 treatment



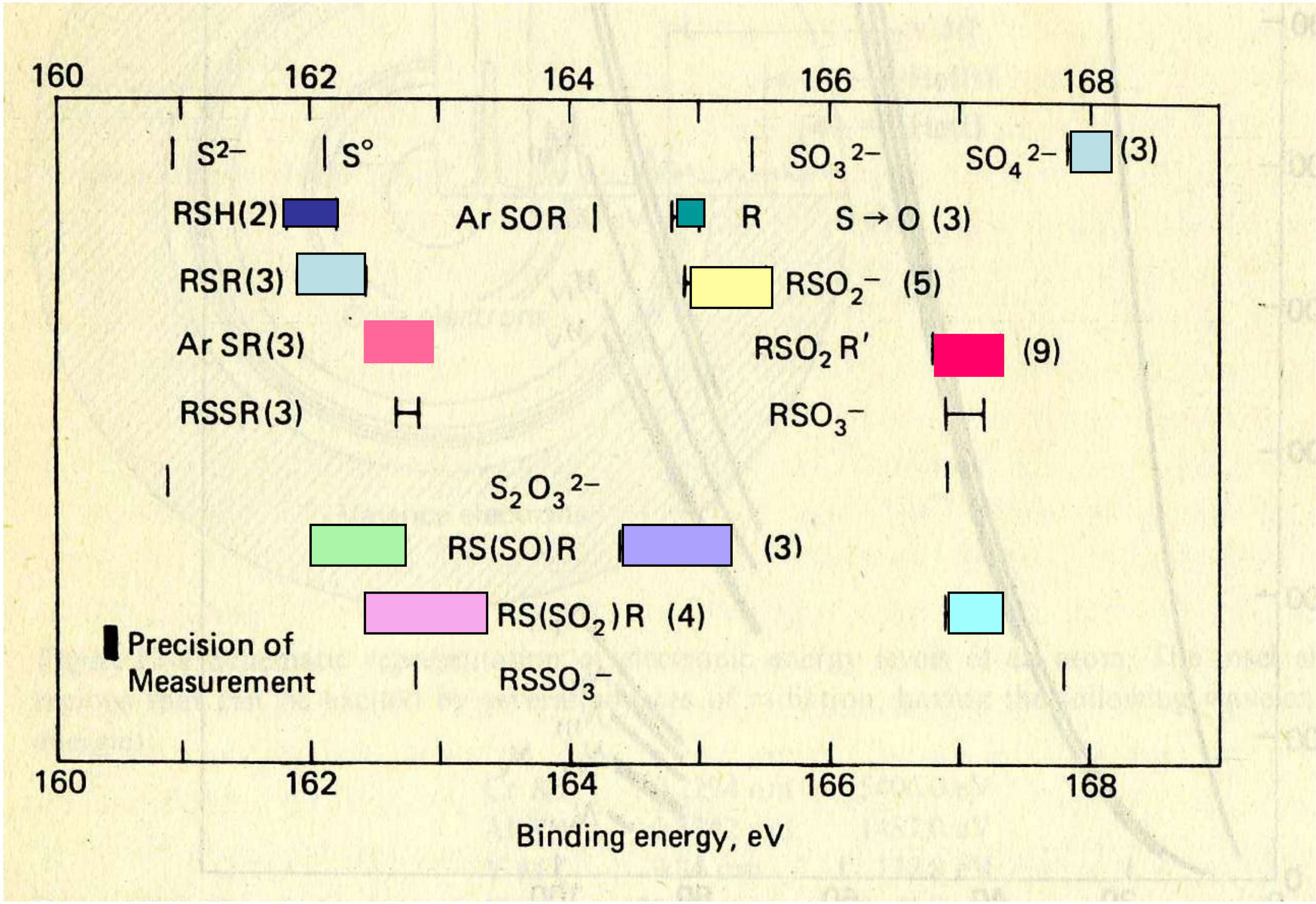
Cl2p: 200 eV, -Cl

198 eV, Cl^-

XPS Spectra of modified SWNTs, SOCl2 treatment



Examples of Binding Energy in Sulfur atom



Influence of functional groups on electron binding energy in a sulfur atom.

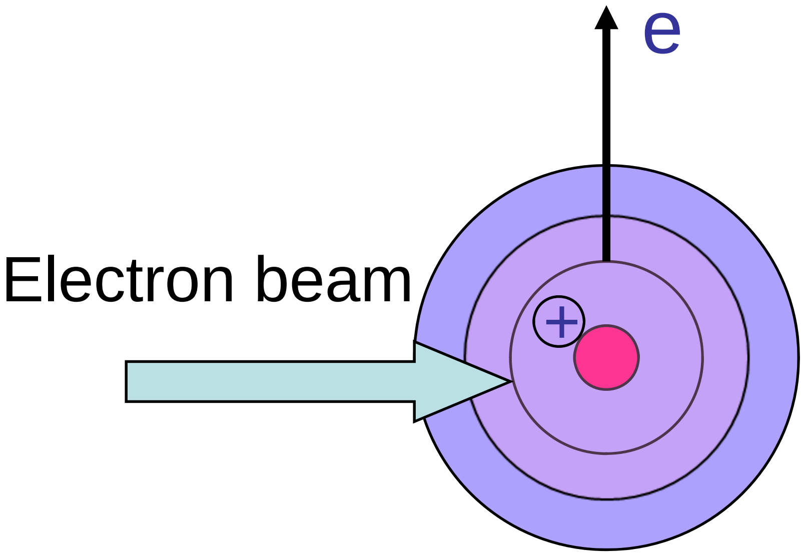
X-ray Photoelectron Spectroscopy, XPS

XPS detects all elements with an atomic number (*Z*) of 3 (lithium) and above. This limitation means that it cannot detect hydrogen (*Z*=1) or helium (*Z*=2).

X-ray Photoelectron Spectroscopy, XPS

Analysis based on detection of electrons emitted from an atom upon X-ray irradiation. Measuring the kinetic energy of ejected electrons, the binding energy can be determined. Binding energy is specific for a given electron in a given element and can be used for element identification, and is sensitive to chemical environment of the emitted electron.

Electron Energy Loss Spectroscopy EELS



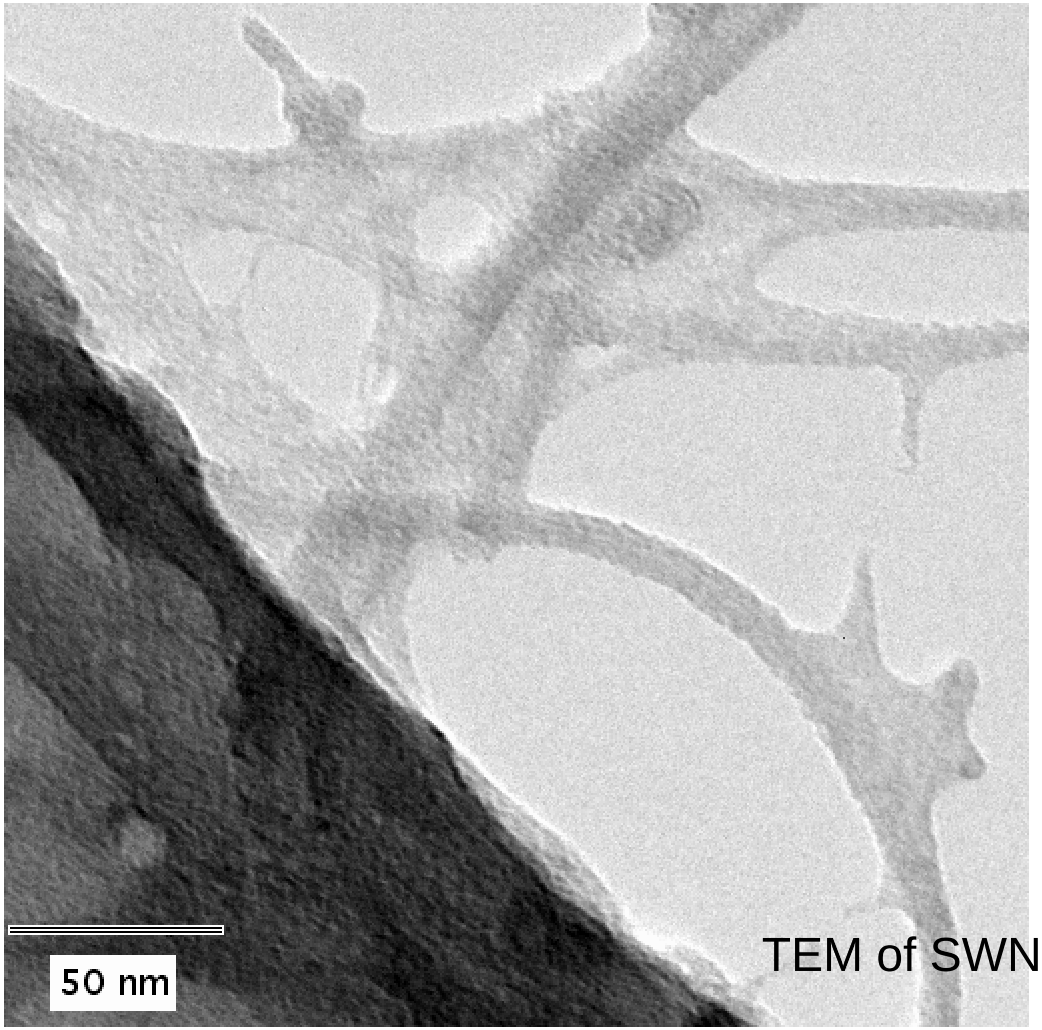
Ionization and emission of electrons

An micro-analysis tool common available on many electron microscopes: TEM, SEM
is complementary to the Energy-Dispersive X-ray spectroscopy, EDX

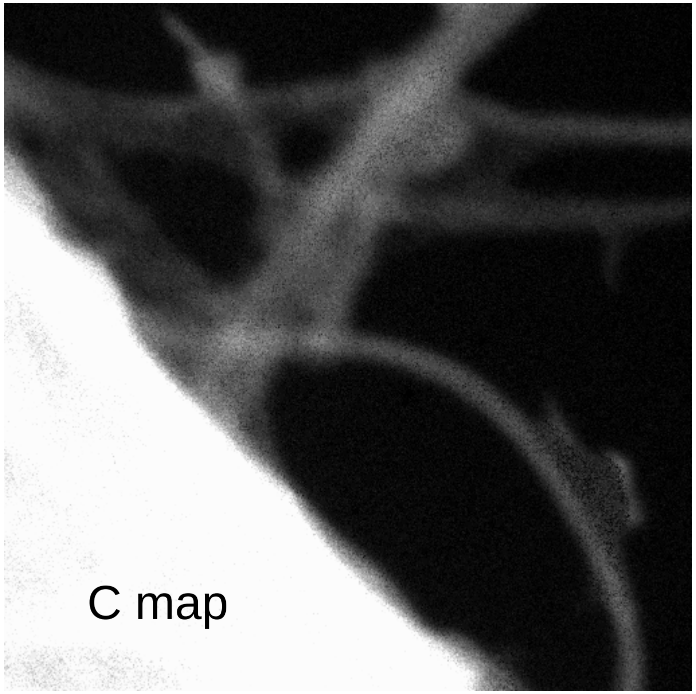
Basic principle

A material is exposed to an electron beam with a known, narrow range of kinetic energy.
Some of the electrons will undergo inelastic scattering, causing core shell ionization of the material atoms.
The electrons lose energy and change their paths.
The amount of energy loss can be measured delivering information about elements in the analyzed material.

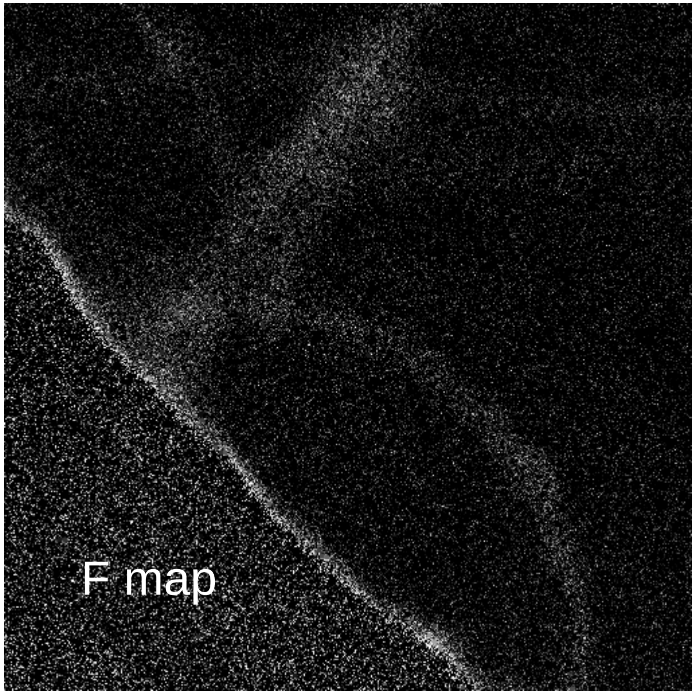
Characterization of fluorinated tubes, elemental mapping by EELS-Analysis



TEM of SWNT



C map



F map

EELS versus EDX

EELS work best at relatively low atomic numbers
reveals "fingerprint" different forms of the same element

EDX is sensitive to heavier elements

Applications

Core-shell ionization EELS provides the same information as x-ray absorption spectroscopy

Determination of sort and amount of elements present in the sample, differentiation between several oxidation states and chemical bondings,

best developed for the elements ranging from carbon through the 3d transition metals, from scandium to zinc,

differences among diamond, graphite, amorphous carbon, and "mineral" carbon (as that appearing in carbonates may be found)

Questions